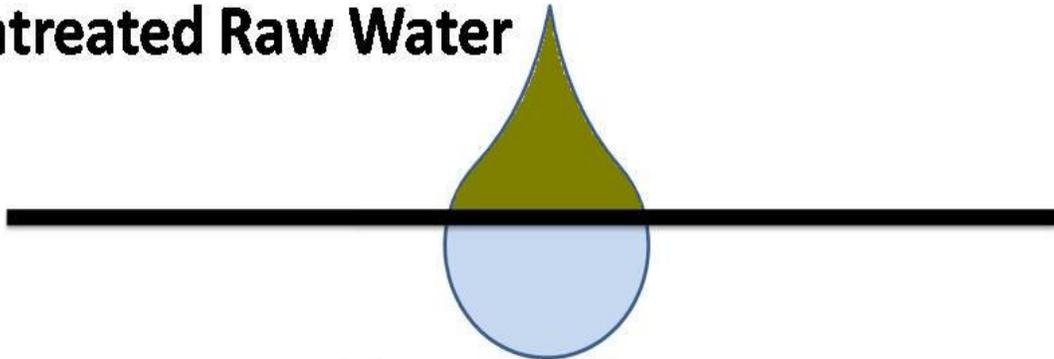


# **WATER CHEMISTRY**

## **CONTINUING EDUCATION**

### **PROFESSIONAL DEVELOPMENT COURSE**

**Untreated Raw Water**



**Treated Water**



**Drinking Water**



## Printing and Saving Instructions

We recommend that you download this pdf document and assignment to your computer desktop and open it with Adobe Acrobat DC reader.

Adobe Acrobat DC reader is a free computer software program and you can find it at Adobe Acrobat's website.

You can complete the course by viewing the course on your computer or you can print it out. This course booklet does not have the assignment (the test). Please visit our website and download the assignment (the test).

**Printing Instructions:** Once you have purchased the program, we will give you permission to print this document. If you are going to print this document, it was designed to be printed double-sided or duplexed but can be printed single-sided.

### Internet Link to Assignment...

<http://www.abctlc.com/downloads/PDF/WaterChemistryAss.pdf>

**State Approval Listing Link,** check to see if your State accepts or has pre-approved this course. Not all States are listed. Not all courses are listed. Do not solely trust our list for it may be outdated. It is your sole responsibility to ensure this course is accepted for credit. No refunds.

**Professional Engineers;** Most states will accept our courses for credit but we do not officially list the States or Agencies acceptance or approvals.

### State Approval Listing URL...

<http://www.ABCTLC.com/downloads/PDF/CEU%20State%20Approvals.pdf>

*You can obtain a printed version from TLC for an additional \$189.95 plus shipping charges.*

*All downloads are electronically tracked and monitored for security purposes.*



**Some States and many employers require the final exam to be proctored.**

**Do not solely depend on TLC's Approval list for it may be outdated.**

Most of our students prefer to do the assignment in Word and e-mail or fax the assignment back to us. We also teach this course in a conventional hands-on class. Call us and schedule a class today.

***Responsibility***

*This course contains EPA's federal rule requirements. Please be aware that each state implements drinking water/wastewater/safety regulations may be more stringent than EPA's or OSHA's regulations. Check with your state environmental agency for more information. You are solely responsible in ensuring that you abide with your jurisdiction or agency's rules and regulations.*

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**Jack White**, Environmental, Health, Safety expert, City of Phoenix. Art Credits.



## Important Information about this Manual

This manual has been prepared to educate students and operators in general safety awareness of dealing with the often-complex and various water disinfectants, including dangerous chemicals, including but not limited to Chlorine and other toxic materials. This CEU course will also cover respirator protection devices, methods, and applications.

This manual will cover general laws, regulations, required procedures and accepted policies relating to the use of disinfectants, DDBPs, Ozone, Ultraviolet Radiation, Respirator Protection Devices, Methods, and Applications.

It should be noted, however, that the regulation of respirator protection devices and hazardous materials is an ongoing process and subject to change over time.

For this reason, a list of resources is provided to assist in obtaining the most up-to-date information on various subjects.

This manual is a not a guidance document for applicators or operators who are involved with pesticides.

It is not designed to meet the requirements of the United States Environmental Protection Agency, Office of Health and Safety Administration (OSHA) or your local State environmental protection agency or health department.

This course manual will provide general respirator protection and safety awareness and should not be used as a basis for respirator protection method/device guidance. This document is not a detailed safety manual or a source or remedy for respirator protection or control.

Technical Learning College or Technical Learning Consultants, Inc. make no warranty, guarantee or representation as to the absolute correctness or appropriateness of the information in this manual and assumes no responsibility in connection with the implementation of this information. It cannot be assumed that this manual contains all measures and concepts required for specific conditions or circumstances.

This document should be used for educational purposes only and is not considered a legal document. Individuals who are responsible for respirator protection should obtain and comply with the most recent federal, state, and local regulations relevant to these sites and are urged to consult with OSHA, EPA and other appropriate federal, state and local agencies.





# Technical Learning College's Scope and Function

Welcome to the Program,

Technical Learning College (TLC) offers affordable continuing education for today's working professionals who need to maintain licenses or certifications. TLC holds several different governmental agency approvals for granting of continuing education credit.

TLC's delivery method of continuing education can include traditional types of classroom lectures and distance-based courses or independent study. TLC's distance based or independent study courses are offered in a print - based distance educational format. We will beat any other training competitor's price for the same CEU material or classroom training.

Our courses are designed to be flexible and for you to finish the material at your convenience. Students can also receive course materials through the mail. The CEU course or e-manual will contain all your lessons, activities and instruction to obtain the assignments. All of TLC's CEU courses allow students to submit assignments using e-mail or fax, or by postal mail. (See the course description for more information.)

Students have direct contact with their instructor—primarily by e-mail or telephone. TLC's CEU courses may use such technologies as the World Wide Web, e-mail, CD-ROMs, videotapes and hard copies. (See the course description.) Make sure you have access to the necessary equipment before enrolling; i.e., printer, Microsoft Word and/or Adobe Acrobat Reader. Some courses may require proctored closed-book exams, depending upon your state or employer requirements.

## **Flexible Learning**

At TLC, there are no scheduled online sessions or passwords you need contend with, nor are you required to participate in learning teams or groups designed for the "typical" younger campus based student. You will work at your own pace, completing assignments in time frames that work best for you. TLC's method of flexible individualized instruction is designed to provide each student the guidance and support needed for successful course completion.

## **Course Structure**

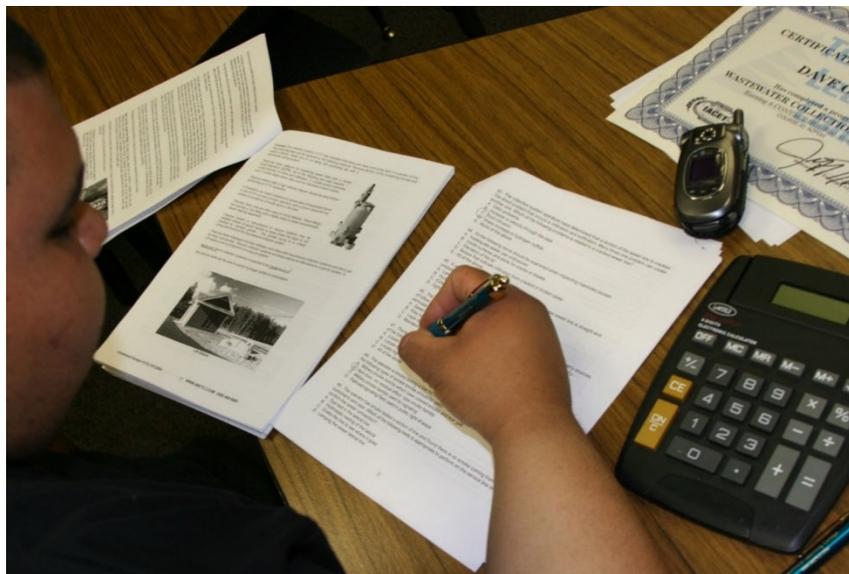
TLC's online courses combine the best of online delivery and traditional university textbooks. You can easily find the course syllabus, course content, assignments, and the post-exam (Assignment). This student-friendly course design allows you the most flexibility in choosing when and where you will study.

## **Classroom of One**

TLC offers you the best of both worlds. You learn on your own terms, on your own time, but you are never on your own. Once enrolled, you will be assigned a personal Student Service Representative who works with you on an individualized basis throughout your program of study. Course specific faculty members (S.M.E.) are assigned at the beginning of each course providing the academic support you need to successfully complete each course. Please call or email us for assistance.

### **Satisfaction Guaranteed**

We have many years of experience, dealing with thousands of students. We assure you, our customer satisfaction is second to none. This is one reason we have taught more than 20,000 students.



We welcome you to do the electronic version of the assignment and submit the answer key and registration to us either by fax or e-mail. If you need this assignment graded and a certificate of completion within a 48-hour turn around, prepare to pay an additional rush charge of \$50.

We welcome you to complete the assignment in Word.

Once we grade it, we will mail a certificate of completion to you. Call us if you need any help.

**Contact Numbers**  
**Fax (928) 468-0675**  
**Email [Info@tlch2o.com](mailto:Info@tlch2o.com)**  
**Telephone (866) 557-1746**

## **Water Chemistry CEU Training Course**

### **CEU Course Introduction**

This distance learning CEU training course will examine various general aspects of commonly found conventional water/wastewater chemistry procedures which are utilized for proper examination of common found contaminants or used water chemicals. (Check with your state Agency for time allocation.) This course was designed to provide continuing education credit to water and/ or wastewater treatment operators.

#### **Course Purpose**

The main purpose of this course is to provide continuing education in understanding various water related laboratory procedures utilized in determining various water quality-water chemistry related concerns and MCL determinations.

#### **Target Audience**

The target audience for this course is primarily for operators who work inside a water laboratory but can include water treatment operators, and wastewater operators. Also people who are interested in working in a water treatment/wastewater treatment or distribution facility and/or wishing to maintain CEUs for a certification license or to learn how to perform their job safely and effectively, and/or to meet education needs for promotion.

There are no prerequisites, and no other materials are needed for this course.

#### **Course Statement of Need**

All water and wastewater operators who work inside a water laboratory need to be able to describe proper basic water chemistry techniques/procedures/reactions and properly demonstrate proper and safe operation of various laboratory equipment utilized for general water and wastewater examination and water quality concerns.

#### **Instructions for Written Assignments**

The ***Water Chemistry*** distance learning course uses a multiple-choice style answer key. You can find the answer key in the front of the assignment.

#### **Feedback Mechanism (Examination Procedures)**

Each student will receive a feedback form as part of his or her study packet. You will be able to find this form in the front of the course assignment or lesson.

#### **Security and Integrity**

All students are required to do their own work. All lesson sheets and final exams are not returned to the student to discourage sharing of answers. Any fraud or deceit and the student will forfeit all fees and the appropriate agency will be notified. A random test generator will be implemented to protect the integrity of the assignment.

#### **Grading Criteria**

TLC will offer the student either pass/fail or a standard letter grading assignment. If TLC is not notified, you will only receive a pass/fail notice. In order to pass your final assignment, you are required to obtain a minimum score of 70% on your assignment.

**Required Texts**

The **Water Chemistry** course comes complete with a short summary of the OSHA's laboratory safety procedure standards. If you need more information or a complete set of Rules, you can download them off the EPA's web page, [www.epa.gov](http://www.epa.gov) or contact your local state environmental agency. You may need to contact a laboratory or state agency for certain sampling information.

**Recordkeeping and Reporting Practices**

TLC will keep all student records for a minimum of seven years. It is the student's responsibility to give the completion certificate to the appropriate agencies. TLC will not release any records to any party, except to the student.

**ADA Compliance**

TLC will make reasonable accommodations for persons with documented disabilities. Students should notify TLC and their instructors of any special needs. Course content may vary from this outline to meet the needs of this particular group. There is an option course assignment available, please contact an Instructor for further assistance.

**Mission Statement**

Our only product is educational service. Our goal is to provide you with the best education service possible. TLC will attempt to make your learning experience an enjoyable opportunity.

**Student Verification**

The student shall submit a driver's license for signature verification and track their time worked on the assignment. The student shall sign an affidavit verifying they have not cheated and worked alone on the assignment. All student attendance is tracked on the student attendance database.

**Feedback Mechanism (Examination Procedures)**

A feedback form is included in the rear of each study packet.

**Environmental Terms, Abbreviations, and Acronyms**

TLC provides a glossary in the rear of this manual that defines, in non-technical language, commonly used environmental terms appearing in publications and materials, as well as abbreviations and acronyms used throughout the EPA and other governmental agencies.

**Record Keeping and Reporting Practices**

TLC keeps all student records for a minimum of five years. It is the student's responsibility to give the completion certificate to the appropriate agencies.

## Educational Mission

The educational mission of TLC is:

To provide TLC students with comprehensive and ongoing training in the theory and skills needed for the environmental education field,

To provide TLC student's opportunities to apply and understand the theory and skills needed for operator certification,

To provide opportunities for TLC students to learn and practice environmental educational skills with members of the community for the purpose of sharing diverse perspectives and experience,

To provide a forum in which students can exchange experiences and ideas related to environmental education,

To provide a forum for the collection and dissemination of current information related to environmental education, and to maintain an environment that nurtures academic and personal growth.

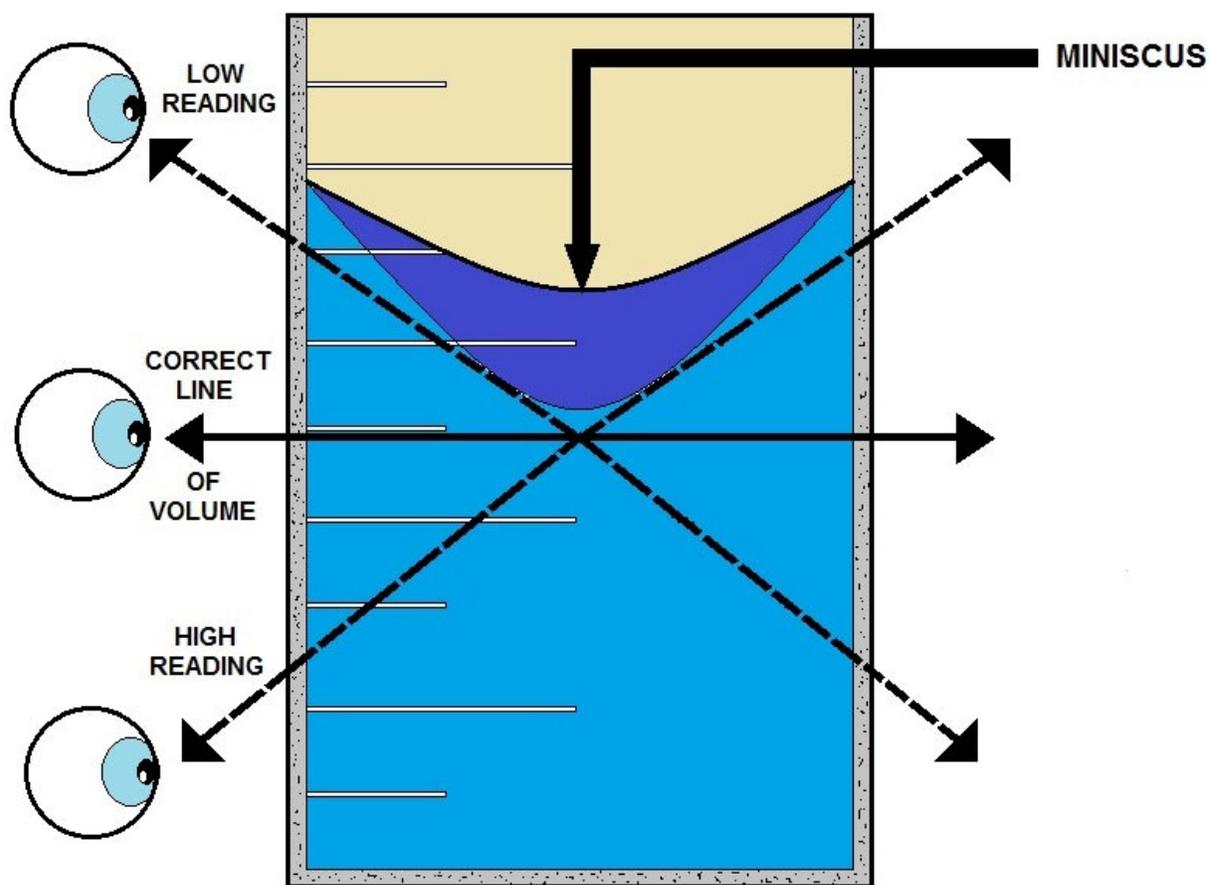
### SAFE DRINKING WATER ACT (SDWA)

<ul style="list-style-type: none"><li>★ DRAFTED IN 1974.</li><li>★ AMENDED IN 1986 AND ALSO IN 1996.</li><li>★ SETS NATIONAL HEALTH-BASED STANDARDS FOR DRINKING WATER TO PROTECT AGAINST BOTH NATURALLY-OCCURRING AND MAN-MADE CONTAMINANTS THAT MAY BE FOUND IN DRINKING WATER.</li><li>★ THE UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (EPA) IS RESPONSIBLE FOR REGULATION AND ENFORCEMENT BY SETTING STANDARDS FOR DRINKING WATER BASED ON SOUND SCIENCE TO PROTECT AGAINST HEALTH RISKS, CONSIDERING AVAILABLE TECHNOLOGY AND ASSOCIATED COSTS.</li><li>★ THE AMENDMENTS REQUIRE MANY ACTIONS TO PROTECT DRINKING WATER AND ITS SOURCES:<ul style="list-style-type: none"><li>RIVERS</li><li>LAKES</li><li>RESERVOIRS</li><li>SPRINGS</li><li>GROUNDWATER WELLS</li></ul></li></ul>	
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### SAFE DRINKING WATER ACT FACTS



*This course contains EPA's federal rule requirements. Please be aware that each state implements drinking water regulations that may be more stringent than EPA's regulations. Check with your state environmental agency for more information.*



## HOW TO READ A MINISCUS

The **meniscus** (plural: *menisci*, from the Greek for "crescent") is the curve in the upper surface of a liquid close to the surface of the container or another object, caused by surface tension. It can be either convex or concave.

A convex meniscus occurs when the molecules have a stronger attraction to each other (cohesion) than to the material of the container (adhesion). This may be seen between mercury and glass in barometers and thermometers.

Conversely, a concave meniscus occurs when the molecules of the liquid attract those of the container's, causing the surface of the liquid to cave downwards. This can be seen in a glass of water.

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## ACRONYMS

CCR	Consumer Confidence Report
CWS	Community Water System
DBP	Disinfection Byproduct
HPC	Heterotrophic Plate Count
IESWTR	Interim Enhanced Surface Water Treatment Rule
IOC	Inorganic Chemical
LCR	Lead and Copper Rule
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MRDL	Maximum Residual Disinfectant Level
MRDLG	Maximum Residual Disinfectant Level Goal
NPDWR	National Primary Drinking Water Regulations
NTNCWS	Non-Transient Non-Community Water System
NTU	Nephelometric Turbidity Units
PN	Public Notification
PWS	Public Water Supply
SDWA	Safe Drinking Water Act
SMCL	Secondary Maximum Contaminant Level
SOC	Synthetic Organic Chemical
SWTR	Surface Water Treatment Rule
TCR	Total Coliform Rule
TT	Treatment Technique
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Chemical



## Common Water Chemistry/Quality Definitions

### Units of Measurement

**mg/l** = Milligrams per liter. One milligram per liter equals one packet of artificial sweetener sprinkled into 250 gallons of iced tea.

**µg/l** = Micrograms per liter. One microgram per liter is equal to one packet of artificial sweetener sprinkled into an Olympic-size swimming pool.

**NTU** = Nephelometric Turbidity Units. A measurement on the cloudiness of the water.

**pCi/l** = Picocuries per liter. A measure of radioactivity.

### Acronyms

**Maximum Contaminant Level (MCL)** - The highest level of a contaminant that is allowed in drinking water.

**Maximum Contaminant Level Goal (MCLG)** - The level of a contaminant in drinking water below which there is no known or expected risk to health.

**Treatment Technique (TT)** - A required process intended to reduce the level of a contaminant in drinking water.

**Action Level (AL)** - The concentration of a contaminant that, if exceeded, triggers treatment or other requirements which a water system must follow.

## Symbols and Characters

These symbols and characters are specific to water sampling methods but have been conformed to common usage as much as possible.

### Units of weight and measure and their abbreviations

#### Symbols

°C degrees Celsius  
μL microliter  
< less than  
> greater than  
% percent

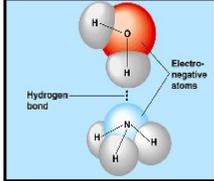
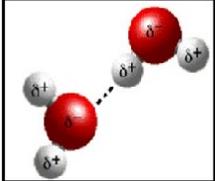
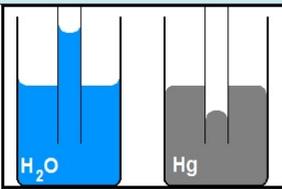
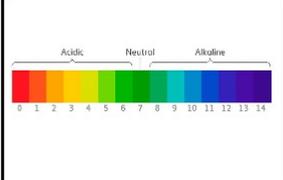
### Alphabetical characters

ACUK - Acid chrome violet K  
AECL - Alternate enhanced coagulant level  
AOC - Assimilable organic carbon  
ASDWA - Association of State Drinking Water Administrators  
AWWA - American Water Works Association  
AWWARF - AWWA Research Foundation  
BAC - Biologically active carbon  
BAF - Biologically active filtration  
BAT - Best Available Technology  
BCAA - Bromochloroacetic acid  
BDOC - Biodegradable organic carbon  
BMP- Best management practice  
BOM - Biodegradable Organic Matter (=BDOC + AOC)  
Br<sup>-</sup> - Bromide ion  
BrO<sup>2-</sup> - Bromite ion  
BrO<sup>3-</sup> - Bromate ion  
CI - Confidence interval  
Cl<sup>2</sup> - Chlorine  
ClO<sup>2</sup> - Chlorine Dioxide  
cm - centimeter  
CT - Concentration-Time  
CWS - Community Water System  
D/DBP - Disinfectants/disinfection byproducts  
DBP - Disinfection byproduct  
DBPFP - Disinfection byproduct formation potential  
DBPP - Disinfection byproduct precursors  
DBPR - Disinfectants/disinfection byproducts rule  
DBPRAM - DBP Regulatory Assessment Model  
DBPs - Disinfection byproducts  
DOC- Dissolved organic carbon  
DPD - N,N-diethyl-p-phenylenediamine  
DWEL - Drinking Water Equivalent Level  
EBCT - Empty bed contact time  
EMSL - EPA Environmental Monitoring and Support Laboratory (Cincinnati)  
EPA - United States Environmental Protection Agency  
ESWTR - Enhanced Surface Water Treatment Rule  
FBR - Filter Backwash Rule

FY - Fiscal year  
G - acceleration due to gravity  
g - gram  
GAC - Granular activated carbon  
GWR - Ground Water Rule  
GWSS - Ground Water Supply Survey  
H<sub>2</sub>O<sub>2</sub> - Hydrogen Peroxide  
HAA5 - Haloacetic acids (five)  
HOBr - Hypobromous acid  
HOCl - Hypochlorous acid  
hr - hour  
IC- Ion chromatography  
ICR- Information Collection Rule  
ID - inside diameter  
IESWTR- Interim Enhanced Surface Water Treatment Rule  
in. - inch  
IOA- International Ozone Association  
IOC - Inorganic chemical  
KMnO<sub>4</sub> - Potassium permanganate  
L - liter  
LOAEL - Lowest observed adverse effect level  
LOQ - Limit of quantitation  
LT1ESWTR - Long Term Stage 1 Enhanced Surface Water Treatment Rule  
m - meter  
MCL - Maximum Contaminant Level  
MCLG - Maximum Contaminant Level Goal  
M-DBP - Microbial and disinfection byproducts  
MDL - Method Detection Limit  
mg - milligram  
mg/L - Milligrams per liter  
mgd - Million gallons per day  
MIB -Methylisoborneol  
mL - milliliter  
mm - millimeter  
mM - millimolar  
MRDL - Maximum Residual Disinfectant Level (as mg/l)  
MRDLG - Maximum Residual Disinfectant Level Goal  
MRL - Minimum Reporting Level  
MX - 3-chloro-4-(dichloromethyl)-5-hydroxyl-2(5H)-furanone  
N - normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per liter of solution  
NaCl - Sodium chloride  
NCI - National Cancer Institute  
ND - Not detected  
NH<sup>2</sup>Cl - Monochloramine  
NIOSH - National Institute for Occupational Safety and Health  
NIPDWR - National Interim Primary Drinking Water Regulation  
NOAEL - No Observed Adverse Effect Level  
NOM - Natural Organic Matter  
NOMS - National Organic Monitoring Survey  
NORS - National Organics Reconnaissance Survey for Halogenated Organics

NPDWR - National Primary Drinking Water Regulation  
NTNCWS - Nontransient noncommunity water system  
NTP - Normal Temperature and Pressure  
O<sup>2</sup> - Oxygen  
O<sup>3</sup> - Ozone  
OBr<sup>-</sup> - Hypobromite ion  
OCI<sup>-</sup> - Hypochlorite ion  
PCE - Perchloroethylene  
PE - Performance evaluation  
POE - Point-of-Entry Technologies  
POU- Point-of-Use Technologies  
ppb - Parts per billion  
ppm - Parts per million  
PQL - Practical Quantitation Level  
PTA - Packed Tower Aeration  
PWS - Public water system  
RIA - Regulatory Impact Analysis  
RMCL - Recommended Maximum Contaminant Level  
RNDB - Regulations Negotiation Data Base  
RSC - Relative Source Contribution  
RSD - relative standard deviation  
SDWA - Safe Drinking Water Act, or the "Act," as amended in 1996  
SM - Standard Method  
SMCL - Secondary Maximum Contaminant Level  
SMR - Standardized mortality ratios  
SOC - Synthetic Organic Chemical  
s<sub>r</sub> - standard deviation of recovery  
SWTR- Surface Water Treatment Rule  
TCE - Trichloroethylene  
THM - Trihalomethane  
THMFP - Trihalomethane formation potential  
TMV - Tobacco mosaic virus  
TOC - Total organic carbon  
TTHM - Total trihalomethanes  
TWG - Technologies Working Group  
UV - Ultraviolet  
VOC - Volatile Organic Chemical  
WIDB - Water Industry Data Base  
WS - Water supply  
X - average percent recovery  
XDBPs - Halogenated DBPs

# WATER PROPERTIES

<p style="text-align: center; background-color: #ADD8E6; margin: 0;"><b>SURFACE TENSION</b></p>  <p style="font-size: small; margin: 5px 0;">WATER PROPERTY OF SURFACE TENSION ALLOWS TO HOLD A CERTAIN WEIGHT ON IT'S SURFACE</p>	<p style="text-align: center; background-color: #ADD8E6; margin: 0;"><b>ADHESION</b></p>  <p style="font-size: small; margin: 5px 0;">WATER'S ADHESIVE PROPERTY IS WHY WATER STICKS TO OTHER OBJECTS, LIKE A LEAF OR YOUR SKIN WHEN IT GETS WET</p>	<p style="text-align: center; background-color: #ADD8E6; margin: 0;"><b>COHESION</b></p>  <p style="font-size: small; margin: 5px 0;">WATER'S COHESIVE PROPERTY IS WHY WATER DROPLETS ARE ROUND BEFORE THEY ARE AFFECTED BY ADHESION</p>	<p style="text-align: center; background-color: #ADD8E6; margin: 0;"><b>CAPILLARY ACTION</b></p>  <p style="font-size: small; margin: 5px 0;">CAPILLARY ACTION IS AN ACTION MADE POSSIBLE BY WATER'S ADHESIVE PROPERTY AND SURFACE TENSION.</p>
<p style="text-align: center; background-color: #ADD8E6; margin: 0;"><b>NEUTRAL pH</b></p>  <p style="font-size: small; margin: 5px 0;">THE pH SCALE SHOWS HOW ACIDIC - BASIC A SUBSTANCE IS. PURE WATER HAS A NEUTRAL pH OF 7</p>	<p style="text-align: center; background-color: #ADD8E6; margin: 0;"><b>3 STATES OF MATTER</b></p>  <p style="font-size: small; margin: 5px 0;">WATER, UNLIKE ANY OTHER MATTER, CAN EXIST IN SOLID, LIQUID OR GAS FORMS</p>	<p style="text-align: center; background-color: #ADD8E6; margin: 0;"><b>HIGH HEAT CAPACITY</b></p>  <p style="font-size: small; margin: 5px 0;">WATER HAS A HIGH SPECIFIC HEAT CAPACITY, MEANING THAT IT TAKES QUITE A LOT OF ENERGY TO MAKE IT WARMER</p>	<p style="text-align: center; background-color: #ADD8E6; margin: 0;"><b>DENSITY</b></p>  <p style="font-size: small; margin: 5px 0;">WATER'S DENSITY IS SLIGHTLY LESS THAN 1g/cm<sup>3</sup></p>



## PROPERTIES OF WATER

### What is Water?

Water is the chemical substance with chemical formula  $H_2O$ : one molecule of water has two hydrogen atoms covalently bonded to a single oxygen atom. Water is a tasteless, odorless liquid at ambient temperature and pressure, and appears colorless in small quantities, although it has its own intrinsic very light blue hue. Ice also appears colorless, and water vapor is essentially invisible as a gas.

Water is primarily a liquid under standard conditions, which is not predicted from its relationship to other analogous hydrides of the oxygen family in the periodic table, which are gases such as hydrogen sulfide. The elements surrounding oxygen in the periodic table, nitrogen, fluorine, phosphorus, sulfur and chlorine, all combine with hydrogen to produce gases under standard conditions. The reason that water forms a liquid are that oxygen is more electronegative than all of these elements with the exception of fluorine.

Oxygen attracts electrons much more strongly than hydrogen, resulting in a net positive charge on the hydrogen atoms, and a net negative charge on the oxygen atom. The presence of a charge on each of these atoms gives each water molecule a net dipole moment.

Electrical attraction between water molecules due to this dipole pulls individual molecules closer together, making it more difficult to separate the molecules and therefore raising the boiling point.

## Introduction to Water Chemistry

*All these principles are good for both water and wastewater.*



**Chemistry** is a branch of physical science that studies the composition, structure, properties and change of matter. Chemistry is chiefly concerned with atoms and molecules and their interactions and transformations, for example, the properties of the chemical bonds formed between atoms to create chemical compounds.

As such, chemistry studies the involvement of electrons and various forms of energy in photochemical reactions, oxidation-reduction reactions, changes in phases of matter, and separation of mixtures. Preparation and properties of complex substances, such as alloys, polymers, biological molecules, and pharmaceutical agents are considered in specialized fields of chemistry.

Chemistry is sometimes called *the central science* because it bridges other natural sciences like physics, geology and biology. Chemistry is a branch of physical science but distinct from physics.

The etymology of the word chemistry has been much disputed. The history of chemistry can be traced to certain practices, known as alchemy, which had been practiced for several millennia in various parts of the world.

## Definition

In retrospect, the definition of chemistry has changed over time, as new discoveries and theories add to the functionality of the science. The term "chymistry", in the view of noted scientist Robert Boyle in 1661, meant the subject of the material principles of mixed bodies. In 1663 the chemist Christopher Glaser described "chymistry" as a scientific art, by which one learns to dissolve bodies, and draw from them the different substances on their composition, and how to unite them again, and exalt them to a higher perfection.

The 1730 definition of the word "chemistry", as used by Georg Ernst Stahl, meant the art of resolving mixed, compound, or aggregate bodies into their principles; and of composing such bodies from those principles. In 1837, Jean-Baptiste Dumas considered the word "chemistry" to refer to the science concerned with the laws and effects of molecular forces. This definition further evolved until, in 1947, it came to mean the science of substances: their structure, their properties, and the reactions that change them into other substances - a characterization accepted by Linus Pauling. More recently, in 1998, Professor Raymond Chang broadened the definition of "chemistry" to mean the study of matter and the changes it undergoes.

## Chemistry Subdisciplines

Chemistry is typically divided into several major sub-disciplines. There are also several main cross-disciplinary and more specialized fields of chemistry.

- Analytical chemistry is the analysis of material samples to gain an understanding of their chemical composition and structure. Analytical chemistry incorporates standardized experimental methods in chemistry. These methods may be used in all subdisciplines of chemistry, excluding purely theoretical chemistry.
- Biochemistry is the study of the chemicals, chemical reactions and chemical interactions that take place in living organisms. Biochemistry and organic chemistry are closely related, as in medicinal chemistry or neurochemistry. Biochemistry is also associated with molecular biology and genetics.
- Inorganic chemistry is the study of the properties and reactions of inorganic compounds. The distinction between organic and inorganic disciplines is not absolute and there is much overlap, most importantly in the sub-discipline of organometallic chemistry.
- Materials chemistry is the preparation, characterization, and understanding of substances with a useful function. The field is a new breadth of study in graduate programs, and it integrates elements from all classical areas of chemistry with a focus on fundamental issues that are unique to materials. Primary systems of study include the chemistry of condensed phases (solids, liquids, polymers) and interfaces between different phases.
- Neurochemistry is the study of neurochemicals; including transmitters, peptides, proteins, lipids, sugars, and nucleic acids; their interactions, and the roles they play in forming, maintaining, and modifying the nervous system.
- Nuclear chemistry is the study of how subatomic particles come together and make nuclei. Modern Transmutation is a large component of nuclear chemistry, and the table of nuclides is an important result and tool for this field.
- Organic chemistry is the study of the structure, properties, composition, mechanisms, and reactions of organic compounds. An organic compound is defined as any compound based on a carbon skeleton.
- Physical chemistry is the study of the physical and fundamental basis of chemical systems and processes. In particular, the energetics and dynamics of such systems and processes are of interest to physical chemists. Important areas of study include chemical thermodynamics, chemical kinetics, electrochemistry, statistical mechanics, spectroscopy, and more recently, astrochemistry. Physical chemistry has large overlap with molecular physics. Physical chemistry involves the use of infinitesimal calculus in deriving equations. It is usually associated with quantum chemistry and theoretical chemistry. Physical

chemistry is a distinct discipline from chemical physics, but again, there is very strong overlap.

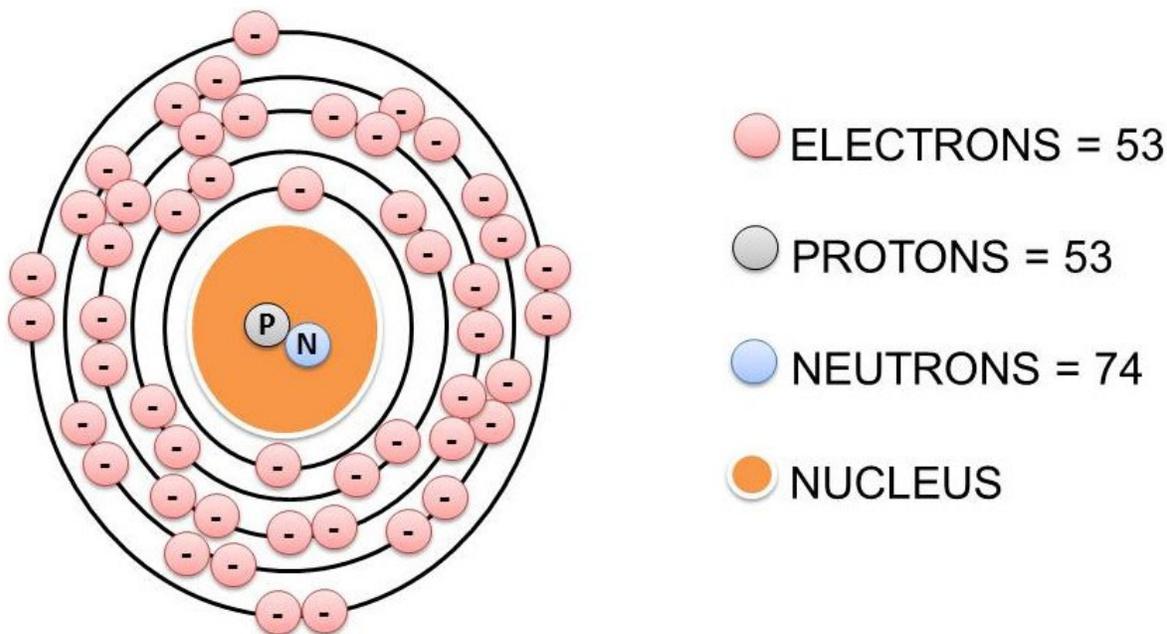
- Theoretical chemistry is the study of chemistry via fundamental theoretical reasoning (usually within mathematics or physics). In particular, the application of quantum mechanics to chemistry is called quantum chemistry. Since the end of the Second World War, the development of computers has allowed a systematic development of computational chemistry, which is the art of developing and applying computer programs for solving chemical problems. Theoretical chemistry has large overlap with (theoretical and experimental) condensed matter physics and molecular physics.

Other disciplines within chemistry are traditionally grouped by the type of matter being studied or the kind of study. These include inorganic chemistry, the study of inorganic matter; organic chemistry, the study of organic (carbon based) matter; biochemistry, the study of substances found in biological organisms; physical chemistry, the study of chemical processes using physical concepts such as thermodynamics and quantum mechanics; and analytical chemistry, the analysis of material samples to gain an understanding of their chemical composition and structure.

Many more specialized disciplines have emerged in recent years, e.g. neurochemistry the chemical study of the nervous system (see subdisciplines).

Other fields include agrochemistry, astrochemistry (and cosmochemistry), atmospheric chemistry, chemical engineering, chemical biology, chemo-informatics, electrochemistry, environmental chemistry, femtochemistry, flavor chemistry, flow chemistry, geochemistry, green chemistry, histochemistry, history of chemistry, hydrogenation chemistry, immunochemistry, marine chemistry, materials science, mathematical chemistry, mechanochemistry, medicinal chemistry, molecular biology, molecular mechanics, nanotechnology, natural product chemistry, oenology, organometallic chemistry, petrochemistry, pharmacology, photochemistry, physical organic chemistry, phytochemistry, polymer chemistry, radiochemistry, solid-state chemistry, sonochemistry, supramolecular chemistry, surface chemistry, synthetic chemistry, thermochemistry, and many others.

## Basic Chemical Structure



# IODINE

At the turn of the twentieth century the theoretical underpinnings of chemistry were finally understood due to a series of remarkable discoveries that succeeded in probing and discovering the very nature of the internal structure of atoms.

In 1897, J. J. Thomson of Cambridge University discovered the electron and soon after the French scientist Becquerel as well as the couple Pierre and Marie Curie investigated the phenomenon of radioactivity.

In a series of pioneering scattering experiments Ernest Rutherford at the University of Manchester discovered the internal structure of the atom and the existence of the proton, classified and explained the different types of radioactivity and successfully transmuted the first element by bombarding nitrogen with alpha particles.

His work on atomic structure was improved on by his students, the Danish physicist Niels Bohr and Henry Moseley. The electronic theory of chemical bonds and molecular orbitals was developed by the American scientists Linus Pauling and Gilbert N. Lewis.

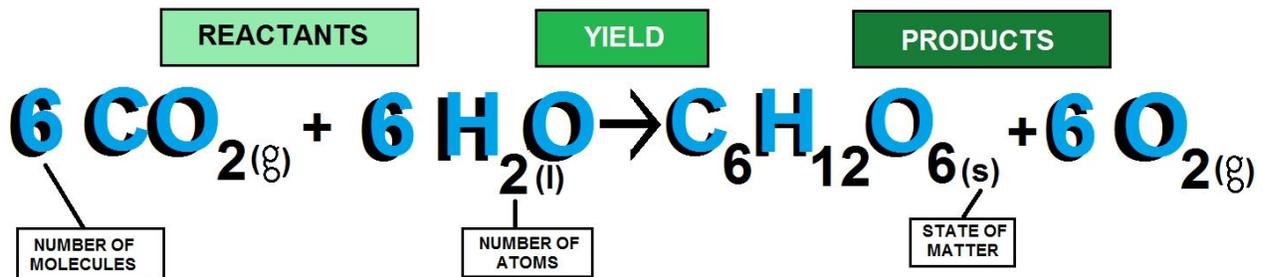
## Commonly found Chemical Types

Many chemicals are commonly available in pure form. Others are available as reagents - inexpensive, convenient sources of chemicals with a bit of processing.

This is convenient for both amateur and professional chemistry work. Common reagents include:

- Metal oxides and carbonates (widely used in pottery)
- Organic acids (used for home brewing)
- Solvents and acids (used in cleaning materials and other hardware applications)
- Photographic chemicals, such as silver nitrate
- Single-chemical fertilizers, such as potassium nitrate (used in agricultural supply)
- Chlorinating agents, such as calcium hypochlorite (used in swimming pool and water purification)
- Mordants, such as potassium dichromate (used in arts and crafts)
- A *chemical substance* is a form of matter that has constant chemical composition and characteristic properties. It cannot be separated into components by physical separation methods, i.e. without breaking chemical bonds. Chemical substances can be chemical elements, chemical compounds, ions or alloys.
- Chemical substances are often called 'pure' to set them apart from mixtures. A common example of a chemical substance is pure water; it has the same properties and the same ratio of hydrogen to oxygen whether it is isolated from a river or made in a laboratory. Other chemical substances commonly encountered in pure form are diamond (carbon), gold, table salt (sodium chloride) and refined sugar (sucrose). However, in practice, no substance is entirely pure, and chemical purity is specified according to the intended use of the chemical.
- Chemical substances exist as solids, liquids, gases or plasma, and may change between these phases of matter with changes in temperature or pressure. Chemical reactions convert one chemical substance into another.
- Forms of energy, such as light and heat, are not considered to be matter, and thus they are not "substances" in this regard.
- Chemical substances (also called pure substances) may well be defined as "any material with a definite chemical composition" in an introductory general chemistry textbook. According to this definition a chemical substance can either be a pure chemical element or a pure chemical compound. But, there are exceptions to this definition; a pure substance can also be defined as a form of matter that has both definite composition and distinct properties. The chemical substance index published by CAS also includes several alloys of uncertain composition. Non-stoichiometric compounds are a special case (in inorganic chemistry) that violates the law of constant composition, and for them, it is sometimes difficult to draw the line between a mixture and a compound, as in the case of palladium hydride.
- In geology, substances of uniform composition are called minerals, while physical mixtures (aggregates) of several minerals (different substances) are defined as rocks.

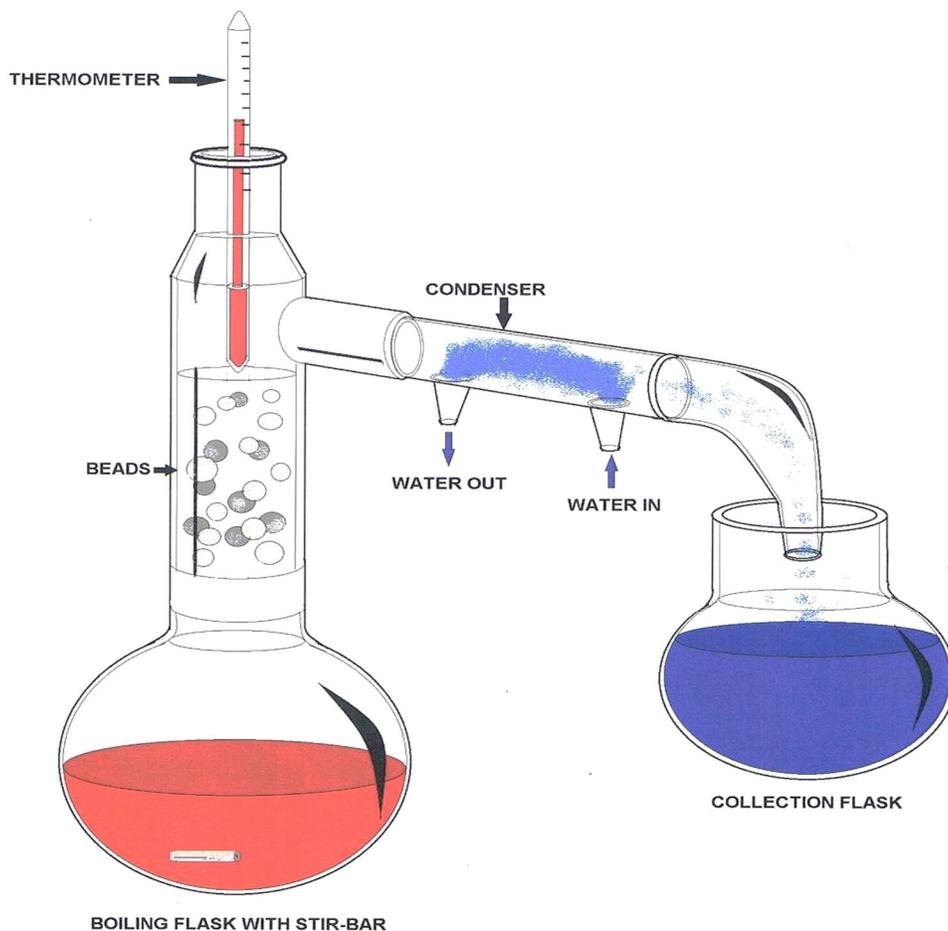
- Many minerals, however, mutually dissolve into solid solutions, such that a single rock is a uniform substance despite being a mixture in stoichiometric terms. Feldspars are a common example: anorthoclase is an alkali aluminum silicate, where the alkali metal is interchangeably either sodium or potassium



## CHEMICAL EQUATION (How to balance)

## Principles of Modern Chemistry

The current model of atomic structure is the quantum mechanical model. Traditional chemistry starts with the study of elementary particles, atoms, molecules, substances, metals, crystals and other aggregates of matter. This matter can be studied in solid, liquid, or gas states, in isolation or in combination. The interactions, reactions and transformations that are studied in chemistry are usually the result of interactions between atoms, leading to rearrangements of the chemical bonds which hold atoms together. Such behaviors are studied in a chemistry laboratory.



The chemistry laboratory stereotypically uses various forms of laboratory glassware. However glassware is not central to chemistry and a great deal of experimental (as well as applied/industrial) chemistry is done without it.

A chemical reaction is a transformation of some substances into one or more different substances. The basis of such a chemical transformation is the rearrangement of electrons in the chemical bonds between atoms. It can be symbolically depicted through a chemical equation, which usually involves atoms as subjects. The number of atoms on the left and the right in the equation for a chemical transformation is equal. (When the number of atoms on either side is unequal, the transformation is referred to as a nuclear reaction or radioactive decay.) The type of chemical reactions a substance may undergo and the energy changes that may accompany it are constrained by certain basic rules, known as chemical laws.

Energy and entropy considerations are invariably important in almost all chemical studies. Chemical substances are classified in terms of their structure, phase, as well as their chemical compositions. They can be analyzed using the tools of chemical analysis, e.g. spectroscopy and chromatography. Scientists engaged in chemical research are known as chemists. Most chemists specialize in one or more sub-disciplines.

## Matter

In chemistry, matter is defined as anything that has rest mass and volume (it takes up space) and is made up of particles. The particles that make up matter have rest mass as well - not all particles have rest mass, such as the photon. Matter can be a pure chemical substance or a mixture of substances.

### Periodic Table of the Elements

**Element Categories**

- alkali metals
- alkaline metals
- other metals
- transition metals
- lanthanoids
- actinoids
- metalloids
- nonmetals
- halogens
- noble gases
- unknown elements

**Electron Configuration Blocks**

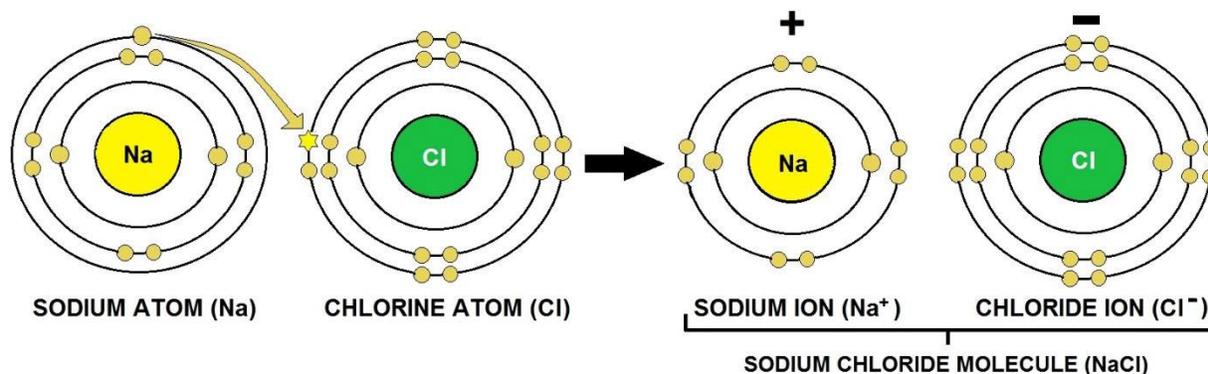
s, d, p, f

**Callout for Iron (Fe):**  
 atomic number: 26  
 chemical symbol: Fe  
 chemical name: iron  
 standard atomic weight: 55.85  
 (lower - upper bounds shown for noble isotopes)

GROUP	1	2											13	14	15	16	17	18	
PERIOD 1	1 <b>H</b> hydrogen [1.0078 - 1.0081]																	2 <b>He</b> helium 4.001	
2	3 <b>Li</b> lithium [6.938 - 6.937]	4 <b>Be</b> beryllium 9.012											5 <b>B</b> boron [10.806 - 10.812]	6 <b>C</b> carbon [12.009 - 12.011]	7 <b>N</b> nitrogen [14.006 - 14.013]	8 <b>O</b> oxygen [15.999 - 15.995]	9 <b>F</b> fluorine 18.998	10 <b>Ne</b> neon 20.18	
3	11 <b>Na</b> sodium [22.989 - 22.99]	12 <b>Mg</b> magnesium 24.31											13 <b>Al</b> aluminum [26.981 - 26.982]	14 <b>Si</b> silicon [28.085 - 28.086]	15 <b>P</b> phosphorus 30.97	16 <b>S</b> sulfur [32.059 - 32.061]	17 <b>Cl</b> chlorine [35.446 - 35.448]	18 <b>Ar</b> argon 39.95	
4	19 <b>K</b> potassium 39.10	20 <b>Ca</b> calcium 40.08	21 <b>Sc</b> scandium 44.96	22 <b>Ti</b> titanium 47.87	23 <b>V</b> vanadium 50.94	24 <b>Cr</b> chromium 52.00	25 <b>Mn</b> manganese 54.94	26 <b>Fe</b> iron 55.85	27 <b>Co</b> cobalt 58.93	28 <b>Ni</b> nickel 58.69	29 <b>Cu</b> copper 63.55	30 <b>Zn</b> zinc 65.38	31 <b>Ga</b> gallium 69.72	32 <b>Ge</b> germanium 72.63	33 <b>As</b> arsenic 74.92	34 <b>Se</b> selenium 78.96	35 <b>Br</b> bromine 79.90	36 <b>Kr</b> krypton 83.80	
5	37 <b>Rb</b> rubidium 85.47	38 <b>Sr</b> strontium 87.62	39 <b>Y</b> yttrium 88.91	40 <b>Zr</b> zirconium 91.22	41 <b>Nb</b> niobium 92.91	42 <b>Mo</b> molybdenum 95.94	43 <b>Tc</b> technetium (98)	44 <b>Ru</b> ruthenium 101.1	45 <b>Rh</b> rhodium 102.9	46 <b>Pd</b> palladium 106.4	47 <b>Ag</b> silver 107.9	48 <b>Cd</b> cadmium 112.4	49 <b>In</b> indium 114.8	50 <b>Sn</b> tin 118.7	51 <b>Sb</b> antimony 121.8	52 <b>Te</b> tellurium 127.6	53 <b>I</b> iodine 126.9	54 <b>Xe</b> xenon 131.3	
6	55 <b>Cs</b> cesium 132.9	56 <b>Ba</b> barium 137.3	57-71 lanthanoids	72 <b>Hf</b> hafnium 178.5	73 <b>Ta</b> tantalum 180.9	74 <b>W</b> tungsten 183.8	75 <b>Re</b> rhenium 186.2	76 <b>Os</b> osmium 190.2	77 <b>Ir</b> iridium 192.2	78 <b>Pt</b> platinum 195.1	79 <b>Au</b> gold 197.0	80 <b>Hg</b> mercury 200.6	81 <b>Tl</b> thallium [204.3 - 204.4]	82 <b>Pb</b> lead 207.2	83 <b>Bi</b> bismuth 208.9	84 <b>Po</b> polonium (209)	85 <b>At</b> astatine (210)	86 <b>Rn</b> radon (222)	
7	87 <b>Fr</b> francium (223)	88 <b>Ra</b> radium (226)	89-103 actinoids	104 <b>Rf</b> rutherfordium (261)	105 <b>Db</b> dubnium (262)	106 <b>Sg</b> seaborgium (263)	107 <b>Bh</b> bohrium (264)	108 <b>Hs</b> hassium (277)	109 <b>Mt</b> meitnerium (268)	110 <b>Ds</b> darmstadtium (271)	111 <b>Rg</b> roentgenium (272)	112 <b>Cn</b> copernicium (285)	113 <b>Uut</b> ununtrium (284)	114 <b>Uuq</b> ununquadium (289)	115 <b>Uup</b> ununpentium (288)	116 <b>Uuh</b> ununhexium (292)	117 <b>Uus</b> ununseptium (293)	118 <b>Uuo</b> ununoctium (294)	
Natural Occurrence																			
<input type="checkbox"/>	primordial																		
<input type="checkbox"/>	from decay																		
<input type="checkbox"/>	synthetic																		
	57 <b>La</b> lanthanum 138.9	58 <b>Ce</b> cerium 140.1	59 <b>Pr</b> praseodymium 140.9	60 <b>Nd</b> neodymium 144.2	61 <b>Pm</b> promethium (145)	62 <b>Sm</b> samarium 150.4	63 <b>Eu</b> europium 151.9	64 <b>Gd</b> gadolinium 157.3	65 <b>Tb</b> terbium 158.9	66 <b>Dy</b> dysprosium 162.5	67 <b>Ho</b> holmium 164.9	68 <b>Er</b> erbium 167.3	69 <b>Tm</b> thulium 168.9	70 <b>Yb</b> ytterbium 173.1	71 <b>Lu</b> lutetium 174.9				
	89 <b>Ac</b> actinium (227)	90 <b>Th</b> thorium 232.0	91 <b>Pa</b> protactinium 231.0	92 <b>U</b> uranium 238.0	93 <b>Np</b> neptunium (237)	94 <b>Pu</b> plutonium (244)	95 <b>Am</b> americium (243)	96 <b>Cm</b> curium (247)	97 <b>Bk</b> berkelium (247)	98 <b>Cf</b> californium (251)	99 <b>Es</b> einsteinium (252)	100 <b>Fm</b> fermium (257)	101 <b>Md</b> mendelevium (258)	102 <b>No</b> nobelium (259)	103 <b>Lr</b> lawrencium (260)				

## Understanding the Atom

The atom is the basic unit of chemistry. It consists of a dense core called the atomic nucleus surrounded by a space called the electron cloud. The nucleus is made up of positively charged protons and uncharged neutrons (together called nucleons), while the electron cloud consists of negatively-charged electrons which orbit the nucleus. In a neutral atom, the negatively-charged electrons balance out the positive charge of the protons. The nucleus is dense; the mass of a nucleon is 1,836 times that of an electron, yet the radius of an atom is about 10,000 times that of its nucleus.



The atom is also the smallest entity that can be envisaged to retain the chemical properties of the element, such as electronegativity, ionization potential, preferred oxidation state(s), coordination number, and preferred types of bonds to form (e.g., metallic, ionic, covalent).

### Element

Standard form of the periodic table of chemical elements. The colors represent different categories of elements.

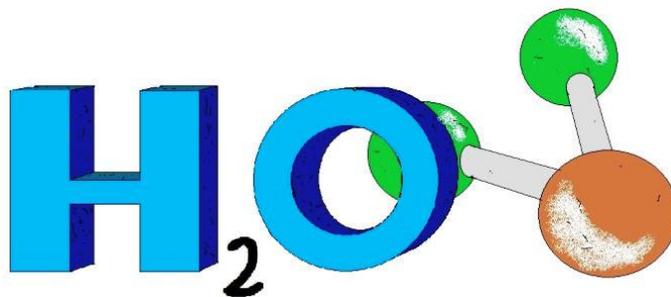
A chemical element is a pure substance which is composed of a single type of atom, characterized by its particular number of protons in the nuclei of its atoms, known as the atomic number and represented by the symbol  $Z$ . The mass number is the sum of the number of protons and neutrons in a nucleus. Although all the nuclei of all atoms belonging to one element will have the same atomic number, they may not necessarily have the same mass number; atoms of an element which have different mass numbers are known as isotopes. For example, all atoms with 6 protons in their nuclei are atoms of the chemical element carbon, but atoms of carbon may have mass numbers of 12 or 13.

The standard presentation of the chemical elements is in the periodic table, which orders elements by atomic number. The periodic table is arranged in groups, or columns, and periods, or rows. The periodic table is useful in identifying periodic trends.

### Compound

A *compound* is a pure chemical substance composed of more than one element. The properties of a compound bear little similarity to those of its elements. The standard nomenclature of compounds is set by the International Union of Pure and Applied Chemistry (IUPAC). Organic compounds are named according to the organic nomenclature system.

Inorganic compounds are named according to the inorganic nomenclature system. In addition the Chemical Abstracts Service has devised a method to index chemical substances. In this scheme each chemical substance is identifiable by a number known as its CAS registry number.



Water (H<sub>2</sub>O), an example of a chemical compound

## Chemical Compounds

A pure chemical compound is a chemical substance that is composed of a particular set of molecules or ions. Two or more elements combined into one substance through a chemical reaction form a chemical compound. All compounds are substances, but not all substances are compounds.

A chemical compound can be either atoms bonded together in molecules or crystals in which atoms, molecules or ions form a crystalline lattice.

Compounds based primarily on carbon and hydrogen atoms are called organic compounds, and all others are called inorganic compounds. Compounds containing bonds between carbon and a metal are called organometallic compounds.

Compounds in which components share electrons are known as covalent compounds. Compounds consisting of oppositely charged ions are known as ionic compounds, or salts.

In organic chemistry, there can be more than one chemical compound with the same composition and molecular weight. Generally, these are called isomers. Isomers usually have substantially different chemical properties, may be isolated and do not spontaneously convert to each other.

A common example is glucose vs. fructose. The former is an aldehyde, the latter is a ketone. Their interconversion requires either enzymatic or acid-base catalysis. However, there are also tautomers, where isomerization occurs spontaneously, such that a pure substance cannot be isolated into its tautomers.

A common example is glucose, which has open-chain and ring forms. One cannot manufacture pure open-chain glucose because glucose spontaneously cyclizes to the hemiacetal form. Materials may also comprise other entities such as polymers. These may be inorganic or organic and sometimes a combination of inorganic and organic.

## Solute – Solution

A solute is a substance that can be dissolved by a solvent to create a solution. A solute can come in many forms. It can be gas, liquid, or solid. The solvent, or substance that dissolves the solute, breaks the solute apart and distributes the solute molecules equally. This creates a *homogenous mixture*, or solution that is equal throughout.

Solutes in solution are measured by their *concentration*. The concentration of a solute is the amount of solute divided by the total volume of solution. A solvent can dilute various amounts of solute, depending on how strong of a solvent is used and how easily the solute molecules come apart. This property of solutes to dissolve in a solvent is known as *solubility*.

### Oxygen in Seawater

An example of a gaseous solute is oxygen. Every fish in the ocean, from the strange creatures in the deepest parts of the ocean to the common coral-dwelling fish that scuba divers love, rely on oxygen dissolved in the water to live. The oxygen, which exists as O<sub>2</sub>, is a polar molecule. As such, the polar water molecules have a natural tendency to attract the oxygen. As the waves mix air into the ocean and the surface of the ocean and atmosphere interact, oxygen is dissolved into the water. The process of diffusion carries the oxygen through the water column, delivering oxygen to organisms throughout the ocean.

In some situations, the organisms in the ocean can use the oxygen in the water faster than it can be diffused into the water. This can happen when excess nutrient runoff from humans runs into the ocean. The nutrients, which are another solute in water, allow huge *algal blooms* to grow. These blooms contain far too many algae. The algae in the lower layers start to die, and bacteria start to consume them. Between the algae and the bacteria, all of the oxygen gets used up. This creates a dead zone in the water column. If fish start to swim through this column, they could suffocate from lack of oxygen.

## Mole

The **mole** (symbol: **mol**) is the unit of measurement for amount of substance in the International System of Units (SI). It is defined as exactly  $6.02214076 \times 10^{23}$  constitutive particles, which may be atoms, molecules, ions, or electrons.

The definition was adopted in November 2018 as one of the seven SI base units, revising the previous definition that specified it as the number of atoms in 12 grams of carbon-12 (<sup>12</sup>C), an isotope of carbon.

The number  $6.02214076 \times 10^{23}$  (the Avogadro number) was chosen so that the mass of one mole of a chemical compound, in grams, is numerically equal (for all practical purposes) to the average mass of one molecule of the compound, in daltons. Thus, for example, one mole of water contains  $6.02214076 \times 10^{23}$  molecules, whose total mass is about 18.015 grams – and the mean mass of one molecule of water is about 18.015 daltons.

The mole is widely used in chemistry as a convenient way to express amounts of reactants and products of chemical reactions. For example, the chemical equation  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$  can be interpreted to mean that 2 mol dihydrogen (H<sub>2</sub>) and 1 mol dioxygen (O<sub>2</sub>) react to form 2 mol water (H<sub>2</sub>O). The mole may also be used to represent the number of atoms, ions, or other entities in a given sample of a substance. The concentration of a solution is commonly expressed by its molarity, defined as the amount of dissolved substance per unit volume of solution, for which the unit typically used is moles per liter (mol/l), commonly abbreviated M.

The term **gram-molecule** (g mol) was formerly used for "mole of molecules", and **gram-atom** (g atom) for "mole of atoms". For example, 1 mole of  $\text{MgBr}_2$  is 1 gram-molecule of  $\text{MgBr}_2$  but 3 gram-atoms of  $\text{MgBr}_2$

## Molarity- Molar Mass -Concentration

Molarity is a chemical term that refers to the amount of a substance, usually a solute or solvent, that exists in a given volume of solution, and is more commonly known by terms such as molar mass or simply concentration. The reference is based on the basic molecular unit of the mol, mole, or gram molecule, which is loosely defined as the molecular weight of a chemical element or compound expressed in grams. Molecular weights vary from substance to substance as they are based upon the sum of the weight of all of the atoms that bind together to make up basic molecules for the substance.

Calculating molarity in most instances in chemistry uses a base number of 12 as a reference point, with the isotope carbon-12 being the foundation for an atomic mass unit. A simple molarity formula as an example would be a combination of two hydrogen atoms that bind together in nature to form hydrogen-2, or deuterium, which has a molarity of two. Since the formula to calculate molarity must take into account the three dimensions present in a volume, molarity is expressed either as mols per cubic meter in standard international units, or as mols per liter, and a basic molar mass is defined as one mol per liter.

## Normality or N

The normality of a solution is the gram equivalent weight of a solute per liter of solution. It may also be called the equivalent concentration. It is indicated using the symbol N, eq/L, or meq/L (= 0.001 N) for units of concentration.

For example, the concentration of a hydrochloric acid solution might be expressed as 0.1 N HCl. A gram equivalent weight or equivalent is a measure of the reactive capacity of a given chemical species (ion, molecule, etc.). The equivalent value is determined using the molecular weight and valence of the chemical species. Normality is the only concentration unit that is reaction dependent.

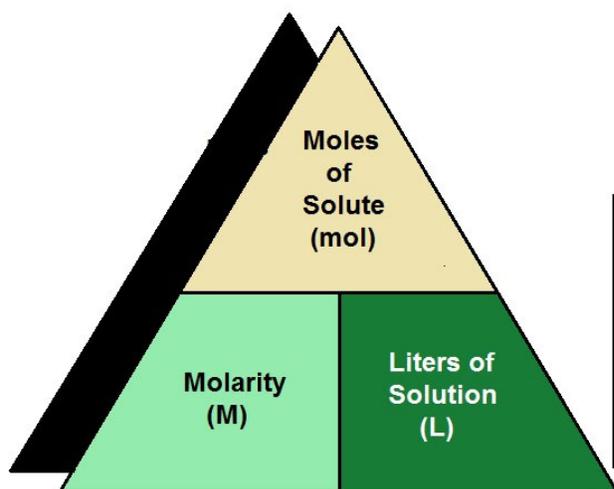
Examples of how to calculate the normality of a solution.

- Normality is a unit of concentration of a chemical solution expressed as gram equivalent weight of solute per liter of solution. A defined equivalence factor must be used to express concentration.
- Common units of normality include N, eq/L, or meq/L.
- Normality is the only unit of chemical concentration that depends on the chemical reaction being studied.
- Normality is not the most common unit of concentration, nor is its use appropriate for all chemical solutions. Typical situations when you might use normality include acid-base chemistry, redox reactions, or precipitation reactions. For most other situations, molarity or molality are better options for units.

## Common Water Treatment Chemicals

Chemical Name	Common Name	Chemical Formula
Aluminum hydroxide		Al(OH) <sub>3</sub>
Aluminum sulfate	Alum, liquid	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 14(H <sub>2</sub> O)
Ammonia		NH <sub>3</sub>
Ammonium		NH <sub>4</sub>
Bentonitic clay	Bentonite	
Calcium bicarbonate		Ca(HCO <sub>3</sub> ) <sub>2</sub>
Calcium carbonate	Limestone	CaCO <sub>3</sub>
Calcium chloride		CaCl <sub>2</sub>
Calcium Hypochlorite	HTH	Ca(OCl) <sub>2</sub> · 4H <sub>2</sub> O
Calcium hydroxide	Slaked Lime	Ca(OH) <sub>2</sub>
Calcium oxide	Unslaked (Quicklime)	CaO
Calcium sulfate	Gypsum	CaSO <sub>4</sub>
Carbon	Activated Carbon	C
Carbon dioxide		CO <sub>2</sub>
Carbonic acid		H <sub>2</sub> CO <sub>3</sub>
Chlorine gas		Cl <sub>2</sub>
Chlorine Dioxide		ClO <sub>2</sub>
Copper sulfate	Blue vitriol	CuSO <sub>4</sub> · 5H <sub>2</sub> O
Dichloramine		NHCl <sub>2</sub>
Ferric chloride	Iron chloride	FeCl <sub>3</sub>
Ferric hydroxide		Fe(OH) <sub>3</sub>
Ferric sulfate	Iron sulfate	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
Ferrous bicarbonate		Fe(HCO <sub>3</sub> ) <sub>2</sub>
Ferrous hydroxide		Fe(OH) <sub>2</sub>
Ferrous sulfate	Copperas	FeSO <sub>4</sub> · 7H <sub>2</sub> O
Hydrofluorsilicic acid		H <sub>2</sub> SiF <sub>6</sub>
Hydrochloric acid	Muriatic acid	HCl
Hydrogen sulfide		H <sub>2</sub> S
Hypochlorous acid		HOCl
Magnesium bicarbonate		Mg(HCO <sub>3</sub> ) <sub>2</sub>
Magnesium carbonate		MgCO <sub>3</sub>
Magnesium chloride		MgCl <sub>2</sub>
Magnesium hydroxide		Mg(OH) <sub>2</sub>
Magnesium dioxide		MgO <sub>2</sub>
Manganous bicarbonate		Mn(HCO <sub>3</sub> ) <sub>2</sub>
Manganous sulfate		MnSO <sub>4</sub>
Monochloramine		NH <sub>2</sub> Cl
Potassium bicarbonate		KHCO <sub>3</sub>

Chemical Name	Common Name	Chemical Formula
Sodium carbonate	Soda ash	Na <sub>2</sub> CO <sub>3</sub>
Sodium chloride	Salt	NaCl
Sodium chlorite		NaClO <sub>2</sub>
Sodium fluoride		NaF
Sodium fluorsilicate		Na <sub>2</sub> SiF <sub>6</sub>
Sodium hydroxide	Lye	NaOH
Sodium hypochlorite		NaOCl
Sodium Metaphosphate	Hexametaphosphate	NaPO <sub>3</sub>
Sodium phosphate	Disodium phosphate	Na <sub>3</sub> PO <sub>4</sub>
Sodium sulfate		Na <sub>2</sub> SO <sub>4</sub>
Sulfuric acid		H <sub>2</sub> SO <sub>4</sub>



#### CALCULATING MOLARITY

Moles = Molarity x Liters  
 Molarity = Moles / Liters  
 Liters = Moles / Molarity

$$\text{MOLARITY} = \frac{\text{Number of Moles}}{\text{Liters of Solution}}$$

OR

$$M = n/v = \frac{\text{Number of Moles}}{\text{Volume}}$$

## CHEMICAL MOLARITY

Number	Element	Valence
1	Hydrogen	(-1), +1
2	Helium	0
3	Lithium	+1
4	Beryllium	+2
5	Boron	-3, +3
6	Carbon	(+2), +4
7	Nitrogen	-3, -2, -1, (+1), +2, +3, +4, +5
8	Oxygen	-2
9	Fluorine	-1, (+1)
10	Neon	0
11	Sodium	+1
12	Magnesium	+2
13	Aluminum	+3
14	Silicon	-4, (+2), +4
15	Phosphorus	-3, +1, +3, +5
16	Sulfur	-2, +2, +4, +6
17	Chlorine	-1, +1, (+2), +3, (+4), +5, +7
18	Argon	0
19	Potassium	+1
20	Calcium	+2
21	Scandium	+3
22	Titanium	+2, +3, +4
23	Vanadium	+2, +3, +4, +5
24	Chromium	+2, +3, +6
25	Manganese	+2, (+3), +4, (+6), +7
26	Iron	+2, +3, (+4), (+6)
27	Cobalt	+2, +3, (+4)
28	Nickel	(+1), +2, (+3), (+4)
29	Copper	+1, +2, (+3)
30	Zinc	+2
31	Gallium	(+2), +3
32	Germanium	-4, +2, +4
33	Arsenic	-3, (+2), +3, +5
34	Selenium	-2, (+2), +4, +6
35	Bromine	-1, +1, (+3), (+4), +5
36	Krypton	0
37	Rubidium	+1
38	Strontium	+2
39	Yttrium	+3
40	Zirconium	(+2), (+3), +4
41	Niobium	(+2), +3, (+4), +5
42	Molybdenum	(+2), +3, (+4), (+5), +6
43	Technetium	+6
44	Rubidium	(+2), +3, +4, (+6), (+7), +8
45	Rhodium	(+2), (+3), +4, (+6)
46	Palladium	+2, +4, (+6)
47	Silver	+1, (+2), (+3)

48	Cadmium	(+1), +2
49	Indium	(+1), (+2), +3
50	Tin	+2, +4
51	Antimony	-3, +3, (+4), +5
52	Tellurium	-2, (+2), +4, +6
53	Iodine	-1, +1, (+3), (+4), +5, +7
54	Xenon	0
55	Cesium	+1
56	Barium	+2
57	Lanthanum	+3
58	Cerium	+3, +4
59	Praseodymium	+3
60	Neodymium	+3, +4
61	Promethium	+3
62	Samarium	(+2), +3
63	Europium	(+2), +3
64	Gadolinium	+3
65	Terbium	+3, +4
66	Dysprosium	+3
67	Holmium	+3
68	Erbium	+3
69	Thulium	(+2), +3
70	Ytterbium	(+2), +3
71	Lutetium	+3
72	Hafnium	+4
73	Tantalum	(+3), (+4), +5
74	Tungsten	(+2), (+3), (+4), (+5), +6
75	Rhenium	(-1), (+1), +2, (+3), +4, (+5), +6, +7
76	Osmium	(+2), +3, +4, +6, +8
77	Iridium	(+1), (+2), +3, +4, +6
78	Platinum	(+1), +2, (+3), +4, +6
79	Gold	+1, (+2), +3
80	Mercury	+1, +2
81	Thallium	+1, (+2), +3
82	Lead	+2, +4
83	Bismuth	(-3), (+2), +3, (+4), (+5)
84	Polonium	(-2), +2, +4, (+6)
85	Astatine	?
86	Radon	0
87	Francium	?
88	Radium	+2
89	Actinium	+3
90	Thorium	+4
91	Protactinium	+5
92	Uranium	(+2), +3, +4, (+5), +6

<b>Common Used Products</b>	<b>Chemical Name</b>
acetone	dimethyl ketone
acid of sugar	oxalic acid
alcohol, grain	ethyl alcohol
alcohol, wood	methyl alcohol
alum	aluminum potassium sulfate
alumina	aluminum oxide
antichlor	sodium thiosulfate
aqua ammonia	aqueous solution of ammonium hydroxide
aqua regia	nitrohydrochloric acid
aqua fortis	nitric acid
aromatic spirit of ammonia	ammonia in alcohol
asbestos	magnesium silicate
aspirin	acetylsalicylic acid
baking soda	sodium bicarbonate
banana oil (artificial)	isoamyl acetate
benzol	benzene
bichloride of mercury	mercuric chloride
black copper oxide	cupric oxide
black lead	graphite (carbon)
bleaching powder	chlorinated lime
blue vitriol	copper sulfate
bluestone	copper sulfate
borax	sodium borate
brimstone	sulfur
brine	aqueous sodium chloride solution
butter of antimony	antimony trichloride
butter of tin	anhydrous stannic chloride
calomel	mercury chloride
carbolic acid	phenol
carbonic acid gas	carbon dioxide
caustic potash	potassium hydroxide
caustic soda	sodium hydroxide
chalk	calcium carbonate
Chile saltpeter	sodium nitrate
chrome, alum	chromic potassium sulfate
chrome, yellow	lead (VI) chromate
copperas	ferrous sulfate
cream of tartar	potassium bitartrate
crocus powder	ferric oxide
emery powder	impure aluminum oxide
Epsom salts	magnesium sulfate
ethanol	ethyl alcohol
fluorspar	natural calcium fluoride
formalin	aqueous formaldehyde solution
French chalk	natural magnesium silicate
galena	natural lead sulfide
Glauber's salt	sodium sulfate
gypsum	natural calcium sulfate

hydrocyanic acid	hydrogen cyanide
hypo (photography)	sodium thiosulfate solution
lime	calcium oxide
limewater	aqueous solution of calcium hydroxide
lunar caustic	silver nitrate
magnesia	magnesium oxide
mercury oxide, black	mercurous oxide
methanol	methyl alcohol
methylated spirits	methyl alcohol
muriatic acid	hydrochloric acid
oil of vitriol	sulfuric acid
oil of wintergreen (artificial)	methyl salicylate
Paris green	copper acetoarsenite
Paris white	powdered calcium carbonate
pear oil (artificial)	isoamyl acetate
pearl ash	potassium carbonate
plaster of Paris	calcium sulfate
plumbago	graphite
potash	potassium carbonate
potassa	potassium hydroxide
Prussic acid	hydrogen cyanide
pyro	tetrasodium pyrophosphate
quicklime	calcium oxide
quicksilver	mercury
red lead	lead tetraoxide
Rochelle salt	potassium sodium tartrate
rouge, jeweler's	ferric oxide
rubbing alcohol	isopropyl alcohol
sal ammoniac	ammonium chloride
sal soda	sodium carbonate
salt, table	sodium chloride
salt of lemon	potassium binoxalate
salt of tartar	potassium carbonate
saltpeter	potassium nitrate
silica	silicon dioxide
soda ash	sodium carbonate
soda lye	sodium hydroxide
soluble glass	sodium silicate
spirit of hartshorn	ammonium hydroxide solution
sugar, table	sucrose
talc or talcum	magnesium silicate
vinegar	impure dilute acetic acid
vitamin C	ascorbic acid
washing soda	sodium carbonate
water glass	sodium silicate

## Substances versus Mixtures

All matter consists of various elements and chemical compounds, but these are often intimately mixed together. Mixtures contain more than one chemical substance, and they do not have a fixed composition. In principle, they can be separated into the component substances by purely mechanical processes. Butter, soil and wood are common examples of mixtures.

Grey iron metal and yellow sulfur are both chemical elements, and they can be mixed together in any ratio to form a yellow-grey mixture. No chemical process occurs, and the material can be identified as a mixture by the fact that the sulfur and the iron can be separated by a mechanical process, such as using a magnet to attract the iron away from the sulfur.

In contrast, if iron and sulfur are heated together in a certain ratio (1 atom of iron for each atom of sulfur, or by weight, 56 grams (1 mol) of iron to 32 grams (1 mol) of sulfur), a chemical reaction takes place and a new substance is formed, the compound iron(II) sulfide, with chemical formula FeS. The resulting compound has all the properties of a chemical substance and is not a mixture. Iron(II) sulfide has its own distinct properties such as melting point and solubility, and the two elements cannot be separated using normal mechanical processes; a magnet will be unable to recover the iron, since there is no metallic iron present in the compound.

### Chemicals Versus Chemical Substances

While the term *chemical substance* is a precise technical term that is synonymous with "chemical" for professional chemists, the meaning of the word *chemical* varies for non-chemists within the English speaking world or those using English.

For industries, government and society in general in some countries, the word *chemical* includes a wider class of substances that contain many mixtures of such chemical substances, often finding application in many vocations. In countries that require a list of ingredients in products, the "chemicals" listed would be equated with "chemical substances".

Within the chemical industry, manufactured "chemicals" are chemical substances, which can be classified by production volume into bulk chemicals, fine chemicals and chemicals found in research only:

- Bulk chemicals are produced in very large quantities, usually with highly optimized continuous processes and to a relatively low price.
- Fine chemicals are produced at a high cost in small quantities for special low-volume applications such as biocides, pharmaceuticals and specialty chemicals for technical applications.
- Research chemicals are produced individually for research, such as when searching for synthetic routes or screening substances for pharmaceutical activity. In effect, their price per gram is very high, although they are not sold.

The cause of the difference in production volume is the complexity of the molecular structure of the chemical. Bulk chemicals are usually much less complex.

While fine chemicals may be more complex, many of them are simple enough to be sold as "building blocks" in the synthesis of more complex molecules targeted for single use, as named above.

The *production* of a chemical includes not only its synthesis but also its purification to eliminate by-products and impurities involved in the synthesis. The last step in production should be the analysis of batch lots of chemicals in order to identify and quantify the percentages of impurities for the buyer of the chemicals.

The required purity and analysis depends on the application, but higher tolerance of impurities is usually expected in the production of bulk chemicals. Thus, the user of the chemical in the US might choose between the bulk or "technical grade" with higher amounts of impurities or a much purer "pharmaceutical grade" (labeled "USP", United States Pharmacopeia).

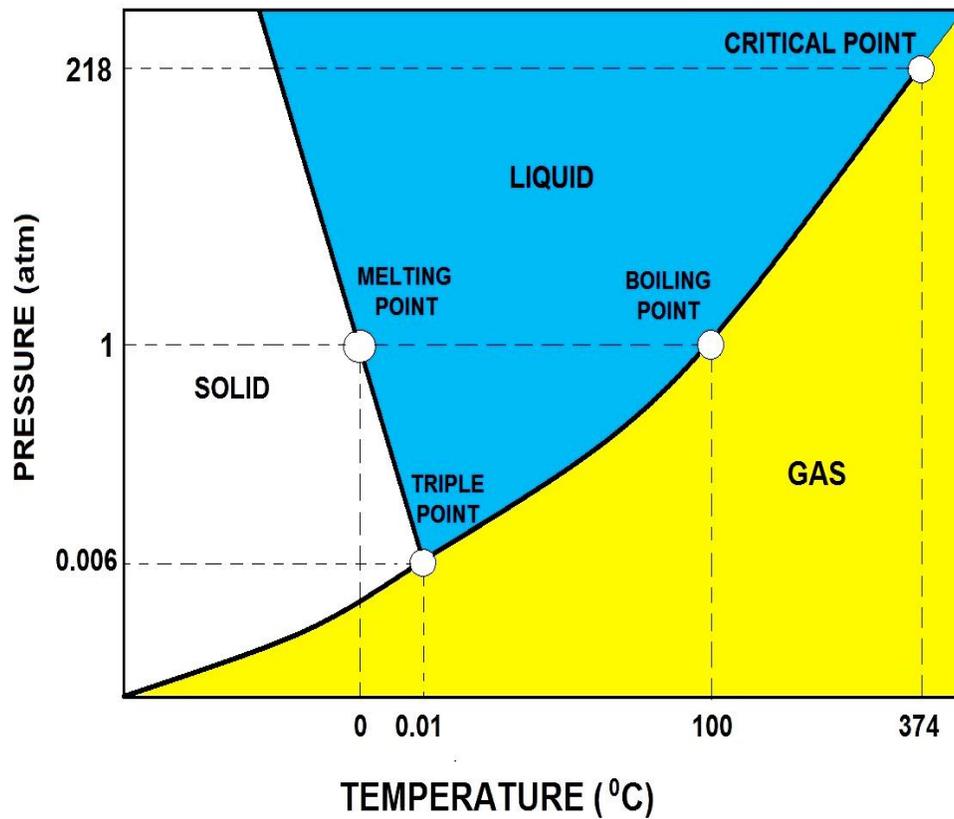
### **Naming and Indexing**

Every chemical substance has one or more systematic names, usually named according to the IUPAC rules for naming. An alternative system is used by the Chemical Abstracts Service (CAS).

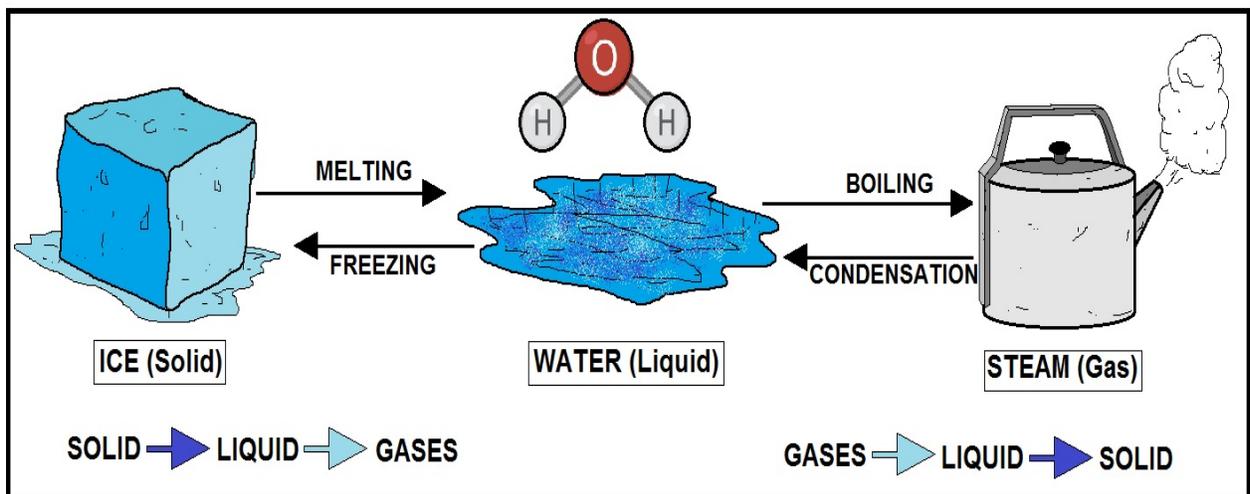
Many compounds are also known by their more common, simpler names, many of which predate the systematic name. For example, the long-known sugar glucose is now systematically named 6-(hydroxymethyl)oxane-2,3,4,5-tetrol. Natural products and pharmaceuticals are also given simpler names, for example the mild pain-killer Naproxen is the more common name for the chemical compound (S)-6-methoxy- $\alpha$ -methyl-2-naphthaleneacetic acid.

Chemists frequently refer to chemical compounds using chemical formulae or molecular structure of the compound. There has been a phenomenal growth in the number of chemical compounds being synthesized (or isolated), and then reported in the scientific literature by professional chemists around the world. An enormous number of chemical compounds are possible through the chemical combination of the known chemical elements.

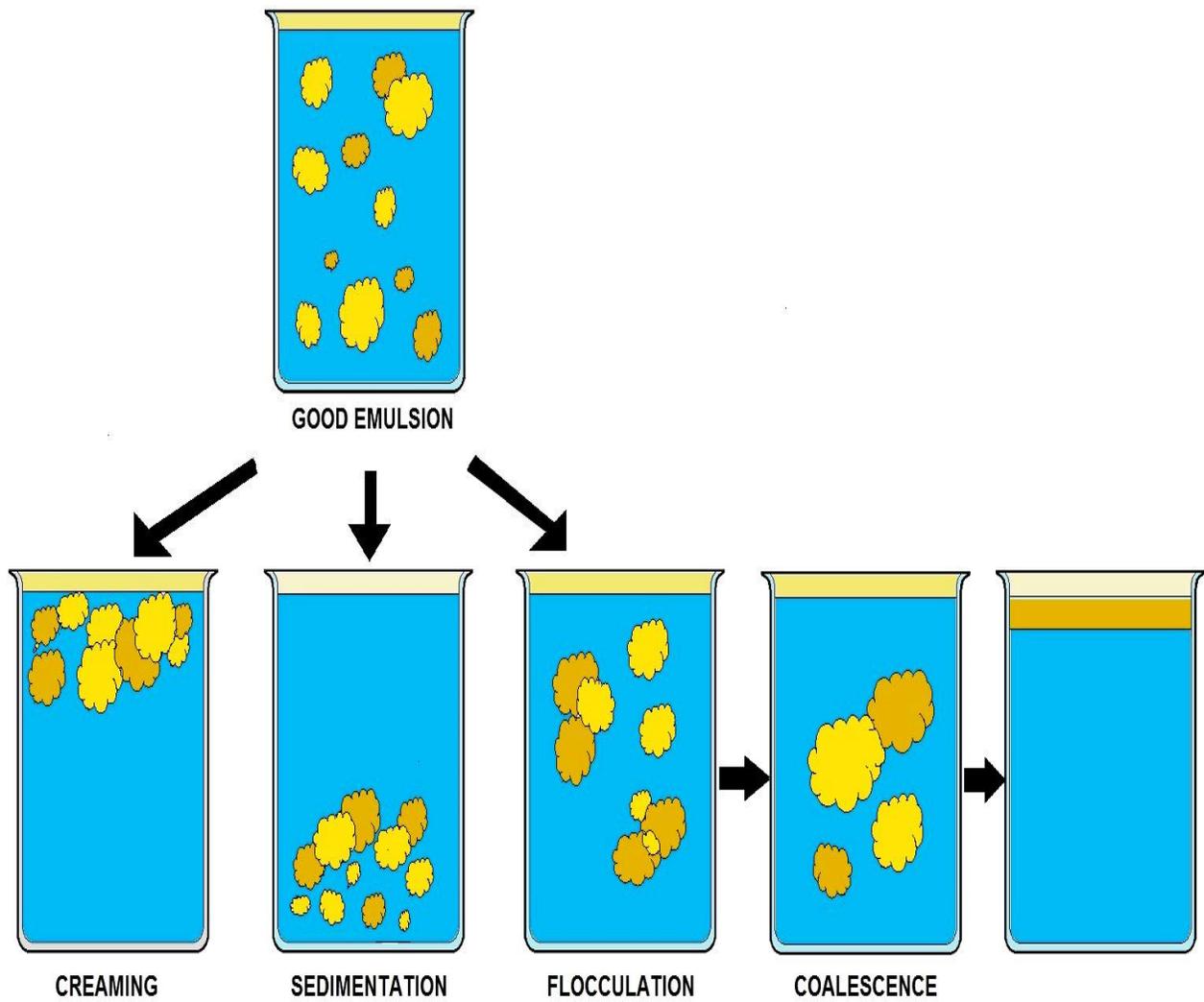
CAS provides the abstracting services of the chemical literature, and provides a numerical identifier, known as CAS registry number to each chemical substance that has been reported in the chemical literature (such as chemistry journals and patents). This information is compiled as a database and is popularly known as the Chemical substances index. Other computer-friendly systems that have been developed for substance information, are: SMILES and the International Chemical Identifier or InChI.



**WATER PHASE DIAGRAM**



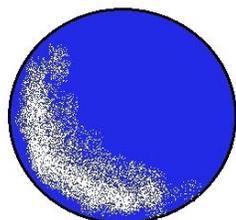
**PHYSICAL CHARACTERISTICS OF WATER**



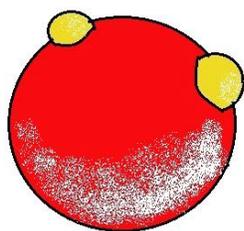
## MECHANISMS OF EMULSION INSTABILITY

## Understanding the Molecule

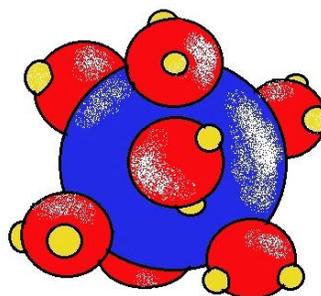
A *molecule* is the smallest indivisible portion of a pure chemical substance that has its unique set of chemical properties, that is, its potential to undergo a certain set of chemical reactions with other substances. However, this definition only works well for substances that are composed of molecules, which is not true of many substances (see below). Molecules are typically a set of atoms bound together by covalent bonds, such that the structure is electrically neutral and all valence electrons are paired with other electrons either in bonds or in lone pairs.



BARE CALCIUM ION



WATER MOLECULE



HYDRATED CALCIUM ION

Thus, molecules exist as electrically neutral units, unlike ions. When this rule is broken, giving the "molecule" a charge, the result is sometimes named a molecular ion or a polyatomic ion. However, the discrete and separate nature of the molecular concept usually requires that molecular ions be present only in well-separated form, such as a directed beam in a vacuum in a mass spectrometer. Charged polyatomic collections residing in solids (for example, common sulfate or nitrate ions) are generally not considered "molecules" in chemistry.

The "inert" or noble gas elements (helium, neon, argon, krypton, xenon and radon) are composed of lone atoms as their smallest discrete unit, but the other isolated chemical elements consist of either molecules or networks of atoms bonded to each other in some way.

Identifiable molecules compose familiar substances such as water, air, and many organic compounds like alcohol, sugar, gasoline, and the various pharmaceuticals.

However, not all substances or chemical compounds consist of discrete molecules, and indeed most of the solid substances that make up the solid crust, mantle, and core of the Earth are chemical compounds without molecules. These other types of substances, such as ionic compounds and network solids, are organized in such a way as to lack the existence of identifiable molecules *per se*. Instead, these substances are discussed in terms of formula units or unit cells as the smallest repeating structure within the substance.

Examples of such substances are mineral salts (such as table salt), solids like carbon and diamond, metals, and familiar silica and silicate minerals such as quartz and granite.

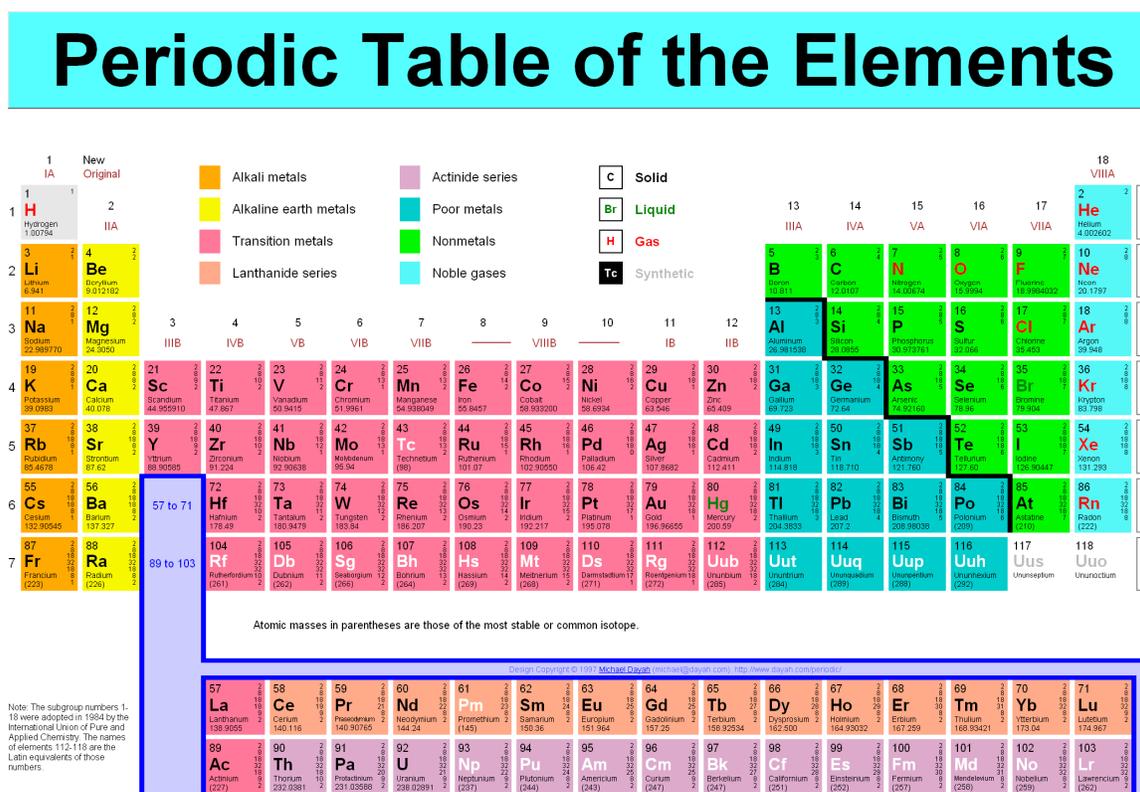
One of the main characteristics of a molecule is its geometry often called its structure. While the structure of diatomic, triatomic or tetra atomic molecules may be trivial, (linear, angular pyramidal etc.) the structure of polyatomic molecules, that are constituted of more than six atoms (of several elements) can be crucial for its chemical nature.

### Substance and Mixture

A chemical substance is a kind of matter with a definite composition and set of properties. A collection of substances is called a mixture. Examples of mixtures are air and alloys.

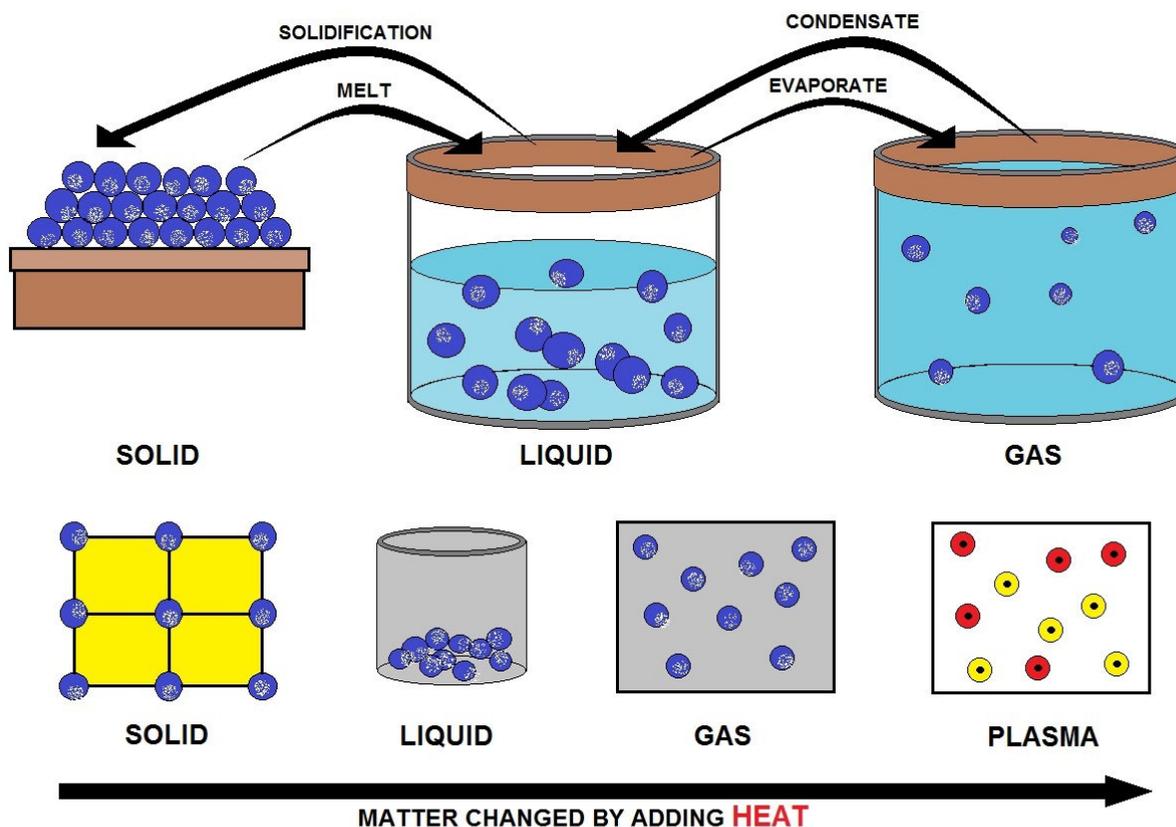
### Mole and Amount of Substance

The mole is a unit of measurement that denotes an amount of substance (also called chemical amount). The mole is defined as the number of atoms found in exactly 0.012 kilogram (or 12 grams) of carbon-12, where the carbon-12 atoms are non-dynamic, at rest and in their ground state. The number of entities per mole is known as the Avogadro constant, and is determined empirically to be approximately  $6.022 \times 10^{23} \text{ mol}^{-1}$ . Molar concentration is the amount of a particular substance per volume of solution, and is commonly reported in  $\text{mol dm}^{-3}$ .



## Phase

In addition to the specific chemical properties that distinguish different chemical classifications, chemicals can exist in several phases. For the most part, the chemical classifications are independent of these bulk phase classifications; however, some more exotic phases are incompatible with certain chemical properties. A *phase* is a set of states of a chemical system that have similar bulk structural properties, over a range of conditions, such as pressure or temperature.



## STATES OF MATTER

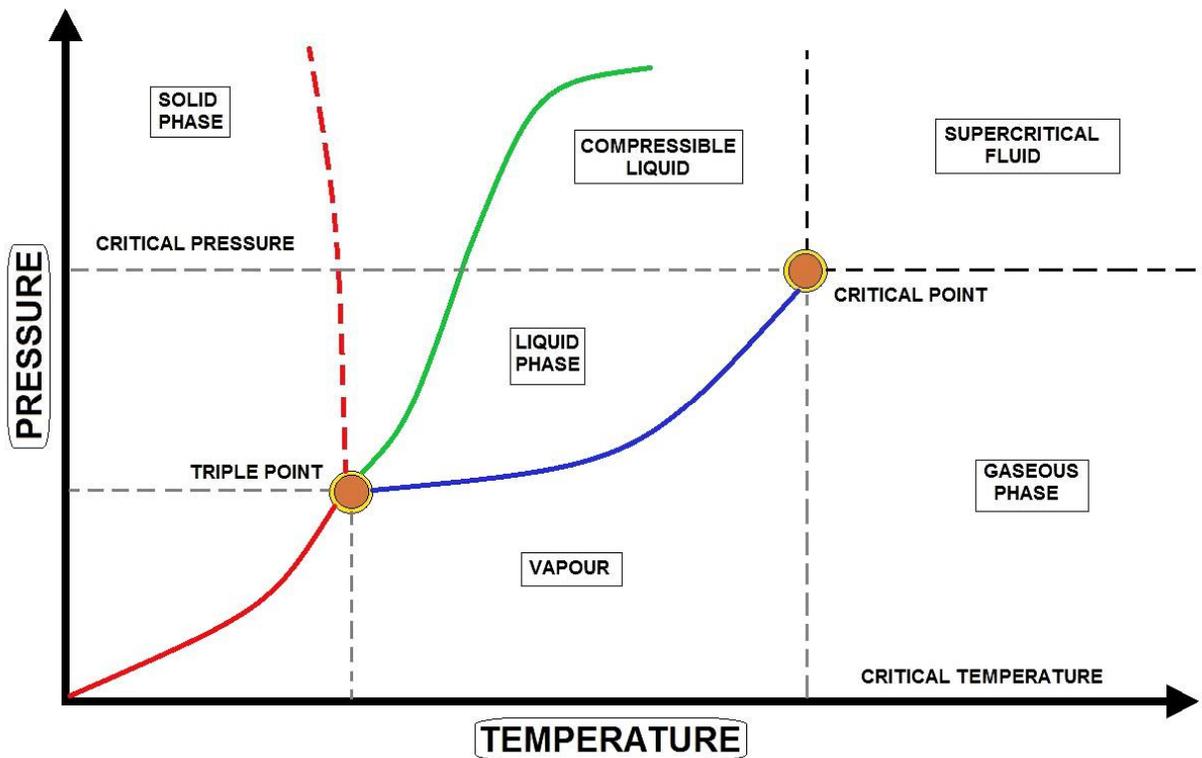
Physical properties, such as density and refractive index tend to fall within values characteristic of the phase. The phase of matter is defined by the *phase transition*, which is when energy put into or taken out of the system goes into rearranging the structure of the system, instead of changing the bulk conditions.

Sometimes the distinction between phases can be continuous instead of having a discrete boundary, in this case the matter is considered to be in a supercritical state. When three states meet based on the conditions, it is known as a triple point and since this is invariant, it is a convenient way to define a set of conditions.

The most familiar examples of phases are solids, liquids, and gases.

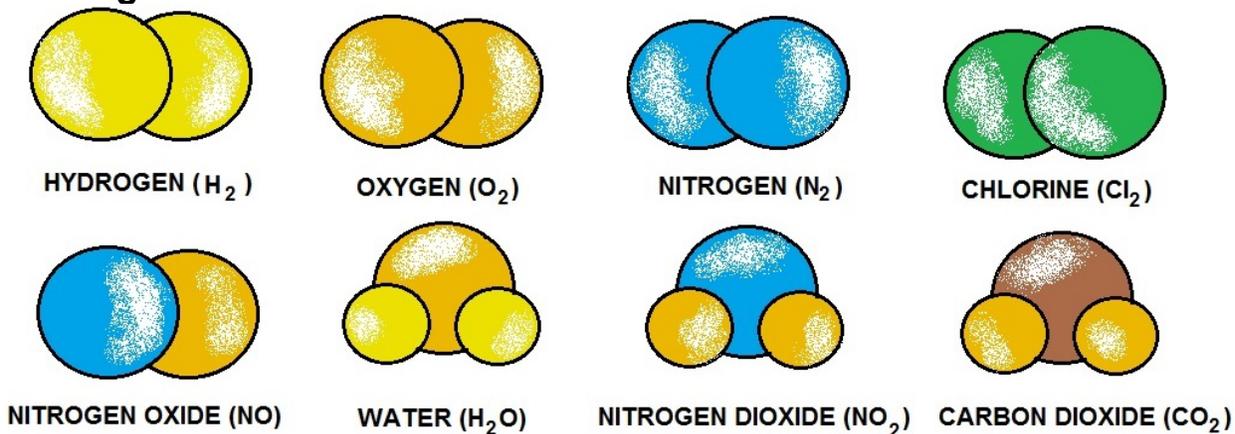
Many substances exhibit multiple solid phases. For example, there are three phases of solid iron (alpha, gamma, and delta) that vary based on temperature and pressure. A principal difference between solid phases is the crystal structure, or arrangement, of the atoms. Another phase commonly encountered in the study of chemistry is the *aqueous* phase, which is the state of substances dissolved in aqueous solution (that is, in water).

Less familiar phases include plasmas, Bose–Einstein condensates and fermionic condensates and the paramagnetic and ferromagnetic phases of magnetic materials. While most familiar phases deal with three-dimensional systems, it is also possible to define analogs in two-dimensional systems, which has received attention for its relevance to systems in biology.

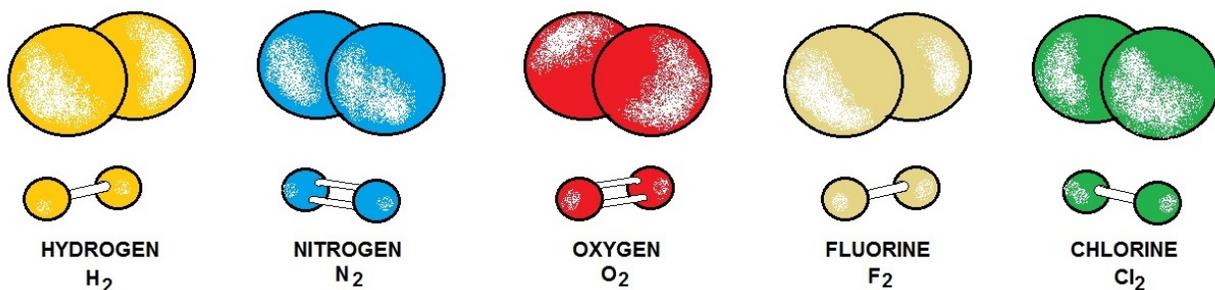


**TRIPLE AND CRITICAL POINTS OF A SUBSTANCE**

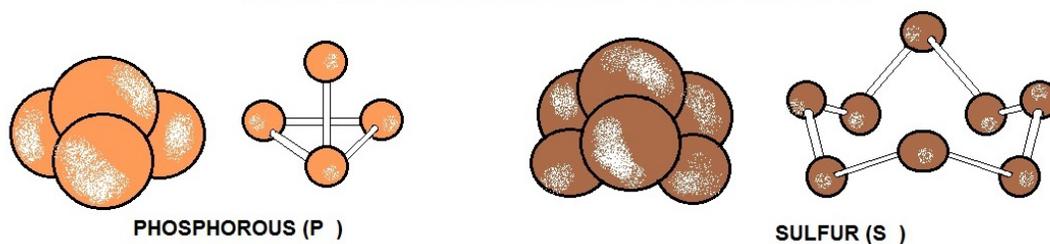
## Bonding



Atoms sticking together in molecules or crystals are said to be bonded with one another. A chemical bond may be visualized as the multipole balance between the positive charges in the nuclei and the negative charges oscillating about them. More than simple attraction and repulsion, the energies and distributions characterize the availability of an electron to bond to another atom.



### ELEMENTS THAT EXIST AS DIATOMIC MOLECULES

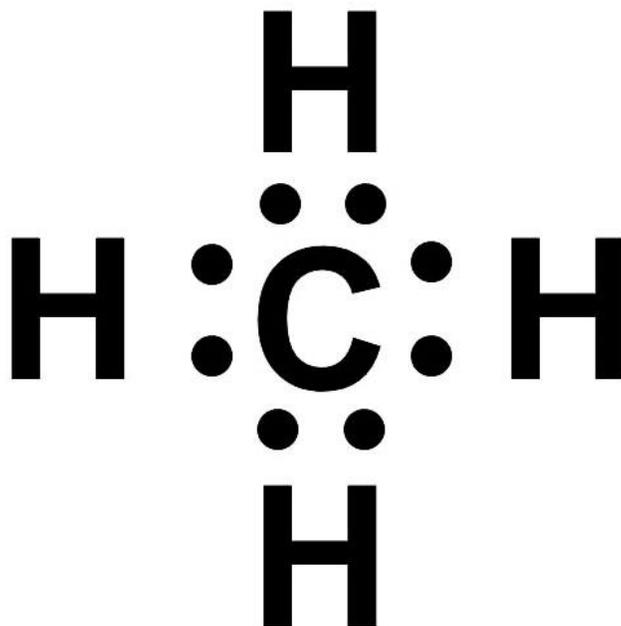


### ELEMENTS THAT EXIST AS POLYATOMIC MOLECULES

A chemical bond can be a covalent bond, an ionic bond, a hydrogen bond or just because of Van der Waals force. Each of these kinds of bonds is ascribed to some potential. These potentials create the interactions which hold atoms together in molecules or crystals. In many simple compounds, valence bond theory, the Valence Shell Electron Pair Repulsion model (VSEPR), and the concept of oxidation number can be used to explain molecular structure and composition.

An ionic bond is formed when a metal loses one or more of its electrons, becoming a positively charged cation, and the electrons are then gained by the non-metal atom, becoming a negatively charged anion.

The two oppositely charged ions attract one another, and the ionic bond is the electrostatic force of attraction between them. For example, sodium (Na), a metal, loses one electron to become an  $\text{Na}^+$  cation while chlorine (Cl), a non-metal, gains this electron to become  $\text{Cl}^-$ . The ions are held together due to electrostatic attraction, and that compound sodium chloride ( $\text{NaCl}$ ), or common table salt, is formed.



### Methane molecule ( $\text{CH}_4$ )

In the methane molecule ( $\text{CH}_4$ ), the carbon atom shares a pair of valence electrons with each of the four hydrogen atoms. Thus, the octet rule is satisfied for C-atom (it has eight electrons in its valence shell) and the duet rule is satisfied for the H-atoms (they have two electrons in their valence shells).

In a covalent bond, one or more pairs of valence electrons are shared by two atoms: the resulting electrically neutral group of bonded atoms is termed a molecule. Atoms will share valence electrons in such a way as to create a noble gas electron configuration (eight electrons in their outermost shell) for each atom.

Atoms that tend to combine in such a way that they each have eight electrons in their valence shell are said to follow the octet rule. However, some elements like hydrogen and lithium need only two electrons in their outermost shell to attain this stable configuration; these atoms are said to follow the *duet rule*, and in this way they are reaching the electron configuration of the noble gas helium, which has two electrons in its outer shell.

Similarly, theories from classical physics can be used to predict many ionic structures. With more complicated compounds, such as metal complexes, valence bond theory is less applicable and alternative approaches, such as the molecular orbital theory, are generally used. See diagram on electronic orbitals.

## Energy

In the context of chemistry, energy is an attribute of a substance as a consequence of its atomic, molecular or aggregate structure. Since a chemical transformation is accompanied by a change in one or more of these kinds of structures, it is invariably accompanied by an increase or decrease of energy of the substances involved. Some energy is transferred between the surroundings and the reactants of the reaction in the form of heat or light; thus the products of a reaction may have more or less energy than the reactants.

A reaction is said to be exergonic if the final state is lower on the energy scale than the initial state; in the case of endergonic reactions the situation is the reverse. A reaction is said to be exothermic if the reaction releases heat to the surroundings; in the case of endothermic reactions, the reaction absorbs heat from the surroundings.

Chemical reactions are invariably not possible unless the reactants surmount an energy barrier known as the activation energy. The *speed* of a chemical reaction (at given temperature  $T$ ) is related to the activation energy  $E$ , by the Boltzmann's population factor - that is the probability of a molecule to have energy greater than or equal to  $E$  at the given temperature  $T$ .

$$e^{-E/kT}$$

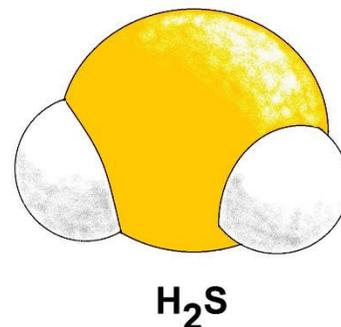
This exponential dependence of a reaction rate on temperature is known as the Arrhenius equation. The activation energy necessary for a chemical reaction to occur can be in the form of heat, light, electricity or mechanical force in the form of ultrasound.

A related concept free energy, which also incorporates entropy considerations, is a very useful means for predicting the feasibility of a reaction and determining the state of equilibrium of a chemical reaction, in chemical thermodynamics. A reaction is feasible only if the total change in the Gibbs free energy is negative, if it is equal to zero the chemical reaction is said to be at equilibrium.

$$\Delta G \leq 0$$

There exist only limited possible states of energy for electrons, atoms and molecules. These are determined by the rules of quantum mechanics, which require quantization of energy of a bound system. The atoms/molecules in a higher energy state are said to be excited. The molecules/atoms of substance in an excited energy state are often much more reactive; that is, more amenable to chemical reactions.

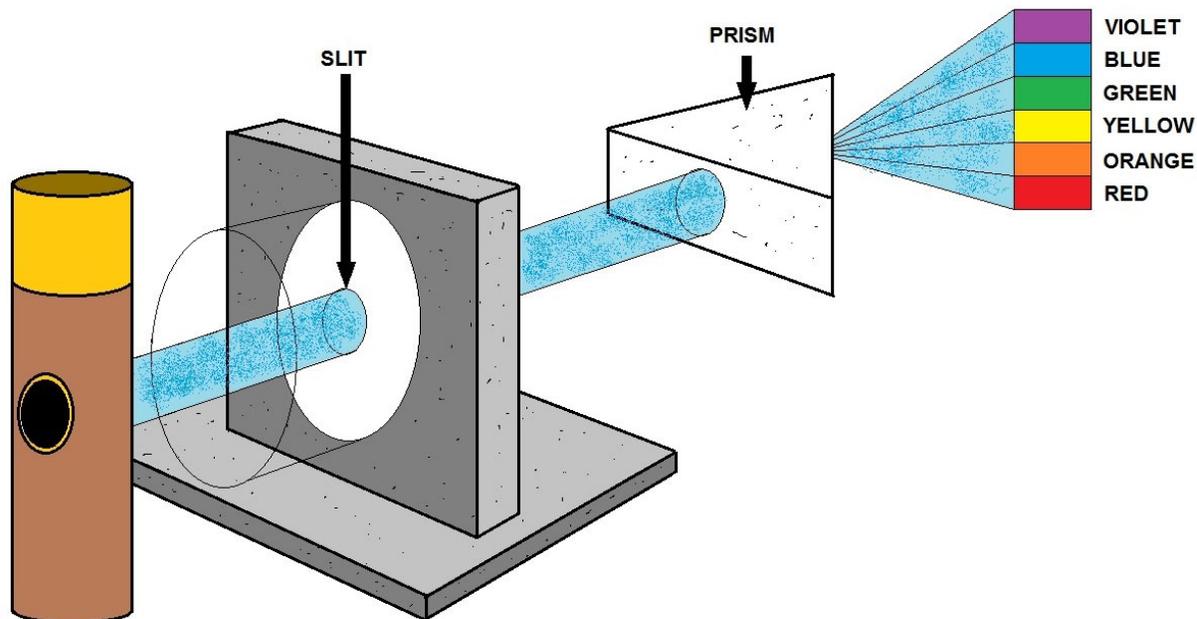
The phase of a substance is invariably determined by its energy and the energy of its surroundings. When the intermolecular forces of a substance are such that the energy of the surroundings is not sufficient to overcome them, it occurs in a more ordered phase like liquid or solid as is the case with water ( $H_2O$ ); a liquid at room temperature because its molecules are bound by hydrogen bonds. Whereas hydrogen sulfide ( $H_2S$ ) is a gas at room temperature and standard pressure, as its molecules are bound by weaker dipole-dipole interactions.



The transfer of energy from one chemical substance to another depends on the *size* of energy quanta emitted from one substance.

However, heat energy is often transferred more easily from almost any substance to another because the phonons responsible for vibrational and rotational energy levels in a substance have much less energy than photons invoked for the electronic energy transfer.

Thus, because vibrational and rotational energy levels are more closely spaced than electronic energy levels, heat is more easily transferred between substances relative to light or other forms of electronic energy. For example, ultraviolet electromagnetic radiation is not transferred with as much efficacy from one substance to another as thermal or electrical energy.



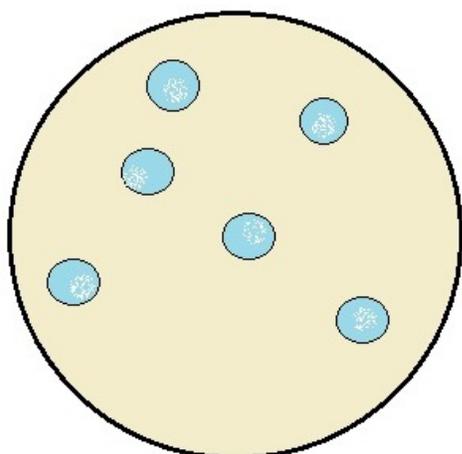
## SPECTROSCOPY

The existence of characteristic energy levels for different chemical substances is useful for their identification by the analysis of spectral lines. Different kinds of spectra are often used in chemical spectroscopy, e.g. IR, microwave, NMR, ESR, etc.

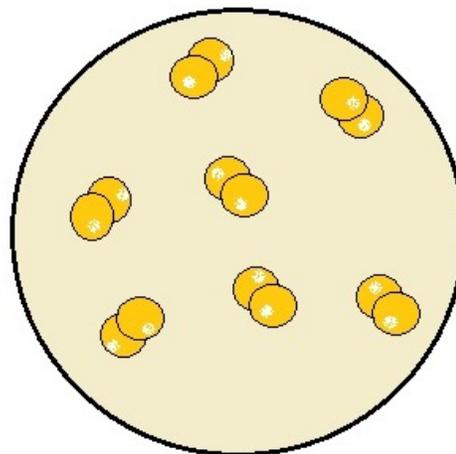
Spectroscopy is also used to identify the composition of remote objects - like stars and distant galaxies - by analyzing their radiation spectra.

The term chemical energy is often used to indicate the potential of a chemical substance to undergo a transformation through a chemical reaction or to transform other chemical substances.

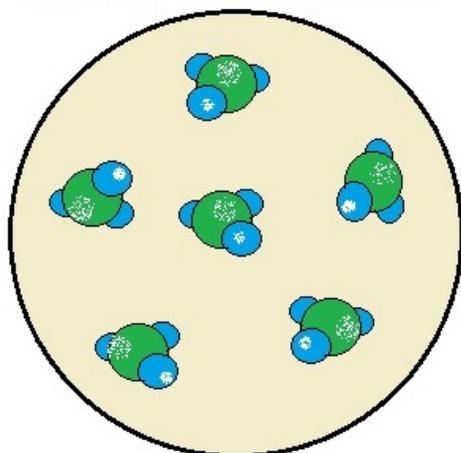
## Reaction



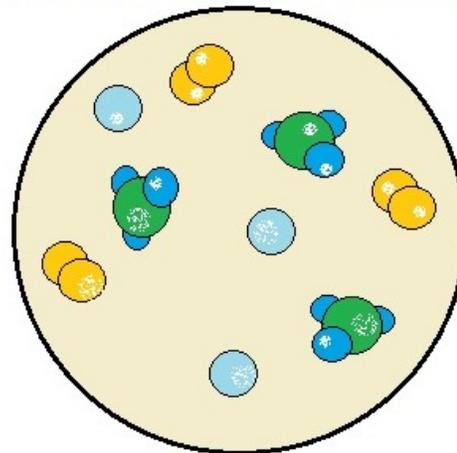
**ATOMS OF AN ELEMENT**



**MOLECULES OF AN ELEMENT**



**MOLECULES OF A COMPOUND**



**MIXTURE OF TWO ELEMENTS  
AND A COMPOUND**

During chemical reactions, bonds between atoms break and form, resulting in different substances with different properties. In a blast furnace, iron oxide, a compound, reacts with carbon monoxide to form iron, one of the chemical elements, and carbon dioxide.

When a chemical substance is transformed as a result of its interaction with another substance or with energy, a chemical reaction is said to have occurred.

A *chemical reaction* is therefore a concept related to the "reaction" of a substance when it comes in close contact with another, whether as a mixture or a solution; exposure to some form of energy, or both. It results in some energy exchange between the constituents of the reaction as well as with the system environment, which may be designed vessels—often laboratory glassware.

Chemical reactions can result in the formation or dissociation of molecules, that is, molecules breaking apart to form two or smaller molecules, or rearrangement of atoms within or across molecules.

Chemical reactions usually involve the making or breaking of chemical bonds. Oxidation, reduction, dissociation, acid-base neutralization and molecular re-arrangement are some of the commonly used kinds of chemical reactions.

A chemical reaction can be symbolically depicted through a chemical equation. While in a non-nuclear chemical reaction the number and kind of atoms on both sides of the equation are equal, for a nuclear reaction this holds true only for the nuclear particles viz. protons and neutrons.

The sequence of steps in which the reorganization of chemical bonds may be taking place in the course of a chemical reaction is called its mechanism. A chemical reaction can be envisioned to take place in a number of steps, each of which may have a different speed. Many reaction intermediates with variable stability can thus be envisaged during the course of a reaction. Reaction mechanisms are proposed to explain the kinetics and the relative product mix of a reaction. Many physical chemists specialize in exploring and proposing the mechanisms of various chemical reactions. Several empirical rules, like the Woodward–Hoffmann rules often come in handy while proposing a mechanism for a chemical reaction.

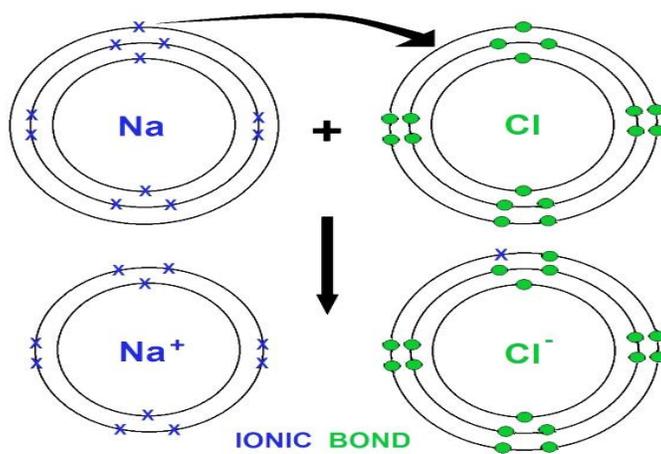
According to the IUPAC gold book, a chemical reaction is "a process that results in the interconversion of chemical species." Accordingly, a chemical reaction may be an elementary reaction or a stepwise reaction. An additional caveat is made, in that this definition includes cases where the interconversion of conformers is experimentally observable. Such detectable chemical reactions normally involve sets of molecular entities as indicated by this definition, but it is often conceptually convenient to use the term also for changes involving single molecular entities (i.e. 'microscopic chemical events').

### Ions and Salts

An *ion* is a charged species, an atom or a molecule, that has lost or gained one or more electrons. When an atom loses an electron and thus has more protons than electrons, the atom is a positively-charged ion or cation. When an atom gains an electron and thus has more electrons than protons, the atom is a negatively-charged ion or anion. Cations and anions can form a crystalline lattice of neutral salts, such as the  $\text{Na}^+$  and  $\text{Cl}^-$  ions forming sodium chloride, or  $\text{NaCl}$ .

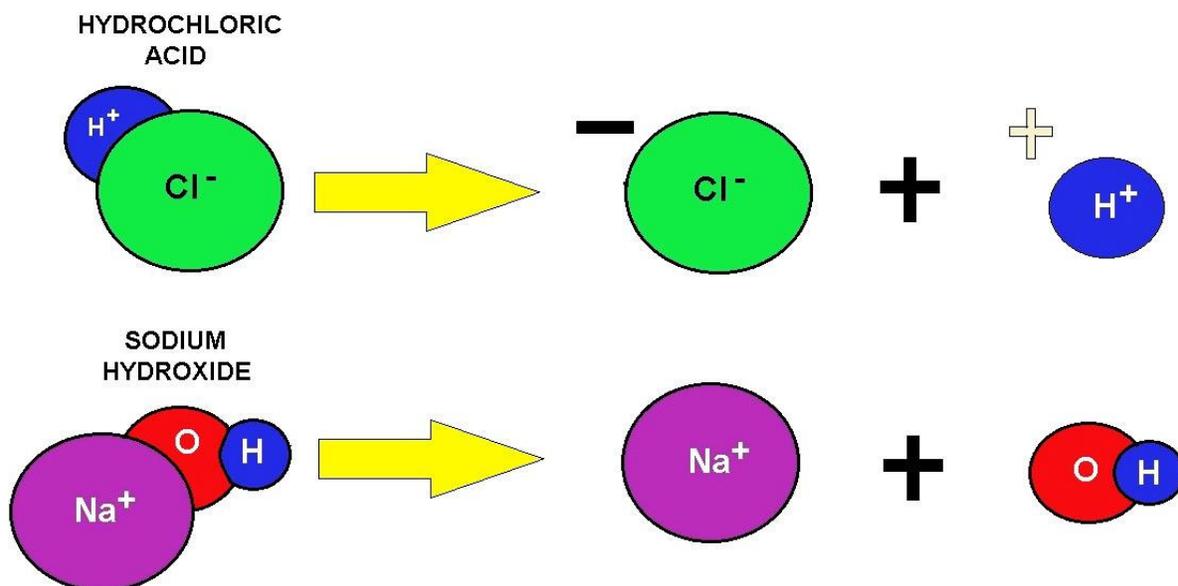
Examples of polyatomic ions that do not split up during acid-base reactions are hydroxide ( $\text{OH}^-$ ) and phosphate ( $\text{PO}_4^{3-}$ ).

Plasma is composed of gaseous matter that has been completely ionized, usually through high temperature.



## SODIUM CHLORIDE

## Acidity and Basicity



## ACIDS AND BASES (comparison)

A substance can often be classified as an acid or a base. There are several different theories which explain acid-base behavior. The simplest is Arrhenius theory, which states that an acid is a substance that produces hydronium ions when it is dissolved in water, and a base is one that produces hydroxide ions when dissolved in water.

According to Brønsted–Lowry acid–base theory, acids are substances that donate a positive hydrogen ion to another substance in a chemical reaction; by extension, a base is the substance which receives that hydrogen ion.

A third common theory is Lewis acid-base theory, which is based on the formation of new chemical bonds. Lewis theory explains that an acid is a substance which is capable of accepting a pair of electrons from another substance during the process of bond formation, while a base is a substance which can provide a pair of electrons to form a new bond.

According to this theory, the crucial things being exchanged are charges. There are several other ways in which a substance may be classified as an acid or a base, as is evident in the history of this concept.

### **Acid strength is commonly measured by two methods:**

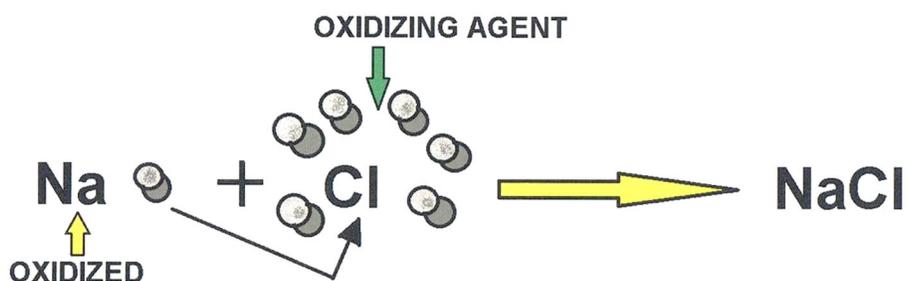
One measurement, based on the Arrhenius definition of acidity, is pH, which is a measurement of the hydronium ion concentration in a solution, as expressed on a negative logarithmic scale. Thus, solutions that have a low pH have a high hydronium ion concentration, and can be said to be more acidic.

The other measurement, based on the Brønsted–Lowry definition, is the acid dissociation constant ( $K_a$ ), which measures the relative ability of a substance to act as an acid under the Brønsted–Lowry definition of an acid. That is, substances with a higher  $K_a$  are more likely to donate hydrogen ions in chemical reactions than those with lower  $K_a$  values.

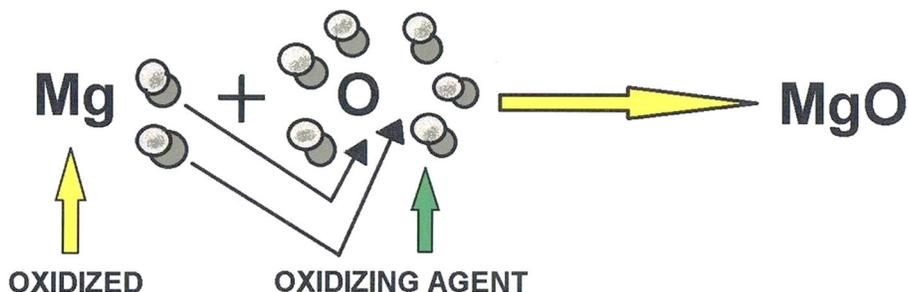
### Redox

Redox (*reduction-oxidation*) reactions include all chemical reactions in which atoms have their oxidation state changed by either gaining electrons (reduction) or losing electrons (oxidation). Substances that have the ability to oxidize other substances are said to be oxidative and are known as oxidizing agents, oxidants or oxidizers.

An oxidant removes electrons from another substance. Similarly, substances that have the ability to reduce other substances are said to be reductive and are known as reducing agents, reductants, or reducers.

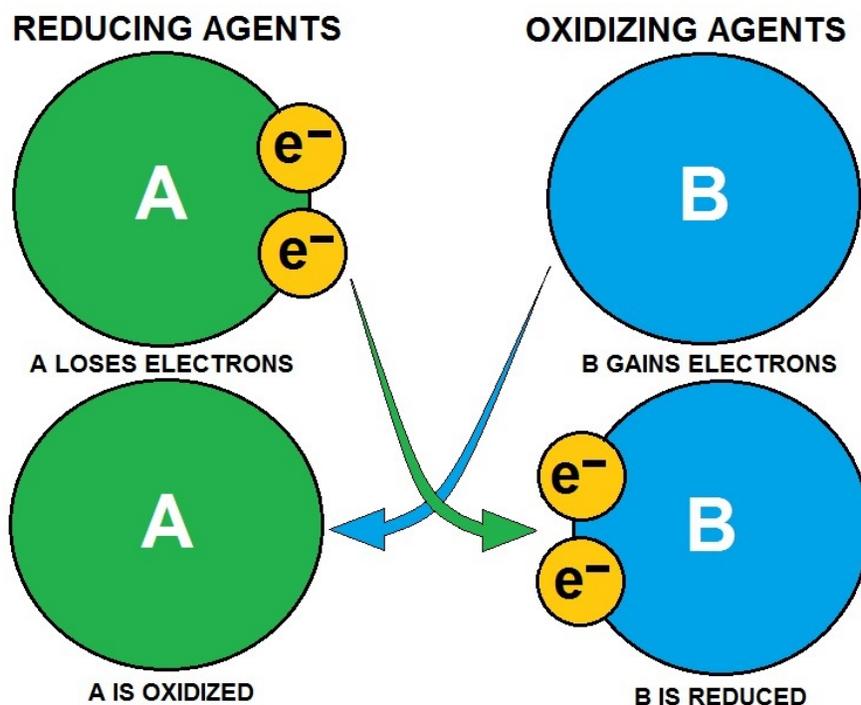


### OXIDIZING AGENT VS. OXIDIZED



A reductant transfers electrons to another substance, and is thus oxidized itself. And because it "donates" electrons it is also called an electron donor.

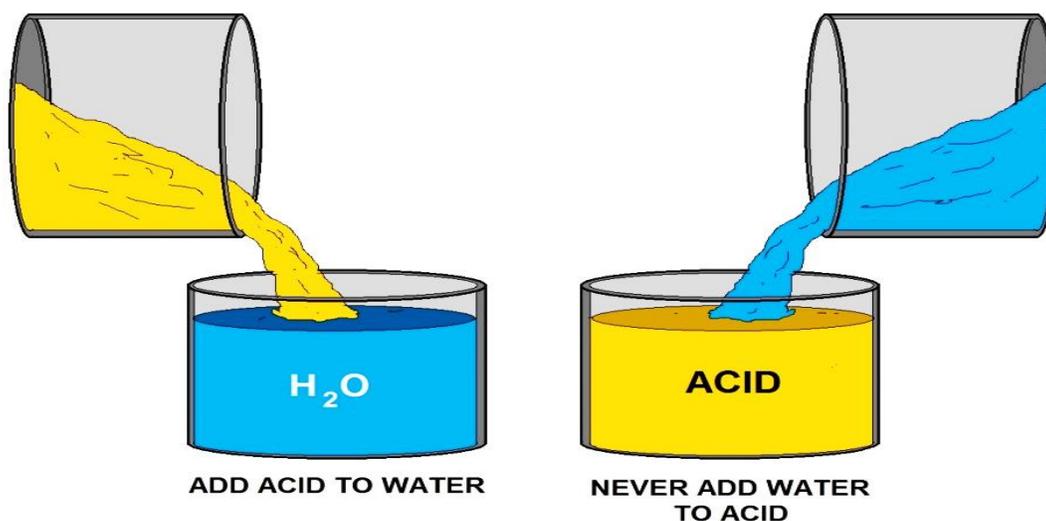
Oxidation and reduction properly refer to a change in oxidation number—the actual transfer of electrons may never occur. Thus, oxidation is better defined as an increase in oxidation number, and reduction as a decrease in oxidation number.

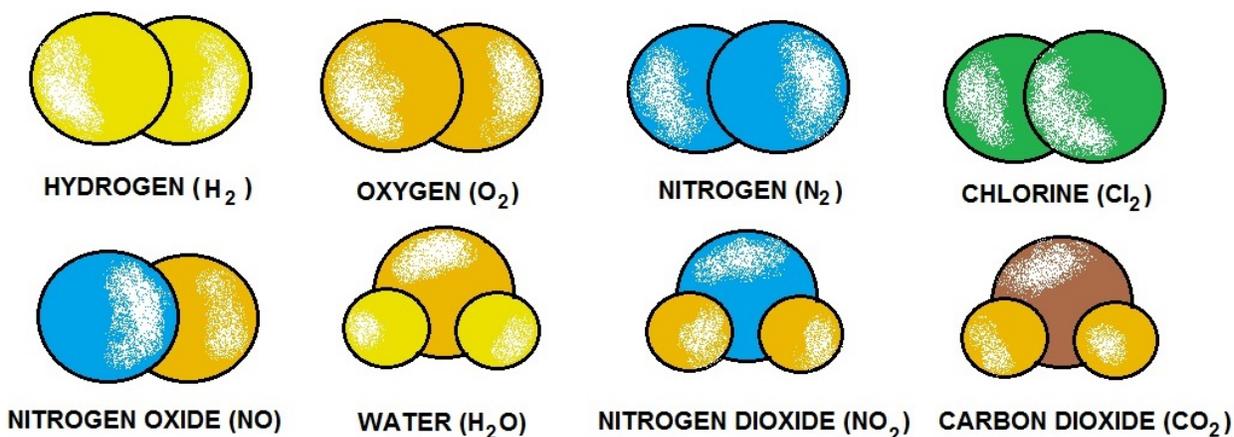


### Equilibrium

Although the concept of equilibrium is widely used across sciences, in the context of chemistry, it arises whenever a number of different states of the chemical composition are possible, as for example, in a mixture of several chemical compounds that can react with one another, or when a substance can be present in more than one kind of phase.

A system of chemical substances at equilibrium, even though having an unchanging composition, is most often not static; molecules of the substances continue to react with one another thus giving rise to a dynamic equilibrium. Thus the concept describes the state in which the parameters such as chemical composition remain unchanged over time.





Water (H<sub>2</sub>O) is the oxide of hydrogen and the most familiar oxygen compound. Its bulk properties partly result from the interaction of its component atoms, oxygen and hydrogen, with atoms of nearby water molecules. Hydrogen atoms are covalently bonded to oxygen in a water molecule but also have an additional attraction (about 23.3 kJ·mol<sup>-1</sup> per hydrogen atom) to an adjacent oxygen atom in a separate molecule. These hydrogen bonds between water molecules hold them approximately 15% closer than what would be expected in a simple liquid with just Van der Waals forces.

Oxides, such as iron oxide or rust, Fe<sub>2</sub>O<sub>3</sub>, form when oxygen combines with other elements

Due to its electronegativity, oxygen forms chemical bonds with almost all other free elements at elevated temperatures to give corresponding oxides. However, some elements, such as iron which oxidizes to iron oxide, or rust, Fe<sub>2</sub>O<sub>3</sub>, readily oxidize at standard conditions for temperature and pressure (STP).

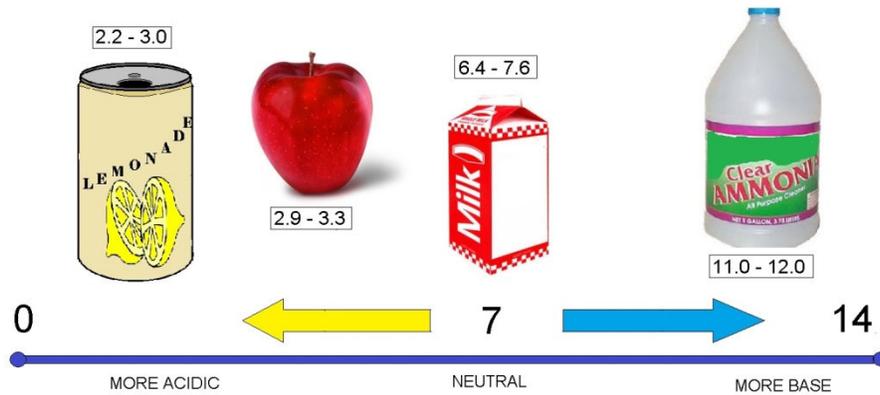
The surface of metals like aluminum and titanium are oxidized in the presence of air and become coated with a thin film of oxide that passivates the metal and slows further corrosion. So-called noble metals, such as gold and platinum, resist direct chemical combination with oxygen, and substances like gold(III) oxide (Au<sub>2</sub>O<sub>3</sub>) must be formed by an indirect route.

The alkali metals and alkali earth metals all react spontaneously with oxygen when exposed to dry air to form oxides, and form hydroxides in the presence of oxygen and water. As a result, none of these elements is found in nature as a free metal.

Caesium is so reactive with oxygen that it is used as a getter in vacuum tubes. Although solid magnesium reacts slowly with oxygen at STP, it is capable of burning in air, generating very high temperatures, and its metal powder may form explosive mixtures with air.

Oxygen is present as compounds in the atmosphere in trace quantities in the form of carbon dioxide (CO<sub>2</sub>) and oxides of nitrogen (NO<sub>x</sub>).

## pH Section



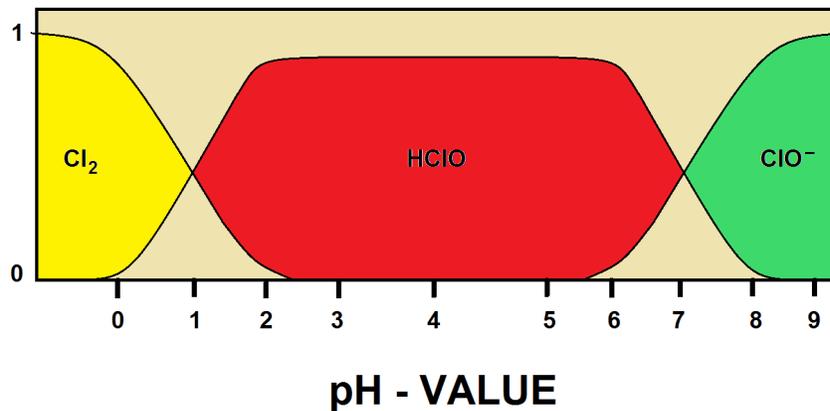
## pH SCALE

In water and wastewater processes, **pH** is a measure of the acidity or basicity of an aqueous solution. Solutions with a pH greater than 7 are basic or alkaline and solution or samples with a pH less than 7 are said to be acidic. Pure water has a pH very close to 7.

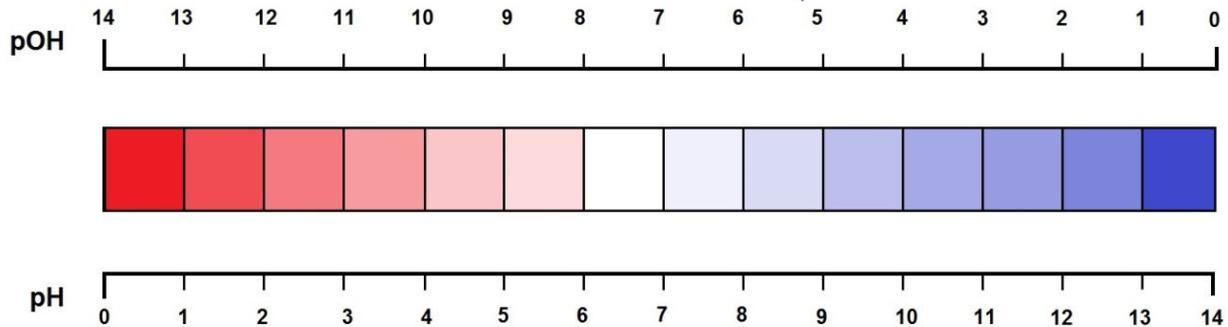
Primary pH standard values are determined using a concentration cell with transference, by measuring the potential difference between a hydrogen electrode and a standard electrode such as the silver chloride electrode. The pH scale is traceable to a set of standard solutions whose pH is established by international agreement.

Measurement of pH for aqueous solutions can be done with a glass electrode and a pH meter, or using indicators like strip test paper.

pH measurements are important in water and wastewater processes (sampling) but also in medicine, biology, chemistry, agriculture, forestry, food science, environmental science, oceanography, civil engineering, chemical engineering, nutrition, water treatment & water purification, and many other applications.



Mathematically, pH is the measurement of hydroxyl ion activity and expressed as the negative logarithm of the activity of the (solvated) hydronium ion, more often expressed as the measure of the hydronium ion concentration.



IN RELATION BETWEEN p(OH) AND p(H) (red= ACIDIC / blue= BASIC)

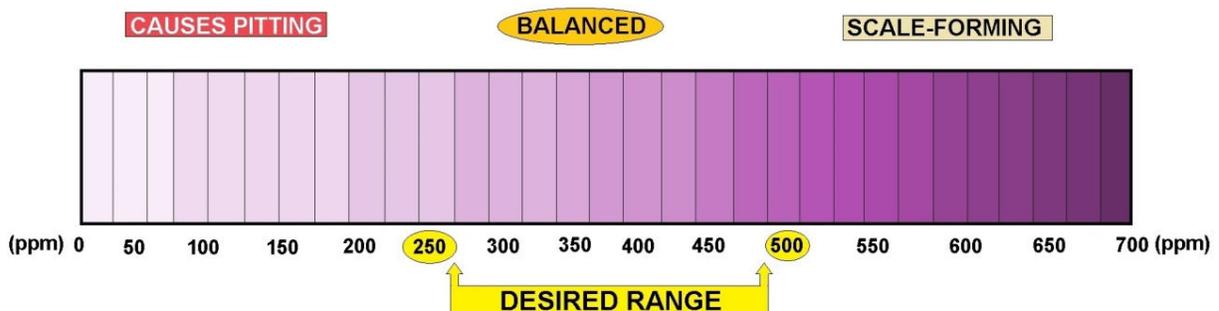
## Contents

### History

The scientific discovery of the p[H] concept of was first introduced by Danish chemist Søren Peder Lauritz Sørensen at the Carlsberg Laboratory back in 1909 and revised to the modern pH in 1924 to accommodate definitions and measurements in terms of electrochemical cells. In the first papers, the notation had the "H" as a subscript to the lowercase "p", as so: pH.

### Alkalinity

Alkalinity is the quantitative capacity of an aqueous solution to neutralize an acid. Measuring alkalinity is important in determining a stream's ability to neutralize acidic pollution from rainfall or wastewater. It is one of the best measures of the sensitivity of the stream to acid inputs. There can be long-term changes in the alkalinity of rivers and streams in response to human disturbances.



## CALCIUM HARDNESS MEASUREMENT

Reference. Bates, Roger G. *Determination of pH: theory and practice*. Wiley, 1973.

## pH Definition and Measurement

CONCENTRATION OF HYDROGEN IONS COMPARED TO DISTILLED H <sub>2</sub> O	1/10,000,000	14	LIQUID DRAIN CLEANER CAUSTIC SODA	EXAMPLES OF SOLUTIONS AND THEIR RESPECTIVE pH
	1/1,000,000	13	BLEACHES OVEN CLEANERS	
	1/100,000	12	SOAPY WATER	
	1/10,000	11	HOUSEHOLD AMMONIA (11.9)	
	1/1,000	10	MILK OF MAGNESIUM (10.5)	
	1/100	9	TOOTHPASTE (9.9)	
	1/10	8	BAKING SODA (8.4) / SEA WATER EGGS	
	0	7	"PURE" WATER (7)	
	10	6	URINE (6) / MILK (6.6)	
	100	5	ACID RAIN (5.6) BLACK COFFEE (5)	
	1000	4	TOMATO JUICE (4.1)	
	10,000	3	GRAPEFRUIT & ORANGE JUICE SOFT DRINK	
	100,000	2	LEMON JUICE (2.3) VINEGAR (2.9)	
	1,000,000	1	HYDROCHLORIC ACID SECRETED FROM STOMACH LINING (1)	
	10,000,000	0	BATTERY ACID	

### pH Scale

#### Technical Definition of pH

In technical terms, pH is defined as the decimal logarithm of the reciprocal of the hydrogen ion activity,  $a_{H^+}$ , in a solution.

$$pH = -\log_{10}(a_{H^+}) = \log_{10}\left(\frac{1}{a_{H^+}}\right)$$

Ion-selective electrodes are often used to measure pH, respond to activity.

In this calculation of electrode potential,  $E$ , follows the Nernst equation, which, for the hydrogen ion can be written as

$$E = E^0 + \frac{RT}{F} \ln(a_{H^+}) = E^0 - \frac{2.303RT}{F} pH$$

where  $E$  is a measured potential,  $E^0$  is the standard electrode potential,  $R$  is the gas constant,  $T$  is the temperature in kelvin,  $F$  is the Faraday constant. For  $H^+$  number of electrons transferred is one. It follows that electrode potential is proportional to pH when pH is defined in terms of activity.

International Standard ISO 31-8 is the standard for the precise measurement of pH as follows: A galvanic cell is set up to measure the electromotive force (EMF) between a reference electrode and an electrode sensitive to the hydrogen ion activity when they are both immersed in the same aqueous solution.

The reference electrode may be a silver chloride electrode or a calomel electrode. The hydrogen-ion selective electrode is a standard hydrogen electrode.

Reference electrode | concentrated solution of KCl || test solution | H<sub>2</sub> | Pt

Firstly, the cell is filled with a solution of known hydrogen ion activity and the emf,  $E_s$ , is measured. Then the emf,  $E_x$ , of the same cell containing the solution of unknown pH is measured.

$$pH(X) = pH(S) + \frac{E_s - E_x}{Z}$$

The difference between the two measured emf values is proportional to pH. This method of calibration avoids the need to know the standard electrode potential. The proportionality

constant,  $1/z$  is ideally equal to  $\frac{1}{2.303RT/F}$  the "Nernstian slope".

If you were to apply this practice the above calculation, a glass electrode is used rather than the cumbersome hydrogen electrode. A combined glass electrode has an in-built reference electrode. It is calibrated against buffer solutions of known hydrogen ion activity. IUPAC has proposed the use of a set of buffer solutions of known H<sup>+</sup> activity.

Two or more buffer solutions should be used in order to accommodate the fact that the "slope" may differ slightly from ideal.

The electrode is first immersed in a standard solution and the reading on a pH meter is adjusted to be equal to the standard buffer's value, to implement the proper calibration. The reading from a second standard buffer solution is then adjusted, using the "slope" control, to be equal to the pH for that solution. Further details, are given in the IUPAC recommendations.

When more than two buffer solutions are used the electrode is calibrated by fitting observed pH values to a straight line with respect to standard buffer values. Commercial standard buffer solutions usually come with information on the value at 25 °C and a correction factor to be applied for other temperatures. The pH scale is logarithmic and pH is a dimensionless quantity.

## pH Indicators

Visual comparison of the color of a test solution with a standard color chart provides a means to measure pH accurate to the nearest whole number. Indicators may be used to measure pH, by making use of the fact that their color changes with pH. More precise measurements are possible if the color is measured spectrophotometrically, using a colorimeter or spectrophotometer. Universal indicator consists of a mixture of indicators such that there is a continuous color change from about pH 2 to pH 10. Universal indicator paper is made from absorbent paper that has been impregnated with universal indicator.

## pOH

pOH is sometimes used as a measure of the concentration of hydroxide ions,  $\text{OH}^-$ , or alkalinity. pOH values are derived from pH measurements. The concentration of hydroxide ions in water is related to the concentration of hydrogen ions by

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

where  $K_w$  is the self-ionization constant of water. Taking logarithms

$$\text{pOH} = \text{p}K_w - \text{pH}$$

So, at room temperature  $\text{pOH} \approx 14 - \text{pH}$ . However this relationship is not strictly valid in other circumstances, such as in measurements of soil alkalinity.

## Extremes of pH

Measurement of pH below about 2.5 (ca.  $0.003 \text{ mol dm}^{-3}$  acid) and above about 10.5 (ca.  $0.0003 \text{ mol dm}^{-3}$  alkali) requires special procedures because, when using the glass electrode, the Nernst law breaks down under those conditions.

Extreme pH measurements imply that the solution may be concentrated, so electrode potentials are affected by ionic strength variation. At high pH the glass electrode may be affected by "alkaline error", because the electrode becomes sensitive to the concentration of cations such as  $\text{Na}^+$  and  $\text{K}^+$  in the solution. Specially constructed electrodes are available which partly overcome these problems. Runoff from industrial outfalls, restaurant grease, mines or mine tailings can produce some very low pH values.

## Non-aqueous Solutions

Hydrogen ion concentrations (activities) can be measured in non-aqueous solvents. pH values based on these measurements belong to a different scale from aqueous pH values, because activities relate to different standard states. Hydrogen ion activity,  $a_{\text{H}^+}$ , can be defined as:

$$a_{\text{H}^+} = \exp\left(\frac{\mu_{\text{H}^+} - \mu_{\text{H}^+}^\ominus}{RT}\right)$$

where  $\mu_{\text{H}^+}$  is the chemical potential of the hydrogen ion,  $\mu_{\text{H}^+}^\ominus$  is its chemical potential in the chosen standard state,  $R$  is the gas constant and  $T$  is the thermodynamic temperature. Therefore pH values on the different scales cannot be compared directly, requiring an intersolvent scale which involves the transfer activity coefficient of hydrolyonium ion.

pH is an example of an acidity function. Other acidity functions can be defined. For example, the Hammett acidity function,  $H_0$ , has been developed in connection with superacids.

The concept of "Unified pH scale" has been developed on the basis of the absolute chemical potential of the proton. This scale applies to liquids, gases and even solids.

## Applications

Water has a pH of  $pK_w/2$ , so the pH of pure water is about 7 at 25 °C; this value varies with temperature. When an acid is dissolved in water, the pH will be less than that of pure water. When a base, or alkali, is dissolved in water, the pH will be greater than that of pure water.

A solution of a strong acid, such as hydrochloric acid, at concentration 1 mol dm<sup>-3</sup> has a pH of 0. A solution of a strong alkali, such as sodium hydroxide, at concentration 1 mol dm<sup>-3</sup>, has a pH of 14. Thus, measured pH values will lie mostly in the range 0 to 14, though negative pH values and values above 14 are entirely possible.

Since pH is a logarithmic scale, a difference of one pH unit is equivalent to a tenfold difference in hydrogen ion concentration.

The pH of an aqueous solution of pure water is slightly different from that of a salt such as sodium chloride even though the salt is neither acidic nor basic. In this case, the hydrogen and hydroxide ions' activity is dependent on ionic strength, so  $K_w$  varies with ionic strength. The pH of pure water decreases with increasing temperatures. One example is the pH of pure water at 50 °C is 6.55.

## Seawater

The pH of seawater plays an important role in the ocean's carbon cycle, and there is evidence of ongoing ocean acidification caused by carbon dioxide emissions. pH measurement can be complicated by the chemical properties of seawater, and several distinct pH scales exist in chemical oceanography.

As part of its operational definition of the pH scale, the IUPAC defines a series of buffer solutions across a range of pH values (often denoted with NBS or NIST designation).

These solutions have a relatively low ionic strength (~0.1) compared to that of seawater (~0.7), and, as a consequence, are not recommended for use in characterizing the pH of seawater, since the ionic strength differences cause changes in electrode potential.

To resolve this problem, an alternative series of buffers based on artificial seawater was developed. This new series resolves the problem of ionic strength differences between samples and the buffers. The newest pH scale is referred to as the **total scale**, often denoted as **pH<sub>T</sub>**.

## Calculations of pH

The calculation of the pH of a solution containing acids and/or bases is an example of a chemical speciation calculation, that is, a mathematical procedure for calculating the concentrations of all chemical species that are present in the solution.

The complexity of the procedure depends on the nature of the solution.

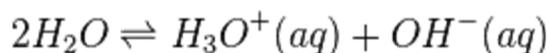
If the pH of a solution contains a weak acid requires the solution of a quadratic equation.

If the pH of a solution contains a weak base may require the solution of a cubic equation.

For strong acids and bases no calculations are necessary except in extreme situations.

The general case requires the solution of a set of non-linear simultaneous equations.

A complicating factor is that water itself is a weak acid and a weak base. It dissociates according to the equilibrium

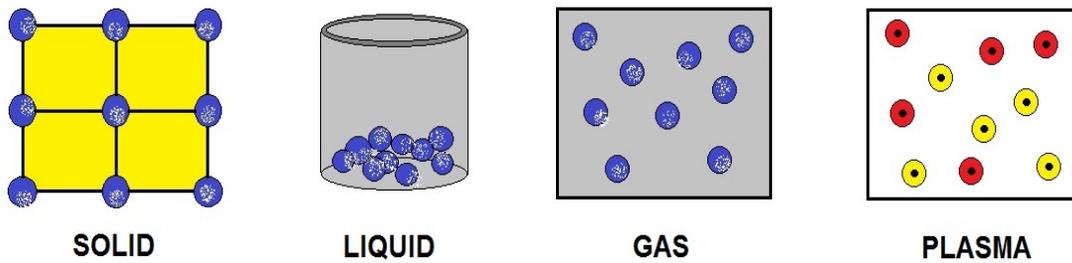
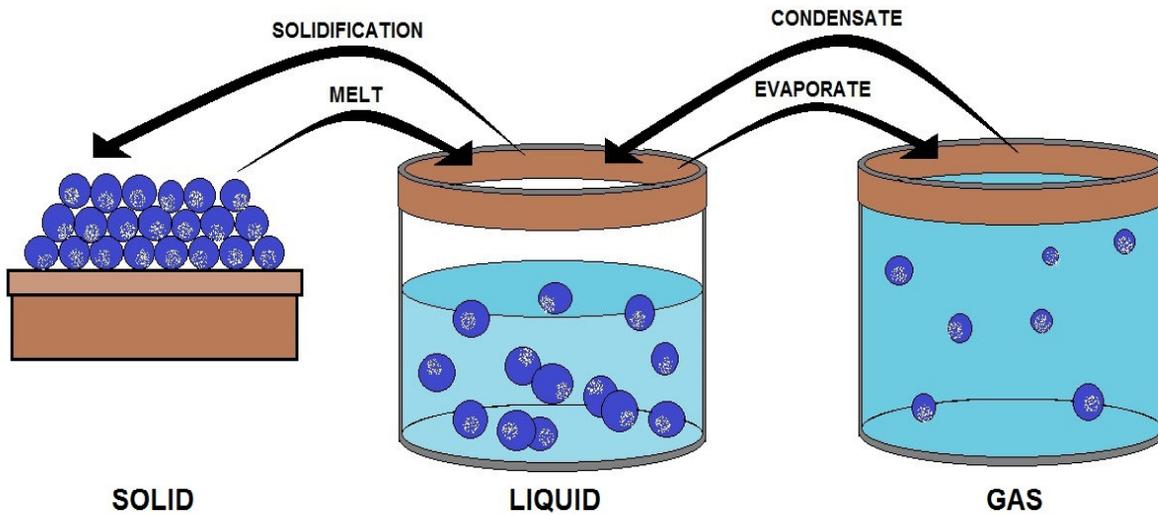


with a dissociation constant,  $K_w$  defined as

$$K_w = [H^+][OH^-]$$

where  $[H^+]$  represents for the concentration of the aquated hydronium ion and  $[OH^-]$  stands for the concentration of the hydroxide ion.  $K_w$  has a value of about  $10^{-14}$  at 25 °C, so pure water has a pH of approximately 7.

This equilibrium needs to be considered at high pH and when the solute concentration is extremely low.



MATTER CHANGED BY ADDING **HEAT**

# STATES OF MATTER

## Strong Acids and Bases



### Strong Acids and Bases

Strong acids and bases are compounds that, for practical purposes, are completely dissociated in water. Under normal circumstances this means that the concentration of hydrogen ions in acidic solution can be taken to be equal to the concentration of the acid. The pH is then equal to minus the logarithm of the concentration value.

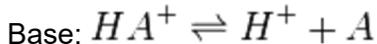
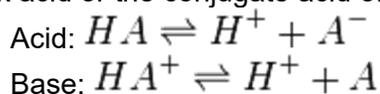
Hydrochloric acid (HCl) is an example of a strong acid. The pH of a 0.01M solution of HCl is equal to  $-\log_{10}(0.01)$ , that is,  $\text{pH} = 2$ .

Sodium hydroxide, NaOH, is an example of a strong base. The p[OH] value of a 0.01M solution of NaOH is equal to  $-\log_{10}(0.01)$ , that is,  $\text{p[OH]} = 2$ .

From the definition of p[OH] above, this means that the pH is equal to about 12. For solutions of sodium hydroxide at higher concentrations the self-ionization equilibrium must be taken into account.

### Weak Acids and Bases

A weak acid or the conjugate acid of a weak base can be treated using the same formalism.



First, an acid dissociation constant is defined as follows. Electrical charges are omitted from subsequent equations for the sake of generality

$$K_a = \frac{[H][A]}{[HA]}$$

and its value is assumed to have been determined by experiment. This being so, there are three unknown concentrations, [HA], [H<sup>+</sup>] and [A<sup>-</sup>] to determine by calculation. Two additional equations are needed.

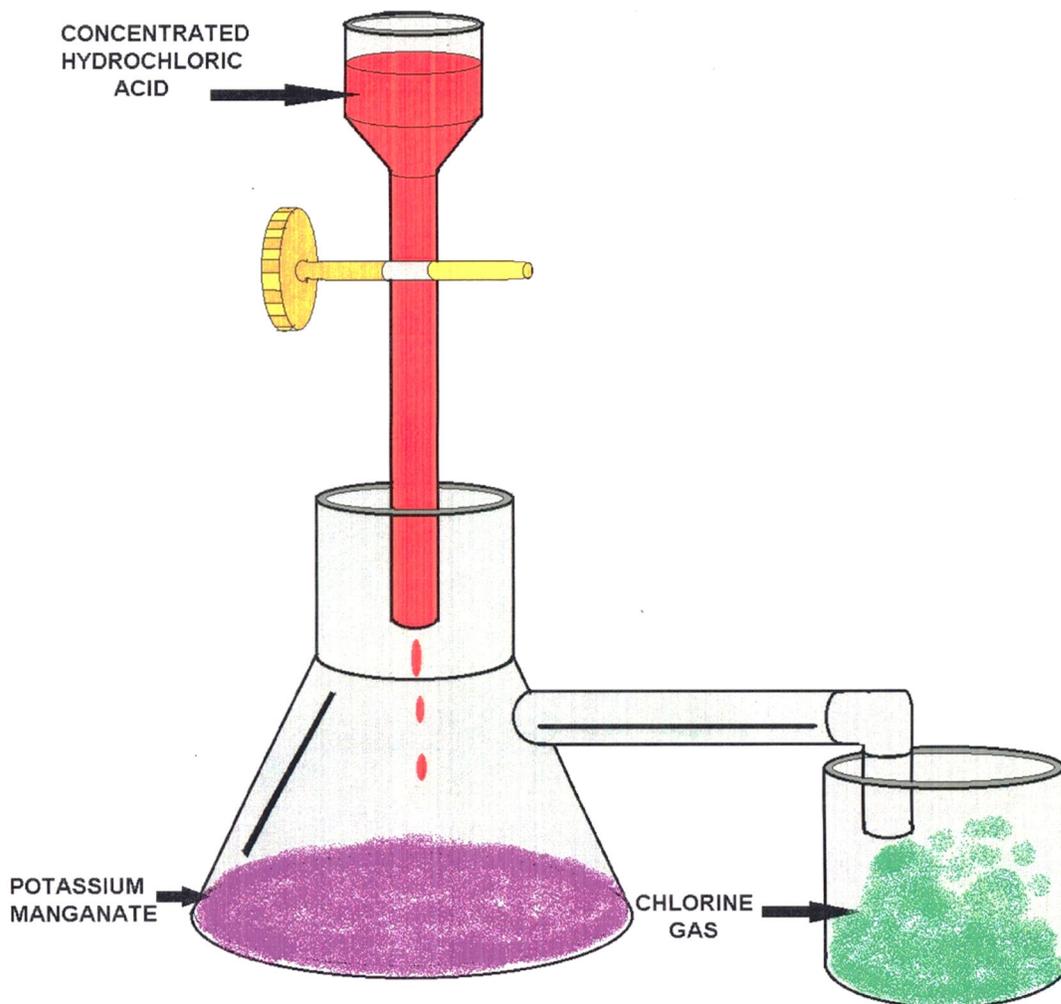
One way to provide them is to apply the law of mass conservation in terms of the two "reagents" H and A.

$$\begin{aligned}C_A &= [A] + [HA] \\C_H &= [H] + [HA]\end{aligned}$$

C stands for analytical concentration. In some texts one mass balance equation is replaced by an equation of charge balance. This is satisfactory for simple cases like this one, but is more difficult to apply to more complicated cases as those below.

Together with the equation defining  $K_a$ , there are now three equations in three unknowns. When an acid is dissolved in water  $C_A = C_H = C_a$ , the concentration of the acid, so  $[A] = [H]$ . After some further algebraic manipulation an equation in the hydrogen ion concentration may be obtained.

$$[H]^2 + K_a[H] - K_aC_a = 0$$



# Alkalinity

## Introduction

Alkalinity of water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the end-point pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents. The measured values also may include contributions from borates, phosphates, silicates or other bases if these are present. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of water for irrigation. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes.

## Titration Method

### a. Principle

Hydroxyl ions present in a sample, as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the end-point pH used.

### b. Reagents

- i) Standard Hydrochloric Acid – 0.02 N.
- ii) Methyl Orange Indicator – Dissolve 0.1 g of methyl orange in distilled water and dilute to 1 liter.
- iii) Sodium carbonate solution, 0.02 N : Dry 3 to 5 g primary standard  $\text{Na}_2\text{CO}_3$  at  $250^\circ\text{C}$  for 4 h and cool in a desiccator. Weigh 1.03 gm. (to the nearest mg), transfer to a 1-L volumetric flask, fill flask to the mark with distilled water, dissolve and mix reagent. Do not keep longer than 1 week.

### c. Procedure

Titrate over a white surface 100 ml of the sample contained in a 250-ml conical flask with standard hydrochloric acid using two or three drops of methyl orange Indicator. (NOTE – If more than 30 ml of acid is required for the titration, a smaller suitable aliquot of the sample shall be taken.)

### d. Calculation

**Total alkalinity** (as  $\text{CaCO}_3$ ),  $\text{mg/l} = 10 V \text{ or } N \times V \times 50 \times 1000$

T.A. (as  $\text{CaCO}_3$ ) = -----  
Sample Amount

Where N = Normality of HCl used

V = volume in ml of standard hydrochloric acid used in the titration.

## Alkalinity to Phenolphthalein

The sample is titrated against standard acid using phenolphthalein indicator.

### a. Reagents

- i) Phenolphthalein Indicator Solution : Dissolve 0.1 g of phenolphthalein in 60 ml of ETHANOL and dilute with Distilled water to 100 ml.
- ii) Standard hydrochloric Acid – 0.02 N.

### b. Procedure

Add 2 drops of phenolphthalein indicator solution to a sample of suitable size, 50 or 100 ml, in a conical flask and titrate over a while surface with standard hydrochloric acid.

### c. Calculation

$$\text{Alkalinity to phenolphthalein (as CaCO}_3\text{), mg/l} = \frac{1000 V_1}{V_2}$$

Where

$V_1$  = volume in ml of standard hydrochloric acid used in the titration, and

$V_2$  = Volume in ml of the sample taken for the test.

### Caustic Alkalinity

#### a. General

Caustic alkalinity is the alkalinity corresponding to the hydroxides present in water and is calculated from total alkalinity (T) and alkalinity to phenolphthalein (P).

<b>b. Procedure</b> Determine total alkalinity and alkalinity to phenolphthalein and calculate caustic alkalinity as shown in Table below. Result of Titration Caustic Alkalinity or Hydroxide Alkalinity as $\text{CaCO}_3$ Carbonate Alkalinity as $\text{CaCO}_3$ Bicarbonate Concentration as $\text{CaCO}_3$ <b>Result of Titration</b>	<b>Caustic Alkalinity or Hydroxide Alkalinity as <math>\text{CaCO}_3</math></b>	<b>Carbonate Alkalinity as <math>\text{CaCO}_3</math></b>	<b>Bicarbonate Concentration as <math>\text{CaCO}_3</math></b>
P=0	0	0	0
P<1/2T	0	2P	T-2P
P=1/2T	0	2P	0
P>1/2T	2P-T	2(T-P)	0
P=T	T	0	0

The alkalinity of water is a measure of its capacity to neutralize acids. The alkalinity of natural water is due to the salts of carbonate, bicarbonate, borates, silicates and phosphates along with the hydroxyl ions in free state.

However, the major portion of the alkalinity in natural waters is caused by hydroxide, carbonate, and bicarbonates which may be ranked in order of their association with high pH values.

Alkalinity values provide guidance in applying proper doses of chemicals in water and waste water treatment processes, particularly in coagulation and softening.

## **Alkalinity (Total)**

References: ASTM D 1067-92, Acidity or Alkalinity of Water.  
APHA Standard Methods, 19th ed., p. 2-26, method 2320B (1995).  
EPA Methods for Chemical Analysis of Water and Wastes, method 310.1 (1983).

The alkalinity of water is a measurement of its buffering capacity or ability to react with strong acids to a designated pH. Alkalinity of natural waters is typically a combination of bicarbonate, carbonate, and hydroxide ions. Sewage and wastewaters usually exhibit higher alkalinities either due to the presence of silicates and phosphates or to a concentration of the ions from natural waters.

Alkalinity inhibits corrosion in boiler and cooling waters and is therefore a desired quality which must be maintained. It is also measured as a means of controlling water and wastewater treatment processes or the quality of various process waters. In natural waters, excessive alkalinity can render water unsuitable for irrigation purposes and may indicate the presence of industrial effluents.

### ***The Titrimetric Method***

CHEMetrics' tests determine total or "M" alkalinity using an acid titrant and a pH indicator. The end point of the titration occurs at pH 4.5. Results are expressed as ppm (mg/L) CaCO<sub>3</sub>.

### **Hardness (calcium)**

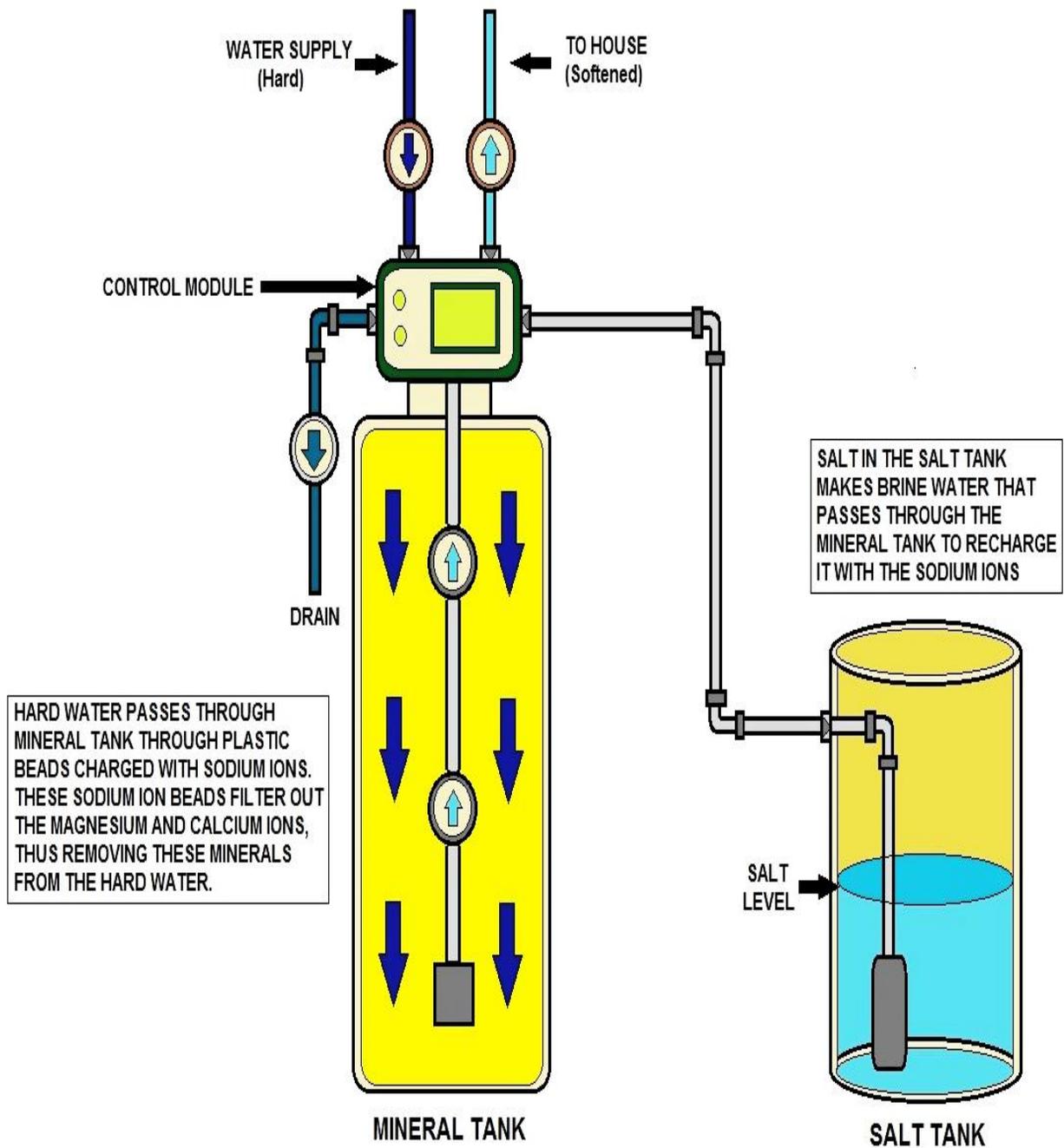
Reference: West, T. S., DSC, Ph.D., Complexometry with EDTA and Related Reagents, 3rd ed., p. 46, 164 (1969).

Originally described as water's capacity to precipitate soap, hardness is one of the most frequently determined qualities of water. It is a composite of the calcium, magnesium, strontium, and barium concentrations in a sample. The current practice is to assume total hardness refers to the calcium and magnesium concentrations only.

Completely de-hardened water, resulting from sodium zeolite or other suitable ion exchange treatment, is required for various processes-including power generation, printing and photo finishing, pulp and paper manufacturing, and food and beverage processing. Hard water can cause scale formation on heat exchange surfaces, resulting in decreased heat transfer and equipment damage.

The Titrimetric Method. This method is specific for calcium hardness. The EGTA titrant in alkaline solution is employed with zincon indicator. Results are expressed as ppm (mg/L) CaCO<sub>3</sub>.

Shelf-life. 8 months. Although the reagent itself is stable, the end point indicator has a limited shelf-life. We recommend stocking quantities that will be used within 7 months.



## BASICS OF HOW A WATER SOFTENER WORKS

## Hard Water Section

Water contains various amounts of dissolved minerals, some of which impart a quality known as hardness. Consumers frequently complain about problems attributed to hard water, such as the formation of scale on cooking utensils and hot water heaters. In this document we will examine the occurrence, and effects, of hard water and the hard water treatment or softening process that removes the hardness-causing minerals. The precipitation process most frequently used is generally known as the lime process or lime soda process. Because of the special facilities required and the complexity of the process, it is generally applicable only to medium- or large-size water systems where all treatment can be accomplished at a central location. This process will provide softened water at the lowest cost. Lime softening can be used for treatment of either groundwater or surface water sources.

The other commonly used method of softening involves the ion exchange process. This process has the advantages of a considerably lower initial cost and ease of use by small systems or by large systems at multiple locations. The principal disadvantage is that operating costs are considerably higher. Ion exchange processes can typically be used for direct treatment of ground-water, so long as turbidity and iron levels are not excessive.

For treatment of surface water, the process normally must be preceded by conventional treatment. Softening can also be accomplished using membrane technology, electrodialysis, distillation, and freezing. Of these, membrane methods seem to have the greatest potential.

### Distillers

Various sizes of distillers are available for home use. They all work on the principle of vaporizing water and then condensing the vapor. In the process, dissolved solids such as salt, metals, minerals, asbestos fibers, and other particles are removed. Some organic chemicals are also removed, but those that are more volatile are often vaporized and condensed with the product water. Distillers are effective in killing all microorganisms.

The principal problem with a distiller is that a small unit can produce only 2-3 gal (7.5 -11 Lt) a day, and that the power cost for operation will be substantially higher than the operating cost of other types of treatment devices.

Water Distillers have a high energy cost (approximately 20-30 cents per gallon). They must be carbon filtered before and/or after to remove volatile chemicals. It is considered "**dead**" water because the process removes all extra oxygen and energy. It has no taste. It is still second only to reverse osmosis water for health. Diet should be rich in electrolytes, as the aggressive nature of distilled water can "**leach**" electrolytes from the body.



## Occurrence of Hard Water

Hard water is caused by soluble, divalent, metallic cations, (positive ions having valence of 2). The principal chemicals that cause water hardness are calcium (**Ca**) and magnesium (**Mg**). Strontium, aluminum, barium, and iron are usually present in large enough concentrations to contribute significantly to the total hardness.

Water hardness varies considerably in different geographic areas of the contiguous 48 states. This is due to different geologic formations, and is also a function of the contact time between water and limestone deposits. Magnesium is dissolved as water passes over and through dolomite and other magnesium-bearing minerals. Because groundwater is in contact with these formations for a longer period of time than surface water, groundwater is normally harder than surface water.

## Expressing Water Hardness Concentration

Water hardness is generally expressed as a concentration of calcium carbonate, in terms of milligrams per liter as  $\text{CaCO}_3$ . The degree of hardness that consumers consider objectionable will vary, depending on other qualities of the water and on the hardness to which they have become accustomed. We will show two different classifications of the relative hardness of water:

### Comparative classifications of water for softness and hardness

Classification	mg/L as $\text{CaCO}_3$ *	mg/L as $\text{CaCO}_3$ †
Soft	0 – 75	0 – 60
Moderately hard	75 – 150	61 – 120
Hard	150 – 300	121 – 180
Very hard	Over 300	Over 180

*Source: Adapted from Sawyer 1960 and Briggs and Ficke 1977.*

\* Per Sawyer (1960)

† Per Briggs and Ficke (1977)

## Types of Water Hardness

Hardness can be categorized by either of two methods: calcium versus magnesium hardness and carbonate versus non-carbonate hardness. The calcium-magnesium distinction is based on the minerals involved. Hardness caused by calcium is called calcium hardness, regardless of the salts associated with it, which include calcium sulfate ( **$\text{CaSO}_4$** ), calcium chloride ( **$\text{CaCl}_2$** ), and others. Likewise, hardness caused by magnesium is called magnesium hardness. Calcium and magnesium are normally the only significant minerals that cause hardness, so it is generally assumed that

$$\text{Total hardness} = \text{calcium hardness} + \text{magnesium hardness}$$

The carbonate-noncarbonate distinction, however, is based on hardness from either the bicarbonate salts of calcium or the normal salts of calcium and magnesium involved in causing water hardness. Carbonate hardness is caused primarily by the bicarbonate salts of calcium and magnesium, which are calcium bicarbonate,  $\text{Ca}(\text{HCO}_3)_2$ , and magnesium bicarbonate  $\text{Mg}(\text{HCO}_3)_2$ . Calcium and magnesium combined with carbonate ( $\text{CO}_3$ ) also contribute to carbonate hardness.

Noncarbonate hardness is a measure of calcium and magnesium salts other than carbonate and bicarbonate salts. These salts are calcium sulfate, calcium chloride, magnesium sulfate ( $\text{MgSO}_4$ ), and magnesium chloride ( $\text{MgCl}_2$ ). Calcium and magnesium combined with nitrate may also contribute to noncarbonate hardness, although it is a very rare condition. For carbonate and noncarbonate hardness,

$$\text{Total hardness} = \text{carbonate hardness} + \text{noncarbonate hardness}$$

When hard water is boiled, carbon dioxide ( $\text{CO}_2$ ) is driven off, and Bicarbonate salts of calcium and magnesium then settle out of the water to form calcium and magnesium carbonate precipitates. These precipitates form the familiar chalky deposits on teapots. Because it can be removed by heating, carbonate hardness is sometimes called “**Temporary hardness.**” Because noncarbonated hardness cannot be removed or precipitated by prolonged boiling, it is sometimes called “**permanent hardness.**”

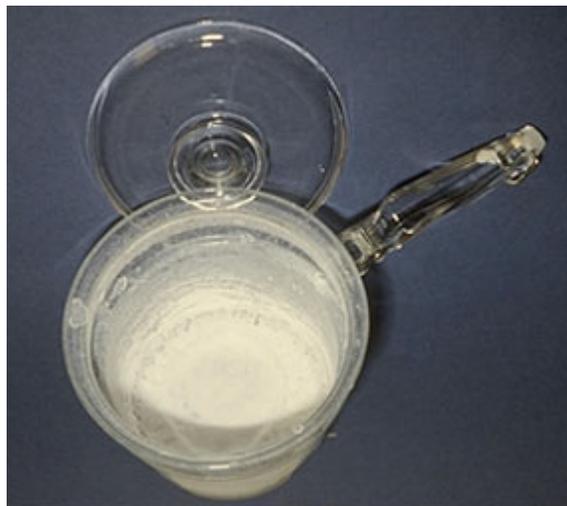
## Objections to Hard Water

### Scale Formation

Hard water forms scale, usually calcium carbonate, which causes a variety of problems. Left to dry on the surface of glassware and plumbing fixtures, including showers doors, faucets, and sink tops; hard water leaves unsightly white scale known as water spots. Scale that forms on the inside of water pipes will eventually reduce the flow capacity or possibly block it entirely. Scale that forms within appliances and water meters causes wear on moving parts.

When hard water is heated, scale forms much faster. In particular, when the magnesium hardness is more than about 40 mg/l (as  $\text{CaCO}_3$ ), magnesium hydroxide scale will deposit in hot water heaters that are operated at normal temperatures of 140-150°F (60-66°C).

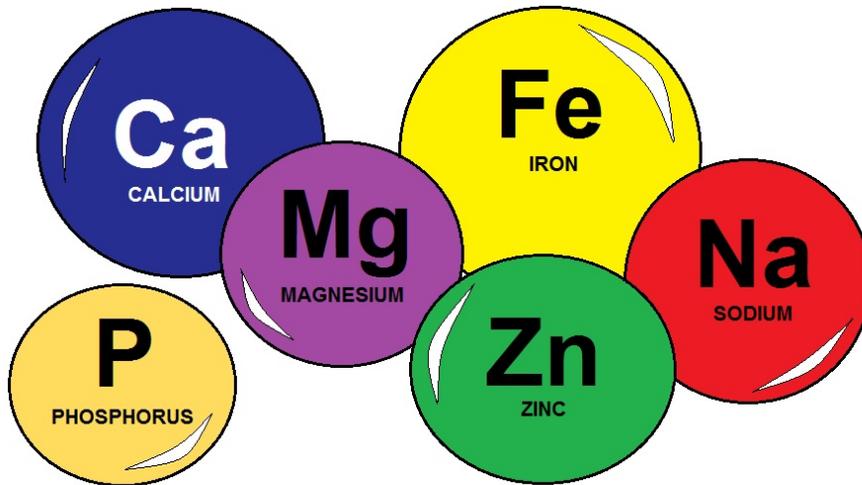
A coating of only 0.04 in. (1 mm) of scale on the heating surfaces of a hot water heater creates an insulation effect that will increase heating costs by about 10 percent.



### Effect on Soap

The historical objection to hardness has been its effect on soap. Hardness ions form precipitates with soap, causing unsightly “**curd,**” such as the familiar bathtub ring, as well as reduced efficiency in washing and laundering. To counteract these problems, synthetic detergents have been developed and are now used almost exclusively for washing clothes and dishes.

These detergents have additives known as sequestering agents that “**tie up**” the hardness ions so that they cannot form the troublesome precipitates. Although modern detergents counteract many of the problems of hard water, many customers prefer softer water. These customers can install individual softening units or use water from another source, such as a cistern, for washing.



**EXAMPLES OF TDS**  
 (Total Dissolved Solids)  
 FOUND IN WATER SOURCES

CAN BE FROM AGRICULTURE OR URBAN RUNOFF, WHICH CARRY EXCESS MINERALS INTO THE WATER SOURCE

MINERAL SPRINGS CONTAIN HIGH LEVELS OF TDS BECAUSE THE ROCKS WHICH THE WATER SOURCE FLOWS THROUGH HAVE A HIGH SALT CONTENT



**MINERALS THAT AFFECT THE QUALITY OF WATER SOURCE**

<b>WATER HARDNESS SCALE</b>		
<b>Grains/Gal.</b>	<b>mg/L or PPM</b>	<b>Classification</b>
LESS THAN 1	LESS THAN 17.1	SOFT
1 - 3.5	17.1 - 60	SLIGHTLY HARD
3.5 - 7	60 - 120	MODERATELY HARD
7 - 10	120 - 180	HARD
Over 10	Over 180	VERY HARD

1 gpg = 17.1 mg/L = 17.1 ppm

## Water Softening

Water softening is a method of removing from water the minerals that make it hard. Hard water does not dissolve soap readily. It forms scale in pipes, boilers, and other equipment in which it is used. The principal methods of softening water are the lime soda process and the ion exchange process.

In the **lime soda process**, soda ash and lime are added to the water in amounts determined by chemical tests. These chemicals combine with the calcium and magnesium in the water to make insoluble compounds that settle to the bottom of the water tank.

In the **ion exchange process**, the water filters through minerals called **zeolites**. As the water passes through the filter, the sodium ions in the zeolite are exchanged for the calcium and magnesium ions in the water, and the water is softened. After household softeners become exhausted, a strong solution of **sodium chloride** (salt) is passed through the filter to replace the sodium that has been lost. The use of two exchange materials makes it possible to remove both metal and acid ions from water.



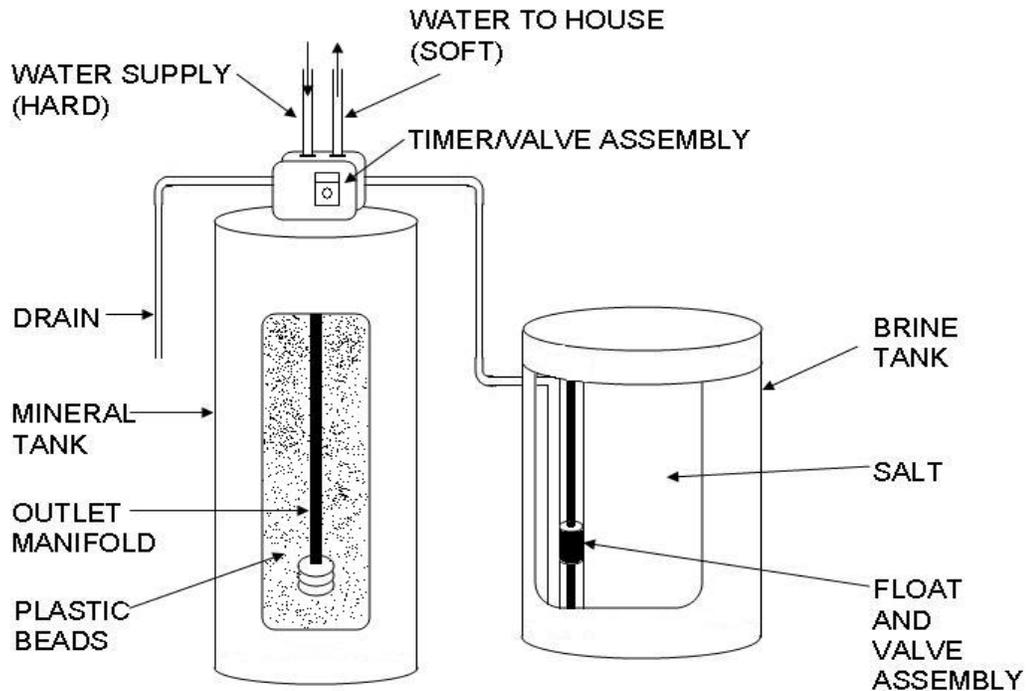
Some cities and towns, however, prohibit or restrict the use of ion exchange equipment on drinking water, pending the results of studies on how people are affected by the consumption of the added sodium in softened water. The containers hold the resin for the deionization. Calcium and magnesium in water create hard water, and high levels can clog pipes. The best way to soften water is to use a water softener unit connected into the water supply line. You may want to consider installing a separate faucet for unsoften water for drinking and cooking. Water softening units also remove iron.

The most common way to soften household water is to use a water softener. Softeners may also be safely used to remove up to about 5 milligrams per liter of dissolved iron if the water softener is rated for that amount of iron removal. Softeners are automatic, semi-automatic, or manual. Each type is available in several sizes and is rated on the amount of hardness it can remove before regeneration is necessary. Using a softener to remove iron in naturally soft water is not advised; a green-sand filter is a better method. When the resin is filled to capacity, it must be recharged. Fully automatic softeners regenerate on a preset schedule and return to service automatically. Regeneration is usually started by a preset time clock; some units are started by water use meters or hardness detectors.

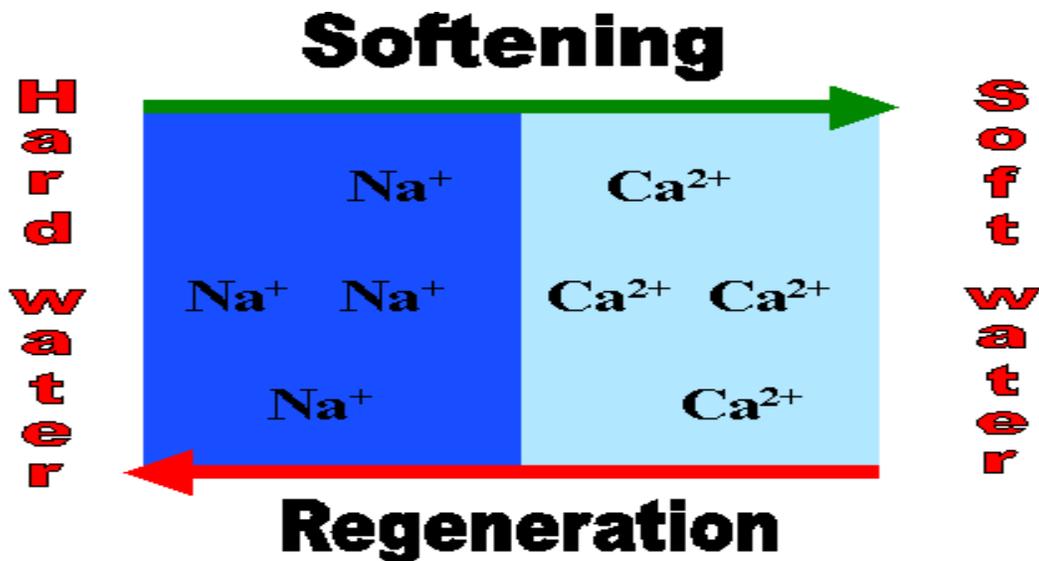
Semi-automatic softeners have automatic controls for everything except for the start of regeneration. Manual units require manual operation of one or more valves to control back washing, brining and rinsing. In many areas, there are companies that provide a water softening service. For a monthly fee the company installs a softener unit and replaces it periodically with a freshly charged unit.

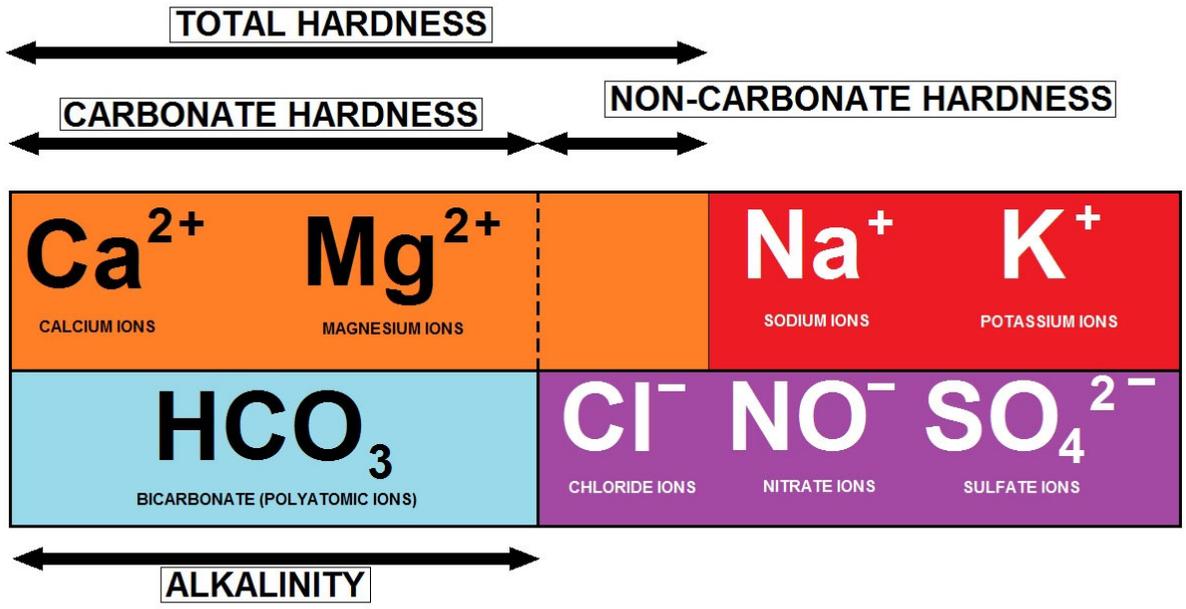
The principle behind water softening is really just simple chemistry. A water softener contains resin beads which hold electrically charged ions. When hard water passes through the softener, calcium and magnesium ions are attracted to the charged resin beads. It's the resulting removal of calcium and magnesium ions that produces "**soft water**."

The diagram below shows the exchange that takes place during the water softening process. When the resin beads in your softener become saturated with calcium and magnesium ions, they need to be recharged. Sodium ions from the water softening salt reactivate the resin beads so they can continue to do their job. Without sufficient softening salt, your water softener is less efficient. As a rule, you should check your water softener once a week to be sure the salt level is always at least one quarter full.

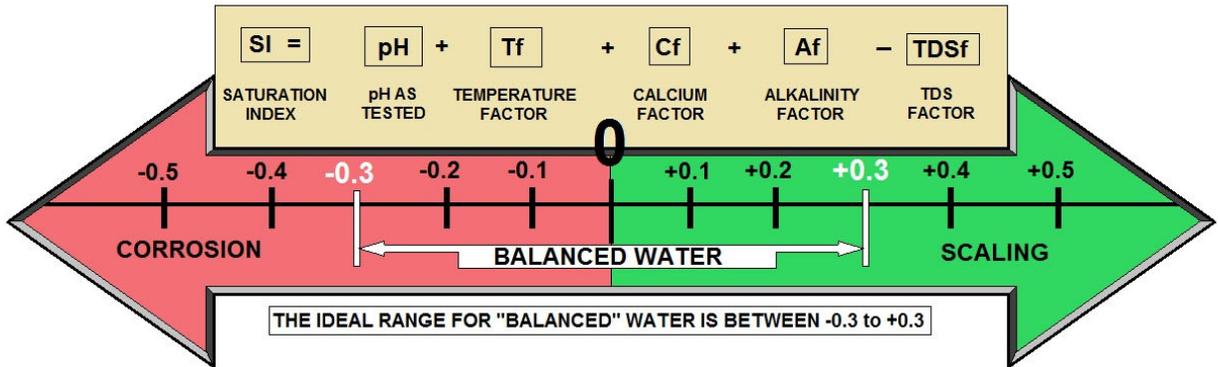


Conventional Household Water Softener





## CARBONATE HARDNESS CHART

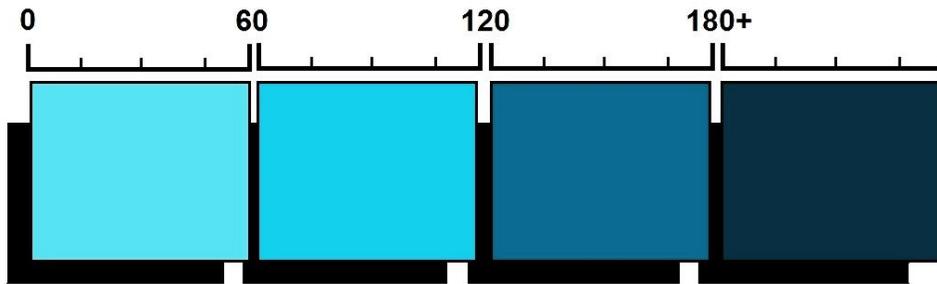


## LANGELIER SATURATION INDEX

GENERAL HARDNESS	
TEMPORARY HARDNESS or CARBONATE HARDNESS (KH)	PERMANENT HARDNESS or NON-CARBONATE HARDNESS (NCH)
CALCIUM (Ca) Carbonate and MAGNESIUM (Mg) Carbonate	CALCIUM (Ca) & MAGNESIUM (Mg) SULFATES
	CALCIUM (Ca) & MAGNESIUM (Mg) CHLORIDES
	CALCIUM (Ca) & MAGNESIUM (Mg) NITRATES



### FORMS OF HARDNESS IN WATER

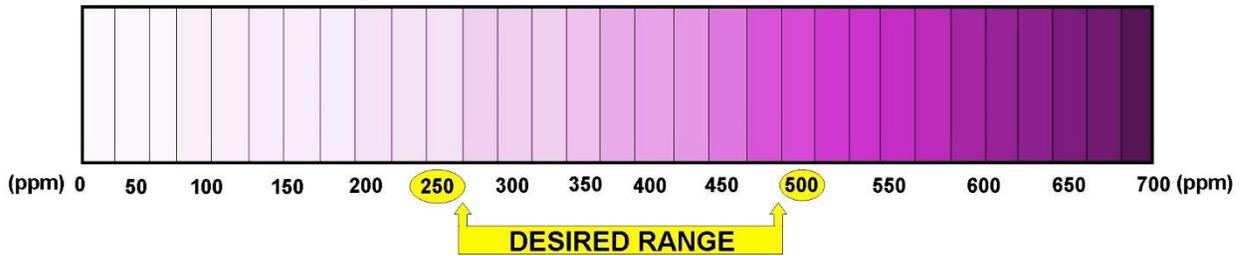


### MEASURING HARDNESS OF WATER (Calcium Ions Present)

CAUSES PITTING

BALANCED

SCALE-FORMING



### CALCIUM HARDNESS MEASUREMENT

## Commonly Found Water Chemistry / Quality Problems

### Turbidity

Turbidity is caused by particles suspended in water. These particles scatter or reflect light rays, making the water appear cloudy.

Turbidity is expressed in nephelometric turbidity units (ntu) and a reading in excess of 5 ntu is generally noticeable to water system customers.

Besides the appearance being unpleasant to customers, turbidity in water is significant from a public health standpoint because suspended particles could shelter microorganisms from the disinfectant and allow them to still be viable when they reach the customer.

EPA regulations direct that, for most water systems, the turbidity of water entering the distribution system must be equal or less than 0.5 ntu in at least 95 percent of the measurements taken each month.

At no time may the turbidity exceed 5 ntu.

Turbidity changes in the distribution system can indicate developing problems.

Increases in turbidity may be caused by changes in velocity or inadequate flushing following main replacement.

### Hardness

Hardness is a measure of the concentration of calcium and magnesium in water. Water hardness usually comes from water contacting rock formations, such as water from wells in limestone formations. Soft ground water may occur where topsoil is thin and limestone formations are sparse or absent. Most surface water is of medium hardness.

Hard and soft water are both satisfactory for human consumption, but customers may object to very hard water because of the scale it forms in plumbing fixtures and on cooking utensils.

Hardness is also a problem for some industrial and commercial users because of scale buildup in boilers and other equipment.

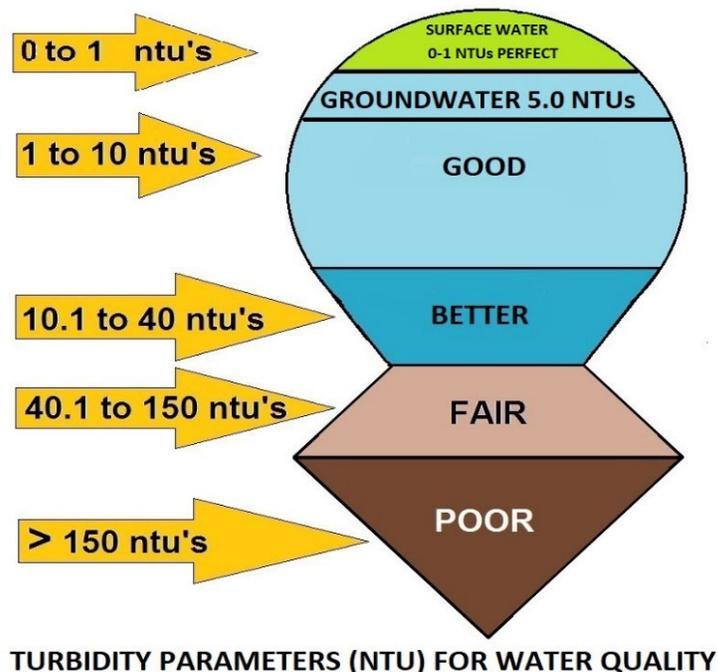
Water generally is considered most satisfactory for household use when the hardness is between 75 and 100 mg/L as calcium carbonate ( $\text{CaCO}_3$ ). Water with 300 mg/L of hardness usually is considered **hard**. Very soft water of 30 mg/L or less is found in some section of the United States. Soft water usually is quite corrosive, and may have to be treated to reduce the corrosivity.



## More on Turbidity

One physical characteristic of water is turbidity. A measure of the cloudiness of water caused by suspended particles. The cloudy appearance of water caused by the presence of tiny particles. High levels of turbidity may interfere with proper water treatment and monitoring. If high quality raw water is low in turbidity, there will be a reduction in water treatment costs. Turbidity is undesirable because it causes health hazards.

An MCL for turbidity established by the EPA because turbidity interferes with disinfection. This characteristic of water changes the most rapidly after a heavy rainfall. The following conditions may cause an inaccurate measure of turbidity; the temperature variation of a sample, a scratched or unclean sample tube in the nephelometer and selecting an incorrect wavelength of a light path.



### Surface Water System Compliance Information

*(Depends on Systems and Rule)*

- ▶ 0.34 NTU in 95% of samples, never to exceed 1.0 NTU spike
- ▶ Sample turbidity at each individual filter effluent
- ▶ Sample the combined filter turbidity at the clear well
- ▶ (Groundwater turbidity = 5.0 NTU)

### Turbidity Key

- ▶ Turbidity can also be measured in ppm (parts per million) and its size is measured in microns. Turbidity can be particles in the water consisting of finely divided solids, larger than molecules, but not visible by the naked eye; ranging in size from .001 to .150mm (1 to 150 microns).
- ▶ 0.34 NTU in 95% of surface water samples, never to exceed 1.0 NTU spike

## Iron

Iron occurs naturally in rocks and soils and is one of the most abundant elements. It occurs in two forms. Ferrous iron ( $\text{Fe}^{2+}$ ) is in a dissolved state, and water containing ferrous iron is colorless. Ferric iron ( $\text{Fe}^{3+}$ ) has been oxidized, and water containing it is rust-colored. Water from some well sources contains significant levels of dissolved iron, which is colorless, but rapidly turns brown as air reaches the water and oxidizes the iron.

There are no known harmful effects to humans from drinking water containing iron, but NSDWR suggest a limit of 0.5 mg/L. At high levels, the staining of plumbing fixtures and clothing becomes objectionable. Iron also provides nutrient source for some bacteria that grow in distribution systems and wells. Iron bacteria, such as *Gallionella*, cause red water, tastes and odors, clogged pipes, and pump failure.

Whenever tests on water samples show increased iron concentrations between the point where water enters the distribution system and the consumer's tap, either corrosion, iron bacteria, or both are probably taking place. If the problem is caused by bacteria, flushing mains, shock chlorination, and carrying increased residual chlorine are alternatives to consider.

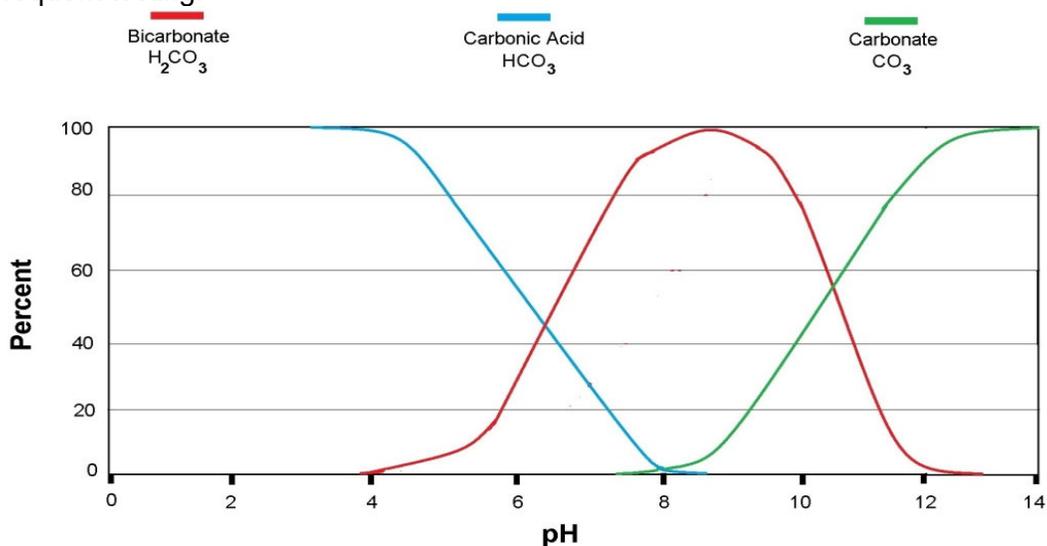
## Manganese

Manganese in ground water creates problems similar to iron. It does not usually discolor the water, but will stain washed clothes and plumbing fixtures black; this is very unpopular with customers. Consumption of manganese has no known harmful effects on humans, but the NSDWR recommend a concentration not to exceed 0.05 mg/L to avoid customer complaints.

## Water Quality Safeguards

The **critical** safeguard for water distribution system operations are

- continuous positive pressure in the mains; 20 pounds per square inch (psi) minimum residual pressure is recommended;
- maintenance of chlorine residual;
- cross-connection control; and
- frequent testing.



**EFFECTS OF ALKALINITY FROM pH**

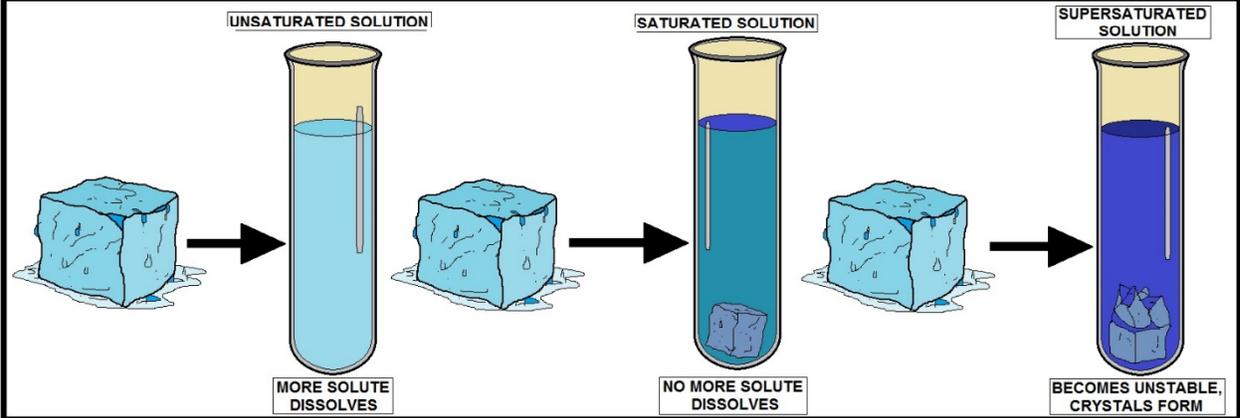
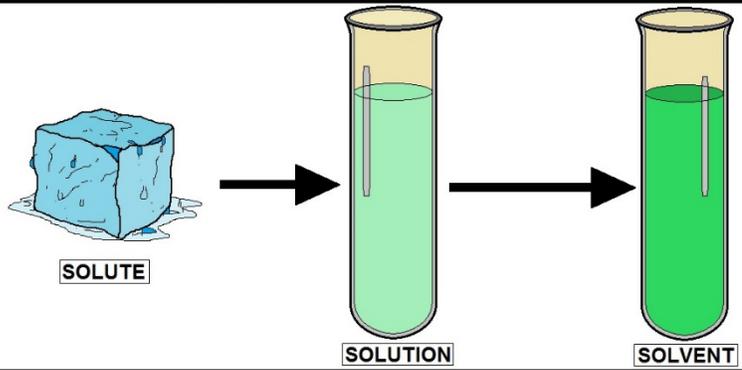
# SOLUBILITY OF SUBSTANCES

WATER SOLUBILITY IS THE MEASUREMENT OF CHEMICAL SUBSTANCE THAT CAN DISSOLVE IN WATER AT A SPECIFIC TEMPERATURE

THE UNIT OF MEASUREMENT FOR SOLUBILITY IS GENERALLY MEASURED IN mg/L (Milligrams per Liter) or ppm (Parts Per Million)

THE SOLUTE CAN BE SOLID, LIQUID OR GAS, WHILE THE SOLVENT IS USUALLY SOLID OR LIQUID. SOLUBILITY MAINLY DEPENDS ON THE COMPOSITION OF SOLUTE AND SOLVENT (Including their pH and presence of other dissolved substances).

THE TERM "SOLUBLE" IS SOMETIMES USED FOR MATERIALS THAT CAN FORM COLLOIDAL SUSPENSIONS OF VERY FINE SOLID PARTICLES IN LIQUID



## SOLUBILITY OF SUBSTANCES EXAMPLE

## Water Quality/Chemistry Key Words

**2,4-D:** A chlorinated phenoxy compound, functions as a systemic herbicide and is used to control many types of broadleaf weeds. There are many forms or derivatives (esters, amines, salts) of 2,4-D and these vary in solubility and volatility. Unless otherwise specified, this document will refer to the acid form of 2,4-D. This compound is used in cultivated agriculture and in pasture and rangeland applications, forest management, home and garden situations and for the control of aquatic vegetation. 2,4-D was a major component (about 50%) of the product Agent Orange used extensively throughout Vietnam. However most of the problems associated with the use of Agent Orange were associated with a contaminant (dioxin) in the 2,4,5-T component of the defoliant. The association of 2,4-D with Agent Orange has prompted a vast amount of study on the herbicide.

**ANTIMONY:** A chemical element with the symbol Sb (Latin: stibium, meaning "mark") and atomic number 51. A metalloid, antimony has four allotropic forms. The stable form of antimony is a blue-white metalloid. Yellow and black antimony are unstable non-metals. Antimony is used in flame-proofing, paints, ceramics, enamels, a wide variety of alloys, electronics, and rubber.

**ASBESTOS:** A mineral fiber that has been used commonly in a variety of building construction materials for insulation and as a fire-retardant. EPA and CPSC have banned several asbestos products. Manufacturers have also voluntarily limited uses of asbestos. Today, asbestos is most commonly found in older homes, in pipe and furnace insulation materials, asbestos shingles, millboard, textured paints and other coating materials, and floor tiles.

**BARIUM:** A chemical element. It has the symbol Ba, and atomic number 56. Barium is a soft silvery metallic alkaline earth metal. It is never found in nature in its pure form due to its reactivity with air. Its oxide is historically known as baryta but it reacts with water and carbon dioxide and is not found as a mineral. The most common naturally occurring minerals are the very insoluble barium sulfate, BaSO<sub>4</sub> (barite), and barium carbonate, BaCO<sub>3</sub> (witherite). Benitoite is a rare gem containing barium.

**BERYLLIUM:** A chemical element with the symbol Be and atomic number 4. A bivalent element, beryllium is a steel grey, strong, light-weight yet brittle alkaline earth metal. It is primarily used as a hardening agent in alloys, most notably beryllium copper. Commercial use of beryllium metal presents technical challenges due to the toxicity (especially by inhalation) of beryllium-containing dusts.

**BROMATE:** An inorganic anion, bromate is tasteless and colorless, with a low volatility. As a moderately strong oxidant, bromate is reactive. BrO<sub>3</sub><sup>-</sup> is a bromine-based oxoanion. A bromate is a chemical compound that contains this ion. Examples of bromates include sodium bromate, (NaBrO<sub>3</sub>), and potassium bromate, (KBrO<sub>3</sub>).

**CADMIUM:** A chemical element with the symbol Cd and atomic number 48. A relatively abundant, soft, bluish-white, transition metal, cadmium is known to cause cancer and occurs with zinc ores. Cadmium is used largely in batteries and pigments, for example in plastic products.

**CHLORITE:** The chlorite ion is ClO<sub>2</sub><sup>-</sup>. A chlorite (compound) is a compound that contains this group, with chlorine in oxidation state +3. Chlorites are also known as salts of chlorous acid.

**CHROMIUM:** A chemical element which has the symbol Cr and atomic number 24. It is a steel-gray, lustrous, hard metal that takes a high polish and has a high melting point. It is also odorless, tasteless, and malleable.

**CONTACT TIME (CT):** To inactivate viruses and bacteria, the minimum disinfection contact time measured before the first customer should be six milligrams per minute per liter (6 mg-min/L). This value is called “Chlorine Contact Time” or CT. To calculate CT, multiply the free chlorine residual concentration (C) times the contact time (T). To get the required CT value of 6, adjust the free chlorine residual concentration or the contact time.

**DISINFECTION BYPRODUCTS:** Disinfection byproducts are chemical, organic and inorganic substances that can form during a reaction of a disinfectant with naturally present organic matter in the water.

**DPD METHOD:** Presence of free chlorine in the distribution network is indication of correct disinfection. Chlorine in water is determined according to ISO 7393-2 by colorimetric HACH method on the basis of DPD (N, N-diethyl - p – phenyldiamine). The photometric detection uses the wave lengths of 490 – 555 nm. Hach elected, for most of his DPD colorimetric systems, the wave length of 530 nm.

**FORMAZIN TURBIDITY UNIT (FTU):** A unit used to measure the clarity of water. The ISO refers to the units as FNU (Formazin Nephelometric Units). The technique is the same as that for the NTU, but the calibration uses microspheres of the polymer formazin.

**HALOACETIC ACIDS:** Haloacetic acids are carboxylic acids in which a halogen atom takes the place of a hydrogen atom in acetic acid. Thus, in a monohaloacetic acid, a single halogen would replace a hydrogen atom. For example, chloroacetic acid would have the structural formula  $\text{CH}_2\text{ClCO}_2\text{H}$ . In the same manner, in dichloroacetic acid two chlorine atoms would take the place of two hydrogen atoms ( $\text{CHCl}_2\text{CO}_2\text{H}$ ).

**HIGH-TEST HYPOCHLORITE:** A composition composed mainly of calcium hypochlorite is commonly called high test hypochlorite. High-Test Hypochlorite contains not less than 60.0% of available chlorine.

**HYDROCHLORIC ACID:** It is the aqueous solution of hydrogen chloride gas (HCl). It is a strong acid, and the major component of gastric acid, and of wide industrial use. Hydrochloric acid must be handled with appropriate safety precautions because it is a highly corrosive liquid.

**INFORMATION COLLECTION RULE (ICR):** EPA collected data required by the Information Collection Rule (May 14, 1996) to support future regulation of microbial contaminants, disinfectants, and disinfection byproducts. The rule was intended to provide EPA with information on chemical byproducts that form when disinfectants used for microbial control react with chemicals already present in source water (disinfection byproducts (DBPs)); disease-causing microorganisms (pathogens), including Cryptosporidium; and engineering data to control these contaminants.

**IRON BACTERIA:** In the management of water-supply wells, iron bacteria are bacteria that derive the energy they need to live and multiply by oxidizing dissolved ferrous iron (or the less frequently available manganese and aluminum). The resulting ferric oxide is insoluble, and appears as brown gelatinous slime that will stain plumbing fixtures, and clothing or utensils washed with the water carrying it, and may contribute to internal corrosion of the pipes and fixtures the water flows through. They are known to grow and proliferate in waters containing as low as 0.1mg/l of iron. However, at least 0.3 ppm of dissolved oxygen is needed to carry out oxidation. The proliferation of iron bacteria, in some way, increases the chance of sulfur bacteria infestation.

**LETHAL CONCENTRATION 50:** Also referred to as LC50, a concentration of a pollutant or effluent at which 50 percent of the test organisms die; a common measure of acute toxicity.

**MANGANESE (IV) OXIDE:** The chemical compound  $MnO_2$ , commonly called manganese dioxide. This blackish or brown solid occurs naturally as the mineral pyrolusite, which is the main ore of manganese. It is also present in manganese nodules. The principal use for  $MnO_2$  is for dry-cell batteries, such as the alkaline battery and the zinc-carbon battery. In 1976 this application accounted for 500,000 tons of pyrolusite.  $MnO_2$  is also used for production of  $MnO_4^-$ . It is used extensively as an oxidizing agent in organic synthesis, for example, for the oxidation of allylic alcohols.

**MAXIMUM CONTAMINANT LEVEL (MCL):** The maximum concentration of a chemical that is allowed in public drinking water systems.

**MAXIMUM CONTAMINANT LEVEL GOAL (MCLG):** The maximum level at which a contaminant can exist in drinking water without having an adverse effect on human health.

**NEPHELOMETRIC TURBIDITY UNIT (NTU):** The unit used to describe turbidity. Nephelometric refers to the way the instrument, a nephelometer, measures how much light is scattered by suspended particles in the water. The greater the scattering, the higher the turbidity. Therefore, low NTU values indicate high water clarity, while high NTU values indicate low water clarity.

**PERMISSIBLE EXPOSURE LIMIT (PEL or OSHA PEL):** A legal limit in the United States for exposure of an employee to a substance or physical agent. For substances it is usually expressed in parts per million (ppm), or sometimes in milligrams per cubic meter ( $mg/m^3$ ). Units of measure for physical agents such as noise are specific to the agent. Permissible Exposure Limits are established by the Occupational Safety and Health Administration (OSHA).

**POWDERED ACTIVATED CARBON TREATMENT (PACT):** A wastewater technology in which powdered activated carbon is added to an anaerobic or aerobic treatment system. The carbon in the biological treatment process acts as a "buffer" against the effects of toxic organics in the wastewater.

**PPM:** Abbreviation for parts per million.

**QUICKLIME:** A calcium oxide material produced by calcining limestone to liberate carbon dioxide, also called "calcined lime" or "pebble lime", commonly used for pH adjustment. Chemical formula is  $CaO$ .

**RECOMMENDED EXPOSURE LIMIT (REL):** An occupational exposure limit that has been recommended by the U.S. National Institute for Occupational Safety and Health to OSHA for adoption as a Permissible Exposure Limit. The REL is a level that NIOSH believes would be protective of worker safety and health over a working lifetime if used in combination with engineering and work practice controls, exposure and medical monitoring, posting and labeling of hazards, worker training and personal protective equipment. No REL has ever been adopted by OSHA, but they have been used as guides by some industry and advocacy organizations.

**SCADA:** A remote method of monitoring pumps and equipment. 130 degrees F is the maximum temperature that transmitting equipment is able to withstand. If the level controller may be set with too close a tolerance 45 could be the cause of a control system that is frequently turning a pump on and off.

**TRANSIENT, NON-COMMUNITY WATER SYSTEM: TNCWS** A water system which provides water in a place such as a gas station or campground where people do not remain for long periods of time. These systems do not have to test or treat their water for contaminants which pose long-term health risks because fewer than 25 people drink the water over a long period. They still must test their water for microbes and several chemicals. A Transient Non-Community Water System: Is not required to sample for VOC's.

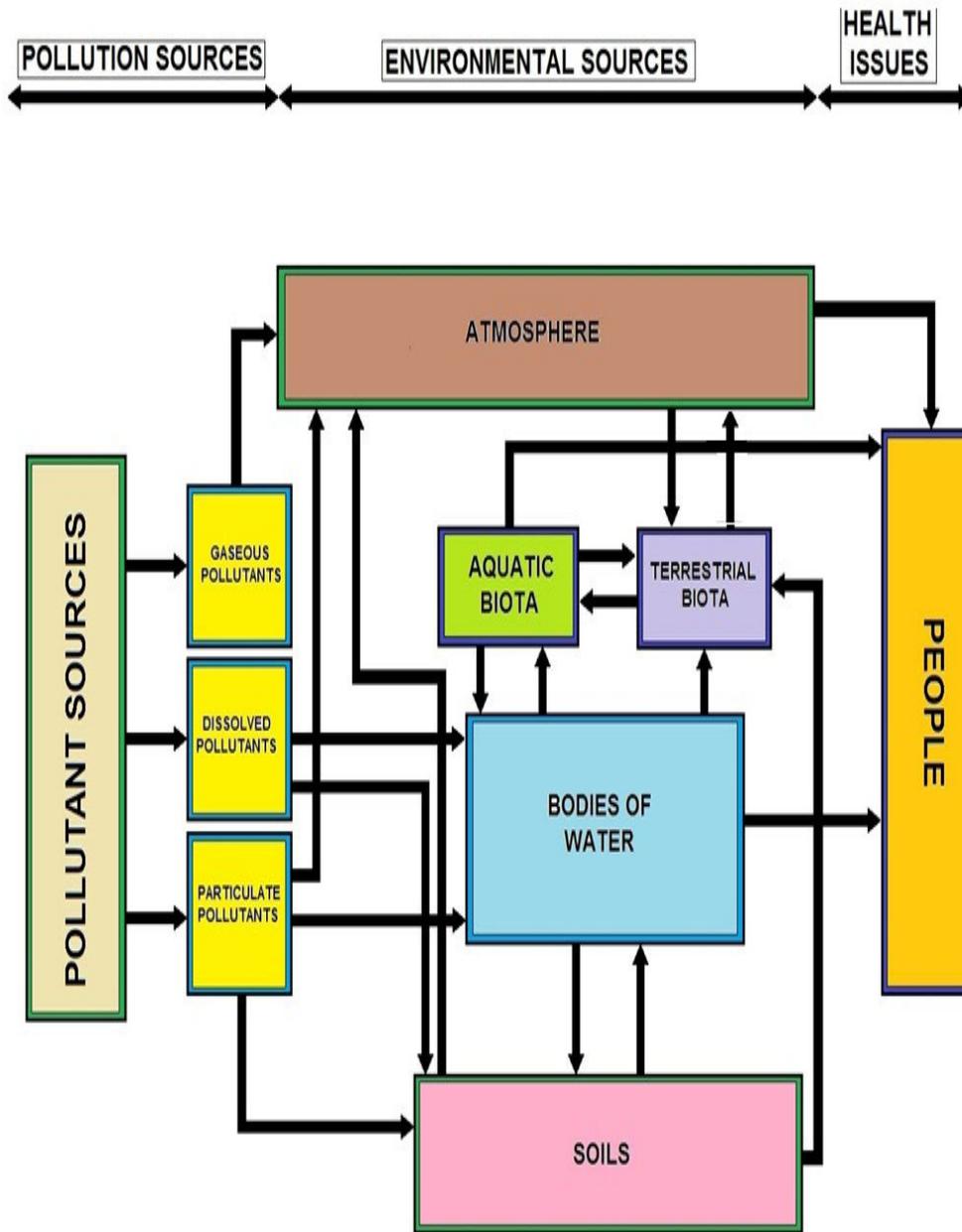
**U.S. ENVIRONMENTAL PROTECTION AGENCY:** In the United States, this agency responsible for setting drinking water standards and for ensuring their enforcement. This agency sets federal regulations which all state and local agencies must enforce.

**VOLATILE ORGANIC COMPOUNDS (VOCs):** Solvents used as degreasers or cleaning agents. Improper disposal of VOCs can lead to contamination of natural waters. VOCs tend to evaporate very easily. This characteristic gives VOCs very distinct chemical odors like gasoline, kerosene, lighter fluid, or dry cleaning fluid. Some VOCs are suspected cancer-causing agents. Volatile organic compounds (VOCs) are organic chemical compounds that have high enough vapor pressures under normal conditions to significantly vaporize and enter the atmosphere. A wide range of carbon-based molecules, such as aldehydes, ketones, and other light hydrocarbons are VOCs. The term often is used in a legal or regulatory context and in such cases the precise definition is a matter of law.

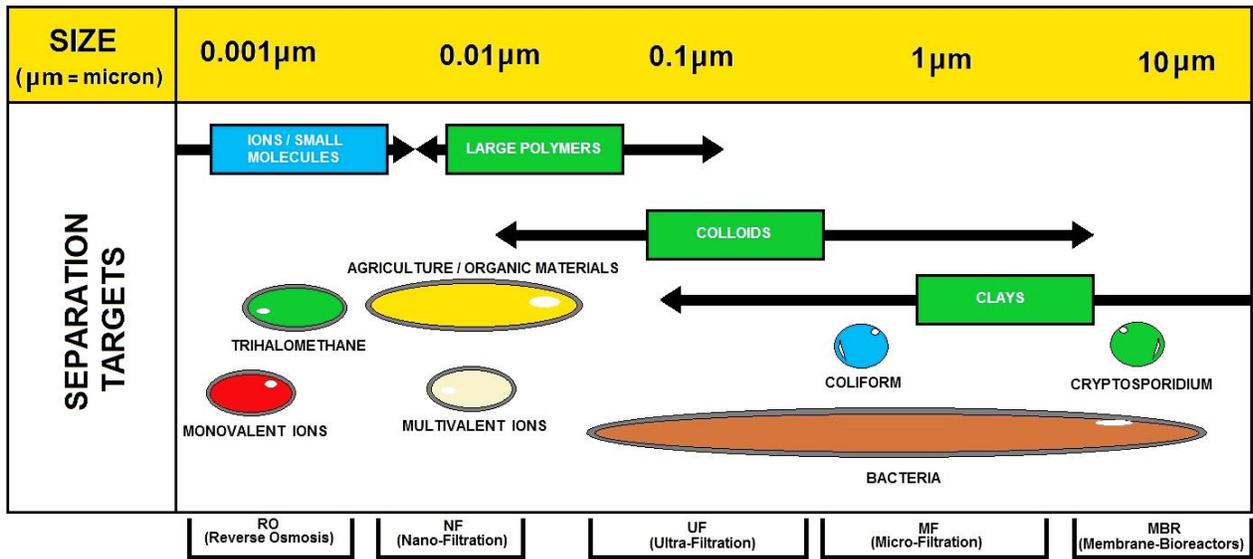
These definitions can be contradictory and may contain "loopholes"; e.g. exceptions, exemptions, and exclusions. The United States Environmental Protection Agency defines a VOC as any organic compound that participates in a photoreaction; others believe this definition is very broad and vague as organics that are not volatile in the sense that they vaporize under normal conditions can be considered volatile by this EPA definition. The term may refer both to well characterized organic compounds and to mixtures of variable composition.

FACTOR	TYPE	SOURCE(S)	PROBLEM
FECAL COLIFORM BACTERIA	BIOLOGICAL	HUMAN SEWAGE; LIVESTOCK WASTE	POSSIBLE PRESENCE OF PATHOGENIC (DISEASE-CAUSING) ORGANISMS
DISSOLVED OXYGEN (DO)	CHEMICAL	AIR; AQUATIC PLANTS	LOW LEVELS CAN KILL AQUATIC ORGANISMS
NITROGEN AND PHOSPHORUS	CHEMICAL	FERTILIZERS AND DETERGENTS FROM LAWNS AND RUNOFF	EXCESSIVE ALGAE GROWTH CAN LEAD TO LOW DO
ZINC, ARSENIC, LEAD, MERCURY, CADMIUM, NICKEL	CHEMICAL	LANDFILLS; INDUSTRIAL DISCHARGES; RUNOFF	GENETIC MUTATIONS OR DEATH IN FISH & WILDLIFE (HUMAN HEALTH THREATS AS WELL)
SALT	CHEMICAL	SALTWATER INTRUSION (IF NEAR OCEAN)	KILLS FRESHWATER SPECIES OF PLANTS AND ANIMALS
MUD, SAND, OTHER SOLID PARTICLES (TURBIDITY)	PHYSICAL	EROSION AND RUNOFF FROM DEVELOPMENT; AGRICULTURE	REDUCES PHOTOSYNTHESIS IN AQUATIC VEGETATION; INTERFERES WITH RESPIRATION IN AQUATIC ANIMALS

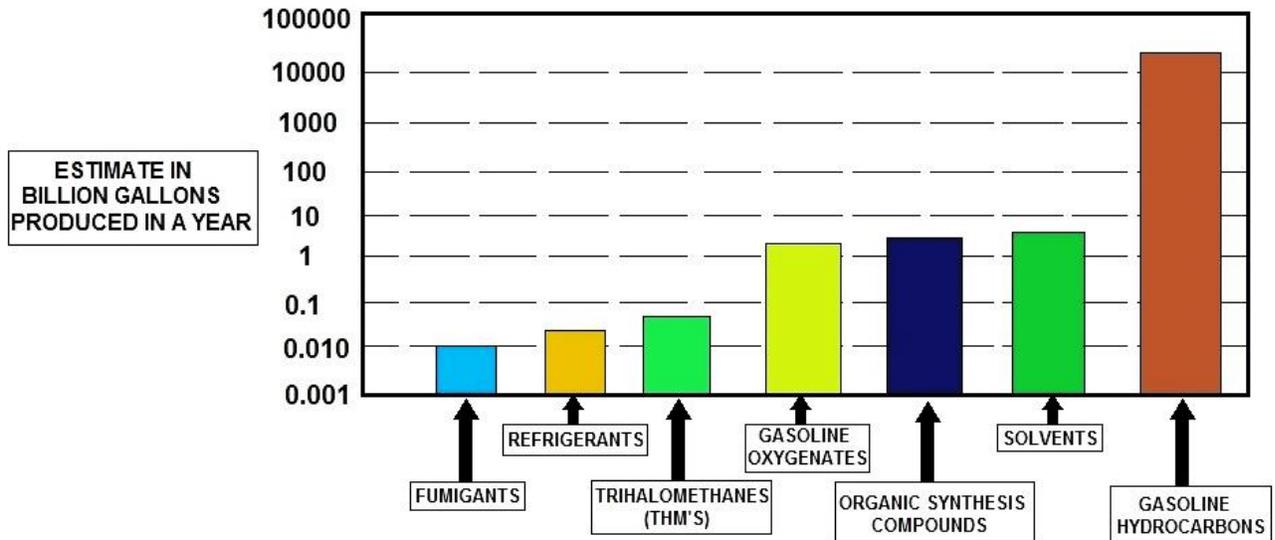
## WATER QUALITY FACTORS



# WATER QUALITY INDICATORS

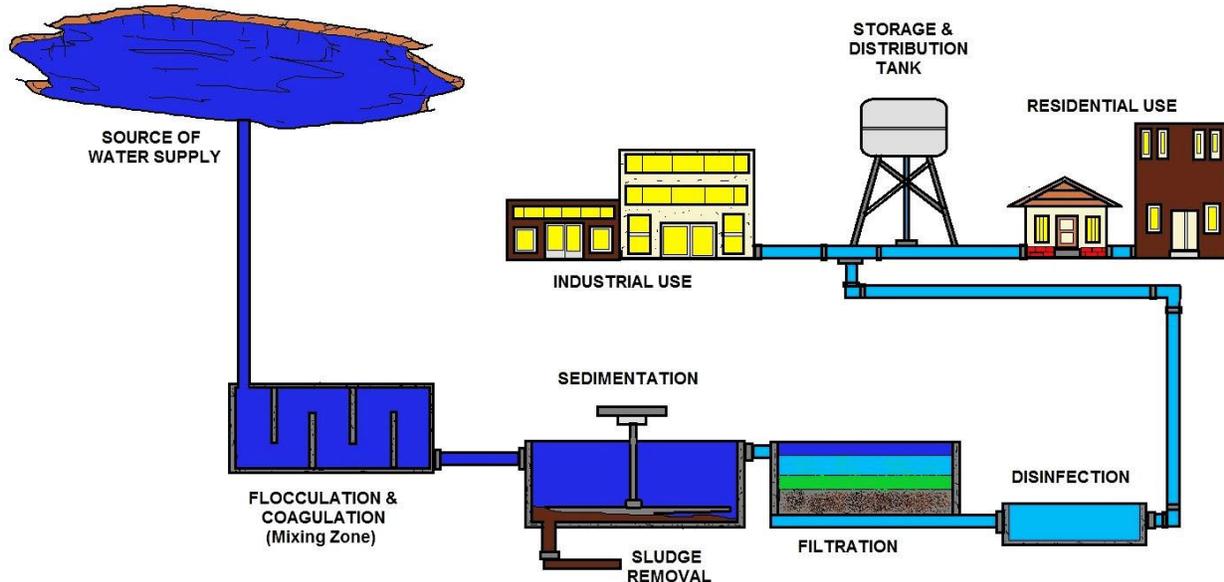


## REMOVAL METHODS



## VOLATILE ORGANIC COMPOUNDS (VOC'S) FOUND IN GROUNDWATER

## Simple Conventional Water Treatment Principles



## DRINKING WATER TREATMENT

Conventional treatment consists of the following unit processes: coagulation, flocculation, clarification, and filtration, and is typically followed by disinfection at full-scale. The above drawing describes conventional treatment. Conventional treatment is often preceded by pre-sedimentation, may be accompanied by powdered activated carbon (PAC) addition, utilize granular activated carbon (GAC) as a filter media, and in some cases be followed by GAC adsorption.

Conventional treatment is often preceded by pre-oxidation, or oxidation takes place concurrently. Oxidants common to conventional treatment are chlorine, chloramine, chlorine dioxide or permanganate. Occasionally membrane processes, either membrane filtration or ultrafiltration, accompany conventional treatment.

In coagulation, a positively charged coagulant (usually an aluminum or iron salt) is added to raw water and mixed in the rapid mix chamber. The coagulant alters or destabilizes negatively charged particulate, dissolved, and colloidal contaminants. Coagulant aid polymers and/or acid may also be added to enhance the coagulation process.

Turbidity and total organic carbon (TOC) are measures of particulates and dissolved organics impacting coagulation.

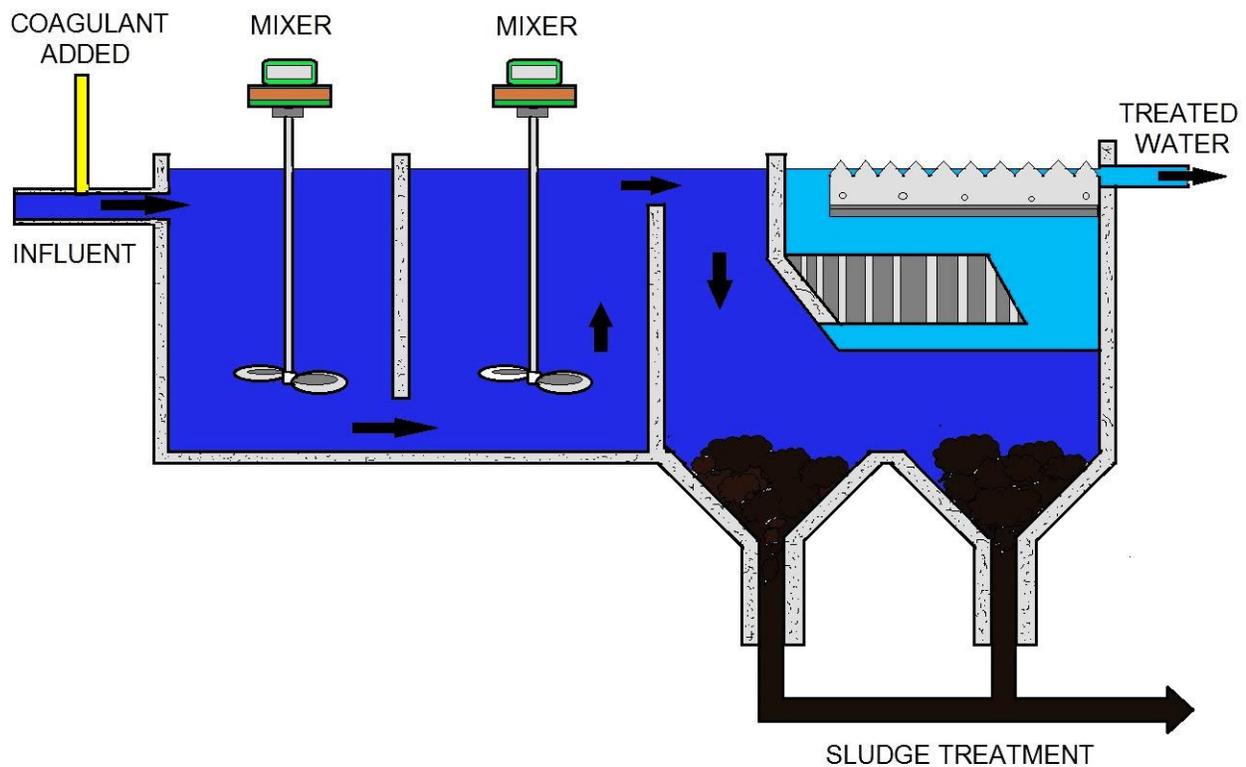
During flocculation, gentle mixing accelerates the rate of particle collision, and the destabilized particles are further aggregated and enmeshed into larger precipitates.

Flocculation is affected by several parameters, including the mixing speed, mixing intensity (G), and mixing time. The product of the mixing intensity and mixing time ( $Gt$ ) is frequently used to describe the flocculation process.

### Destabilization Mechanisms

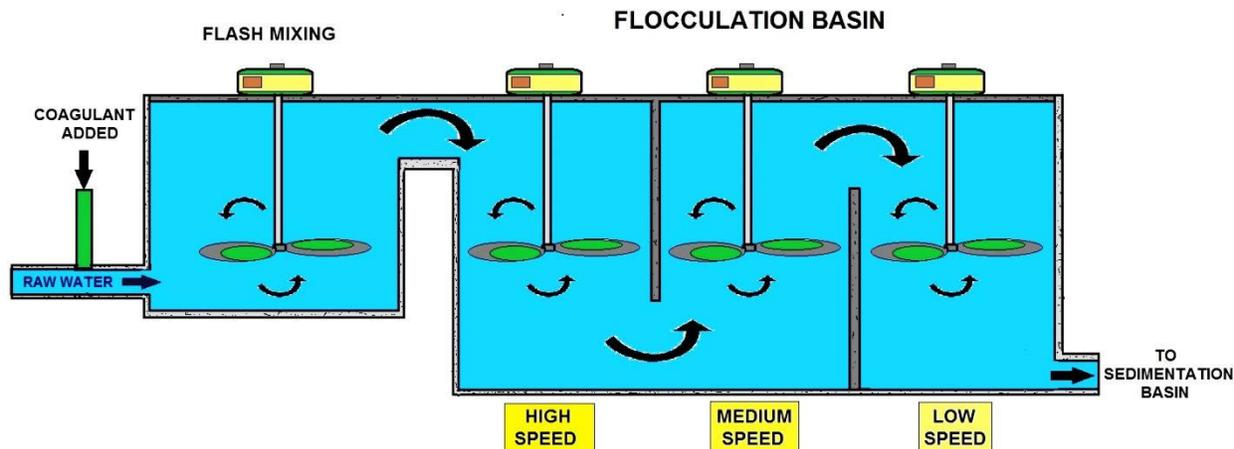
There are two primary destabilization mechanisms in drinking water treatment: charge neutralization and sweep flocculation. The mechanism is dependent upon the coagulant dose. Most drinking water treatment plants operate using sweep flocculation, which requires a higher coagulant dose, rather than charge neutralization. In charge neutralization, the positively charged metal coagulant is attracted to the negatively charged colloids via electrostatic interaction.

Flocs start to form during the neutralization step as particle collisions occur. Adding excess coagulant beyond charge-neutralization results in the formation of metal coagulant precipitates. These metal hydroxide compounds (e.g.,  $\text{Al}(\text{OH})_3$  or  $\text{Fe}(\text{OH})_3$ ) are heavy, sticky and larger in particle size. Sweep flocculation occurs when colloidal contaminants are entrained or swept down by the precipitates as they settle in the suspension.



FLOCCULATION BASIN

*This course contains EPA's federal rule requirements. Please be aware that each state implements drinking water regulations that may be more stringent than EPA's regulations. Check with your state environmental agency for more information.*

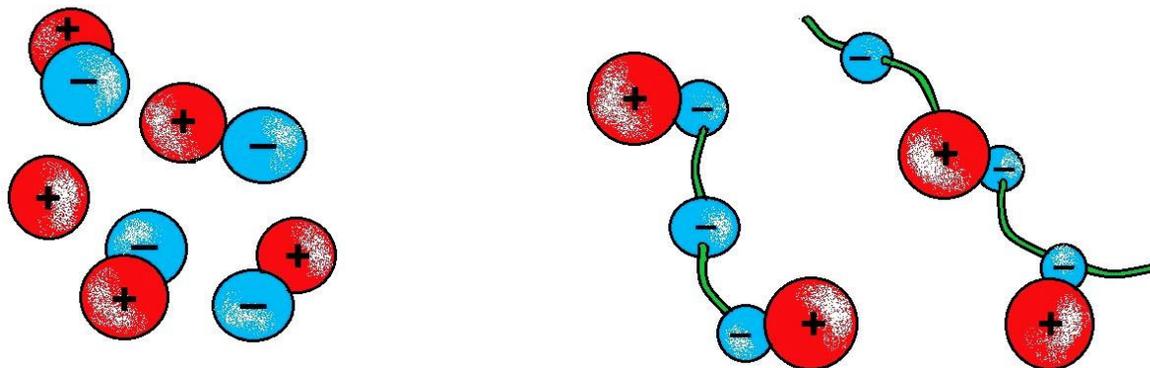


## FLASH FLOCCULATION

### Coagulation

The optimal pH range for coagulation is 6 to 7 when using alum and 5.5 to 6.5 when using iron. For high alkalinity water, excessive amounts of coagulant may be needed to lower the pH to the optimal pH range. In these cases, it may be beneficial to use acid in addition to the coagulant to reduce the amount of coagulant needed and effectively lower chemical costs. Enhanced coagulation is now widely practiced for removing disinfection byproduct (DBP) precursors, and it also removes inorganics, particulates, and color causing compounds.

Removing these contaminants using coagulation depends on the amount of coagulant added. It is important to determine the optimal dose for coagulation; insufficient doses will not effectively destabilize the particles and adding excessive doses can cause detrimental effects such as re-stabilization, excessive sludge production, or corrosion.



## COAGULATION vs. FLOCCULATION

Coagulation invariably requires addition of a chemical with a strong positive charge, such as aluminum sulfate (alum), to neutralize the negative electrostatic charges that allow particles to remain suspended in the raw water. Coagulation involves turbulent mixing of the coagulant chemical with the raw water.

Flocculation involves gentle mixing of the coagulated water to allow the small particles to come together to form larger particles. Flocculation may occur naturally to some extent following coagulation, or may be encouraged by the addition of a chemical, such as a flocculant polymer.

Coagulation and flocculation are necessary steps in conventional water treatment processes and occur in successive steps intended to overcome the forces stabilizing the suspended particles, allowing particle collision and growth of floc. If step one is incomplete, the following step will be unsuccessful.

Coagulation and flocculation are necessary steps in conventional water treatment processes and occur in successive steps intended to overcome the forces stabilizing the suspended particles, allowing particle collision and growth of floc. If step one is incomplete, the following step will be unsuccessful.

The first step destabilizes the particle's charges. Coagulants with charges opposite those of the suspended solids are added to the water to neutralize the negative charges on dispersed non-settleable solids such as clay and color-producing organic substances.

Once the charge is neutralized, the small suspended particles are capable of sticking together. The slightly larger particles formed through this process and called microflocs, are not visible to the naked eye.

The water surrounding the newly formed microflocs should be clear. If it is not, all the particles' charges have not been neutralized, and coagulation has not been carried to completion. More coagulant may need to be added.

A high-energy, rapid-mix to properly disperse the coagulant and promote particle collisions is needed to achieve good coagulation. Over-mixing does not affect coagulation, but insufficient mixing will leave this step incomplete. Contact time in the rapid-mix chamber is typically 1 to 3 minutes.

### **Dissolved and Suspended Particles**

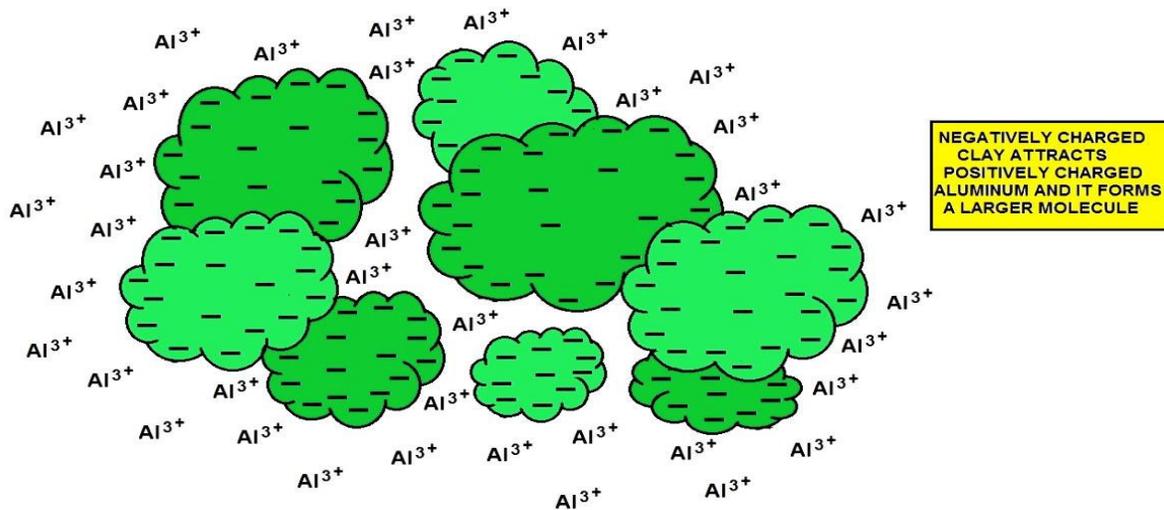
All waters, especially surface waters, contain both dissolved and suspended particles. Coagulation and flocculation processes are used to separate the suspended solids portion from the water.

The suspended particles vary considerably in source, composition charge, particle size, shape, and density. Correct application of coagulation and flocculation processes and selection of the coagulants depend upon understanding the interaction between these factors. The small particles are stabilized (kept in suspension) by the action of physical forces on the particles themselves.

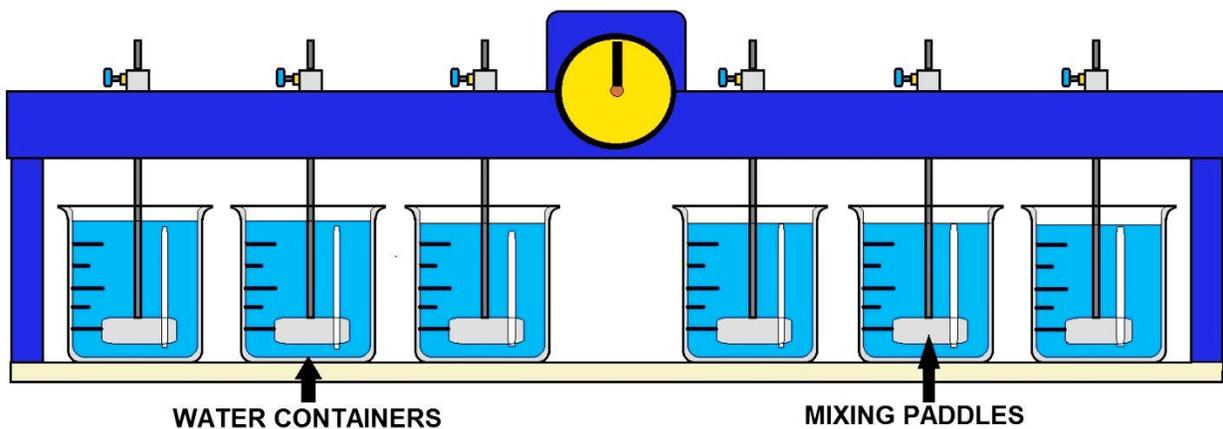
One of the forces playing a dominant role in stabilization results from the surface charge present on the particles. Most solids suspended in water possess a negative charge and, since they have the same type of surface charge, repel each other when they come close together. Therefore, they will remain in suspension rather than clump together and settle out of the water.

# Understanding Water Quality Parameters

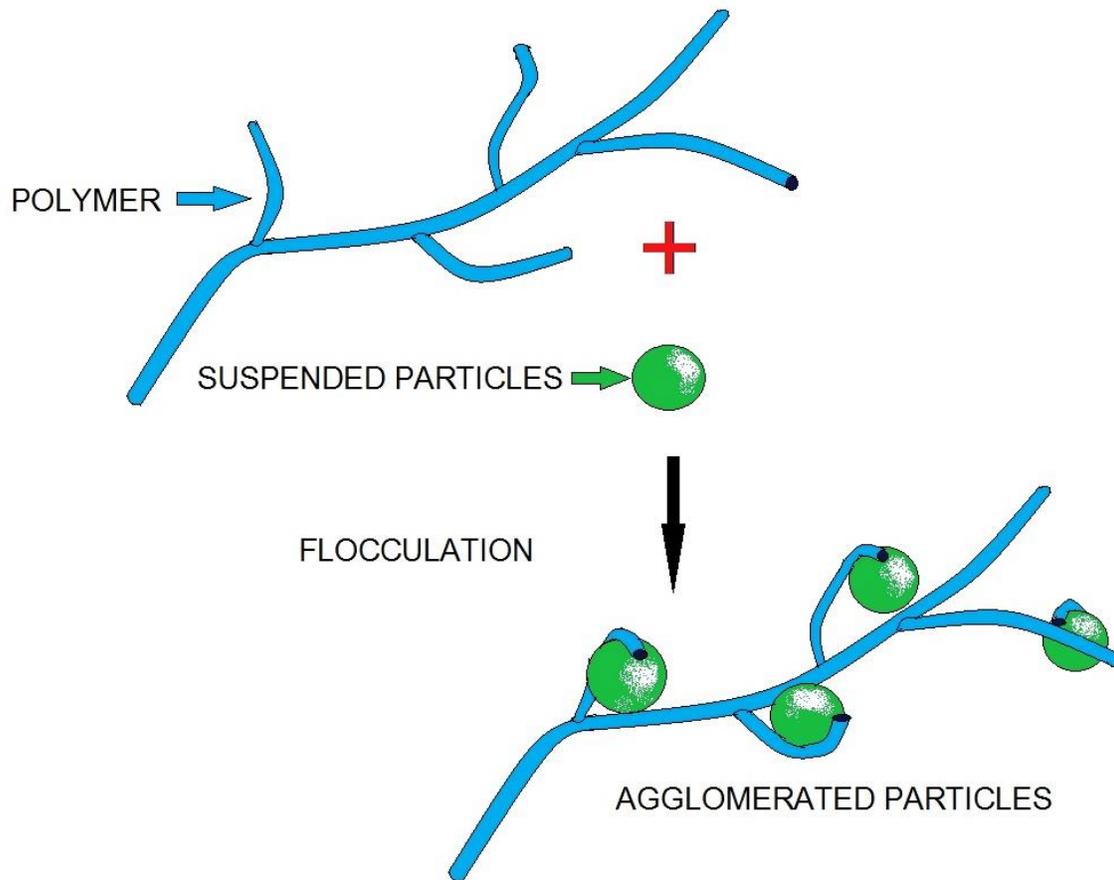
Water quality parameters such as pH, temperature, and alkalinity may dictate effectiveness of the coagulation-filtration process. The pH during coagulation has a profound influence on the effectiveness during the destabilization process. The pH controls both the speciation of the coagulant as well as its solubility, and it also affects the speciation of the contaminants. For high alkalinity water, an excessive amount of coagulant may be required to lower the pH to the optimal pH ranges (alum pH 6 to 7, iron 5.5 to 6.5). Temperature also impacts the coagulation process because it affects the viscosity of the water. Thus lower temperature waters can decrease the hydrolysis and precipitation kinetics. For some treatment objectives, other parameters like iron, manganese or sulfate impact coagulation.



## FLOCCULATION



## FLOCCULATION / COAGULATION JAR TEST UNIT



## FLOCCULATION

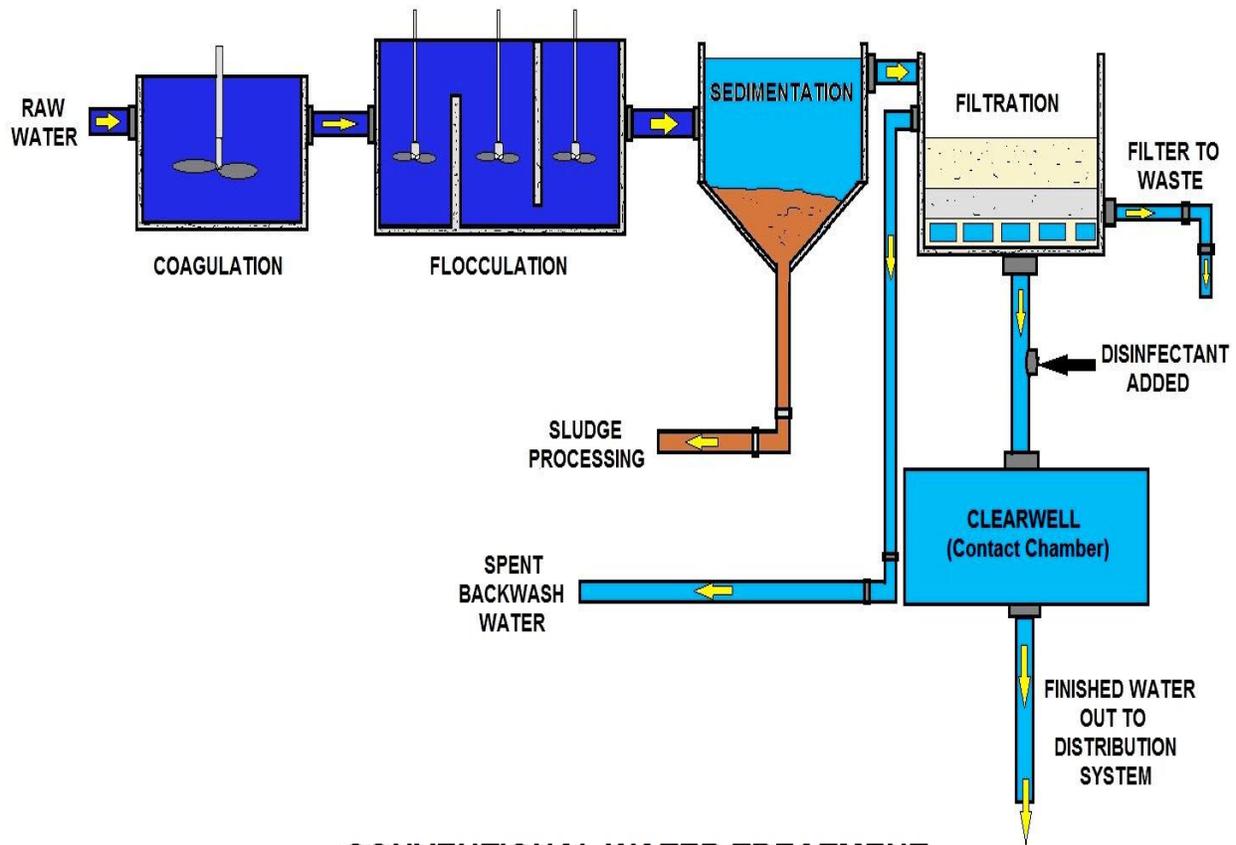
### **Polyaluminium Chloride (PACl)**

Some of the alternative coagulants such as polyaluminium chloride (PACl) can be advantageous over the traditional coagulants in low temperature conditions as these coagulants are already hydrolyzed, and therefore temperature tends to have less effect on the coagulation process.

Following flocculation, agglomerated particles enter the clarification unit where they are removed by sedimentation by gravity or are floated and skimmed from the surface of the clarification unit.

In the sedimentation processes, the majority of the solids are removed by gravitational settling; particles that do not settle and are still suspended are removed during the filtration process.

Sedimentation is generally accomplished in rectangular or circular basins and is often enhanced by the addition of inclined plates or tubes which increase effectiveness of the process by effectively increasing the surface area of the sedimentation basin.



## CONVENTIONAL WATER TREATMENT

### Dissolved Air Flotation (DAF)

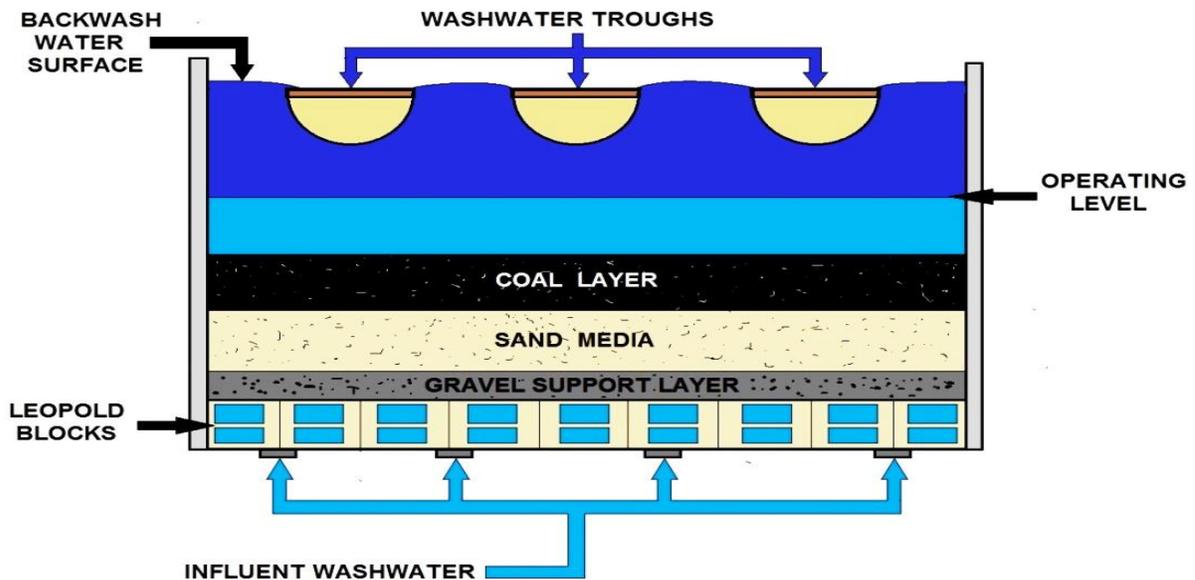
Dissolved air flotation (DAF) is another clarification process in which air is diffused as fine bubbles and suspended particles are floated to the surface and removed by skimming.

Generally, DAF is most effective for small, fine, low-density particles like algae and may not be effective in all instances. Like conventional sedimentation, solids not removed by DAF are removed during filtration.

### Clarification Process

Two parameters frequently used to describe the clarification process are the overflow rate and the detention time. The overflow rate is the process loading rate and is usually expressed in gpm/sf or gpd/sf. Overflow rates for conventional sedimentation generally range from 0.3 to 1 gpm/sf (500 to 1500 gpd/sf).

Overflow rates for other processes can vary significantly. There are proprietary sand-ballasted clarification systems that have been demonstrated to operate effectively at overflow rates as high as 20 gpm/sf. Typical detention times range from 1 to 2 hours, although many states require up to 4 hours for full-scale surface water treatment.

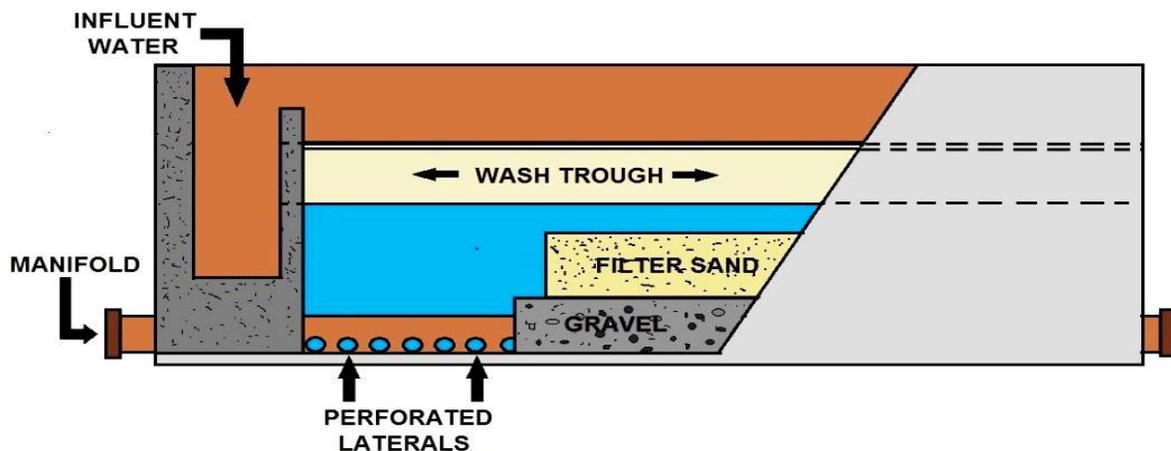


## DUAL MEDIA FILTER

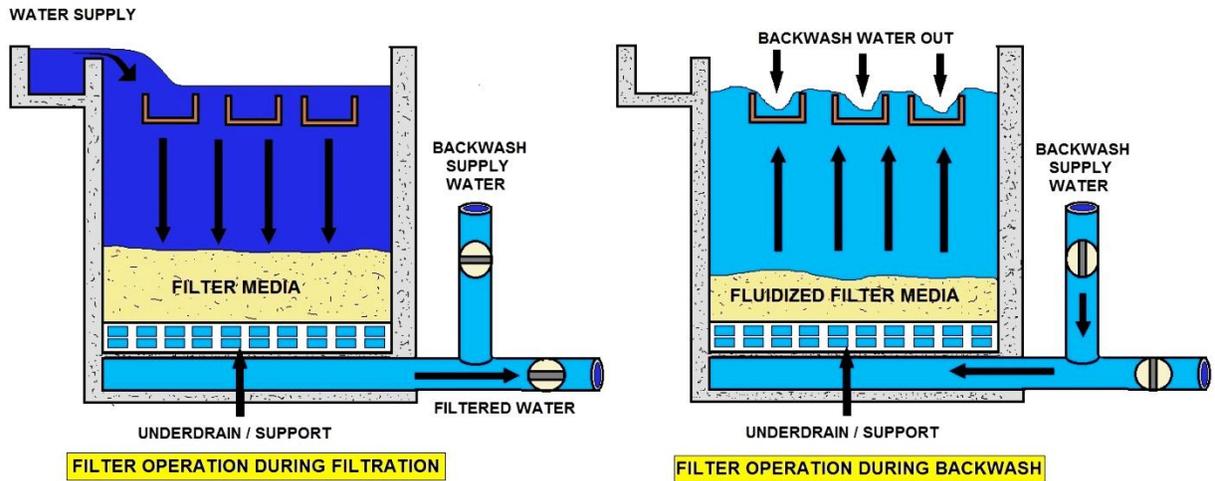
### Dual-media Filter

The most commonly used filter type in the conventional treatment process is a dual-media filter comprised of anthracite and sand; however, mono-media (sand), multi-media (garnet, anthracite, and sand), and other media configurations, including the use of granular activated carbon, are also used in drinking water treatment.

During filtration, the majority of suspended particles are removed in the top portion of the filter media. Filters are backwashed to dislodge and remove particles trapped within the filter bed, to reduce head loss (pressure build up), and to keep the filter media clean.



## RAPID SAND FILTER



## RAPID SAND FILTER

### Filter Loading Rate

The filter loading rate is a measure of the filter production per unit area and is typically expressed in gpm/sf. Typical filter loading rates range from 2 to 4 gpm/sf; however, higher filter loading rates, 4 to 6 gpm/sf, are becoming more common at full-scale.

This can be a critical parameter because it determines the water velocity through the filter bed and can impact the depth to which particles pass through the media.

The filter run time describes the length of time between filter backwashes during which a filter is in production mode. The filter run time is not only an indicator of the effectiveness of prior treatment (i.e., the ability of the coagulation and clarification steps to remove suspended solids), but also plays a role in the effectiveness of the filter itself.

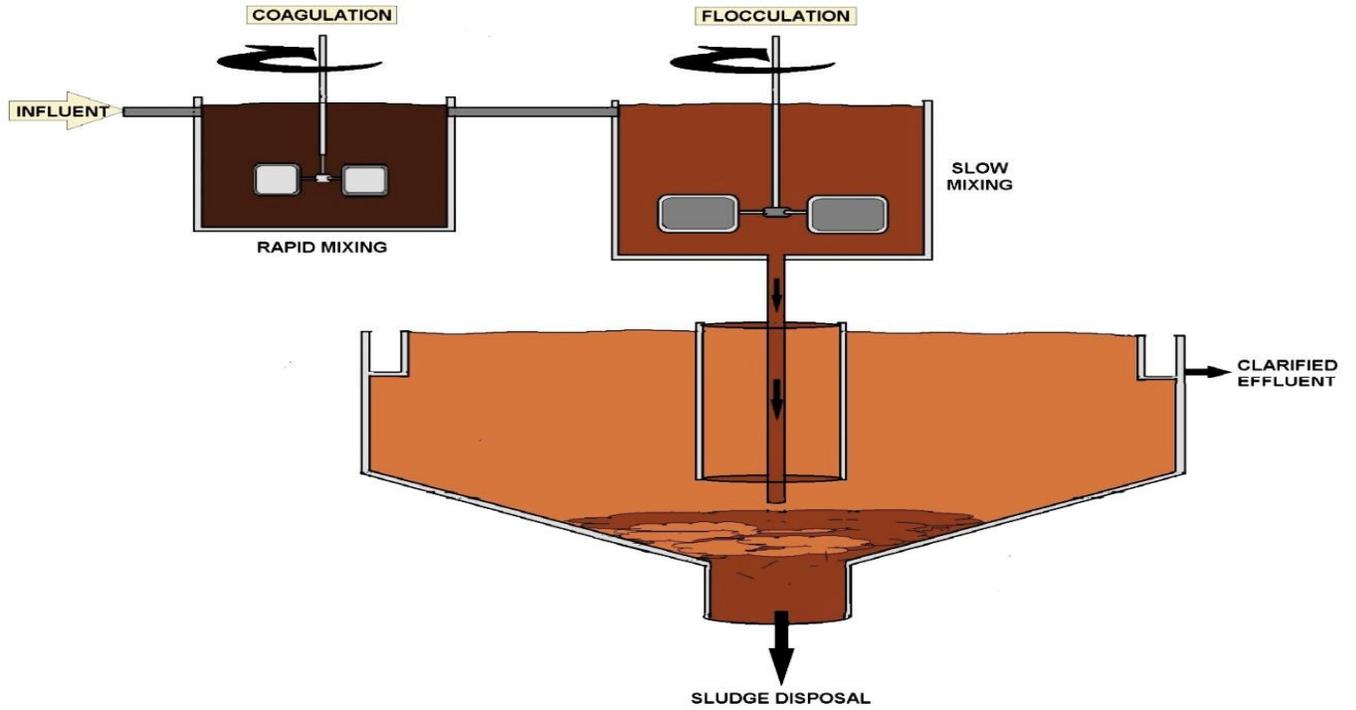
### Filter Performance

Filter performance, particularly with regard to particulate contaminants, is often poorest immediately following a backwash. As the filter run time increases and the concentration of solids in the media increases, the filtration process often performs better with regard to particulate contaminant removal.

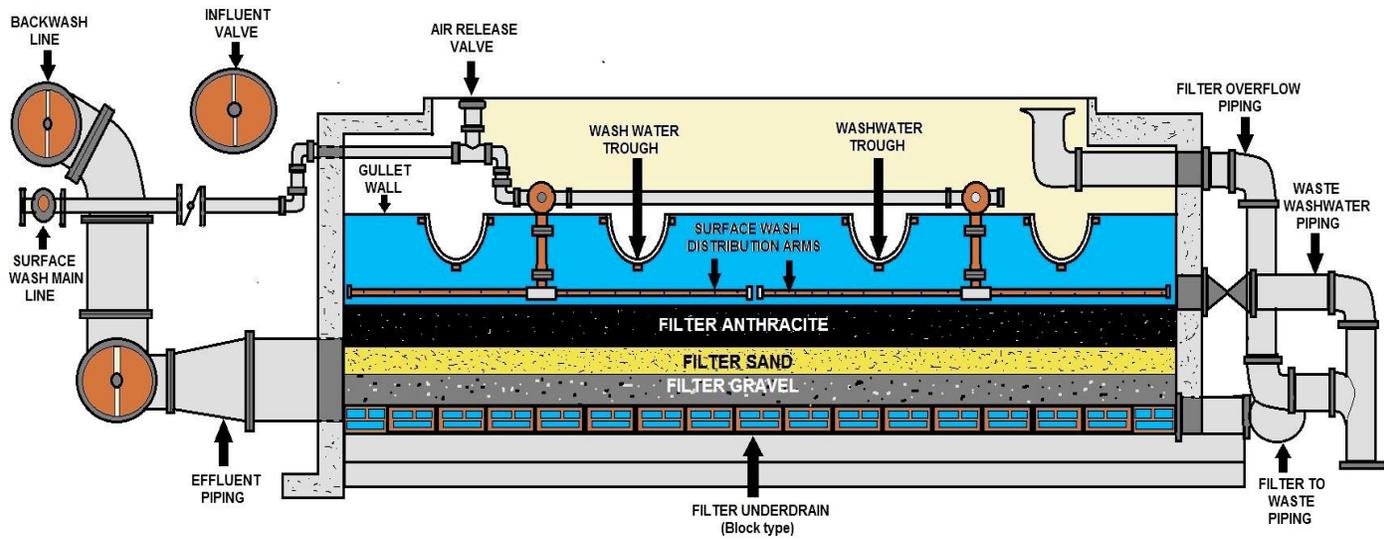
### Spent Backwash

Residuals generated by the conventional treatment process include coagulation solids (sludge) and spent backwash. Spent backwash is often returned to the treatment process as a means to minimize water loss. Sludge may also be recycled to minimize coagulant and coagulant aid doses and improve process performance.

Process solids (i.e., coagulation sludge and filtered solids) will contain elevated concentrations of contaminants removed during the treatment process. Depending on the source water concentration of a particular contaminant and any disposal limitations, it may be necessary evaluate the disposal of process solids with respect to state and local hazardous waste regulations.



**BASIC COAGULATION / FLOCCULATION PROCESS**



**TYPICAL FILTER SECTIONS**

## Solubility of Substances in Water

Water is an excellent solvent for many compounds. Some dissolve in it as molecules while others, called electrolytes, dissociate and dissolve not as neutral molecules but as charged species called ions. Compounds which exist as solid ionic crystals dissolve in water as ions, and most of them are highly soluble in water. "Highly soluble" is a somewhat elastic description, but generally means soluble to at least the extent of forming 0.1 to 1.0 molar aqueous solutions. Salts which are less soluble in water than this at room temperature are called slightly soluble salts.

The solubility of an ionic salt depends both upon its cations and its anions, but for simple salts in aqueous solution at room temperature the following general observations are useful. Almost all sodium, potassium, and ammonium salts are highly soluble; the only significant exception is  $\text{KClO}_4$ , which is moderately soluble almost without exception.

Metal carbonates and phosphates are generally insoluble or slightly soluble, with the exception of those of sodium, potassium, and ammonium which are highly soluble; magnesium ammonium phosphate is used for the precipitation of magnesium ion.

Metal halides are generally highly soluble, with the exception of those of silver, lead, and mercury (I). Lead chloride is slightly soluble while silver and mercury (I) chlorides are much less soluble. Sulfate salts are generally highly soluble as well, with more exceptions; calcium, barium, strontium, lead, and mercury (I) sulfates are almost insoluble while silver sulfate is slightly soluble. Metal sulfides are generally insoluble in water.

### Solid-Solution (Solubility) Reactions

When solids dissolve, the solutes are no longer pure substances and their activity can no longer be taken as unity. In dilute solutions, aqueous or otherwise, activities of solutes are often taken as equal to their molar concentrations. These equilibria are called solubility equilibria and are taken up under the following main heading. The example below shows how the form in which they are written compares to other equilibrium constants.

**Example.** The equilibrium constant for the reaction  $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$  is written as  $K = \frac{a(\text{Ag}^+)a(\text{Cl}^-)}{a(\text{AgCl})}$ ; more commonly, it is written in the form  $K_a(\text{AgCl}) = a(\text{Ag}^+)a(\text{Cl}^-) = K_{sp}$ . If the molar concentrations are taken as good approximations to the activities, which in dilute solutions they are, then  $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$ .

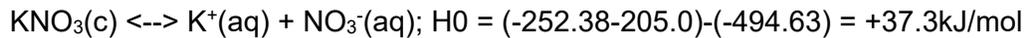
**Example.** Let us write and simplify to the extent possible the equilibrium constant for the equilibrium  $\text{Al}^{3+}(aq) + 3\text{OH}^-(aq) \rightleftharpoons \text{Al}(\text{OH})_3(s)$  For this equilibrium  $K = \frac{1}{[\text{Al}^{3+}][\text{OH}^-]^3} = 1/K_{sp}$ . where  $K$  has the units  $\text{dm}^{12}/\text{mol}^4$ , or  $(\text{dm}^3)^4/\text{mol}^4$ .

The form of equilibrium constant indicated as  $K_{sp}$  is called the solubility product constant or, more commonly, the solubility product. This constant therefore must refer to the process of a solid going into solution (solubility) rather than the reverse, precipitation of solid from solution. As a consequence, the ions are products and appear in the numerator.

The value of the solubility product is temperature-dependent and is generally found to increase with increasing temperature. As a consequence, the molar solubility of ionic salts generally increases with increasing temperature. The extent of this increase varies from one salt to another.

It is sometimes possible to take advantage of the difference in the effect of temperature to separate mixtures of different soluble salts. As the chart in the following Figure shows, a solution originally of equal concentration in  $\text{KClO}_3$  and  $\text{KNO}_3$  should upon heating and evaporation of water precipitate  $\text{KClO}_3$  because  $\text{KNO}_3$  is by far the more soluble near the boiling point of water.

The solubility of solid salts in water, and in most other solvents, increases with temperature while that of gases decreases. The heat or enthalpy change of the dissolution reaction for most solids is positive so the dissolution reaction is endothermic. For some solids, such as  $\text{NaCl}$ , the heat of solution is very small and so the effect of temperature is small also. For other salts, such as  $\text{KNO}_3$ , the effect of temperature is much larger:



**Chemical coagulation** in the water/wastewater treatment is the process of bringing suspended matter in untreated water together for the purpose of settling and for the preparation of the water for filtration.

**Coagulation involves three specific steps, which are:**

- Coagulation
- Flocculation
- Sedimentation



Primary Clarifier

## Principles of Coagulation

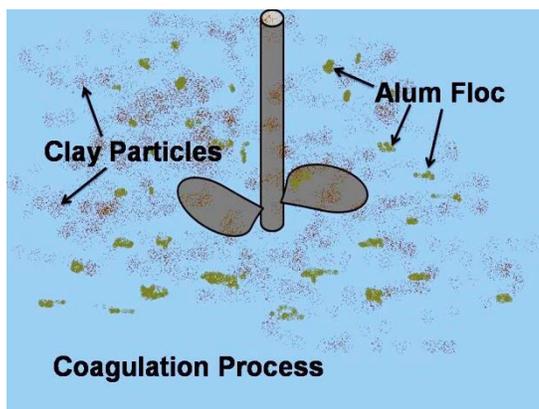
Untreated surface waters contain clay, minerals, bacteria, inert solids, microbiological organisms, oxidized metals, organic color producing particles, and other suspended materials. Some of the microbiological organisms can include Giardia cysts, pathogenic bacteria, and viruses. Oxidized metals include iron and manganese. All of these materials can inhibit disinfection, cause problems in the distribution system, and leave the water cloudy rather than clear. The purpose of coagulation is to remove these particles.

The ability of particles to remain suspended in water is a function of both the particle size and specific gravity. Turbidity particles can range in size from molecular to 50 microns. Particles which are greater than one micron in diameter are considered silt, and settle out due to their relatively large size and density without the need to coagulate in a matter of seconds or minutes.

Colloidal material ranges in size from 0.001 to one micron in diameter. These materials require days to months for complete settling. Since detention times in the water treatment process are generally less than twelve hours, the rate of settling of these colloidal particles must be increased in the water treatment process. This is accomplished in the coagulation process when tiny particles agglomerate into larger, denser particles which will settle more quickly as shown in the picture on the right.

These tiny colloidal particles have a very large surface area to mass ratio, and this factor is important in keeping the particles suspended for long periods of time. In fact, the surface area to mass ratio is so high that electric charges and ionic groups become important in keeping the particles suspended. Two types of colloids exist.

These are hydrophobic or water hating colloids, and hydrophilic or water loving colloids. Hydrophilic colloids form suspensions easily, and can be difficult to remove. These colloids can, however, react chemically with the coagulants commonly added to water under proper conditions. Examples of hydrophilic colloids would be organic color forming compounds. Hydrophobic colloids do not easily form suspensions. The reactions between hydrophobic colloids and the coagulants commonly added to water are largely physical rather than chemical. Examples of hydrophobic colloids would be clays and metal oxides.



### The Coagulation Process

Coagulation is accomplished by the addition of ions having the opposite charge to that of the colloidal particles. Since the colloidal particles are almost always negatively charged, the ions which are added should be cations or positively charged. The coagulating power of an ion is dependent on its valency or magnitude of charge. A bivalent ion (+2 charge) is 30 to 60 times more effective than a monovalent ion (+1 charge). A trivalent ion (+3 charge) is 700 to 1000 times more effective than a monovalent ion.

Typically, two major types of coagulants are added to water. These are aluminum salts and iron salts. The most common aluminum salt is aluminum sulfate, or alum.

When aluminum sulfate is added to water, the aluminum ions enter into a series of complicated reactions. The aluminum ions become hydrated, meaning that water molecules attach themselves to the aluminum ions. In addition, anions present in the water, such as hydroxide and sulfate ions can attach to the aluminum ions.

These reactions result in large, positively charged molecules having aluminum ions at their center. These particles may have charges as high as +4. Following these reactions, a second type of reaction occurs, called Olation. This reaction involves the bridging of two or more of these large molecules to form even larger, positively charged ions. A typical molecule can contain eight aluminum ions, twenty hydroxide ions, and will have a +4 charge. Iron salts behave in a similar manner when added to water.

Once these large polymeric aluminum or iron compounds are formed, the magnitude of their high positive charge allows these species to rapidly move toward the colloid, where they are adsorbed onto the negatively charged surface of the turbidity particle. The coagulant compounds can penetrate the bound water layer because of their high positive charge.

This rapid adsorption results in the compression of the electrical double layer, and results in the colloid becoming coated with the coagulant compounds. The net result of this process is that the electrical charges on the particle are reduced.

The suspension is now considered to be destabilized, and the particles can be brought together through, among other forces, Brownian Movement, and will be held together by the Van der Waals forces.

An additional process occurs which assists this process. As the coagulant continues to undergo the hydrolyzation and olation reactions, progressively larger masses of flocculent material are formed. These compounds can become large enough to settle on their own, and tend to trap turbidity particles as they settle. This is commonly referred to as sweep floc.

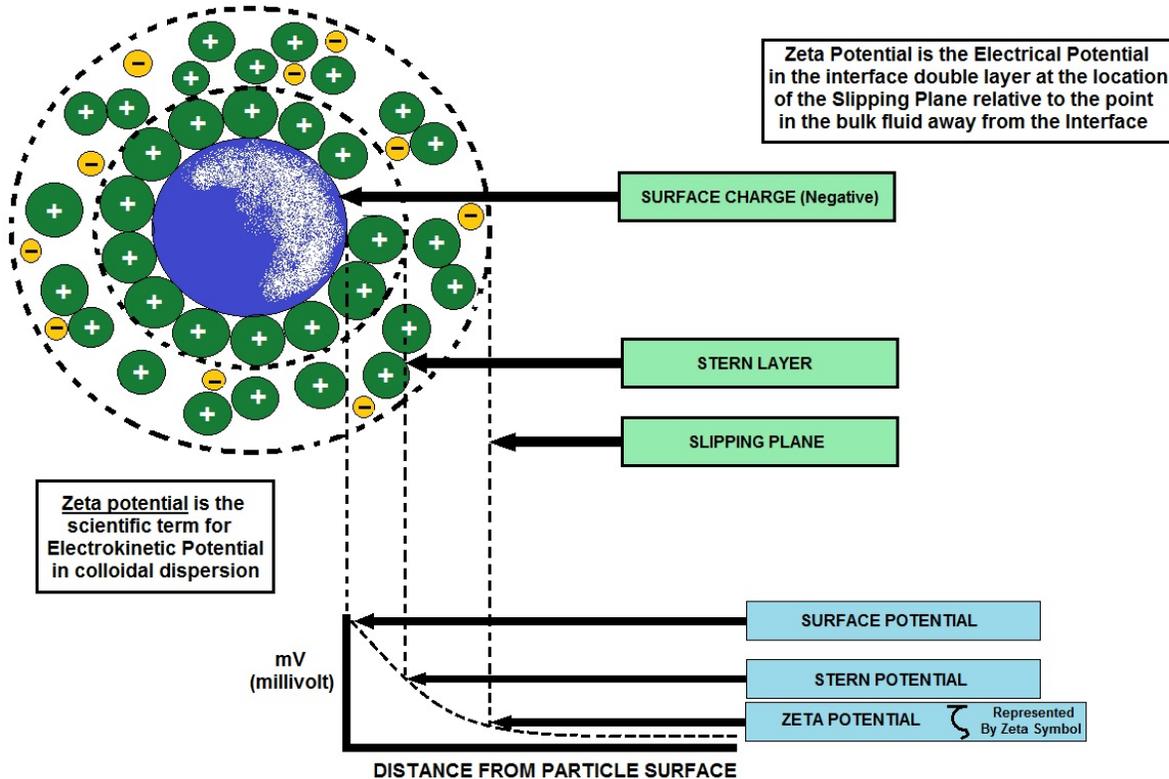
As the coagulation reactions and destabilization are occurring, the Zeta Potential at the surface of the colloid is also found to be reducing. Typically, the Zeta Potential for a naturally occurring water may be in the range of -10 to -25 millivolts. As the reactions occur, this Zeta Potential will be reduced to approximately -5 millivolts.

These figures are only examples of what might be considered typical waters. Since all waters exhibit a specific set of characteristics, these numbers will vary. It is interesting to note that the Zeta Potential does not have to be reduced to zero in order for coagulation to occur, because the forces of attraction can become predominant before complete destabilization occurs.

Hydrophilic colloids participate in the coagulation process in a slightly different way. These colloids tend to attract water molecules and attach these water molecules to their surfaces. This is also a hydration process, and the water molecules act as a barrier to contact between particles.

Also attached to the surfaces are hydroxyl, carboxyl, and phosphate groups, all to which are negatively charged. Coagulant products react chemically with the negatively charged groups attached to the hydrophilic colloids, forming an insoluble product which is electrically neutral and destabilized.

## Zeta Potential



## ZETA POTENTIAL

In water treatment, monitoring dosage using zeta potential measurements can significantly reduce the cost of chemical additives by optimizing the dosage control in real time.

The zeta potential (also known as electrokinetic potential) is established on the surface of any material when it comes in contact with a liquid medium. It is thus an interfacial property. It is typically given in millivolt unit.

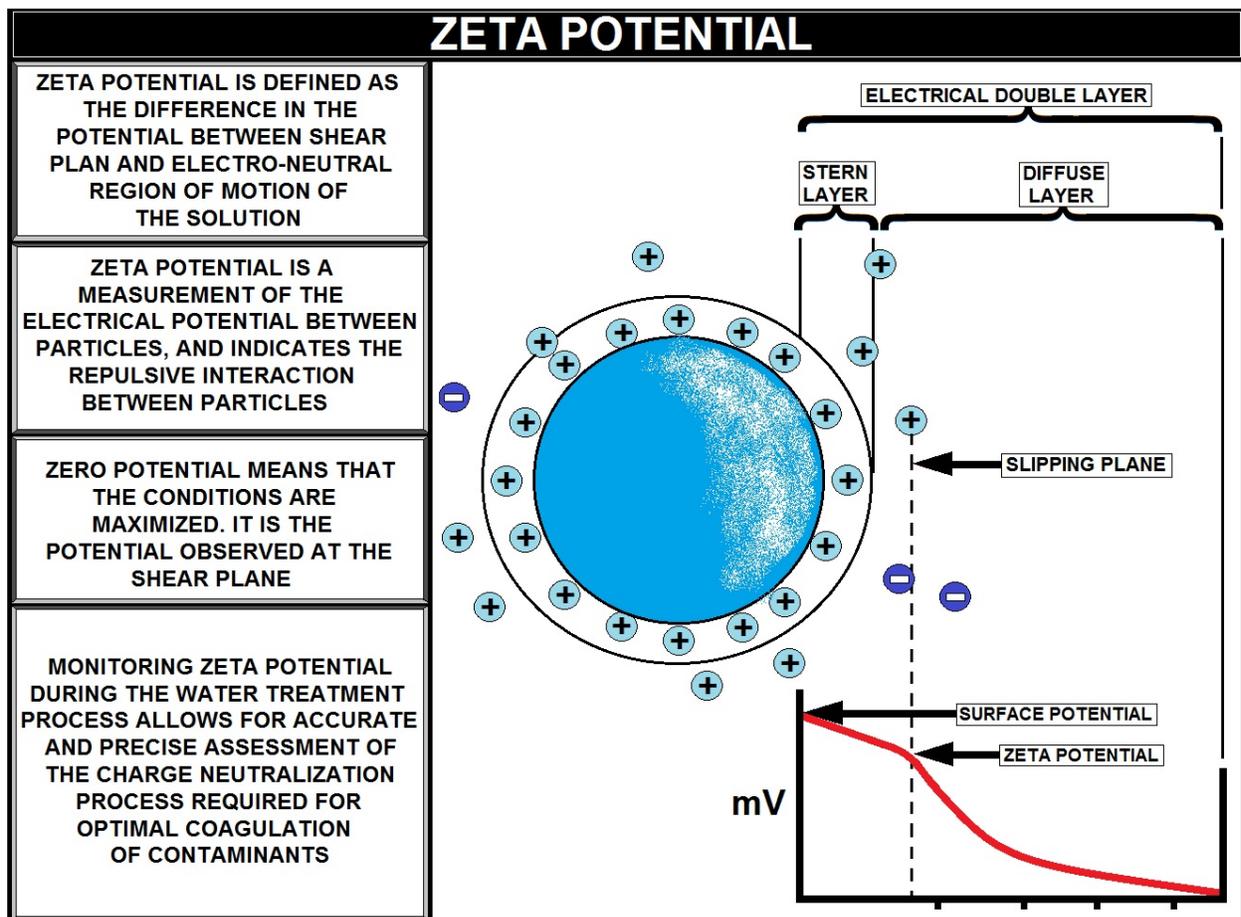
Zeta potential is a measure of the magnitude of the electrostatic or charge repulsion/attraction between particles and is one of the fundamental parameters known to affect stability. Its measurement brings detailed insight into the causes of dispersion, aggregation or flocculation, and can be applied to improve the formulation of dispersions, emulsions and suspensions.

Speed of introduction of new formulations is the key to product success. Measurement of zeta potential is one of the ways to shorten stability testing by reducing the number of candidate formulations, hence reducing the time and cost of testing as well as improving shelf life.

If a material comes in contact with a liquid, the functional groups on its surface will react with the surrounding medium. This process results in a surface charge, which attracts the accumulation of oppositely charged ions. These counter ions arrange themselves spontaneously in a so-called electrochemical double layer. The zeta potential is defined as the sum of the initial surface charge and the accumulated layer.

The following needs to be kept in mind when talking about zeta potential:

- The zeta potential is only present if a material comes in contact with a liquid. It represents the effective net charge in this condition.
- The zeta potential can be measured on macroscopic surfaces (e.g. membranes, hair, polymers) as well as from particles dispersed in a liquid (e.g. colloids, nanoparticles, liposomes). Both types are considered “material”. However, the differentiation is important in order to choose the right technology to measure the zeta potential.
- The properties of the liquid medium play an important role in the formation of the zeta potential, which is highly dependent on the pH value or buffer concentration.
- A surface charge can be observed for solid materials (solid-liquid interface) as well as liquid droplets (liquid-liquid interface).



**ZETA POTENTIAL EXPLAINED**

## Coagulation Influencing Factors

**Effects of pH:** The pH range in which a coagulation process occurs may be the single most important factor in proper coagulation. The vast majority of coagulation problems are related to improper pH levels. Whenever possible, coagulation should be conducted in the optimum pH zone. When this is not done, lower coagulation efficiency results, generally resulting in a waste of chemicals and a lowered water quality.

Each of the inorganic salt coagulants has its own characteristic optimum pH range. In many plants, it is necessary to adjust the pH level in the coagulation process. In most cases this involves the addition of lime, caustic soda, or soda ash to maintain a minimum pH level. In some cases, however, acids may be necessary to lower the pH level to an optimum range. In some water plants, the acidic reactions of the inorganic salts are taken advantage of when the raw water pH levels are higher than desired. In these instances, overfeed of the coagulant is intentionally induced in order for the coagulation process to occur in the optimum range.

**Effects of salts:** Since no natural waters are completely pure, each will have various levels of cations and anions such as calcium, sodium, magnesium, iron, manganese, sulfate, chloride, phosphate, and others. Some of these ions may affect the efficiency of the coagulation process. Generally, mono and divalent cations such as sodium, calcium, and magnesium have little or no effect on the coagulation process. Trivalent cations do not have an adverse effect on the process in most instances. In fact, significant concentrations of naturally occurring iron in a water supply has resulted in the ability to feed lower than normal dosages of inorganic salt coagulants.

Some anions can have a more pronounced effect. Generally, monovalent anions such as chloride have little effect on the coagulation process. As the concentration of the divalent anion sulfate in a water supply increases, the optimum pH range of the inorganic salt coagulants tends to broaden, generally toward the lower pH levels.

As the concentration of phosphate ions increase, the optimum range of pH tends to shift to lower pH levels, without broadening. These effects could cause a disruption of the coagulation process if abrupt changes in the concentrations of these anions occur in the water supply.

**Nature of turbidity:** The turbidity in natural surface waters is composed of a large number of sizes of particles. The sizes of particles can be changing constantly, depending on precipitation and manmade factors. When heavy rains occur, runoff into streams, rivers, and reservoirs occurs, causing turbidity levels to increase. In most cases, the particle sizes are relatively large and settle relatively quickly in both the water treatment plant and the source of supply. However, in some instances, fine, colloidal material may be present in the supply, which may cause some difficulty in the coagulation process.

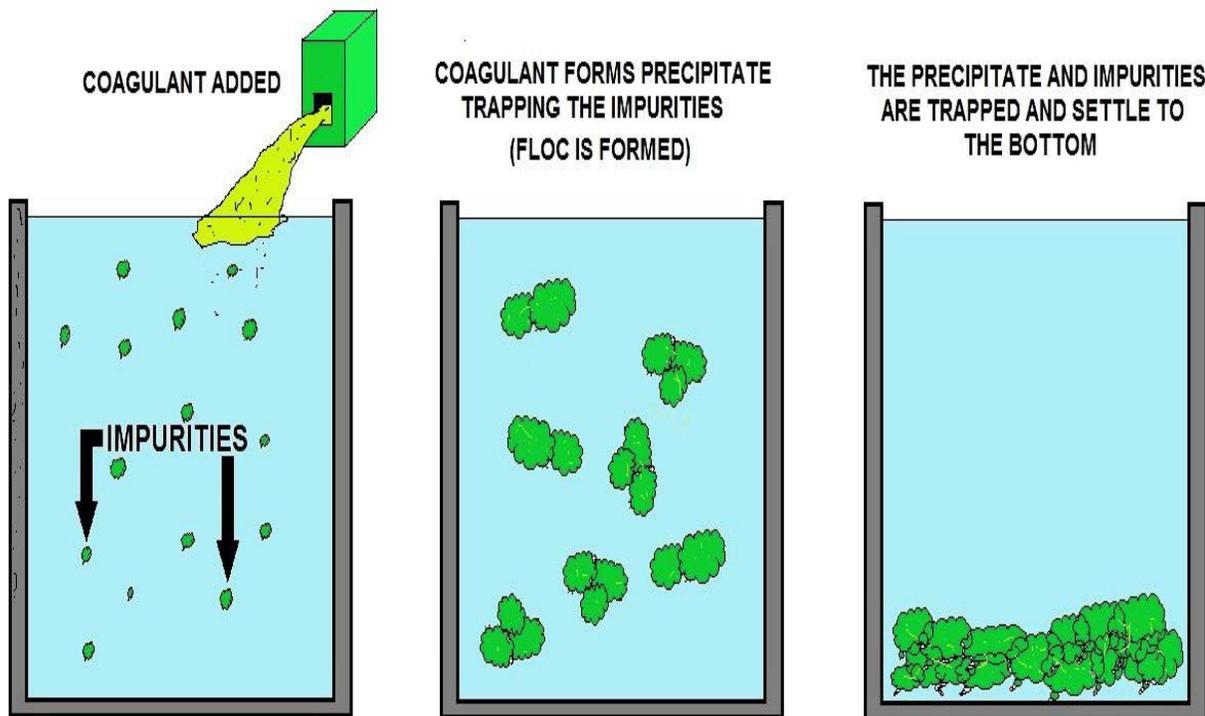
Generally, higher turbidity levels require higher coagulant dosages. However, seldom is the relationship between turbidity level and coagulant dosage linear. Usually, the additional coagulant required is relatively small when turbidities are much higher than normal due to higher collision probabilities of the colloids during high turbidities.

Conversely, low turbidity waters can be very difficult to coagulate due to the difficulty in inducing collision between the colloids. In this instance, floc formation is poor, and much of the turbidity is carried directly to the filters. Organic colloids may be present in a water supply due to pollution, and these colloids can be difficult to remove in the coagulation process. In this situation, higher coagulant dosages are generally required.

**Water temperature:** Cold water temperatures can cause two factors which add to the difficulty of the coagulation process. As water temperatures approach freezing, almost all chemical reactions occur more slowly. It can be more difficult therefore to evenly disperse the coagulants into the water. As a result, the coagulant process becomes less efficient, and higher coagulant dosages are generally used to compensate for these effects. In addition, floc settling characteristics become poor due to the higher density of the water during near freezing temperatures.

**Mixing Effects:** Poor or inadequate mixing results in an uneven dispersion of the coagulant. Unfortunately, many older plants were designed with mixing facilities which generally do not accomplish mixing in the most efficient manner. As a result, it becomes necessary to use higher than necessary dosages of coagulant to achieve an optimum level of efficiency in the process. The effects of low turbidity and cold water temperatures can tend to aggravate the lack of adequate mixing facilities in some plants.

**Effect of the coagulant:** The choice of the proper coagulant for the given conditions is of critical importance in maintaining an efficient coagulation scheme under widely varying conditions. The chemicals most commonly used in the coagulation process are Aluminum Sulfate, Ferric Chloride, Ferric Sulfate, and Cationic Polymers.

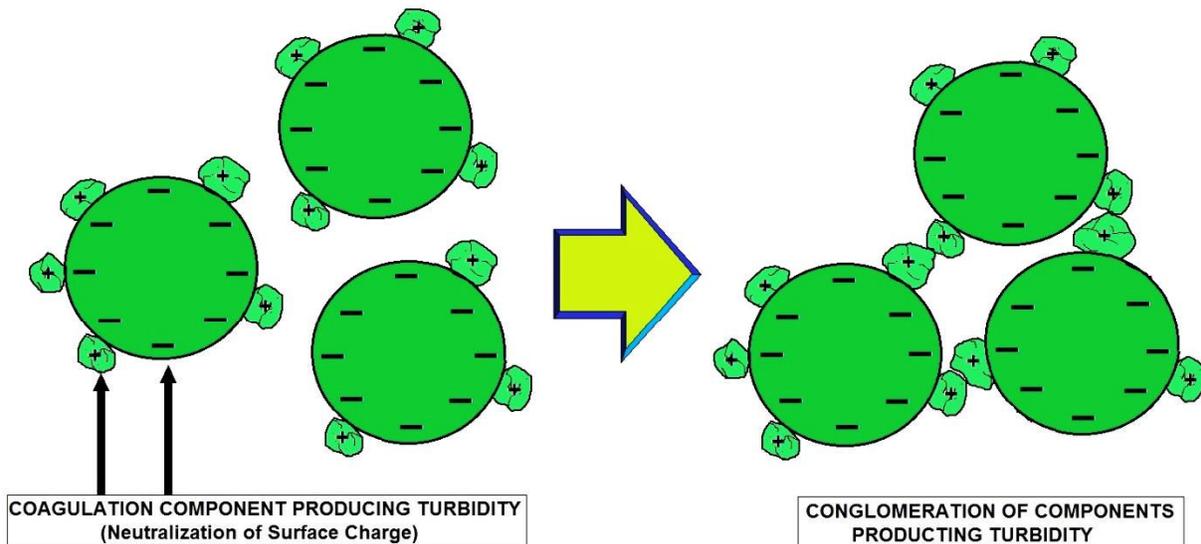


## BASICS OF COAGULATION / FLOCCULATION PROCESS

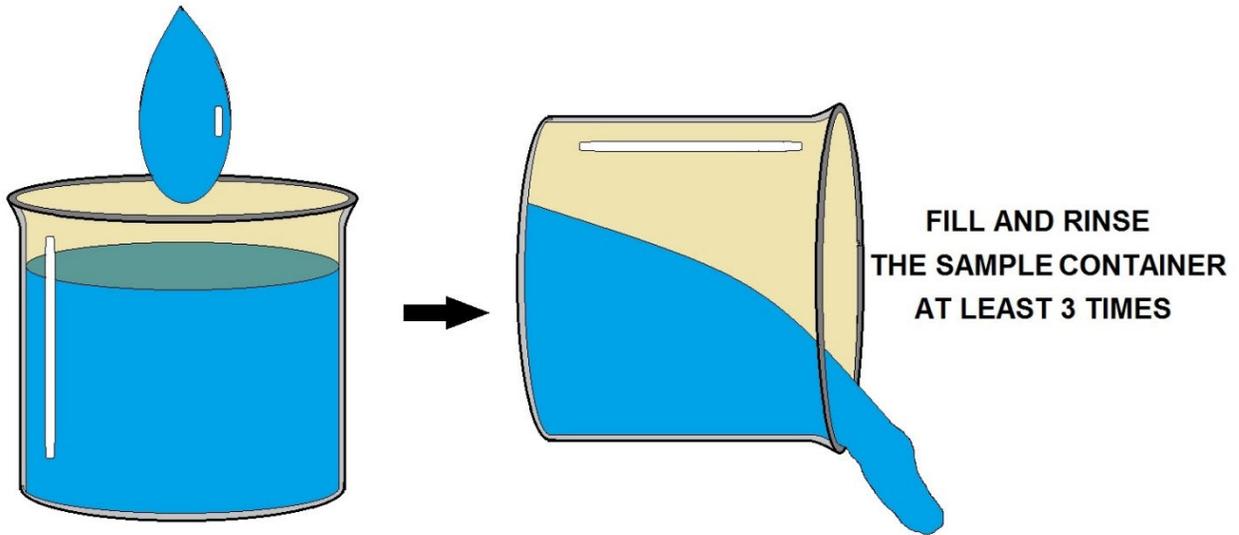
CHEMICAL NAME	CHEMICAL FORMULA	PRIMARY COAGULANT	COAGULANT AID
ALUMINUM SULFATE (Alum)	$Al_2(SO_4)_3 \cdot 14 H_2O$	X	
FERROUS SULFATE	$FeSO_4 \cdot 7 H_2O$	X	
FERRIC SULFATE	$Fe_2(SO_4)_3 \cdot 9 H_2O$	X	
FERRIC CHLORIDE	$FeCl_3 \cdot 6 H_2O$	X	
CATIONIC POLYMER	VARIOUS	X	X
CALCIUM HYDROXIDE	$Ca(OH)_2$	X*	X
CALCIUM OXIDE	CaO	X*	X
SODIUM ALUMINATE	$Na_2Al_2O_4$	X*	X
BENTONITE	CLAY		X
CALCIUM CARBONATE	$CaCO_3$		X
SODIUM SILICATE	$Na_2SiO_3$		X
ANIONIC POLYMER	VARIOUS		X
NONIONIC POLYMER	VARIOUS		X

\* Used as Primary Coagulant only in Water Softening Process

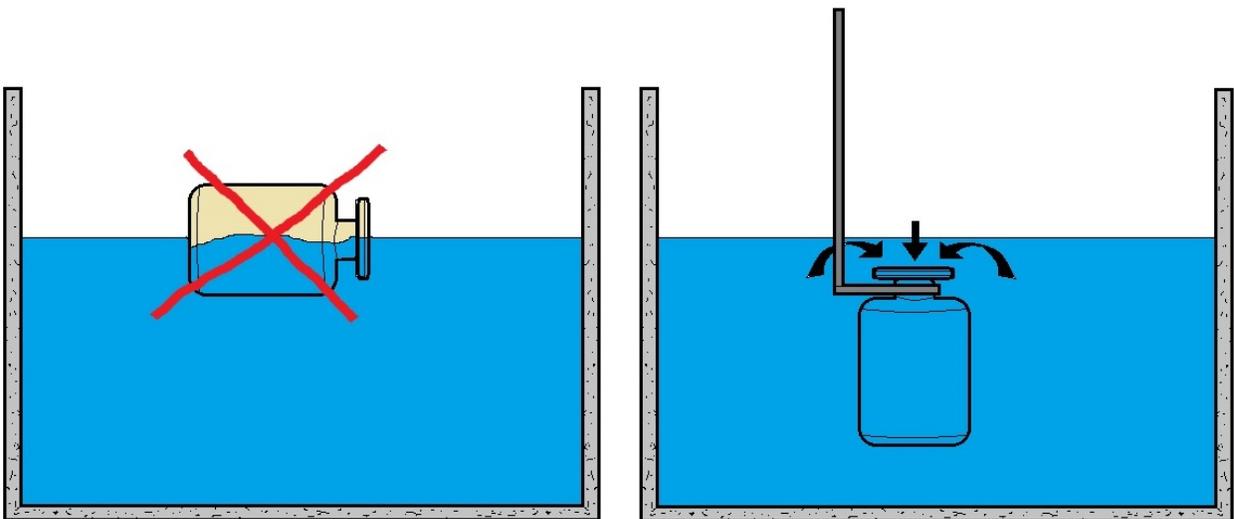
## COAGULANT CHEMICALS CHART



## COAGULATION PROCESS



## PROPER SAMPLING PROCEDURE



## PROPER WAY TO TAKE A SAMPLE (Immerse sample container in source)

## Common Coagulants

**Aluminum Sulfate (Alum):** Aluminum Sulfate is also known as alum, filter alum, and alumina sulfate. Alum is the most widely used coagulant. Alum is available in dry form as a powder or in lump form. It can also be purchased and fed as a liquid. Alum has no exact formula due to the varying water molecules of hydration which may be attached to the aluminum sulfate molecule. Once in water, alum can react with hydroxides, carbonates, bicarbonates, and other anions as discussed previously to form large, positively charged molecules. Carbon dioxide and sulfate are generally byproducts of these reactions. During the reactions, alum acts as an acid to reduce the pH and alkalinity of the water supply. It is important that sufficient alkalinity be present in the water supply for the various reactions to occur.

**On a theoretical basis, 1.0 mg/l of dry alum will react with:**

- 0.50 mg/l of natural alkalinity as calcium carbonate
- 0.33 mg/l of 85% quicklime as calcium oxide
- 0.39 mg/l of 95% hydrated lime as calcium hydroxide
- 0.54 mg/l of soda ash as sodium carbonate

Alum can be effective in the pH range of 5.5 to 7.8, but seems to work best in most water supplies in a pH range of 6.8 to 7.5. Below a pH range of 5.5, alkalinity in the water supply is generally insufficient.

The aluminum ions become soluble rather than insoluble and do not participate in the hydration and olation reactions necessary to make the alum effective as a coagulant. In these instances the plant may experience higher than normal filtered water turbidities, and much of the aluminum will pass through the filters.

When the pH level of the water is above 7.8 after the addition of the alum, the aluminum ions again become soluble, and the efficiency of coagulation is decreased. Under these conditions, aluminum ions again penetrate the filters, and post filtration alum coagulation can occur in the clear well and in the distribution system in some cases.

### **Ferric Chloride (Ferric)**

Traditionally, ferric chloride has not been used widely as a coagulant, but this trend is not continuing. Ferric chloride is becoming more extensively used as a coagulant due partially to the fact that the material can be purchased as a liquid.

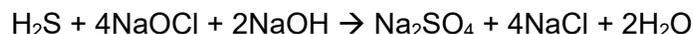
Ferric chloride may also be purchased as an anhydrous solid. Liquid ferric chloride is highly corrosive, and must be isolated from all corrodible metals. Like ferric sulfate, ferric chloride exhibits a wide pH range for coagulation, and the ferric ion does not easily become soluble.

As a result, many plants are replacing alum with ferric chloride to eliminate the penetration of aluminum ions through the plant filters. Ferric chloride also reacts as an acid in water to reduce alkalinity.

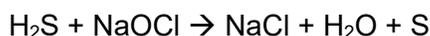
Other inorganic coagulants are available, such as potash alum, ammonia alum, ferrous sulfate (copperas), and chlorinated copperas. None of these materials are widely used. Typical dosages of the inorganic coagulants range from 50 pounds per million gallons of water treated under ideal conditions to as high as 800 to 1000 pounds per million gallons of water treated under worst case conditions.

## H<sub>2</sub>S Control – Traditional Wet Scrubbing using Chemicals

The most common method of control of H<sub>2</sub>S gas is to pass the smelly gas through a vertical, packed bed wet scrubber. The air passes up the tower as the scrubbing liquid containing caustic (NaOH) and oxidizing agent (most often bleach or NaOCl, sodium hypochlorite) flows down the tower in the counter-current fashion. The high pH provided by the caustic drives the mass transfer from gas to liquid phase by solubilizing H<sub>2</sub>S as HS<sup>-</sup> bisulfide and S<sup>-2</sup> sulfide ions. Once in solution, the reaction between hydrogen sulfide and oxidizing agent is almost instantaneous (assuming sufficient oxidizing agent is present). This reaction converts the sulfide to sulfate (SO<sub>4</sub><sup>-2</sup>) ion. The overall chemical reaction is described by the following equation:



Therefore, theoretically, for each molecule of H<sub>2</sub>S destroyed, four molecules of bleach and two molecules of caustic are consumed. However, the chemistry is not quite so simple, as partial oxidation of H<sub>2</sub>S also takes place which forms elemental sulfur:



This reaction represents about 1% of the chemistry present in a wet scrubber. The presence of excess bleach helps to minimize the formation of elemental sulfur. But bleach is an expensive chemical.

The use of two stage scrubbing is often employed both to minimize chemical consumption as well as to control sulfur deposits when scrubbing H<sub>2</sub>S. The first stage operates at 80% efficiency and uses a caustic only scrub at high pH (12.5). The air then passes to the second stage, where the remaining H<sub>2</sub>S is scrubbed with caustic / bleach solution at pH 9.5. The H<sub>2</sub>S present is destroyed at 99%+ efficiency. The blowdown from the 2<sup>nd</sup> stage, which will contain some amount of unused NaOCl, is sent to the sump of the 1<sup>st</sup> stage. In this way additional H<sub>2</sub>S is destroyed and maximum consumption of expensive oxidizing agent is assured.

Never the less, there are losses of chemicals which cannot be prevented, which of course raise the cost of odor scrubbing. These losses are due to the facts that bleach, NaOCl, slowly decomposes in storage as well as the fact that some amount of caustic is constantly lost to CO<sub>2</sub> absorption in both scrubbing stages.

### Emissions

Volatile organic compounds (VOCs) are the primary air pollutants emitted from rendering operations. The major constituents that have been qualitatively identified as potential emissions include organic sulfides, disulfides, C-4 to C-7 aldehydes, trimethylamine, C-4 amines, quinoline, dimethyl pyrazine, other pyrazines, and C-3 to C-6 organic acids. In addition, lesser amounts of C-4 to C-7 alcohols, ketones, aliphatic hydrocarbons, and aromatic compounds are potentially emitted. No quantitative emission data were presented.

Historically, the VOCs are considered an odor nuisance in residential areas in close proximity to rendering plants, and emission controls are directed toward odor elimination. The odor detection threshold for many of these compounds is low; some as low as 1 part per billion (ppb). Of the specific constituents listed, only quinoline is classified as a hazardous air pollutant (HAP). In addition to emissions from rendering operations, VOCs may be emitted from the boilers used to generate steam for the operation.

# Inorganic Chemical Introduction

## What are Inorganic Compounds?

**Inorganic compounds** are of inanimate, not biological origin. Inorganic compounds lack carbon and hydrogen atoms and are synthesized by the agency of geological systems. In contrast, the synthesis of organic compounds in biological systems incorporates carbohydrates into the molecular structure.

Organic chemists traditionally refer to any molecule containing carbon as an organic compound and by default this means that inorganic chemistry deals with molecules lacking carbon. However, biologists may distinguish organic from inorganic compounds in a different way that does not hinge on the presence of a carbon atom.

Pools of organic matter, for example, that have been metabolically incorporated into living tissues persist in decomposing tissues, but as molecules become oxidized into the open environment, such as atmospheric CO<sub>2</sub>, this creates a separate pool of inorganic compounds.

The distinction between inorganic and organic compounds is not always clear when dealing with open and closed systems, because everything is ultimately connected to everything else on the planet.

Some scientists, for example, view the open environment (i.e., the ecosphere) as an extension of life and from this perspective may consider atmospheric CO<sub>2</sub> as an organic compound. IUPAC, an agency widely recognized for defining chemical terms, does not offer definitions of inorganic or organic.

Inorganic compounds are rather simple chemicals present in ground water. These chemicals are generally described as mineral in nature and usually exist as ions (chemical substances with a positive or negative charge) when dissolved in water.

Typical examples include sodium, iron, calcium, magnesium, manganese, nitrate, chloride, sulfate, and zinc. Many of these chemicals are naturally occurring minerals that are dissolved from the rock/soil which make up the aquifer or water-bearing rock formations below the soil surface.

However, some of these compounds may be introduced into ground water by human activities. Nitrate (an agricultural fertilizer) and sodium chloride (road salt) are two examples.

Water purveyors need to test for 30 different inorganic compounds including all arsenic, barium, cadmium, lead, mercury, selenium, and thallium

- ✓ **Organic compounds** - these are once living, or are living and can bring life to cells. These contain carbon, and their electrons spin clockwise, just like those of the human body. Additionally, these cells can form an ionic bond with the body and can easily break down into materials to help with bodily function, such as tissue repair.
- ✓ **Inorganic compounds**- these were never living, without carbon and cannot bring life to cells. The body treats these metals like toxins and are tightly held together; they cannot be easily broken down. And, their electrons spin counterclockwise, out of sync with the rest of the body.

## Drinking Water Standards

The US Environmental Protection Agency is responsible for establishing maximum contaminant levels for drinking water. These standards are expressed as MCL (Maximum Contaminant Level). In most cases, this measurement is expressed as milligrams per liter of water (mg/l) or as parts per million (ppm).

In general terms, inorganic compounds are those materials that do not contain carbon. These compounds are often able to be dissolved in water. For example, dissolved gases such as nitrogen, oxygen, radon, and methane can be classified as inorganic compounds.

In addition to dissolved gases, some metals may be present in water as well. Some of these metals can be hazardous to human health, and may be introduced into water either naturally or through man-made activities.

Some of the more common metals include arsenic and aluminum which the EPA has established a MCL of no more than .05. Lead with a MCL of .015. Mercury MCL of .002. In addition, zinc, calcium, sodium, magnesium, potassium, and copper, all with a 1.3 MCL.

Lead, mercury, and arsenic can be dangerous to human health even at low concentrations, and as mentioned above can be introduced to our water from a variety of sources, including old pipes and lead solder.

Conversely, some of the other inorganic compounds such as sodium, potassium, calcium, and magnesium are important to our overall health and well-being.

Another class of inorganic compounds are known as negative ions. These include substances such as fluoride: MCL 4.0 PPM (parts per million). Chloride and nitrate: MCL 10.0 ppm. Nitrite MCL 1.0. Sulfate, phosphate, carbonate, and cyanide: MCL 0.2

### **Inorganic Chemistry**

**Inorganic chemistry** is the study of the synthesis and behavior of inorganic and organometallic compounds. This field covers all chemical compounds except the myriad organic compounds (carbon based compounds, usually containing C-H bonds), which are the subjects of organic chemistry.

The distinction between the two disciplines is far from absolute, and there is much overlap, most importantly in the sub-discipline of organometallic chemistry. It has applications in every aspect of the chemical industry—including catalysis, materials science, pigments, surfactants, coatings, medicine, fuel, and agriculture.

## Subdivisions of Inorganic Chemistry

Many inorganic compounds are ionic compounds, consisting of cations and anions joined by ionic bonding. Examples of salts (which are ionic compounds) are magnesium chloride  $\text{MgCl}_2$ , which consists of magnesium cations  $\text{Mg}^{2+}$  and chloride anions  $\text{Cl}^-$ ; or sodium oxide  $\text{Na}_2\text{O}$ , which consists of sodium cations  $\text{Na}^+$  and oxide anions  $\text{O}^{2-}$ .

In any salt, the proportions of the ions are such that the electric charges cancel out, so that the bulk compound is electrically neutral. The ions are described by their oxidation state and their ease of formation can be inferred from the ionization potential (for cations) or from the electron affinity (anions) of the parent elements.

Important classes of inorganic salts are the oxides, the carbonates, the sulfates and the halides. Many inorganic compounds are characterized by high melting points. Inorganic salts typically are poor conductors in the solid state. Another important feature is their solubility in water, e.g., and ease of crystallization. Where some salts (e.g.,  $\text{NaCl}$ ) are very soluble in water, others (e.g.,  $\text{SiO}_2$ ) are not.

The simplest inorganic reaction is double displacement when in mixing of two salts the ions are swapped without a change in oxidation state. In redox reactions one reactant, the *oxidant*, lowers its oxidation state and another reactant, the *reductant*, has its oxidation state increased. The net result is an exchange of electrons.

Electron exchange can occur indirectly as well, e.g., in batteries, a key concept in electrochemistry.

When one reactant contains hydrogen atoms, a reaction can take place by exchanging protons in acid-base chemistry. In a more general definition, an acid can be any chemical species capable of binding to electron pairs is called a Lewis acid; conversely any molecule that tends to donate an electron pair is referred to as a Lewis base. As a refinement of acid-base interactions, the HSAB theory takes into account polarizability and size of ions.

Inorganic compounds are found in nature as minerals. Soil may contain iron sulfide as pyrite or calcium sulfate as gypsum. Inorganic compounds are also found multitasking as biomolecules: as electrolytes (sodium chloride), in energy storage (ATP) or in construction (the polyphosphate backbone in DNA).

The first important man-made inorganic compound was ammonium nitrate for soil fertilization through the Haber process. Inorganic compounds are synthesized for use as catalysts such as vanadium(V) oxide and titanium(III) chloride, or as reagents in organic chemistry such as lithium aluminum hydride.

Subdivisions of inorganic chemistry are organometallic chemistry, cluster chemistry and bioinorganic chemistry. These fields are active areas of research in inorganic chemistry, aimed toward new catalysts, superconductors, and therapies.

## Industrial Inorganic Chemistry

Inorganic chemistry is a highly practical area of science. Traditionally, the scale of a nation's economy could be evaluated by their productivity of sulfuric acid. The top 20 inorganic chemicals manufactured in Canada, China, Europe, India, Japan, and the US (2005 data): aluminum sulfate, ammonia, ammonium nitrate, ammonium sulfate, carbon black, chlorine, hydrochloric acid, hydrogen, hydrogen peroxide, nitric acid, nitrogen, oxygen, phosphoric acid, sodium carbonate, sodium chlorate, sodium hydroxide, sodium silicate, sodium sulfate, sulfuric acid, and titanium dioxide. The manufacturing of fertilizers is another practical application of industrial inorganic chemistry.

## Descriptive Inorganic Chemistry

Descriptive inorganic chemistry focuses on the classification of compounds based on their properties. Partly the classification focuses on the position in the periodic table of the heaviest element (the element with the highest atomic weight) in the compound, partly by grouping compounds by their structural similarities. When studying inorganic compounds, one often encounters parts of the different classes of inorganic chemistry (an organometallic compound is characterized by its coordination chemistry, and may show interesting solid state properties).

Different classifications are:

## Coordination Compounds

Classical coordination compounds feature metals bound to "lone pairs" of electrons residing on the main group atoms of ligands such as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{Cl}^-$ , and  $\text{CN}^-$ . In modern coordination compounds almost all organic and inorganic compounds can be used as ligands.

The "metal" usually is a metal from the groups 3-13, as well as the *trans*-lanthanides and *trans*-actinides, but from a certain perspective, all chemical compounds can be described as coordination complexes.

The stereochemistry of coordination complexes can be quite rich, as hinted at by Werner's separation of two enantiomers of  $[\text{Co}((\text{OH})_2\text{Co}(\text{NH}_3)_4)_3]^{6+}$ , an early demonstration that chirality is not inherent to organic compounds. A topical theme within this specialization is supramolecular coordination chemistry.

- **Examples:**  $[\text{Co}(\text{EDTA})]^-$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $\text{TiCl}_4(\text{THF})_2$ .

## Main Group Compounds

These species feature elements from groups 1, 2 and 13-18 (excluding hydrogen) of the periodic table. Due to their often similar reactivity, the elements in group 3 (Sc, Y, and La) and group 12 (Zn, Cd, and Hg) are also generally included.

Main group compounds have been known since the beginnings of chemistry, e.g., elemental sulfur and the distillable white phosphorus. Experiments on oxygen,  $\text{O}_2$ , by Lavoisier and Priestley not only identified an important diatomic gas, but opened the way for describing compounds and reactions according to stoichiometric ratios.

The discovery of a practical synthesis of ammonia using iron catalysts by Carl Bosch and Fritz Haber in the early 1900s deeply impacted mankind, demonstrating the significance of inorganic chemical synthesis.

Typical main group compounds are  $\text{SiO}_2$ ,  $\text{SnCl}_4$ , and  $\text{N}_2\text{O}$ . Many main group compounds can also be classed as “organometallic”, as they contain organic groups, e.g.,  $\text{B}(\text{CH}_3)_3$ . Main group compounds also occur in nature, e.g., phosphate in DNA, and therefore may be classed as bioinorganic. Conversely, organic compounds lacking (many) hydrogen ligands can be classed as “inorganic”, such as the fullerenes, buckytubes and binary carbon oxides.

- **Examples:** tetrasulfur tetranitride  $\text{S}_4\text{N}_4$ , diborane  $\text{B}_2\text{H}_6$ , silicones, buckminsterfullerene  $\text{C}_{60}$ .

### Transition Metal Compounds

Compounds containing metals from group 4 to 11 are considered transition metal compounds. Compounds with a metal from group 3 or 12 are sometimes also incorporated into this group, but also often classified as main group compounds.

Transition metal compounds show a rich coordination chemistry, varying from tetrahedral for titanium (e.g.,  $\text{TiCl}_4$ ) to square planar for some nickel complexes to octahedral for coordination complexes of cobalt. A range of transition metals can be found in biologically important compounds, such as iron in hemoglobin.

- **Examples:** iron pentacarbonyl, titanium tetrachloride, cisplatin

### Organometallic Compounds

Usually, organometallic compounds are considered to contain the M-C-H group. The metal (M) in these species can either be a main group element or a transition metal. Operationally, the definition of an organometallic compound is more relaxed to include also highly lipophilic complexes such as metal carbonyls and even metal alkoxides.

Organometallic compounds are mainly considered a special category because organic ligands are often sensitive to hydrolysis or oxidation, necessitating that organometallic chemistry employs more specialized preparative methods than was traditional in Werner-type complexes.

Synthetic methodology, especially the ability to manipulate complexes in solvents of low coordinating power, enabled the exploration of very weakly coordinating ligands such as hydrocarbons,  $\text{H}_2$ , and  $\text{N}_2$ .

Because the ligands are petrochemicals in some sense, the area of organometallic chemistry has greatly benefited from its relevance to industry.

- **Examples:** Cyclopentadienyliron dicarbonyl dimer  $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$ , Ferrocene  $\text{Fe}(\text{C}_5\text{H}_5)_2$ , Molybdenum hexacarbonyl  $\text{Mo}(\text{CO})_6$ , Diborane  $\text{B}_2\text{H}_6$ , Tetrakis(triphenylphosphine)palladium(0)  $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$

### Cluster Compounds

Clusters can be found in all classes of chemical compounds. According to the commonly accepted definition, a cluster consists minimally of a triangular set of atoms that are directly bonded to each other. But metal-metal bonded dimetallic complexes are highly relevant to the area. Clusters occur in “pure” inorganic systems, organometallic chemistry, main group chemistry, and bioinorganic chemistry. The distinction between very large clusters and bulk solids is increasingly blurred. This interface is the chemical basis of nanoscience or nanotechnology and specifically arise from the study of quantum size effects in cadmium selenide clusters. Thus, large clusters can be described as an array of bound atoms intermediate in character between a molecule and a solid.

- **Examples:**  $\text{Fe}_3(\text{CO})_{12}$ ,  $\text{B}_{10}\text{H}_{14}$ ,  $[\text{Mo}_6\text{Cl}_{14}]^{2-}$ , 4Fe-4S

## Bioinorganic Compounds

By definition, these compounds occur in nature, but the subfield includes anthropogenic species, such as pollutants (e.g., methylmercury) and drugs (e.g., Cisplatin). The field, which incorporates many aspects of biochemistry, includes many kinds of compounds, e.g., the phosphates in DNA, and also metal complexes containing ligands that range from biological macromolecules, commonly peptides, to ill-defined species such as humic acid, and to water (e.g., coordinated to gadolinium complexes employed for MRI). Traditionally bioinorganic chemistry focuses on electron- and energy-transfer in proteins relevant to respiration. Medicinal inorganic chemistry includes the study of both non-essential and essential elements with applications to diagnosis and therapies.

- **Examples:** hemoglobin, methylmercury, carboxypeptidase

## Solid State Compounds

This important area focuses on structure, bonding, and the physical properties of materials. In practice, solid state inorganic chemistry uses techniques such as crystallography to gain an understanding of the properties that result from collective interactions between the subunits of the solid. Included in solid state chemistry are metals and their alloys or intermetallic derivatives. Related fields are condensed matter physics, mineralogy, and materials science.

- **Examples:** silicon chips, zeolites,  $\text{YBa}_2\text{Cu}_3\text{O}_7$

## Theoretical Inorganic Chemistry

An alternative perspective on the area of inorganic chemistry begins with the Bohr model of the atom and, using the tools and models of theoretical chemistry and computational chemistry, expands into bonding in simple and then more complex molecules.

Precise quantum mechanical descriptions for multielectron species, the province of inorganic chemistry, is difficult. This challenge has spawned many semi-quantitative or semi-empirical approaches including molecular orbital theory and ligand field theory. In parallel with these theoretical descriptions, approximate methodologies are employed, including density functional theory.

Exceptions to theories, qualitative and quantitative, are extremely important in the development of the field. For example,  $\text{Cu}^{II}_2(\text{OAc})_4(\text{H}_2\text{O})_2$  is almost diamagnetic below room temperature whereas Crystal Field Theory predicts that the molecule would have two unpaired electrons. The disagreement between qualitative theory (paramagnetic) and observation (diamagnetic) led to the development of models for "magnetic coupling."

These improved models led to the development of new magnetic materials and new technologies.

## Qualitative Theories

Inorganic chemistry has greatly benefited from qualitative theories. Such theories are easier to learn as they require little background in quantum theory. Within main group compounds, VSEPR theory powerfully predicts, or at least rationalizes, the structures of main group compounds, such as an explanation for why  $\text{NH}_3$  is pyramidal whereas  $\text{ClF}_3$  is T-shaped.

For the transition metals, crystal field theory allows one to understand the magnetism of many simple complexes, such as why  $[\text{Fe}^{III}(\text{CN})_6]^{3-}$  has only one unpaired electron, whereas  $[\text{Fe}^{III}(\text{H}_2\text{O})_6]^{3+}$  has five. A particularly powerful qualitative approach to assessing the structure and reactivity begins with classifying molecules according to electron counting, focusing on the numbers of valence electrons, usually at the central atom in a molecule.

### **Molecular Symmetry Group Theory**

A central construct in inorganic chemistry is the theory of molecular symmetry. Mathematical group theory provides the language to describe the shapes of molecules according to their point group symmetry. Group theory also enables factoring and simplification of theoretical calculations.

Spectroscopic features are analyzed and described with respect to the symmetry properties of the, *inter alia*, vibrational or electronic states. Knowledge of the symmetry properties of the ground and excited states allows one to predict the numbers and intensities of absorptions in vibrational and electronic spectra. A classic application of group theory is the prediction of the number of C-O vibrations in substituted metal carbonyl complexes. The most common applications of symmetry to spectroscopy involve vibrational and electronic spectra.

As an instructional tool, group theory highlights commonalities and differences in the bonding of otherwise disparate species, such as  $WF_6$  and  $Mo(CO)_6$  or  $CO_2$  and  $NO_2$ .

### **Thermodynamics and Inorganic Chemistry**

An alternative quantitative approach to inorganic chemistry focuses on energies of reactions. This approach is highly traditional and empirical, but it is also useful. Broad concepts that are couched in thermodynamic terms include redox potential, acidity, phase changes.

A classic concept in inorganic thermodynamics is the Born-Haber cycle, which is used for assessing the energies of elementary processes such as electron affinity, some of which cannot be observed directly.

### **Mechanistic Inorganic Chemistry**

An important and increasingly popular aspect of inorganic chemistry focuses on reaction pathways. The mechanisms of reactions are discussed differently for different classes of compounds.

### **Main Group Elements and Lanthanides**

The mechanisms of main group compounds of groups 13-18 are usually discussed in the context of organic chemistry (organic compounds are main group compounds, after all).

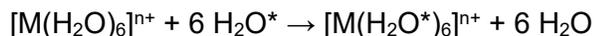
Elements heavier than C, N, O, and F often form compounds with more electrons than predicted by the octet rule, as explained in the article on hypervalent molecules. The mechanisms of their reactions differ from organic compounds for this reason.

Elements lighter than carbon (B, Be, Li) as well as Al and Mg often form electron-deficient structures that are electronically akin to carbocations. Such electron-deficient species tend to react via associative pathways. The chemistry of the lanthanides mirrors many aspects of chemistry seen for aluminum.

## Transition Metal Complexes

Mechanisms for the reactions of transition metals are discussed differently from main group compounds. The important role of d-orbitals in bonding strongly influences the pathways and rates of ligand substitution and dissociation. These themes are covered in articles on coordination chemistry and ligand. Both associative and dissociative pathways are observed.

An overarching aspect of mechanistic transition metal chemistry is the kinetic lability of the complex illustrated by the exchange of free and bound water in the prototypical complexes  $[M(H_2O)_6]^{n+}$ :

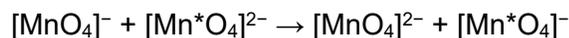


where  $H_2O^*$  denotes isotopically enriched water, e.g.,  $H_2^{17}O$

The rates of water exchange varies by 20 orders of magnitude across the periodic table, with lanthanide complexes at one extreme and Ir(III) species being the slowest.

## Redox Reactions

Redox reactions are prevalent for the transition elements. Two classes of redox reaction are considered: atom-transfer reactions, such as oxidative addition/reductive elimination, and electron-transfer. A fundamental redox reaction is "self-exchange", which involves the degenerate reaction between an oxidant and a reductant. For example, permanganate and its one-electron reduced relative manganate exchange one electron:



## Reactions at Ligands

Coordinated ligands display reactivity distinct from the free ligands. For example, the acidity of the ammonia ligands in  $[Co(NH_3)_6]^{3+}$  is elevated relative to  $NH_3$  itself. Alkenes bound to metal cations are reactive toward nucleophiles whereas alkenes normally are not. The large and industrially important area of catalysis hinges on the ability of metals to modify the reactivity of organic ligands.

Homogeneous catalysis occurs in solution and heterogeneous catalysis occurs when gaseous or dissolved substrates interact with surfaces of solids.

Traditionally homogeneous catalysis is considered part of organometallic chemistry and heterogeneous catalysis is discussed in the context of surface science, a subfield of solid state chemistry. But the basic inorganic chemical principles are the same.

Transition metals, almost uniquely, react with small molecules such as  $CO$ ,  $H_2$ ,  $O_2$ , and  $C_2H_4$ . The industrial significance of these feedstocks drives the active area of catalysis. Ligands can also undergo ligand transfer reactions such as transmetalation.

## Inorganic Compound Characterization

Because of the diverse range of elements and the correspondingly diverse properties of the resulting derivatives, inorganic chemistry is closely associated with many methods of analysis. Older methods tended to examine bulk properties such as the electrical conductivity of solutions, melting points, solubility, and acidity. With the advent of quantum theory and the corresponding expansion of electronic apparatus, new tools have been introduced to probe the electronic properties of inorganic molecules and solids. Often these measurements provide insights relevant to theoretical models.



For example, measurements on the photoelectron spectrum of methane demonstrated that describing the bonding by the two-center, two-electron bonds predicted between the carbon and hydrogen using Valence Bond Theory is not appropriate for describing ionization processes in a simple way. Such insights led to the popularization of molecular orbital theory as fully delocalized orbitals are a more appropriate simple description of electron removal and electron excitation.

### Commonly encountered techniques are:

- X-ray crystallography: This technique allows for the 3D determination of molecular structures.
- Dual polarization interferometer: This technique measures the conformation and conformational change of molecules.
- Various forms of spectroscopy
  - Ultraviolet-visible spectroscopy: Historically, this has been an important tool, since many inorganic compounds are strongly colored
  - NMR spectroscopy: Besides  $^1\text{H}$  and  $^{13}\text{C}$  many other "good" NMR nuclei (e.g.,  $^{11}\text{B}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ , and  $^{195}\text{Pt}$ ) give important information on compound properties and structure. Also the NMR of paramagnetic species can result in important structural information. Proton NMR is also important because the light hydrogen nucleus is not easily detected by X-ray crystallography.

- Infrared spectroscopy: Mostly for absorptions from carbonyl ligands
- Electron nuclear double resonance (ENDOR) spectroscopy
- Mössbauer spectroscopy
- Electron-spin resonance: ESR (or EPR) allows for the measurement of the environment of paramagnetic metal centers.
- Electrochemistry: Cyclic voltammetry and related techniques probe the redox characteristics of compounds.



## Synthetic Inorganic Chemistry

Although some inorganic species can be obtained in pure form from nature, most are synthesized in chemical plants and in the laboratory.

Inorganic synthetic methods can be classified roughly according to the volatility or solubility of the component reactants. Soluble inorganic compounds are prepared using methods of organic synthesis.

For metal-containing compounds that are reactive toward air, Schlenk line and glove box techniques are followed.

Volatile compounds and gases are manipulated in “vacuum manifolds” consisting of glass piping interconnected through valves, the entirety of which can be evacuated to 0.001 mm Hg or less.

Compounds are condensed using liquid nitrogen (b.p. 78K) or other cryogenics. Solids are typically prepared using tube furnaces, the reactants and products being sealed in containers, often made of fused silica (amorphous  $\text{SiO}_2$ ) but sometimes more specialized materials such as welded Ta tubes or Pt “boats”. Products and reactants are transported between temperature zones to drive reactions.

## Drinking Water Analysis Chart

<u>ANALYSIS</u>	<u>METHOD</u>	<u>HOLDING TIME</u>
<b>Inorganic Compounds (IOC)</b> Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Copper, Iron, Lead, Manganese, Mercury, Nickel, Selenium, Silver, Sodium, Thallium, Zinc, Hardness, Conductivity, Turbidity, Color, Chloride, Cyanide, Fluoride, Nitrate, Nitrite, Sulfate, and Total Dissolved Solids.	(various)	48 hours
<b>Primary Pollutants</b> (Short IOC) Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Lead, Mercury, Selenium, Silver, Sodium, Thallium, Turbidity, Fluoride, Cyanide, Nitrate, and Nitrite.	(various)	48 hours
<b>Municipal Testing</b>		
<b>Lead and Copper</b>	EPA 200.9 for Pb EPA 200.7 for Cu	14 days
<b>Public or Individual Water Source Testing</b>		
<b>Nitrate</b>	SM-4500 NO3 D	48 hours
<b>Total Coliform &amp; E. Coli</b>	SM-9223 B	30 Hours
<b>Metals Analysis on Drinking Water (per element)</b>		
<b>GFAA</b> (As, Pb, Sb, Se, Tl)	EPA 200.9	6 months
<b>ICP</b> (Ag, Al, B, Ba, Be, Cd, Cr, Cu, Fe, Mn, Mo, Na, Ni, Zn)	EPA 200.7	6 months
<b>CVAA</b> (Hg)	EPA 245.1	6 months
<b>Primary Pollutant Metals</b>	GFAA/ICP/CVAA	6 months
<b><u>Drinking Water Analysis</u></b>		
<b>PH</b>	EPA 150.1	
<b>Acidity</b>	SM-2310 B (4b)	14 days
<b>Alkalinity (Bicarbonate &amp; Carbonate)</b>	SM-2320 B (4a)	14 days
<b>BOD</b>	SM-5210 B	48 hours
<b>Calcium</b>	EPA 200.7	6 months
<b>Chloride</b>	SM-4500 CI	8 days
<b>Chlorine, total</b>	SM-4500 CI	5 hours
<b>Color</b>	SM-2120 B	8 hours
<b>COD</b>	EPA 410.4 (7.3)	28 days
<b>Cyanide</b>	EPA 335.2 (8.7)	28 days
<b>Dissolved Oxygen</b>	SM-4500 O C	8 hours
<b>Fluoride</b>	SM-4500 F C	28 days
<b>Hardness</b>	SM-2340 B	6 months
<b>Magnesium</b>	EPA 200.7	6 months
<b>Nitrogen, ammonia</b>	SM-4500 NH3 E SM-4500 NH3 H	28 days

Nitrogen, nitrate	SM-4500 NO3 D	48 hours
Nitrogen, nitrite	SM-4500 NO2	48 hours
Nitrate + Nitrite	SM-4500 NO3 E	48 hours
Nitrogen, TKN	EPA 351.4	28 days
Odor	SM-2150	6 days
Phosphorous, ortho	EPA 200.7	48 hours
Phosphorous, total	SM-4500 P	28 days
Solids, settle able	SM-2540	7 days
Solids, suspended	SM-2540 D	7 days
<b><u>Drinking Water Analysis</u></b>		
Solids, total	SM-2540 B	7 days
Solids, volatile	SM-2540 E	7 days
Specific Conductance	SM-2510 B	28 days
Sulfate	SM-4500 SO-4 E	28 days
Sulfide	SM-4500 S-2 D	28 days
Sulfite	EPA 377.1	28 days
Silica	SM-4500 SI E	28 days
Total Organic Carbon	EPA 415.1	28 days
Turbidity	SM- 2130 B	48 hours

*This course contains EPA's federal rule requirements. Please be aware that each state implements drinking water regulations that may be more stringent than EPA's regulations. Check with your state environmental agency for more information.*

<b><u>ORGANICS</u></b>		
<b>Semi-volatile Organics in Water (SOC)*</b>	<b>(various)</b>	<b>7 days</b>
<b>Volatile Organics in Water*</b>	<b>(various)</b>	<b>7 days</b>
<b>Trihalomethanes*</b>	<b>EPA 501.1</b>	<b>7 days</b>
<b>Gross Alpha &amp; Beta (Radionuclides)*</b>	<b>(various)</b>	<b>7 days</b>
<b>BOD</b>	<b>SM-5210 B</b>	<b>48 hours</b>
<b>COD</b>	<b>EPA 410.4(7.3)</b>	<b>28 days</b>
<b>Oil and Grease</b>	<b>EPA 413.1(1.2)</b>	<b>28 days</b>
<b>Hardness W/digestion</b>	<b>SM-2340 B</b>	<b>6 months</b>
<b>Nitrogen, TKN</b>	<b>EPA 351.4</b>	<b>28 days</b>
<b>Nitrogen, ammonia</b>	<b>SM-4500 NH3 F</b>	<b>28 days</b>
<b>Nitrogen, Total Organic</b>	<b>SM-4500 NorgNH3</b>	<b>28 days</b>
<b>Nitrogen, nitrate</b>	<b>SM-4500 NO3 D</b>	<b>48 hours</b>
<b>Nitrogen, nitrite</b>	<b>SM-4500 NO2 B</b>	<b>48 hours</b>
<b>Phosphorous, ortho</b>	<b>SM-4500 P E</b>	<b>48 hours</b>
<b>Sulfate</b>	<b>SM-4500 SO4 E</b>	<b>28 days</b>
<b>Solids, dissolved</b>	<b>SM-2540</b>	<b>7 days</b>
<b>Solids, settle able</b>	<b>SM-2540 F</b>	<b>7 days</b>
<b>Solids, suspended</b>	<b>SM-2540 D</b>	<b>7 days</b>
<b>Solids, total</b>	<b>SM-2540 B</b>	<b>7 days</b>
<b>Solids, volatile</b>	<b>SM-2540 E</b>	<b>7 days</b>
<b>Total Organic Carbon</b>	<b>EPA 415.1</b>	<b>28 days</b>
<b>PH</b>	<b>EPA 150.1</b>	
<b>Metals (per element)</b>		
<b>ICP (Ag, Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Sb, V,</b>	<b>EPA 200.7</b>	<b>6 months</b>

GFAA (As, Pb, Ba, Se, Tl)	EPA 200.9	6 months
CVAA (Hg)	EPA 245.1	6 months

## Definitions

**Action level** - the concentration of a contaminant which, if exceeded, triggers treatment or other requirements which a water system must follow.

**Maximum Contaminant Level** - the “Maximum Allowed” (MCL) is the highest level of a contaminant that is allowed in drinking water. MCLs are set as close to the MCLGs as feasible using the best available treatment technology.

**Maximum Contaminant Level Goal** - the “Goal” (MCLG) is the level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety.

**Non-Detects (ND)** - laboratory analysis indicates that the constituent is not present.

**Parts per million (ppm) or Milligrams per liter (mg/L)** - one part per million corresponds to one minute in two years or a single penny in \$10,000.

**Parts per billion (ppb) or Micrograms per liter (ug/L)** - one part per billion corresponds to one minute in 2,000 years, or a single penny in \$10,000,000.

**Picocuries per liter (pCi/L)** - picocuries per liter is a measure of the radioactivity in water.

*This course contains EPA’s federal rule requirements. Please be aware that each state implements drinking water regulations that may be more stringent than EPA’s regulations. Check with your state environmental agency for more information.*

## Sample Containers and Preservation Techniques

Methods used by the laboratory usually specify what type of container and how much sample is required to run an analysis. The following table provides a summary of the sample handling and preservation requirements for some of the most common tests.

Parameter	Bottle Type	Minimum Sample Size	Maximum Holding Time	Storage & Preservation
<b>Acidity</b>	P or G <sup>B</sup>	100ml	24 hrs/14 days	refrigerate
<b>Alkalinity</b>	P or G	200ml	24 hrs/14 days	refrigerate
<b>BOD (5 day)</b>	P or G	1L	6 hrs/48 hrs	refrigerate
<b>Boron</b>	P	100ml	28 days/6 months	
<b>Chloride</b>	P or G	250ml	28 days	
<b>Chlorine, residual</b>	P or G	500ml	0.5 hr/stat	analyze on site ASAP
<b>COD</b>	P or G	500ml	28 days/28 days	analyze on site ASAP
<b>Color</b>	P or G	500ml	48 hrs/48 hrs	refrigerate
<b>Coliform, Total</b>	P or G	125ml	30 hrs	refrigerate
<b>Conductivity</b>	P or G	500ml	48 hrs/48 hrs	refrigerate
<b>Cyanide, Total</b>	P or G	500ml	28 days/28 days	add NaOH to pH>12
				refrigerate in dark
<b>Fluoride</b>	P	300ml	28days/ 28 days	
<b>Hardness</b>	P or G	100ml	6 months/6 months	add HNO <sub>3</sub> to pH<2
<b>Metals, general</b>	P <sup>A</sup> or G <sup>A</sup>	250ml	6 months/6 months	add HNO <sub>3</sub> to pH<2
<i>Furnace</i>	P <sup>A</sup> or G <sup>A</sup>	250ml	6 months/6 months	
<i>Flame</i>	P <sup>A</sup> or G <sup>A</sup>	250ml	6 months/6 months	
<b>Mercury</b>	P <sup>A</sup> or G <sup>A</sup>	500ml	28 days/28 days	add HNO <sub>3</sub> to pH<2
<b>Nitrogen Ammonia</b>	P or G	500ml	7 days/ 28 days	ASAP or add H <sub>2</sub> SO <sub>4</sub> to pH<2 & refrigerate
<i>Nitrate</i>	P or G	100ml	48 hrs/48 hrs	ASAP & refrigerate
<i>Nitrate + Nitrite</i>	P or G	200ml	48 hrs/28 days	ASAP & refrigerate
<i>Nitrite</i>	P or G	100ml	none/48 hrs	ASAP & refrigerate

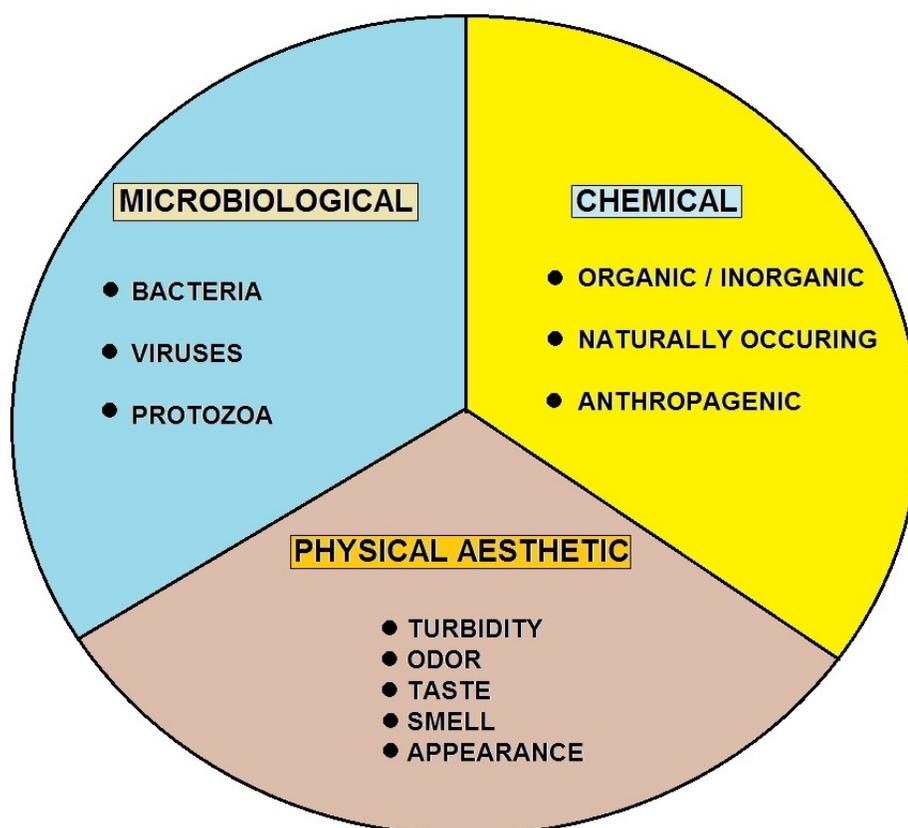
<i>TKN</i>	P or G	500ml	7 days/28 days	add H <sub>2</sub> SO <sub>4</sub> to pH<2
<b>Oxygen, dissolved</b>	G (BOD)	300ml		
<i>Electrode</i>			0.5 hrs/stat	ASAP on site
<i>Winkler</i>			8hrs/8 hrs	ASAP on site
<b>pH</b>	P or G	50ml	2 hrs/stat	ASAP on site
<b>Phosphate,</b>	G <sup>A</sup>			
<i>Ortho</i>		100ml	48hrs	filter ASAP refrigerate
<i>Total</i>		100ml	28 days/28 days	refrigerate
<b>Solids,</b>	P or G			
<i>Dissolved</i>		250ml	7 days	refrigerate
<i>Settleable</i>		1L	48 hrs	refrigerate
<i>Suspended</i>		250ml	7 days	refrigerate
<i>Total</i>		250ml	7 days	refrigerate
<i>Volatile</i>		250ml	7 days	refrigerate
<b>Silica</b>	P	200ml	28 days/28 days	refrigerate
<b>Sulfate</b>	P or G	100ml	28 days/28 days	refrigerate
<b>Turbidity</b>	P or G	100ml	24 hrs/48 hrs	ASAP/refrigerate, store in dark up to 24 hrs

Refrigerate = storage at 4 degrees C, in the dark. P = plastic (polyethylene or equivalent); G = glass, G<sup>A</sup> or P<sup>A</sup> = rinsed with 1:1 HNO<sub>3</sub>; G<sup>B</sup> = glass, borosilicate, G<sup>S</sup> = glass rinsed with organic solvents; NS = not stated in cited reference; stat = no storage allowed; analyze immediately.

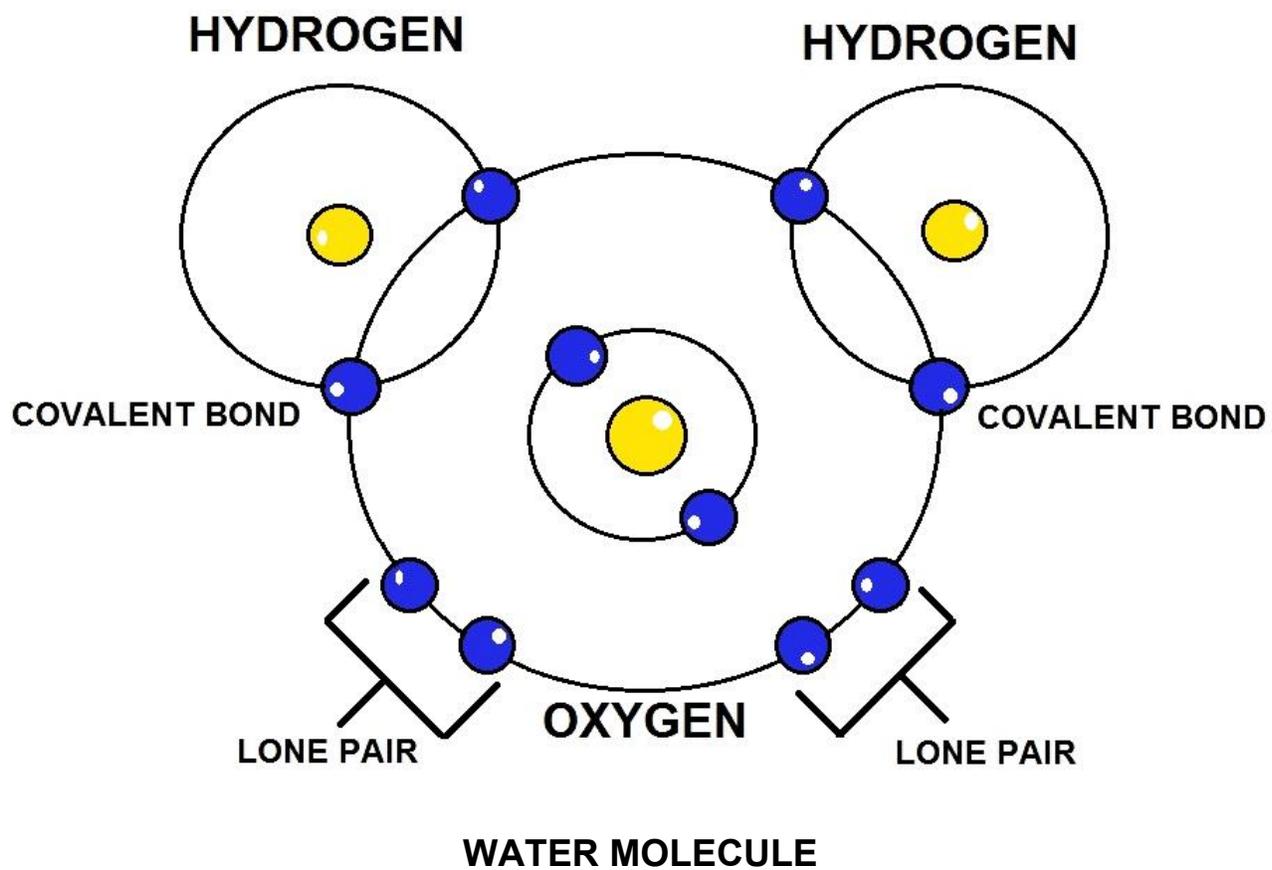
*This course contains EPA's federal rule requirements. Please be aware that each state implements drinking water regulations that may be more stringent than EPA's regulations. Check with your state environmental agency for more information.*

FACTOR	TYPE	SOURCE(S)	PROBLEM
FECAL COLIFORM BACTERIA	BIOLOGICAL	HUMAN SEWAGE; LIVESTOCK WASTE	POSSIBLE PRESENCE OF PATHOGENIC (DISEASE-CAUSING) ORGANISMS
DISSOLVED OXYGEN (DO)	CHEMICAL	AIR; AQUATIC PLANTS	LOW LEVELS CAN KILL AQUATIC ORGANISMS
NITROGEN AND PHOSPHORUS	CHEMICAL	FERTILIZERS AND DETERGENTS FROM LAWNS AND RUNOFF	EXCESSIVE ALGAE GROWTH CAN LEAD TO LOW DO
ZINC, ARSENIC, LEAD, MERCURY, CADMIUM, NICKEL	CHEMICAL	LANDFILLS; INDUSTRIAL DISCHARGES; RUNOFF	GENETIC MUTATIONS OR DEATH IN FISH & WILDLIFE (HUMAN HEALTH THREATS AS WELL)
SALT	CHEMICAL	SALTWATER INTRUSION (IF NEAR OCEAN)	KILLS FRESHWATER SPECIES OF PLANTS AND ANIMALS
MUD, SAND, OTHER SOLID PARTICLES (TURBIDITY)	PHYSICAL	EROSION AND RUNOFF FROM DEVELOPMENT; AGRICULTURE	REDUCES PHOTOSYNTHESIS IN AQUATIC VEGETATION; INTERFERES WITH RESPIRATION IN AQUATIC ANIMALS

## WATER QUALITY FACTORS



## WATER QUALITY BROKEN DOWN INTO 3 BROAD CATEGORIES



# IOC Section

## Periodic Table of the Elements

**Element Categories**

- alkali metals
- alkaline metals
- other metals
- transition metals
- lanthanoids
- actinoids
- metalloids
- nonmetals
- halogens
- noble gases
- unknown elements

**Electron Configuration Blocks**

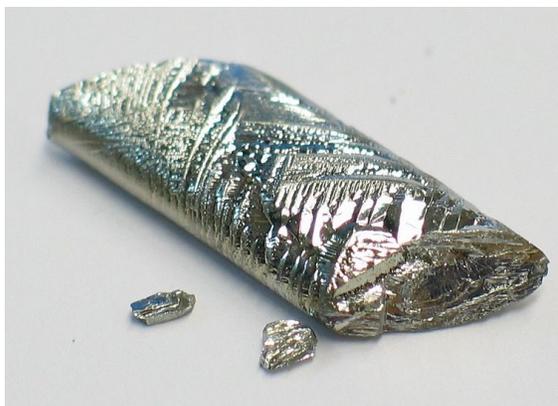
s, p, d, f

**Callout for Iron (Fe):**

- atomic number: 26
- chemical symbol: Fe
- chemical name: iron
- standard atomic weight: 55.85
- lower: liquid at STP
- liquid: no stable isotopes

**Natural Occurrence Legend:**

- primordial (solid box)
- from decay (dashed box)
- synthetic (dotted box)



Left, Tellurium, right Astatine with Fluorine



Common water sample bottles for distribution systems.

Radiochems, VOCs, (Volatile Organic Compounds), TTHMs, Total Trihalomethanes), Nitrate, Nitrite.

Most of these sample bottles will come with the preservative already inside the bottle.

Some bottles will come with a separate preservative (acid) for the field preservation.

Slowly add the acid or other preservative to the water sample; not water to the acid or preservative.

## Inorganic Chemicals

Contaminant	MCLG <sup>1</sup> (mg/L) <sup>2</sup>	MCL or TT <sup>1</sup> (mg/L) <sup>2</sup>	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
<b>Antimony</b>	0.006	0.006	Increase in blood cholesterol; decrease in blood sugar	Discharge from petroleum refineries; fire retardants; ceramics; electronics; solder
<b>Arsenic</b>	0 <sup>2</sup>	0.010 as of 01/23/06	Skin damage or problems with circulatory systems, and may have increased risk of getting cancer	Erosion of natural deposits; runoff from orchards, runoff from glass & electronics production wastes
<b>Asbestos (fiber &gt;10 micrometers)</b>	7 million fibers per liter	7 MFL	Increased risk of developing benign intestinal polyps	Decay of asbestos cement in water mains; erosion of natural deposits
<b>Barium</b>	2	2	Increase in blood pressure	Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits
<b>Beryllium</b>	0.004	0.004	Intestinal lesions	Discharge from metal refineries and coal-burning factories; discharge from electrical, aerospace, and defense industries
<b>Cadmium</b>	0.005	0.005	Kidney damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints
<b>Chromium (total)</b>	0.1	0.1	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits
<b>Copper</b>	1.3	TT <sup>2</sup> ; Action Level=1.3	Short term exposure: Gastrointestinal distress Long term exposure: Liver or kidney damage People with Wilson's Disease should consult their personal doctor if the amount of copper in their water exceeds the action level	Corrosion of household plumbing systems; erosion of natural deposits
<b>Cyanide (as free cyanide)</b>	0.2	0.2	Nerve damage or thyroid problems	Discharge from steel/metal factories;

## Inorganic Chemicals

Contaminant	MCLG <sup>1</sup> (mg/L) <sup>2</sup>	MCL or TT <sup>1</sup> (mg/L) <sup>2</sup>	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
				discharge from plastic and fertilizer factories
<b>Fluoride</b>	4.0	4.0	Bone disease (pain and tenderness of the bones); Children may get mottled teeth	Water additive which promotes strong teeth; erosion of natural deposits; discharge from fertilizer and aluminum factories
<b>Lead</b>	zero	TT <sup>2</sup> ; Action Level=0.015	Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities Adults: Kidney problems; high blood pressure	Corrosion of household plumbing systems; erosion of natural deposits
<b>Mercury (inorganic)</b>	0.002	0.002	Kidney damage	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands
<b>Nitrate (measured as Nitrogen)</b>	10	10	Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits
<b>Nitrite (measured as Nitrogen)</b>	1	1	Infants below the age of six months who drink water containing nitrite in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits
<b>Selenium</b>	0.05	0.05	Hair or fingernail loss; numbness in fingers or toes; circulatory problems	Discharge from petroleum refineries; erosion of natural deposits; discharge from mines
<b>Thallium</b>	0.0005	0.002	Hair loss; changes in blood; kidney, intestine, or liver problems	Leaching from ore-processing sites; discharge from electronics, glass, and drug factories

## Chemical Treatment before the Filter

The coagulation and flocculation stages of the water treatment must be monitored continuously. Adjustments in the amount of coagulant added must be made frequently to prevent the filter from becoming overloaded with suspended material. This overload may cause the filter to prematurely reach its maximum headloss.

If there is early turbidity breakthrough in the filter effluent, more coagulant may have to be added to the coagulation process. There may be a need for better mixing during the coagulation or the addition of more filter aid.

If there is a rapid increase in filter head loss, too much coagulant may be clogging the filter. Less coagulant or less filter aid should be used. The operator needs to learn to recognize these problems and choose the proper corrections.



Filter aid being fed at the weirs of sedimentation.



In the photograph above, overfeeding flocculants to meet federal regulations caused Iron to precipitate on the filter walls.

## IOC Sample Collection – Things to Remember

Sample instructions should be supplied with the sample containers from the laboratory. If the laboratory fails to include sample instructions, contact the laboratory and request sample instructions.

### Some general practices to remember:

- Samples should be collected at the entry point to the distribution system after all treatment (finished water)
- Select a sampling faucet that does NOT have an aerator (sampling must be done with minimum aeration)
- Run the water until the temperature is as cold as it gets
- Just before sample collection, adjust to a very low flow. Do not change the flow while collecting the sample
- Routine nitrate and nitrite samples should be collected on a Monday or a Tuesday
- When filling sample bottle, tip bottle slightly so that water flows down the side wall of the container. Bring bottle to an upright position as it fills
- Call the laboratory if bottles are received broken (or break while collecting samples)
- The owner or operator of a water supply must maintain chemical analysis reports (results) or a summary of those reports for at least 10 years.



### Chain of Custody Procedures

Because a sample is physical evidence, chain of custody procedures are used to maintain and document sample possession from the time the sample is collected until it is introduced as evidence. Chain of custody requirements will vary from agency to agency.

However, these procedures are similar and the chain of custody outlined in this manual is only a guideline. Consult your project manager for specific requirements.

If you have *Physical possession* of a sample, have it in view, or have physically secured it to prevent tampering then it is defined as being in "custody." A chain of custody record, therefore, begins when the sample containers are obtained from the laboratory. From this point on, a chain of custody record will accompany the sample containers.

## Chemical Monitoring

The final federal rules regarding Phase II and V contaminants were promulgated by the U.S. EPA in 1992 and initial monitoring began in January 1993. This group of contaminants consists of Inorganic Chemicals (**IOC**), Volatile Organic Chemicals (**VOC**) and Synthetic Organic Chemicals (**SOC**) and the rule applies to all community and non-transient non-community public water systems.

The monitoring schedule for these contaminants is phased in by water system population size according to a **“standardized monitoring framework”** established by the U.S. EPA. This standardized monitoring framework establishes nine-year compliance cycles consisting of three 3-year compliance periods. The first compliance cycle began in January 1993 and ended December 31, 2001, with subsequent compliance cycles following the nine-year timeframe. The three-year compliance period of each cycle is the standard monitoring period for the water system.



## Turbidity Monitoring

Monitoring for turbidity is applicable to all public water systems using surface water sources or ground water sources under the direct influence of surface water in whole or part. Check with your state drinking water section or health department for further instructions.

### **The maximum contaminant level for turbidity for systems that provide filtration treatment:**

1. Conventional or direct filtration: less than or equal to 0.5 NTU in at least 95% of the measurements taken each month. Conventional filtration treatment plants should be able to achieve a level of 0.1 NTU with proper chemical addition and operation.
2. Slow sand filtration, cartridge and alternative filtration: less than or equal to 1 NTU in at least 95% of the measurements taken each month. The turbidity levels must not exceed 5 NTU at any turbidity measurements must be performed on representative samples of the filtered water every four (4) hours that the system serves water to the public.

A water system may substitute continuous turbidity monitoring for grab sample monitoring if it validates the continuous measurement for accuracy on a regular basis using a protocol approved by the Health or Drinking Water Agency, such as confirmation by a bench top turbidimeter.

For systems using slow sand filtration, cartridge, or alternative filtration treatment the Health or Drinking Water Agency may reduce the sampling frequency to once per day if it determines that less frequent monitoring is sufficient to indicate effective filtration performance.

## **Inorganic Chemical Monitoring**

All systems must monitor for inorganics. The monitoring for these contaminants is also complex with reductions, waivers and detections affecting the sampling frequency. Please refer to the monitoring schedules provided by your state health or drinking water sections for assistance in determining individual requirements. All transient non-community water systems are required to complete a one-time inorganic chemical analysis. The sample is to be collected at entry points (POE) to the distribution system representative of each source after any application of treatment.

### **Nitrates**

Nitrate is an inorganic chemical that occurs naturally in some groundwater but most often is introduced into ground and surface waters by man. The most common sources are from fertilizers and treated sewage or septic systems. At high levels (over 10 mg/l) it can cause the “**blue baby**” syndrome in young infants, which can lead to serious illness and even death. It is regarded as an “**acute health risk**” because it can quickly cause illness.

Every water system must test for **Nitrate** at least yearly. Systems that use ground water only must test yearly. Systems that use surface water and those that mix surface and ground water must test every quarter. A surface water system may go to yearly testing if community and nontransient noncommunity water must do quarterly monitoring whenever they exceed 5 mg/l in a test. After 4 quarters of testing and the results show that the nitrate level is not going up, they may go back to yearly testing.

### **Radiological Contaminants**

All community water systems shall monitor for gross alpha activity every four years for each source. Depending on your state rules, compliance will be based on the annual composite of 4 consecutive quarters or the average of the analyses of 4 quarterly samples. If the average annual concentration is less than one half the MCL, an analysis of a single sample may be substituted for the quarterly sampling procedure.

### **Total Trihalomethanes (TTHM)**

All community water systems serving a population of 10,000 or more and which add a disinfectant in any part of the drinking water treatment process shall monitor for total trihalomethanes (**TTHM**). The MCL is 0.1 mg/l and consists of a calculation of the running average of quarterly analyses of the sum of the concentrations of bromodichloromethane, di-bromochloromethane, bromoform and chloroform.

### **Lead and Copper Rule**

The Lead and Copper Rule was promulgated by the U.S. EPA on June 7, 1991, with monitoring to begin in January 1992 for larger water systems. This rule applies to all community and nontransient, noncommunity water systems and establishes action levels for these two contaminants at the consumer’s tap. Action levels of 0.015 mg/l for lead and 1.3 mg/l for copper have been established.

This rule establishes maximum contaminant level goals (**MCLGs**) for lead and copper, treatment technique requirements for optimal corrosion control, source water treatment, public education and lead service line replacement. Whenever an action level is exceeded, the corrosion control treatment requirement is triggered. This is determined by the concentration measured in the 90th percentile highest sample from the samples collected at consumers’ taps.

Sample results are assembled in ascending order (lowest to highest) with the result at the 90th percentile being the action level for the system. For example, if a water system collected 20 samples, the result of the 18th highest sample would be the action level for the system.

The rule also includes the best available technology (**BAT**) for complying with the treatment technique requirements, mandatory health effects language for public notification of violations and analytical methods and laboratory performance requirements.

Initial monitoring began in January 1992 for systems with a population of 50,000 or more, in July 1992 for medium-sized systems (3,300 to 50,000 population) and in July 1993 for small-sized systems (less than 3,300 population),

One-liter tap water samples are to be collected at high-risk locations by either water system personnel or residents. Generally, high-risk locations are homes with lead-based solder installed after 1982 or with lead pipes or service lines. If not enough of these locations exist in the water system, the rule provides specific guidelines for selecting other sample sites.

The water must be allowed to stand motionless in the plumbing pipes for at least six (6) hours and collected from a cold water tap in the kitchen or bathroom. It is a first draw sample, which means the line is not to be flushed prior to sample collection.

The number of sampling sites is determined by the population of the system and sample collection consists of two, six-month monitoring periods; check with your state rule or drinking water section for more information.

### **Sampling Sites by Population**

*System size - No. of sites - No. of sites*

*(no. of persons served) (standard monitoring) (reduced monitoring)*

>100,000	100	50
10,001-100,000	60	30
3,301 to 10,000	40	20
501 to 3,300	20	10
101 to 500	10	5
< 100	5	5

If a system meets the lead and copper action levels or maintains optimal corrosion control treatment for two consecutive six-month monitoring periods, then reduced monitoring is allowed and sampling frequency drops to once per year.

After three consecutive years of reduced monitoring, sample frequency drops to once every three years. In addition to lead and copper testing, all large water systems and those medium- and small-sized systems that exceed the lead or copper action levels will be required to monitor for the following water quality parameters: pH, alkalinity, calcium, conductivity, orthophosphate, silica and water temperature.

These parameters are used to identify optimal corrosion control treatment and determine compliance with the rule once treatment is installed. The sampling locations for monitoring water quality parameters are at entry points and representative taps throughout the distribution system.

Coliform sampling sites can be used for distribution system sampling. The number of sites required for monitoring water quality during each six-month period is shown below.

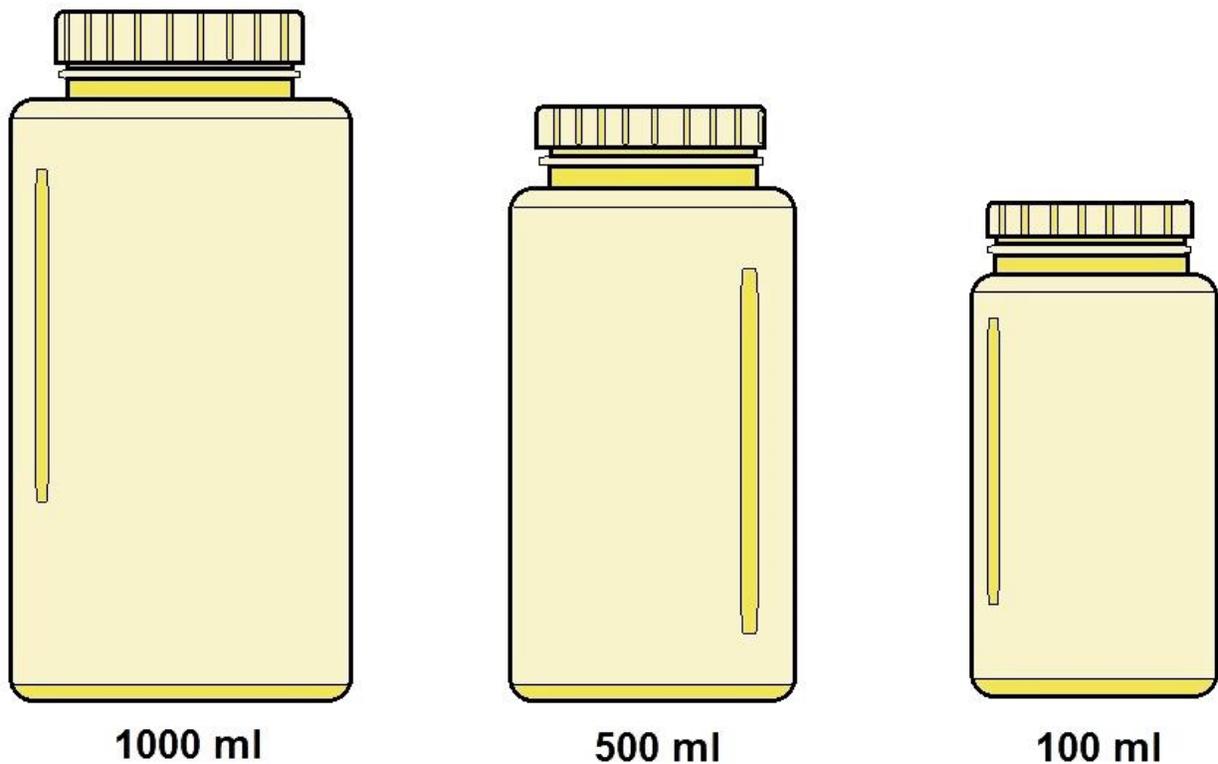
## Number of Water Quality Parameters per Population

*System size # of sites for water (no. of persons served) quality parameters*

>100,000	25
10,001-100,000	10
3,301 to 10,000	3
501 to 3,300	2
101 to 500	1
<100	1

Water systems which maintain water quality parameters reflecting optimal corrosion control for two consecutive six-month monitoring periods qualify for reduced monitoring. After three consecutive years, the monitoring frequency can drop to once per year.

All large water systems must demonstrate that their water is minimally corrosive or install corrosion control treatment regardless of lead and copper sampling results.



# SAMPLING CONTAINERS

## Antimony - Inorganic Contaminant 0.006 mg/L MCL Metalloid

**Antimony** is a toxic chemical element with symbol **Sb** and atomic number 51. A lustrous gray metalloid, it is found in nature mainly as the sulfide mineral stibnite ( $\text{Sb}_2\text{S}_3$ ). Antimony compounds have been known since ancient times and were used for cosmetics; metallic antimony was also known, but it was erroneously identified as lead. It was established to be an element around the 17th century.

For some time, China has been the largest producer of antimony and its compounds, with most production coming from the Xikuangshan Mine in Hunan. The industrial methods to produce antimony are roasting and subsequent carbothermal reduction or direct reduction of stibnite with iron.

### What are EPA's drinking water regulations for antimony?

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.



The MCLG for antimony is 0.006 mg/L or 6 ppb. EPA has set this level of protection based on the best available science to prevent potential health problems. EPA has set an enforceable regulation for antimony, called a maximum contaminant level (MCL), at 0.006 mg/L or 6 ppb. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.

The Phase V Rule, the regulation for antimony, became effective in 1994. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed antimony as part of the Six Year Review and determined that the 0.006 mg/L or 6 ppb MCLG and 0.006 mg/L or 6 ppb MCL for antimony are still protective of human health.

### Applications

The largest applications for metallic antimony are as alloying material for lead and tin and for lead antimony plates in lead-acid batteries. Alloying lead and tin with antimony improves the properties of the alloys which are used in solders, bullets and plain bearings. Antimony compounds are prominent additives for chlorine- and bromine-containing fire retardants found in many commercial and domestic products. An emerging application is the use of antimony in microelectronics.

Antimony is in the nitrogen group (group 15) and has an electronegativity of 2.05. As expected by periodic trends, it is more electronegative than tin or bismuth, and less electronegative than tellurium or arsenic.

Antimony is stable in air at room temperature, but reacts with oxygen if heated to form antimony trioxide,  $\text{Sb}_2\text{O}_3$ . Antimony is a silvery, lustrous gray metal that has a Mohs scale hardness of 3. Therefore, pure antimony is not used to make hard objects: coins made of antimony were issued in China's Guizhou province in 1931, but because of their rapid wear, their minting was discontinued. Antimony is resistant to attack by acids.

Four allotropes of antimony are known, a stable metallic form and three metastable forms, explosive, black and yellow. Metallic antimony is a brittle, silver-white shiny metal. When molten antimony is slowly cooled, metallic antimony crystallizes in a trigonal cell, isomorphous with that of the gray allotrope of arsenic. A rare explosive form of antimony can be formed from the electrolysis of antimony (III) trichloride. When scratched with a sharp implement, an exothermic reaction occurs and white fumes are given off as metallic antimony is formed; when rubbed with a pestle in a mortar, a strong detonation occurs.

Black antimony is formed upon rapid cooling of vapor derived from metallic antimony. It has the same crystal structure as red phosphorus and black arsenic; it oxidizes in air and may ignite spontaneously. At 100 °C, it gradually transforms into the stable form. The yellow allotrope of antimony is the most unstable. It has only been generated by oxidation of stibine ( $\text{SbH}_3$ ) at -90 °C. Above this temperature and in ambient light, this metastable allotrope transforms into the more stable black allotrope.

Metallic antimony adopts a layered structure (space group  $R\bar{3}m$  No. 166) in which layers consist of fused ruffled six-membered rings. The nearest and next-nearest neighbors form a distorted octahedral complex, with the three atoms in the same double-layer being slightly closer than the three atoms in the next. This relatively close packing leads to a high density of 6.697 g/cm<sup>3</sup>, but the weak bonding between the layers leads to the low hardness and brittleness of antimony.

### Isotopes

Antimony exists as two stable isotopes,  $^{121}\text{Sb}$  with a natural abundance of 57.36% and  $^{123}\text{Sb}$  with a natural abundance of 42.64%. It also has 35 radioisotopes, of which the longest-lived is  $^{125}\text{Sb}$  with a half-life of 2.75 years.

In addition, 29 metastable states have been characterized. The most stable of these is  $^{124}\text{Sb}$  with a half-life of 60.20 days, which has an application in some neutron sources. Isotopes that are lighter than the stable  $^{123}\text{Sb}$  tend to decay by  $\beta^+$  decay, and those that are heavier tend to decay by  $\beta^-$  decay, with some exceptions.

### Occurrence

The abundance of antimony in the Earth's crust is estimated at 0.2 to 0.5 parts per million, comparable to thallium at 0.5 parts per million and silver at 0.07 ppm. Even though this element is not abundant, it is found in over 100 mineral species. Antimony is sometimes found natively, but more frequently it is found in the sulfide stibnite ( $\text{Sb}_2\text{S}_3$ ) which is the predominant ore mineral.

Antimony compounds are often classified into those of Sb(III) and Sb(V). Relative to its congener arsenic, the +5 oxidation state is more stable.

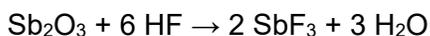
## Oxides and hydroxides

Antimony trioxide ( $\text{Sb}_2\text{O}_3$ ) is formed when antimony is burnt in air. In the gas phase, this compound exists as  $\text{Sb}_4\text{O}_6$ , but it polymerizes upon condensing. Antimony pentoxide ( $\text{Sb}_2\text{O}_5$ ) can only be formed by oxidation by concentrated nitric acid. Antimony also forms a mixed-valence oxide, antimony tetroxide ( $\text{Sb}_2\text{O}_4$ ), which features both Sb(III) and Sb(V). Unlike phosphorus and arsenic, these various oxides are amphoteric, do not form well-defined oxoacids and react with acids to form antimony salts.

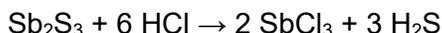
Antimonous acid  $\text{Sb}(\text{OH})_3$  is unknown, but the conjugate base sodium antimonite ( $[\text{Na}_3\text{SbO}_3]_4$ ) forms upon fusing sodium oxide and  $\text{Sb}_2\text{O}_3$ . Transition metal antimonites are also known. Antimonic acid exists only as the hydrate  $\text{HSb}(\text{OH})_6$ , forming salts containing the antimonate anion  $\text{Sb}(\text{OH})_6^-$ . Dehydrating metal salts containing this anion yields mixed oxides. Many antimony ores are sulfides, including stibnite ( $\text{Sb}_2\text{S}_3$ ), pyrrargyrite ( $\text{Ag}_3\text{SbS}_3$ ), zinkenite, jamesonite, and boulangerite. Antimony pentasulfide is non-stoichiometric and features antimony in the +3 oxidation state and S-S bonds. Several thioantimonides are known, such as  $[\text{Sb}_6\text{S}_{10}]^{2-}$  and  $[\text{Sb}_8\text{S}_{13}]^{2-}$ .

## Halides

Antimony forms two series of halides,  $\text{SbX}_3$  and  $\text{SbX}_5$ . The trihalides  $\text{SbF}_3$ ,  $\text{SbCl}_3$ ,  $\text{SbBr}_3$ , and  $\text{SbI}_3$  are all molecular compounds having trigonal pyramidal molecular geometry. The trifluoride  $\text{SbF}_3$  is prepared by the reaction of  $\text{Sb}_2\text{O}_3$  with HF:



It is Lewis acidic and readily accepts fluoride ions to form the complex anions  $\text{SbF}_4^-$  and  $\text{SbF}_6^-$ . Molten  $\text{SbF}_3$  is a weak electrical conductor. The trichloride  $\text{SbCl}_3$  is prepared by dissolving  $\text{Sb}_2\text{S}_3$  in hydrochloric acid:

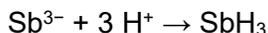


The pentahalides  $\text{SbF}_5$  and  $\text{SbCl}_5$  have trigonal bipyramidal molecular geometry in the gas phase, but in the liquid phase,  $\text{SbF}_5$  is polymeric, whereas  $\text{SbCl}_5$  is monomeric.  $\text{SbF}_5$  is a powerful Lewis acid used to make the super acid fluoroantimonic acid (" $\text{HSbF}_6$ ").

Oxyhalides are more common for antimony than arsenic and phosphorus. Antimony trioxide dissolves in concentrated acid to form oxoantimonyl compounds such as  $\text{SbOCl}$  and  $(\text{SbO})_2\text{SO}_4$ .

## Antimonides, hydrides, and organoantimony compounds

Compounds in this class generally are described as derivatives of  $\text{Sb}^{3-}$ . Antimony forms antimonides with metals, such as indium antimonide ( $\text{InSb}$ ) and silver antimonide ( $\text{Ag}_3\text{Sb}$ ). The alkali metal and zinc antimonides, such as  $\text{Na}_3\text{Sb}$  and  $\text{Zn}_3\text{Sb}_2$ , are more reactive. Treating these antimonides with acid produces the unstable gas stibine,  $\text{SbH}_3$ :



Stibine can also be produced by treating  $\text{Sb}^{3+}$  salts with hydride reagents such as sodium borohydride. Stibine decomposes spontaneously at room temperature. Because stibine has a positive heat of formation, it is thermodynamically unstable and thus antimony does not react with hydrogen directly.

Organoantimony compounds are typically prepared by alkylation of antimony halides with Grignard reagents. A large variety of compounds are known with both Sb(III) and Sb(V) centers, including mixed chloro-organic derivatives, anions, and cations. Examples include  $\text{Sb}(\text{C}_6\text{H}_5)_3$  (triphenylstibine),  $\text{Sb}_2(\text{C}_6\text{H}_5)_4$  (with an Sb-Sb bond), and cyclic  $[\text{Sb}(\text{C}_6\text{H}_5)]_n$ . Pentacoordinated organoantimony compounds are common, examples being  $\text{Sb}(\text{C}_6\text{H}_5)_5$  and several related halides.

### History

Antimony(III) sulfide,  $\text{Sb}_2\text{S}_3$ , was recognized in predynastic Egypt as an eye cosmetic (kohl) as early as about 3100 BC, when the cosmetic palette was invented.

An artifact, said to be part of a vase, made of antimony dating to about 3000 BC was found at Telloh, Chaldea (part of present-day Iraq), and a copper object plated with antimony dating between 2500 BC and 2200 BC has been found in Egypt. Austen, at a lecture by Herbert Gladstone in 1892 commented that "we only know of antimony at the present day as a highly brittle and crystalline metal, which could hardly be fashioned into a useful vase, and therefore this remarkable 'find' (artifact mentioned above) must represent the lost art of rendering antimony malleable."

Moorey was unconvinced the artifact was indeed a vase, mentioning that Selimkhanov, after his analysis of the Tello object (published in 1975), "attempted to relate the metal to Transcaucasian natural antimony" (i.e. native metal) and that "the antimony objects from Transcaucasia are all small personal ornaments." This weakens the evidence for a lost art "of rendering antimony malleable."

The first European description of a procedure for isolating antimony is in the book *De la pirotechnia* of 1540 by Vannoccio Biringuccio; this predates the more famous 1556 book by Agricola, *De re metallica*. In this context Agricola has been often incorrectly credited with the discovery of metallic antimony.

The book *Currus Triumphalis Antimonii* (The Triumphal Chariot of Antimony), describing the preparation of metallic antimony, was published in Germany in 1604. It was purported to have been written by a Benedictine monk, writing under the name Basilius Valentinus, in the 15th century; if it were authentic, which it is not, it would predate Biringuccio.

The first natural occurrence of pure antimony in the Earth's crust was described by the Swedish scientist and local mine district engineer Anton von Swab in 1783; the type-sample was collected from the Sala Silver Mine in the Bergslagen mining district of Sala, Västmanland, Sweden.

## **Arsenic- Inorganic Contaminant 0.010 mg/L MCL Metalloid**

Arsenic is a chemical element with symbol **As** and the atomic number is 33. Arsenic occurs in many minerals, usually in conjunction with sulfur and metals, and also as a pure elemental crystal. It was first documented by Albertus Magnus in 1250. Arsenic is a metalloid. It can exist in various allotropes, although only the gray form has important use in industry.

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.



The MCLG for arsenic is zero. EPA has set this level of protection based on the best available science to prevent potential health problems. Based on the MCLG, EPA has set an enforceable regulation for arsenic, called a maximum contaminant level (MCL), at 0.010 mg/L or 10 ppb. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies.

The Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring Final Rule, the regulation for arsenic, became effective in 2002. The Safe Drinking Water Act requires EPA to periodically review and revise contaminants, if appropriate, based on new scientific data. The regulation for arsenic will be included in a future review cycle.

The main uses of metallic arsenic is for strengthening alloys of copper and especially lead (for example, in car batteries).

Arsenic is a common n-type dopant in semiconductor electronic devices, and the optoelectronic compound gallium arsenide is the most common semiconductor in use after doped silicon.

Arsenic and its compounds, especially the trioxide, are used in the production of pesticides (treated wood products), herbicides, and insecticides. These applications are declining, however.

Arsenic is notoriously poisonous to multicellular life, although a few species of bacteria are able to use arsenic compounds as respiratory metabolites. Arsenic contamination of groundwater is a problem that affects millions of people across the world.

Arsenic, a naturally occurring element, is found throughout the environment; for most people, food is the major source of exposure. Acute (short-term) high-level inhalation exposure to arsenic dust or fumes has resulted in gastrointestinal effects (nausea, diarrhea, abdominal pain); central and peripheral nervous system disorders have occurred in workers acutely exposed to inorganic arsenic. Chronic (long-term) inhalation exposure to inorganic arsenic in humans is associated with irritation of the skin and mucous membranes.

Chronic oral exposure has resulted in gastrointestinal effects, anemia, peripheral neuropathy, skin lesions, hyperpigmentation, and liver or kidney damage in humans. Inorganic arsenic exposure in humans, by the inhalation route, has been shown to be strongly associated with lung cancer, while ingestion of inorganic arsenic in humans has been linked to a form of skin cancer and also to bladder, liver, and lung cancer. EPA has classified inorganic arsenic as a Group A, human carcinogen.

### **Contamination of Groundwater**

Arsenic contamination of groundwater is often due to naturally occurring high concentrations of arsenic in deeper levels of groundwater. It is a high-profile problem due to the use of deep tubewells for water supply in the Ganges Delta, causing serious arsenic poisoning to large numbers of people. In addition, mining techniques such as hydraulic fracturing mobilize arsenic in groundwater and aquifers due to enhanced methane transport and resulting changes in redox conditions, and inject fluid containing additional arsenic.

A 2007 study found that over 137 million people in more than 70 countries are probably affected by arsenic poisoning of drinking water. Arsenic contamination of ground water is found in many countries throughout the world, including the USA.

Approximately 20 incidents of groundwater arsenic contamination have been reported from all over the world. Of these, four major incidents were in Asia, including locations in Thailand, Taiwan, and Mainland China. In South America, Argentina and Chile are affected. There are also many locations in the United States where the groundwater contains arsenic concentrations in excess of the Environmental Protection Agency standard of 10 parts per billion adopted in 2001. Millions of private wells have unknown arsenic levels, and in some areas of the US, over 20% of wells may contain levels that are not safe.

### **Arsine**

Arsine is a gas consisting of arsenic and hydrogen. It is extremely toxic to humans, with headaches, vomiting, and abdominal pains occurring within a few hours of exposure. EPA has not classified arsine for carcinogenicity.

Drinking water regulations require public water systems to monitor for arsenic at the entry point to the distribution system. There is no federal requirement for systems to monitor for arsenic within the distribution system. You may, however, want to test your distribution system water for arsenic to be sure that the water being delivered has arsenic levels below the MCL. If you decide to monitor your distribution system, consider testing for arsenic at locations where the settling and accumulation of iron solids or pipe scales are likely (i.e., areas with cast iron pipe, ductile iron pipe, or galvanized iron pipe).

If your water system has installed some form of arsenic treatment, keep in mind that the treatment you installed may change the water quality in other ways. It might cause the water to react differently in the distribution system. Depending on the kind of treatment you've installed, consider what distribution system problems might result.

A change in the taste, odor or appearance of the water at customers' taps may be the first indication of a problem. Some water quality parameters to consider monitoring, depending on your arsenic treatment technology, include iron, pH, manganese, alkalinity, and aluminum.

The current drinking water standard or Maximum Contaminant Level (MCL) set by the U.S. Environmental Protection Agency (EPA) is 0.010 mg/L or parts per million (ppm). This is equivalent to 10 ug/L (micrograms per liter) or 10 ppb. In 2001, the U.S. Environmental Protection Agency (EPA) reduced the regulatory MCL from 50 ppb to 10 ppb on the basis on bladder and lung cancer risks. The MCL is based on the average individual consuming 2 liters of water a day for a lifetime. Long term exposure to drinking water containing arsenic at levels higher than 10 ppb increases the chances of getting cancer, while for lower arsenic water levels the chances are less.

If your water has arsenic levels above 10 ppb, you should obtain drinking water from another source or install a home treatment device. Concentrations above 10 ppb will increase the risk of long-term or chronic health problems, the higher the level and length of exposure, the greater the risk. It is especially important to reduce arsenic water concentrations if you have children or are pregnant. Children are at greater risk (to any agent in water) because of their greater water consumption on a per unit body weight basis.

Pregnant women may wish to reduce their arsenic exposures because arsenic has been found at low levels in mother's milk and will cross the placenta, increasing exposures and risks for the fetus. If your water has arsenic levels above 200 ppb, you should immediately stop drinking the water until you can either obtain water from another source or install and maintain treatment.

### Physical Characteristics

The three most common arsenic allotropes are *metallic gray*, *yellow* and *black arsenic*, with gray being the most common. *Gray arsenic* ( $\alpha$ -As, space group R3m No. 166) adopts a double-layered structure consisting of many interlocked ruffled six-membered rings. Because of weak bonding between the layers, gray arsenic is brittle and has a relatively low Mohs hardness of 3.5. Nearest and next-nearest neighbors form a distorted octahedral complex, with the three atoms in the same double-layer being slightly closer than the three atoms in the next. This relatively close packing leads to a high density of 5.73 g/cm<sup>3</sup>. Gray arsenic is a semimetal, but becomes a semiconductor with a bandgap of 1.2–1.4 eV if amorphized. *Yellow arsenic* is soft and waxy, and somewhat similar to tetraphosphorus (P<sub>4</sub>). Both have four atoms arranged in a tetrahedral structure in which each atom is bound to each of the other three atoms by a single bond. This unstable allotrope, being molecular, is the most volatile, least dense and most toxic. Solid yellow arsenic is produced by rapid cooling of arsenic vapor, As<sub>4</sub>. It is rapidly transformed into the gray arsenic by light. The yellow form has a density of 1.97 g/cm<sup>3</sup>. *Black arsenic* is similar in structure to red phosphorus.

### Isotopes

Naturally occurring arsenic is composed of one stable isotope, <sup>75</sup>As. As of 2003, at least 33 radioisotopes have also been synthesized, ranging in atomic mass from 60 to 92. The most stable of these is <sup>73</sup>As with a half-life of 80.3 days. Isotopes that are lighter than the stable <sup>75</sup>As tend to decay by  $\beta^+$  decay, and those that are heavier tend to decay by  $\beta^-$  decay, with some exceptions.

At least 10 nuclear isomers have been described, ranging in atomic mass from 66 to 84. The most stable of arsenic's isomers is <sup>68m</sup>As with a half-life of 111 seconds.

### Chemistry

When heated in air, arsenic oxidizes to arsenic trioxide; the fumes from this reaction have an odor resembling garlic. This odor can be detected on striking arsenide minerals such as arsenopyrite with a hammer.

Arsenic (and some arsenic compounds) sublimes upon heating at atmospheric pressure, converting directly to a gaseous form without an intervening liquid state at 887 K (614 °C). The triple point is 3.63 MPa and 1,090 K (820 °C). Arsenic makes arsenic acid with concentrated nitric acid, arsenious acid with dilute nitric acid, and arsenic trioxide with concentrated sulfuric acid.

### Compounds

Arsenic compounds resemble in some respects those of phosphorus, which occupies the same group (column) of the periodic table. Arsenic is less commonly observed in the pentavalent state, however. The most common oxidation states for arsenic are: -3 in the arsenides, such as alloy-like intermetallic compounds; and +3 in the arsenites, arsenates (III), and most organoarsenic compounds. Arsenic also bonds readily to itself as seen in the square  $\text{As}_3-4$  ions in the mineral skutterudite. In the +3 oxidation state, arsenic is typically pyramidal, owing to the influence of the lone pair of electrons.

### Inorganic

Arsenic forms colorless, odorless, crystalline oxides  $\text{As}_2\text{O}_3$  ("white arsenic") and  $\text{As}_2\text{O}_5$ , which are hygroscopic and readily soluble in water to form acidic solutions. Arsenic (V) acid is a weak acid. Its salts are called arsenates, which is the basis of arsenic contamination of groundwater, a problem that affects many people. Synthetic arsenates include Paris Green (copper(II) acetoarsenite), calcium arsenate, and lead hydrogen arsenate. The latter three have been used as agricultural insecticides and poisons.

The protonation steps between the arsenate and arsenic acid are similar to those between phosphate and phosphoric acid. Unlike phosphorus acid, arsenous acid is genuinely tribasic, with the formula  $\text{As}(\text{OH})_3$ .

A broad variety of sulfur compounds of arsenic are known. Orpiment ( $\text{As}_2\text{S}_3$ ) and realgar ( $\text{As}_4\text{S}_4$ ) are somewhat abundant and were formerly used as painting pigments. In  $\text{As}_4\text{S}_{10}$ , arsenic has a formal oxidation state of +2 in  $\text{As}_4\text{S}_4$ , which features As-As bonds so that the total covalency of As is still three.

The trifluoride, trichloride, tribromide, and triiodide of arsenic (III) are well known, whereas only Arsenic pentafluoride ( $\text{AsF}_5$ ) is the only important pentahalide. Again reflecting the lower stability of the 5+ oxidation state, the pentachloride is stable only below -50 °C.

### Organoarsenic Compounds

A large variety of organoarsenic compounds are known. Several were developed as chemical warfare agents during World War I, including vesicants such as lewisite and vomiting agents such as adamsite. Cacodylic acid, which is of historic and practical interest, arises from the methylation of arsenic trioxide, a reaction that has no analogy in phosphorus chemistry.

### Alloys

Arsenic is used as the group 5 element in the III-V semiconductors gallium arsenide, indium arsenide, and aluminum arsenide. The valence electron count of GaAs is the same as a pair of Si atoms, but the band structure is completely different, which results in distinct bulk properties. Other arsenic alloys include the II-IV semiconductor cadmium arsenide.

## Occurrence and Production

Minerals with the formula  $MAsS$  and  $MAs_2$  ( $M = Fe, Ni, Co$ ) are the dominant commercial sources of arsenic, together with realgar (an arsenic sulfide mineral) and native arsenic. An illustrative mineral is arsenopyrite ( $FeAsS$ ), which is structurally related to iron pyrite. Many minor As-containing minerals are known. Arsenic also occurs in various organic forms in the environment. Inorganic arsenic and its compounds, upon entering the food chain, are progressively metabolized to a less toxic form of arsenic through a process of methylation.

Other naturally occurring pathways of exposure include volcanic ash, weathering of arsenic-containing minerals and ores, and dissolved in groundwater. It is also found in food, water, soil, and air. Arsenic is absorbed by all plants, but is more concentrated in leafy vegetables, rice, apple and grape juice, and seafood. An additional route of exposure is through inhalation.

In 2005, China was the top producer of white arsenic with almost 50% world share, followed by Chile, Peru, and Morocco, according to the British Geological Survey and the United States Geological Survey. Most operations in the US and Europe have closed for environmental reasons. The arsenic is recovered mainly as a side product from the purification of copper. Arsenic is part of the smelter dust from copper, gold, and lead smelters.

On roasting in air of arsenopyrite, arsenic sublimes as arsenic (III) oxide leaving iron oxides, while roasting without air results in the production of metallic arsenic. Further purification from sulfur and other chalcogens is achieved by sublimation in vacuum or in a hydrogen atmosphere or by distillation from molten lead-arsenic mixture.

## Health Hazard Information

### Arsenic

Arsenic is known to cause cancer, as well as many other serious health problems. Here we review the hazards of arsenic exposure and ways people can protect themselves from these hazards.

Arsenic is an element in the environment that can be found naturally in rocks and soil, water, air, and in plants and animals. It can also be released into the environment from some agricultural and industrial sources.

Arsenic has no taste or smell. Although sometimes found in its pure form as a steel grey metal, arsenic is usually part of chemical compounds. These compounds are divided into 2 groups:

- Inorganic compounds (combined with oxygen, iron, chlorine, and sulfur)
- Organic compounds (combined with carbon and other atoms)

Inorganic arsenic compounds are found in industry, in building products (in some "pressure-treated" woods), and in arsenic-contaminated water. This is the form of arsenic that tends to be more toxic and has been linked to cancer.

Organic arsenic compounds are much less toxic than the inorganic arsenic compounds and are not thought to be linked to cancer. These compounds are found in some foods, such as fish and shellfish.

While arsenic levels may fluctuate over time, what is most significant from the standpoint of cancer risk is long-term exposure.

For water systems in the 25 states that reported arsenic data to the EPA, we have calculated two estimates of average long-term levels: one is a very conservative estimate, the other our best estimate, based on what we believe to be the most reasonable analytical techniques (details on how we arrived at the estimates are included with the charts).

The table below shows the lifetime risks of dying of cancer from arsenic in tap water, based on the National Academy of Sciences' 1999 risk estimates.

<b>Arsenic Level in Tap Water (in parts per billion, or ppb)</b>	<b>Approximate Total Cancer Risk (assuming 2 liters consumed/day)</b>
0.5 ppb	1 in 10,000
1 ppb	1 in 5,000
3 ppb	1 in 1,667
4 ppb	1 in 1,250
5 ppb	1 in 1,000
10 ppb	1 in 500
20 ppb	1 in 250
25 ppb	1 in 200
50 ppb	1 in 100

### **Arsenic Diabetes**

New research findings from the National Health and Nutrition Examination Survey suggest that exposure to levels of arsenic commonly found in drinking water may be a risk factor for type 2 diabetes. The findings suggest that millions of Americans may be at increased risk for type 2 diabetes based on the level of arsenic in their drinking water.

Data on the nearly 800 participants in the study for which urinary arsenic concentrations were available, indicated that urine levels of arsenic were significantly associated with the prevalence of type 2 diabetes.

After splitting the subjects into 5 groups based on the level of arsenic in their urine, the researchers determined that those in the highest category were more than three and one-half times more likely to have diabetes. The strength of arsenic as a risk factor for diabetes is similar to other factors such as obesity.

Inorganic arsenic in drinking water at concentrations higher than 100 parts per million has been linked to type 2 diabetes in studies that took place in Taiwan, Mexico, and Bangladesh where drinking water is commonly contaminated with high levels of arsenic. The US drinking water standard is currently 10 parts per million, but most people on private wells have not had their water tested and aren't required to. The researchers estimate that about 13 million Americans live in areas where public water systems exceed the EPA standard for arsenic and this number does not include private wells and water systems.

Animal studies have shown that arsenic affects the production of glucose, insulin secretion and can cause insulin resistance. The current findings reinforce the need to evaluate the role of arsenic in diabetes development in prospective epidemiologic studies conducted in populations exposed to a wide range of arsenic levels.

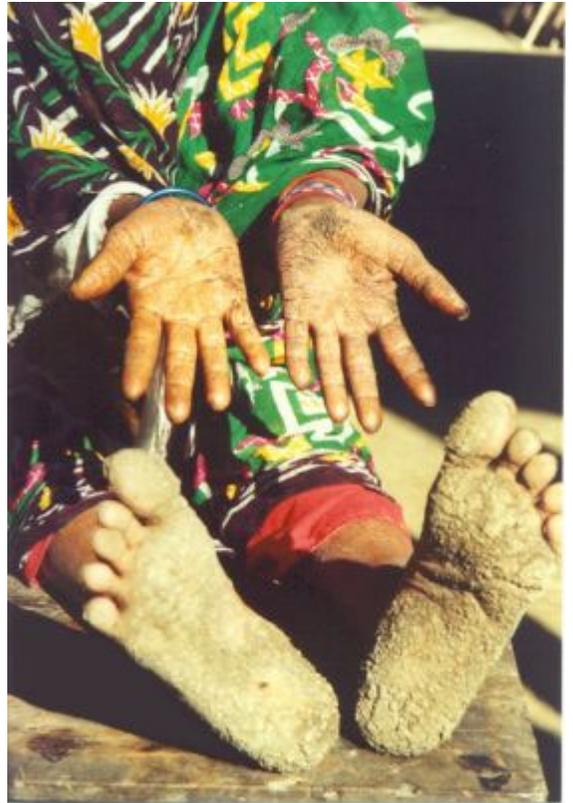
**Acute Effects:**

**Inorganic Arsenic**

- Acute inhalation exposure of workers to high levels of arsenic dusts or fumes has resulted in gastrointestinal effects (nausea, diarrhea, abdominal pain), while acute exposure of workers to inorganic arsenic has also resulted in central and peripheral nervous system disorders.
- Acute oral exposure to inorganic arsenic, at doses of approximately 600 micrograms per kilogram body weight per day ( $\mu\text{g}/\text{kg}/\text{d}$ ) or higher in humans, has resulted in death. Oral exposure to lower levels of inorganic arsenic has resulted in effects on the gastrointestinal tract (nausea, vomiting), central nervous system (CNS) (headaches, weakness, delirium), cardiovascular system (hypotension, shock), liver, kidney, and blood (anemia, leukopenia).
- Acute animal tests in rats and mice have shown inorganic arsenic to have moderate to high acute toxicity.

**Arsine**

- Acute inhalation exposure to arsine by humans has resulted in death; it has been reported that a half-hour exposure to 25 to 50 parts per million (ppm) can be lethal.
- The major effects from acute arsine exposure in humans include headaches, vomiting, abdominal pains, hemolytic anemia, hemoglobinuria, and jaundice; these effects can lead to kidney failure.
- Arsine has been shown to have extreme acute toxicity from acute animal tests.



### **Chronic Effects (Non-cancer):**

#### **Inorganic arsenic**

- Chronic inhalation exposure to inorganic arsenic in humans is associated with irritation of the skin and mucous membranes (dermatitis, conjunctivitis, pharyngitis, and rhinitis).
- Chronic oral exposure to inorganic arsenic in humans has resulted in gastrointestinal effects, anemia, peripheral neuropathy, skin lesions, hyperpigmentation, gangrene of the extremities, vascular lesions, and liver or kidney damage.
- No chronic inhalation exposure studies have been performed in animals for any inorganic arsenic compound.
- Some studies have suggested that inorganic arsenic is an essential dietary nutrient in goats, chicks, and rats. However, no comparable data are available for humans. EPA has concluded that essentiality, although not rigorously established, is plausible.
- EPA has not established a Reference Concentration (RfC) for inorganic arsenic.
- The California Environmental Protection Agency (CalEPA) has established a chronic inhalation reference level of 0.00003 milligrams per cubic meter (mg/m<sup>3</sup>) based on developmental effects in mice. The CalEPA reference exposure level is a concentration at or below which adverse health effects are not likely to occur. It is not a direct estimator of risk, but rather a reference point to gauge the potential effects. At lifetime exposures increasingly greater than the reference exposure level, the potential for adverse health effects increases.
- The Reference Dose (RfD) for inorganic arsenic is 0.0003 milligrams per kilogram body weight per day (mg/kg/d) based on hyperpigmentation, keratosis, and possible vascular complications in humans. The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious noncancer effects during a lifetime.
- EPA has medium confidence in the study on which the RfD for inorganic arsenic was based because, although an extremely large number of people were included in the assessment (>40,000), the doses were not well characterized and other contaminants were present. The supporting human toxicity database, while extensive, is somewhat flawed and, consequently, EPA has assigned medium confidence to the RfD.

#### **Arsine**

- No information is available on the chronic effects of arsine in humans.
- The RfC for arsine is 0.00005 mg/m<sup>3</sup> based on increased hemolysis, abnormal red blood cell morphology, and increased spleen weight in rats, mice, and hamsters.
- EPA has medium confidence in the RfC based on: (1) high confidence in the studies on which the RfC for arsine was based because the sample sizes were adequate, statistical significance was reported, concentration dose-response relationships were documented, three species were investigated, and both a no-observed-adverse-effect level (NOAEL) and a lowest-observed-adverse-effect level (LOAEL) were identified, and (2) medium confidence in the database because while there were three inhalation animal studies and a developmental/reproductive study, there were no data available on human exposure.

### ***Reproductive/Developmental Effects:***

#### **Inorganic arsenic**

- Several studies have suggested that women who work in, or live near, metal smelters may have higher than normal spontaneous abortion rates, and their children may exhibit lower than normal birth weights. However, these studies are limited because they were designed to evaluate the effects of smelter pollutants in general, and are not specific for inorganic arsenic.
- Ingested inorganic arsenic can cross the placenta in humans, exposing the fetus to the chemical.
- Oral animal studies have reported inorganic arsenic at very high doses to be fetotoxic and to cause birth defects.

#### **Arsine**

- Human studies have indicated higher than expected spontaneous abortion rates in women in the microelectronics industry who were exposed to arsine. However, these studies have several limitations, including small sample size and exposure to other chemicals in addition to arsine.

### ***Cancer Risk:***

#### **Inorganic arsenic**

- Human, inhalation studies have reported inorganic arsenic exposure to be strongly associated with lung cancer.
- Ingestion of inorganic arsenic in humans has been associated with an increased risk of nonmelanoma skin cancer and also to an increased risk of bladder, liver, and lung cancer.
- Animal studies have not associated inorganic arsenic exposure via the oral route with cancer, and no cancer inhalation studies have been performed in animals for inorganic arsenic.
- EPA has classified inorganic arsenic as a Group A, human carcinogen.
- EPA used a mathematical model, using data from an occupational study of arsenic-exposed copper smelter workers, to estimate the probability of a person developing cancer from continuously breathing air containing a specified concentration of inorganic arsenic. EPA calculated an inhalation unit risk estimate of  $4.3 \times 10^{-3}(\mu\text{g}/\text{m}^3)^{-1}$ . EPA estimates that, if an individual were to continuously breathe air containing inorganic arsenic at an average of  $0.0002 \mu\text{g}/\text{m}^3$  ( $2 \times 10^{-7} \text{mg}/\text{m}^3$ ) over his or her entire lifetime, that person would theoretically have no more than a one-in-a-million increased chance of developing cancer as a direct result of breathing air containing this chemical. Similarly, EPA estimates that continuously breathing air containing  $0.002 \mu\text{g}/\text{m}^3$  ( $2 \times 10^{-6} \text{mg}/\text{m}^3$ ) would result in not greater than a one-in-a-hundred thousand increased chance of developing cancer, and air containing  $0.02 \mu\text{g}/\text{m}^3$  ( $2 \times 10^{-5} \text{mg}/\text{m}^3$ ) would result in not greater than a one-in-ten thousand increased chance of developing cancer. For a detailed discussion of confidence in the potency estimates, please see IRIS.
- EPA has calculated an oral cancer slope factor of  $1.5 (\text{mg}/\text{kg}/\text{d})^{-1}$  for inorganic arsenic.

#### **Arsine**

- No cancer inhalation studies in humans or animals are available for arsine.
- EPA has not classified arsine for carcinogenicity.

## Physical Properties

- Inorganic arsenic is a naturally occurring element in the earth's crust.
- Pure inorganic arsenic is a gray-colored metal, but inorganic arsenic is usually found combined with other elements such as oxygen, chlorine, and sulfur.
- The chemical symbol for inorganic arsenic is As, and it has an atomic weight of 74.92 g/mol.
- The chemical formula for arsine is AsH<sub>3</sub>, and it has a molecular weight of 77.95 g/mol.
- Arsine is a colorless gas with a disagreeable garlic odor.
- Arsenic combined with elements such as oxygen, chlorine, and sulfur forms inorganic arsenic; inorganic arsenic compounds include arsenic pentoxide, arsenic trioxide, and arsenic acid. Arsenic combined with carbon and hydrogen forms organic arsenic; organic arsenic compounds include arsanilic acid, arsenobetaine, and dimethylarsinic acid.

## History

The word "Arsenic" was adopted in Latin *arsenicum* and Old French *arsenic*, from which the English word *arsenic* is derived. Arsenic sulfides (orpiment, realgar) and oxides have been known and used since ancient times. Zosimos (circa 300 AD) describes roasting *sandarach* (realgar) to obtain *cloud of arsenic* (arsenious oxide), which he then reduces to metallic arsenic.

As the symptoms of arsenic poisoning were somewhat ill-defined, it was frequently used for murder until the advent of the Marsh test, a sensitive chemical test for its presence. (Another less sensitive but more general test is the Reinsch test.) Owing to its use by the ruling class to murder one another and its potency and discreetness, arsenic has been called the *Poison of Kings* and the *King of Poisons*.

During the Bronze Age, arsenic was often included in bronze, which made the alloy harder (so-called "arsenical bronze"). Albertus Magnus (Albert the Great, 1193–1280) is believed to have been the first to isolate the element from a compound in 1250, by heating soap together with arsenic trisulfide. In 1649, Johann Schröder published two ways of preparing arsenic. Crystals of elemental (native) arsenic are found in nature, although rare.

Cadet's fuming liquid (impure cacodyl), often claimed as the first synthetic organometallic compound, was synthesized in 1760 by Louis Claude Cadet de Gassicourt by the reaction of potassium acetate with arsenic trioxide.

In the Victorian era, "arsenic" ("white arsenic" or arsenic trioxide) was mixed with vinegar and chalk and eaten by women to improve the complexion of their faces, making their skin paler to show they did not work in the fields. Arsenic was also rubbed into the faces and arms of women to "improve their complexion".

The accidental use of arsenic in the adulteration of foodstuffs led to the Bradford sweet poisoning in 1858, which resulted in approximately 20 deaths.

## Arsenic Applications

### Agricultural

The toxicity of arsenic to insects, bacteria and fungi led to its use as a wood preservative. In the 1950s a process of treating wood with chromated copper arsenate (also known as CCA or Tanalith) was invented, and for decades this treatment was the most extensive industrial use of arsenic. An increased appreciation of the toxicity of arsenic resulted in a ban for the use of CCA in consumer products; the European Union and United States initiated this process in 2004. CCA remains in heavy use in other countries however, e.g. Malaysian rubber plantations.

Arsenic was also used in various agricultural insecticides, termination and poisons. For example, lead hydrogen arsenate was a common insecticide on fruit trees, but contact with the compound sometimes resulted in brain damage among those working the sprayers. In the second half of the 20th century, monosodium methyl arsenate (MSMA) and disodium methyl arsenate (DSMA) – less toxic organic forms of arsenic – have replaced lead arsenate in agriculture.

Arsenic is still added to animal food, in particular in the US as a method of disease prevention and growth stimulation. One example is roxarsone, which is used as a broiler starter by about 70% of the broiler growers since 1995.

The Poison-Free Poultry Act of 2009 proposes to ban the use of roxarsone in industrial swine and poultry production. Alpharma, a subsidiary of Pfizer Inc., which produces Roxarsone, has voluntarily suspended sales of the drug in response to studies showing elevated levels of arsenic in treated chickens.

### Medical use

During the 18th, 19th, and 20th centuries, a number of arsenic compounds have been used as medicines, including arsphenamine (by Paul Ehrlich) and arsenic trioxide (by Thomas Fowler). Arsphenamine as well as neosalvarsan was indicated for syphilis and trypanosomiasis, but has been superseded by modern antibiotics.

Arsenic trioxide has been used in a variety of ways over the past 500 years, but most commonly in the treatment of cancer. The US Food and Drug Administration in 2000 approved this compound for the treatment of patients with acute promyelocytic leukemia that is resistant to ATRA.

It was also used as Fowler's solution in psoriasis. Recently new research has been done in locating tumors using arsenic-74 (a positron emitter). The advantages of using this isotope instead of the previously used iodine-124 is that the signal in the PET scan is clearer as the body tends to transport iodine to the thyroid gland producing a lot of noise. In subtoxic doses, soluble arsenic compounds act as stimulants, and were once popular in small doses as medicine by people in the mid-18th century.

### Alloys

The main use of metallic arsenic is for alloying with lead. Lead components in car batteries are strengthened by the presence of a few percent of arsenic. Dezincification can be strongly reduced by adding arsenic to brass, a copper-zinc alloy. Gallium arsenide is an important semiconductor material, used in integrated circuits. Circuits made from GaAs are much faster (but also much more expensive) than those made in silicon. Unlike silicon it has a direct bandgap, and so can be used in laser diodes and LEDs to directly convert electricity into light.

## Military

After World War I, the United States built up a stockpile of 20,000 tons of lewisite ( $\text{ClCH}=\text{CHAsCl}_2$ ), a chemical weapon that is a vesicant (blister agent) and lung irritant. The stockpile was neutralized with bleach and dumped into the Gulf of Mexico after the 1950s. During the Vietnam War the United States used Agent Blue, a mixture of sodium cacodylate and its acid form, as one of the rainbow herbicides to deprive invading North Vietnamese soldiers of foliage cover and rice.

## Other uses

- Copper acetoarsenite was used as a green pigment known under many names, including 'Paris Green' and 'Emerald Green'. It caused numerous arsenic poisonings. Scheele's Green, a copper arsenate, was used in the 19th century as a coloring agent in sweets.
- Also used in bronzing and pyrotechnics.
- Up to 2% of arsenic is used in lead alloys for lead shots and bullets.
- Arsenic is added in small quantities to alpha-brass to make it dezincification resistant. This grade of brass is used to make plumbing fittings or other items that are in constant contact with water.
- Arsenic is also used for taxonomic sample preservation.
- Until recently arsenic was used in optical glass. Modern glass manufacturers, under pressure from environmentalists, have removed it, along with lead.

## Bacteria

Some species of bacteria obtain their energy by oxidizing various fuels while reducing arsenate to arsenite. Under oxidative environmental conditions some bacteria use arsenite, which is oxidized to arsenate as fuel for their metabolism. The enzymes involved are known as arsenate reductases (Arr).

In 2008, bacteria were discovered that employ a version of photosynthesis in the absence of oxygen with arsenites as electron donors, producing arsenates (just as ordinary photosynthesis uses water as electron donor, producing molecular oxygen). Researchers conjecture that, over the course of history, these photosynthesizing organisms produced the arsenates that allowed the arsenate-reducing bacteria to thrive.

One strain PHS-1 has been isolated and is related to the Gammaproteobacterium *Ectothiorhodospira shaposhnikovii*. The mechanism is unknown, but an encoded Arr enzyme may function in reverse to its known homologues. Although the arsenate and phosphate anions are similar structurally, no evidence exists for the replacement of phosphate in ATP or nucleic acids by arsenic.

It is known that even if your water has detectable levels of arsenic that are below the 0.010 mg/L MCL, and you have iron pipes or components in your distribution system, your system's pipes may have arsenic-rich scales attached to them. As long as the scales are not disturbed, they will remain attached to the pipes or other distribution system components.

Certain conditions, such as flushing of mains or fire flow conditions, may result in those scales being sloughed off and suspended in the water, releasing the arsenic. Other conditions, such as changes in water chemistry, may result in some of the arsenic dissolving back into the water. Both of these situations could cause high arsenic levels at consumers' taps.

### **Arsenic Control Measures Can Affect Finished Water Quality**

Public water systems installing arsenic treatment should be informed about possible changes to their finished water that may result from the arsenic treatment they install. For example, systems may need to adjust their finished water quality to address new concerns about corrosion. Changes in water chemistry due to using new sources, blending different source waters, or installing arsenic treatment are some of the factors that can affect distribution system water quality. In some cases, this may cause an increase in arsenic levels in the distribution system or create simultaneous compliance issues with other drinking water regulations.

Water systems may also find deposits of arsenic-rich particles in their storage tanks or at locations in their distribution system with low flows. If the flow is increased or a storage tank is drawn down to a low level, these arsenic-rich particles can get stirred up and transported to consumers' taps.

This situation occurs primarily when iron media used in treatment are released into the distribution system, or when iron particles are not properly filtered out during iron removal treatment. If these treatment technologies are operated correctly, this should not be a problem for most water systems.

### **Is Arsenic in your Storage Tank?**

#### **Is Your Ground Water System Installing Disinfection for Pathogen Control?**

Water systems that disinfect their water should be aware of the possibility of an increase in arsenic concentrations in their distribution system, particularly if the water contains high concentrations of dissolved iron.

When chlorinated, the dissolved iron forms particles on which arsenic can accumulate. As a result, high arsenic concentrations may occur in distribution system water even if arsenic concentrations in the raw water are below the MCL.

This happened to a small community water system in the Midwest that began chlorinating water from a series of wells that had raw water arsenic levels between 0.003 and 0.008 mg/L and iron concentrations up to 0.4 mg/L. At the same time, the system installed a polyphosphate feed system for corrosion control. Soon after chlorination began, the system received intermittent colored-water complaints from its customers with increasing frequency across the distribution system.

Samples collected from several representative locations throughout the service area had a reddish-brown color and contained particles. A metals analysis showed high levels of copper and iron oxides in the finished water, along with arsenic concentrations approaching 5 mg/L. Because of the water's colored appearance, it was considered unlikely that customers would consume the water. Doctors and health care professionals were notified of the situation and instructed to watch for signs of arsenic poisoning.

Researchers found that chlorinating the water caused the formation of ferri-hydroxide solids. The minimal arsenic present in the groundwater was being concentrated as it absorbed onto the solids. Copper oxide particulates also formed and were released. To some extent, the polyphosphates served a useful role by keeping iron in solution and counteracting the tendency for the iron oxides to form, but additional steps were needed.

For six months the system alternated their chlorination schedule: on for one day then off two days. The system then returned to full-time chlorination, starting with a low distribution system residual of 0.2 mg/L and gradually increasing it to 0.5 mg/L.

The system continued to flush water mains on a semi-annual schedule using a unidirectional approach. In the last year, the system received only one colored water complaint.

### **Heredity**

Arsenic has been linked to epigenetic changes, heritable changes in gene expression that occur without changes in DNA sequence. These include DNA methylation, histone modification, and RNA interference. Toxic levels of arsenic cause significant DNA hypermethylation of tumor suppressor genes p16 and p53, thus increasing risk of carcinogenesis. These epigenetic events have been studied *in vitro* using human kidney cells and *in vivo* using rat liver cells and peripheral blood leukocytes in humans. Inductive coupled plasma mass spectrometry (ICP-MS) is used to detect precise levels of intracellular arsenic and its other bases involved in epigenetic modification of DNA. Studies investigating arsenic as an epigenetic factor will help in developing precise biomarkers of exposure and susceptibility.

The Chinese brake fern (*Pteris vittata*) hyperaccumulates arsenic present in the soil into its leaves and has a proposed use in phytoremediation.

### **Biomethylation**

Inorganic arsenic and its compounds, upon entering the food chain, are progressively metabolized through a process of methylation. For example, the mold *Scopulariopsis brevicaulis* produce significant amounts of trimethylarsine if inorganic arsenic is present. The organic compound arsenobetaine is found in some marine foods such as fish and algae, and also in mushrooms in larger concentrations. The average person's intake is about 10–50 µg/day. Values about 1000 µg are not unusual following consumption of fish or mushrooms, but there is little danger in eating fish because this arsenic compound is nearly non-toxic.

### **Arsenic Environmental Issues**

#### **Arsenic Control Measures Can Affect Finished Water Quality**

Public water systems installing arsenic treatment should be informed about possible changes to their finished water that may result from the arsenic treatment they install. For example, systems may need to adjust their finished water quality to address new concerns about corrosion.

Changes in water chemistry due to using new sources, blending different source waters, or installing arsenic treatment are some of the factors that can affect distribution system water quality. In some cases, this may cause an increase in arsenic levels in the distribution system or create simultaneous compliance issues with other drinking water regulations.

### **Occurrence in drinking water**

Widespread arsenic contamination of groundwater has led to a massive epidemic of arsenic poisoning in Bangladesh and neighboring countries. It is estimated that approximately 57 million people in the Bengal basin are drinking groundwater with arsenic concentrations elevated above the World Health Organization's standard of 10 parts per billion (ppb). However, a study of cancer rates in Taiwan suggested that significant increases in cancer mortality appear only at levels above 150 ppb.

The arsenic in the groundwater is of natural origin, and is released from the sediment into the groundwater, owing to the anoxic conditions of the subsurface. This groundwater began to be used after local and western NGOs and the Bangladeshi government undertook a massive shallow tube well drinking-water program in the late twentieth century.

This program was designed to prevent drinking of bacteria-contaminated surface waters, but failed to test for arsenic in the groundwater. Many other countries and districts in Southeast Asia, such as Vietnam and Cambodia have geological environments conducive to generation of high-arsenic groundwaters. Arsenicosis was reported in Nakhon Si Thammarat, Thailand in 1987, and the dissolved arsenic in the Chao Phraya River is suspected of containing high levels of naturally occurring arsenic, but has not been a public health problem owing to the use of bottled water.

In the United States, arsenic is most commonly found in the ground waters of the southwest. Parts of New England, Michigan, Wisconsin, Minnesota and the Dakotas are also known to have significant concentrations of arsenic in ground water. Increased levels of skin cancer have been associated with arsenic exposure in Wisconsin, even at levels below the 10 part per billion drinking water standard, although this link has not been proven. According to a recent film funded by the US Superfund, millions of private wells have unknown arsenic levels, and in some areas of the US, over 20% of wells may contain levels that exceed established limits.

Low-level exposure to arsenic at concentrations found commonly in US drinking water compromises the initial immune response to H1N1 or swine flu infection according to NIEHS-supported scientists. The study, conducted in laboratory mice, suggests that people exposed to arsenic in their drinking water may be at increased risk for more serious illness or death in response to infection from the virus.

Some Canadians are drinking water that contains inorganic arsenic. Private dug well waters are most at risk for containing inorganic arsenic. Preliminary well water analyses typically does not test for arsenic. Researchers at the Geological Survey of Canada have modeled relative variation in natural arsenic hazard potential for the province of New Brunswick. This study has important implications for potable water and health concerns relating to inorganic arsenic.

Epidemiological evidence from Chile shows a dose-dependent connection between chronic arsenic exposure and various forms of cancer, in particular when other risk factors, such as cigarette smoking, are present. These effects have been demonstrated to persist below 50 ppb.

Analyzing multiple epidemiological studies on inorganic arsenic exposure suggests a small but measurable risk increase for bladder cancer at 10 ppb. According to Peter Ravenscroft of the Department of Geography at the University of Cambridge, roughly 80 million people worldwide consume between 10 and 50 ppb arsenic in their drinking water. If they all consumed exactly 10 ppb arsenic in their drinking water, the previously cited multiple epidemiological study analysis would predict an additional 2,000 cases of bladder cancer alone. This represents a clear underestimate of the overall impact, since it does not include lung or skin cancer, and explicitly underestimates the exposure. Those exposed to levels of arsenic above the current WHO standard should weigh the costs and benefits of arsenic remediation.

Early (1973) evaluations of the removal of dissolved arsenic by drinking water treatment processes demonstrated that arsenic is very effectively removed by co-precipitation with either iron or aluminum oxides. The use of iron as a coagulant, in particular, was found to remove arsenic with efficiencies exceeding 90%. Several adsorptive media systems have been approved for point-of-service use in a study funded by the United States Environmental Protection Agency (US EPA) and the National Science Foundation (NSF).

A team of European and Indian scientists and engineers have set up six arsenic treatment plants in West Bengal based on in-situ remediation method (SAR Technology).

This technology does not use any chemicals and arsenic is left as an insoluble form (+5 state) in the subterranean zone by recharging aerated water into the aquifer and thus developing an oxidation zone to support arsenic oxidizing micro-organisms. This process does not produce any waste stream or sludge and is relatively cheap.

Another effective and inexpensive method to remove arsenic from contaminated well water is to sink wells 500 feet or deeper to reach purer waters. A recent 2011 study funded by the US National Institute of Environmental Health Sciences' Superfund Research Program shows that deep sediments can remove arsenic and take it out of circulation.

Through this process called adsorption in which arsenic sticks to the surfaces of deep sediment articles, arsenic can be naturally removed from well water.

Magnetic separations of arsenic at very low magnetic field gradients have been demonstrated in point-of-use water purification with high-surface-area and monodisperse magnetite ( $\text{Fe}_3\text{O}_4$ ) nanocrystals. Using the high specific surface area of  $\text{Fe}_3\text{O}_4$  nanocrystals the mass of waste associated with arsenic removal from water has been dramatically reduced.

Epidemiological studies have suggested a correlation between chronic consumption of drinking water contaminated with arsenic and the incidence of all leading causes of mortality. The literature provides reason to believe arsenic exposure is causative in the pathogenesis of diabetes.

Hungarian engineer László Schremmer has recently discovered that by the use of chaff-based filters it is possible to reduce the arsenic content of water to 3  $\mu\text{g/L}$ . This is especially important in areas where the potable water is provided by filtering the water extracted from the underground aquifer.

### **Wood Preservation in the US**

As of 2002, US-based industries consumed 19,600 metric tons of arsenic. Ninety percent of this was used for treatment of wood with chromated copper arsenate (CCA). In 2007, 50% of the 5,280 metric tons of consumption was still used for this purpose. In the United States, the use of arsenic in consumer products was discontinued for residential and general consumer construction on December 31, 2003 and alternative chemicals are now used, such as Alkaline Copper Quaternary, borates, copper azole, cyproconazole, and propiconazole.

Although discontinued, this application is also one of the most concerns to the general public. The vast majority of older pressure-treated wood was treated with CCA. CCA lumber is still in widespread use in many countries, and was heavily used during the latter half of the 20th century as a structural and outdoor building material.

Although the use of CCA lumber was banned in many areas after studies showed that arsenic could leach out of the wood into the surrounding soil (from playground equipment, for instance), a risk is also presented by the burning of older CCA timber. The direct or indirect ingestion of wood ash from burnt CCA lumber has caused fatalities in animals and serious poisonings in humans; the lethal human dose is approximately 20 grams of ash. Scrap CCA lumber from construction and demolition sites may be inadvertently used in commercial and domestic fires.

Protocols for safe disposal of CCA lumber do not exist evenly throughout the world; there is also concern in some quarters about the widespread landfill disposal of such timber.

## **Water Purification Solutions**

### **Small-scale water treatment**

A review of methods to remove arsenic from groundwater in Pakistan summarizes the most technically viable inexpensive methods. A simpler and less expensive form of arsenic removal is known as the Sono arsenic filter, using three pitchers containing cast iron turnings and sand in the first pitcher and wood activated carbon and sand in the second.

Plastic buckets can also be used as filter containers. It is claimed that thousands of these systems are in use and can last for years while avoiding the toxic waste disposal problem inherent to conventional arsenic removal plants. Although novel, this filter has not been certified by any sanitary standards such as NSF, ANSI, WQA and does not avoid toxic waste disposal similar to any other iron removal process.

In the United States small "under the sink" units have been used to remove arsenic from drinking water. This option is called "point of use" treatment. The most common types of domestic treatment use the technologies of adsorption (using media such as Bayoxide E33, GFH, or titanium dioxide) or reverse osmosis. Ion exchange and activated alumina have been considered but not commonly used.

### **Arsenic Large-scale water treatment**

In some places, such as the United States, all the water supplied to residences by utilities must meet primary (health-based) drinking water standards. Regulations may necessitate large-scale treatment systems to remove arsenic from the water supply. The effectiveness of any method depends on the chemical makeup of a particular water supply. The aqueous chemistry of arsenic is complex, and may affect the removal rate that can be achieved by a particular process.

Some large utilities with multiple water supply wells could shut down those wells with high arsenic concentrations, and produce only from wells or surface water sources that meet the arsenic standard. Other utilities, however, especially small utilities with only a few wells, may have no available water supply that meets the arsenic standard.

**Coagulation/filtration** (also known as flocculation) removes arsenic by coprecipitation and adsorption using iron coagulants. Coagulation/filtration using alum is already used by some utilities to remove suspended solids and may be adjusted to remove arsenic. But the problem of this type of filtration system is that it gets clogged very easily, mostly within two to three months. The toxic arsenic sludge are disposed of by concrete stabilization, but there is no guarantee that they won't leach out in future.

**Iron oxide adsorption** filters the water through a granular medium containing ferric oxide. Ferric oxide has a high affinity for adsorbing dissolved metals such as arsenic. The iron oxide medium eventually becomes saturated, and must be replaced. The sludge disposal is a problem here too.

**Activated alumina** is an adsorbent that effectively removes arsenic. Activated alumina columns connected to shallow tube wells in India and Bangladesh have successfully removed both As(III) and As(V) from groundwater for decades.

Long-term column performance has been possible through the efforts of community-elected water committees that collect a local water tax for funding operations and maintenance. It has also been used to remove undesirably high concentrations of fluoride.

**Ion Exchange** has long been used as a water-softening process, although usually on a single-home basis. Traditional anion exchange is effective in removing As(V), but not As (III), or arsenic trioxide, which doesn't have a net charge. Effective long-term ion exchange removal of arsenic requires a trained operator to maintain the column.

Both **Reverse osmosis** and **electrodialysis** (also called *electrodialysis reversal*) can remove arsenic with a net ionic charge. (Note that arsenic oxide,  $As_2O_3$ , is a common form of arsenic in groundwater that is soluble, but has no net charge.) Some utilities presently use one of these methods to reduce total dissolved solids and therefore improve taste. A problem with both methods is the production of high-salinity waste water, called brine, or concentrate, which then must be disposed of.

### **Subterranean Arsenic Removal (SAR) Technology**

In subterranean arsenic removal (SAR), aerated groundwater is recharged back into the aquifer to create an oxidation zone which can trap iron and arsenic on the soil particles through adsorption process. The oxidation zone created by aerated water boosts the activity of the arsenic-oxidizing microorganisms which can oxidize arsenic from +3 to +5 state SAR Technology.

No chemicals are used and almost no sludge is produced during operational stage since iron and arsenic compounds are rendered inactive in the aquifer itself. Thus toxic waste disposal and the risk of its future mobilization is prevented. Also, it has very long operational life, similar to the long lasting tube wells drawing water from the shallow aquifers.

Six such SAR plants, funded by the World Bank and constructed by Ramakrishna Vivekananda Mission, Barrackpore & Queen's University Belfast, UK are operating in West Bengal. Each plant has been delivering more than 3,000 liters of arsenic and iron-free water daily to the rural community. The first community water treatment plant based on SAR technology was set up at Kashimpore near Kolkata in 2004 by a team of European and Indian engineers led by Dr. Bhaskar Sen Gupta of Queen's University Belfast for TiPOT.

SAR technology had been awarded Dhirubhai Ambani Award, 2010 from IChemE UK for Chemical Innovation. Again, SAR was the winner of the St. Andrews Award for Environment, 2010. The SAR Project was selected by the Blacksmith Institute - New York & Green Cross- Switzerland as one of the "12 Cases of Cleanup & Success" in the World's Worst Polluted Places Report 2009.

### **The Hungarian Solution**

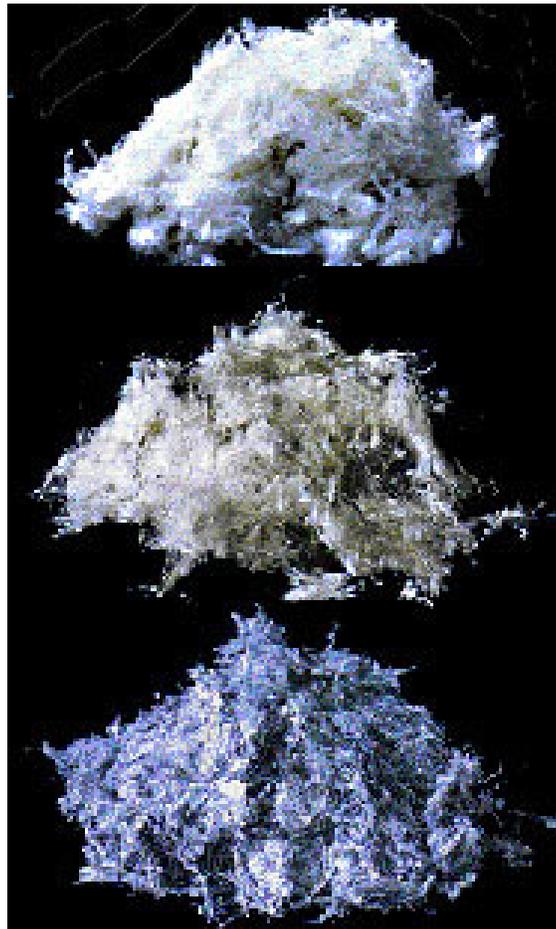
Hungarian engineer László Schremmer has recently discovered that by the use of chaff-based filters it is possible to reduce the arsenic content of water to 3 microgram/liter. This is especially important in areas where the potable water is provided by filtering the water extracted from the underground aquifer.

### **Arsenic Can Build Up on and Release in Pipes and Storage Tanks**

Water systems may also find deposits of arsenic-rich particles in their storage tanks or at locations in their distribution system with low flows. If the flow is increased or a storage tank is drawn down to a low level, these arsenic-rich particles can get stirred up and transported to consumers' taps. This situation occurs primarily when iron media used in treatment are released into the distribution system, or when iron particles are not properly filtered out during iron removal treatment. If these treatment technologies are operated correctly, this should not be a problem for most water systems.

Public water systems with arsenic in their raw water may find that scales on pipes and other components in their distribution systems contain relatively high arsenic concentrations. These arsenic-rich scales can become dislodged and suspended in the water, and may be ultimately delivered to consumers.

Arsenic has been shown to attach to iron in distribution system pipes. Because iron is so effective at binding with arsenic, corrosion deposits can have high concentrations of arsenic solids. In a recent study, arsenic levels found in solids that were collected after pipe sections and hydrants were flushed were as high as 13.65 milligrams of arsenic per gram of solid.



Asbestos minerals which have been used commercially from the top: chrysotile, amosite and crocidolite.



## **Asbestos - Inorganic Contaminant 7 MFL**

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for asbestos is 7 MFL. EPA has set this level of protection based on the best available science to prevent potential health problems. EPA has set an enforceable regulation for asbestos, called a maximum contaminant level (MCL), at 7 MFL.

MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.

The Phase II Rule, the regulation for asbestos, became effective in 1992. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed asbestos as part of the Six Year Review and determined that the 7 MFL MCLG and 7 MFL MCL for asbestos are still protective of human health.

### **How does Asbestos get into my Drinking Water?**

The major sources of asbestos in drinking water are decay of asbestos cement water mains; and erosion of natural deposits.

A federal law called the Emergency Planning and Community Right to Know Act (EPCRA) requires facilities in certain industries, which manufacture, process, or use significant amounts of toxic chemicals, to report annually on their releases of these chemicals. For more information on the uses and releases of chemicals in your state, contact the Community Right-to-Know Hotline: (800) 424-9346.

### **How will I know if Asbestos is in my Drinking Water?**

When routine monitoring indicates that asbestos levels are above the MCL, your water supplier must take steps to reduce the amount of asbestos so that it is below that level. Water suppliers must notify their customers as soon as practical, but no later than 30 days after the system learns of the violation. Additional actions, such as providing alternative drinking water supplies, may be required to prevent serious risks to public health.

### **How will Asbestos be removed from my Drinking Water?**

The following treatment method(s) have proven to be effective for removing asbestos to below 7 MFL: coagulation/filtration, direct and diatomite filtration, and corrosion control.



### **Asbestos Cement Pipe (ACP)**

Common water distribution pipe, notice that both pipes have been cut with a power saw. You are not allowed to cut this type of pipe with a power saw, because it will spread the Asbestos.

Wetting agents may be applied with garden sprayers or hoses. Garden sprayers are hand-held, portable, and have a one- to five-gallon capacity. Water hoses are usually attached to a faucet tap, fire hydrant or water tank. Generally, the hose has a nozzle attached which spreads the water stream so that a fine mist is created.

### **Asbestos-Cement Products**

Asbestos-cement products (such as transite) are commonly used for duct insulation, pipes, and siding. Being a Category II nonfriable ACM, asbestos-cement products need to be removed prior to demolition if they have a high probability of becoming crumbled, pulverized, or reduced to powder during demolition activities. EPA believes that most demolition activities will subject such Category II nonfriable ACM to the regulation.

### ***Asbestos is an Excellent ...***

#### **Heat Stability**

Asbestos will maintain its structural integrity at temperatures well above 800 F. The melting point is at about 2800 F

#### **Thermal Insulation**

The fibers have a relatively large surface area, along with numerous pores, and cracks. This allows for a low heat transfer. This makes it useful as an insulator in homes and machinery. The large surface area also absorbs water making it practical as pipe insulator to prevent sweating.

#### **Chemical Resistance**

The amphiboles are resistant to aqueous media and chemical attack. They also show high resistance to acids. This makes this class of asbestos useful for battery packing. Chrysotile is significantly less resistant to chemical destruction.

## Sound Absorption

Asbestos has a large internal volume, large surface area, and the fibers are flexible. This makes it ideal for the absorption of sound energy. It is often used to help acoustics.



Serpent

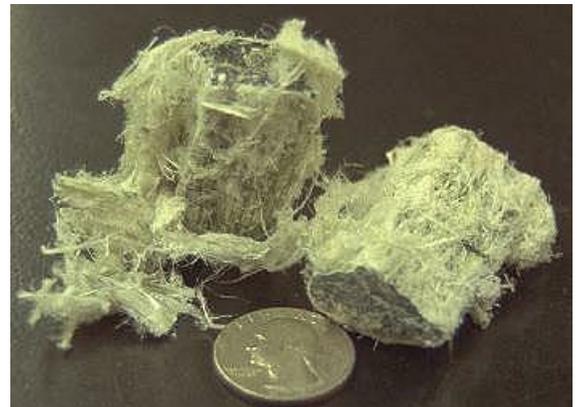
## Asbestos

OSHA requires that employees who may be exposed to dangerous levels of asbestos must be made aware of the hazards and how to protect themselves. Employees must be told where in their workplace they can find copies of all applicable asbestos standards. Employers must provide any employee with the opportunity to review the regulations if they so desire. It is an employee's right to have access to the regulations.

### What Is Asbestos?

Asbestos is the name given to a number of naturally occurring fibrous silicate minerals that have been mined for their useful properties such as thermal insulation, chemical and thermal stability, and high tensile strength. The three most common types of asbestos are: a) chrysotile, b) amosite and c) crocidolite.

Chrysotile, also known as white asbestos and a member of the Serpentine mineral group is the commonest. Asbestos can only be identified under a microscope.



Asbestos differs from other minerals in its crystal development. The crystal formation of asbestos is in the form of long thin fibers. Asbestos is divided into two mineral groups **Serpentine** and **Amphibole**. The division between the two types of asbestos is based upon the crystalline structure.

Serpentines have a sheet or layered structure where amphiboles have a chain-like structure. As the only member of the serpentine group, Chrysotile (A, B) is the most common type of asbestos found in buildings. Chrysotile makes up approximately 90%-95% of all asbestos contained in buildings in the United States.

Unlike most minerals, which turn into dust particles when crushed, asbestos breaks up into fine fibers that are too small to be seen by the human eye. Often, individual fibers are mixed with a material that binds them together, producing asbestos-containing material (**ACM**).

### **Health Effects of Asbestos Exposure**

Asbestos is the largest single cause of fatal disease and ill-health caused by work in Great Britain. Although almost all the deaths and ill health related to asbestos today are due to exposures that happened several decades ago, if you work with asbestos, or come into contact with it as a result of repair and maintenance work, you need to be particularly careful. Asbestos can be found in most buildings built between 1950 and 1980, as insulation and lagging. It is still used in some brake pads and clutch linings and can be met in vehicle servicing and repair.

### **Asbestos-Related Health Problems**

Some people exposed to asbestos develop asbestos-related health problems; some do not. Once inhaled, asbestos fibers can easily penetrate body tissues. They may be deposited and retained in the airways and lung tissue. Because asbestos fibers remain in the body, each exposure increases the likelihood of developing an asbestos-related disease.

Asbestos-related diseases may not appear until years after exposure. A medical examination that includes a medical history, breathing capacity test, and chest X ray may detect problems early.

Many substances have a "**safe dose**" or an exposure that is unlikely to cause any harm. Above the safe dose, a health effect is expected. This concept is known as a dose response. As the dose increases, so does the expected severity of the health effect.

However, in the case of asbestos, scientists have not determined a "**safe dose**" or threshold level for exposure to airborne asbestos. Still, the less exposure a person receives over a lifetime, the less likely it is that that person will develop an asbestos-related health problem.

In addition to breathing it, ingesting asbestos may also be harmful to you, but the consequences of this type of exposure have not been clearly documented. People who touch asbestos may get a rash similar to the rash caused by fiberglass. While the effects of skin exposure to asbestos have not been scientifically documented, it is best to minimize all contact with asbestos.

Asbestos was used in approximately 3,000 products. Two-thirds of this total (2,000) was used in construction products. Appendix A includes a short list of products where asbestos may be found.

## Barium - Inorganic Contaminant 2 mg/L MCL

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for barium is 2 mg/L or 2 ppm. EPA has set this level of protection based on the best available science to prevent potential health problems. EPA has set an enforceable regulation for barium, called a maximum contaminant level (MCL), at 2 mg/L or 2 ppm. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.



The Phase IIB Rule, the regulation for barium, became effective in 1993. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed barium as part of the Six Year Review and determined that the 2 mg/L or 2 ppm MCLG and 2 mg/L or 2 ppm MCL for barium are still protective of human health.

The major sources of barium in drinking water are discharge of drilling wastes; discharge from metal refineries; and erosion of natural deposits.

A federal law called the Emergency Planning and Community Right to Know Act (EPCRA) requires facilities in certain industries, which manufacture, process, or use significant amounts of toxic chemicals, to report annually on their releases of these chemicals. For more information on the uses and releases of chemicals in your state, contact the Community Right-to-Know Hotline: (800) 424-9346.

When routine monitoring indicates that barium levels are above the MCL, your water supplier must take steps to reduce the amount of barium so that it is below that level. Water suppliers must notify their customers as soon as practical, but no later than 30 days after the system learns of the violation. Additional actions, such as providing alternative drinking water supplies, may be required to prevent serious risks to public health.

### **How will barium be removed from my Drinking Water?**

The following treatment method(s) have proven to be effective for removing barium to below 2 mg/L or 2 ppm: ion exchange, reverse osmosis, lime softening, and electrodialysis.

### **How do I learn more about my Drinking Water?**

EPA strongly encourages people to learn more about their drinking water, and to support local efforts to protect the supply of safe drinking water and upgrade the community water system. Your water bill or telephone book's government listings are a good starting point for local information.

**Barium** is a chemical element with symbol **Ba** and atomic number 56. It is the fifth element in Group 2, a soft silvery metallic alkaline earth metal. Because of its high chemical reactivity barium is never found in nature as a free element. Its hydroxide was known in pre-modern history as baryta; this substance does not occur as a mineral, but can be prepared by heating barium carbonate.

The most common naturally occurring minerals of barium are barite (barium sulfate, BaSO<sub>4</sub>) and witherite (barium carbonate, BaCO<sub>3</sub>), both being insoluble in water. Barium's name originates from the alchemical derivative "baryta", which itself comes from Greek βαρύς (*barys*), meaning "heavy." Barium was identified as a new element in 1774, but not reduced to a metal until 1808, shortly after electrolytic isolation techniques became available.

Barium has only a few industrial applications. The metal has been historically used to scavenge air in vacuum tubes. It is a component of YBCO (high-temperature superconductors) and electroceramics, and is added to steel and cast iron to reduce the size of carbon grains within the microstructure of the metal. Barium compounds are added to fireworks to impart a green color. For instance, barium sulfate is used as an insoluble heavy additive to oil well drilling fluid, and in purer form, as X-ray radiocontrast agents for imaging the human gastrointestinal tract. Soluble barium compounds are poisonous due to release of the soluble barium ion, and therefore have been used as rodenticides.

### Physical Properties

Barium is a soft, silvery-white metal, with a slight golden shade when ultrapure. The silvery-white color of barium metal rapidly vanishes upon oxidation in air yielding a dark gray oxide layer. Barium has a medium specific weight and good electrical conductivity. Ultrapure barium is very hard to prepare, and therefore many properties of barium have not been accurately measured yet.

At room temperature and pressure, barium has a body-centered cubic structure, with a barium–barium distance of 503 picometers, expanding with heating at a rate of approximately  $1.8 \times 10^{-5}/^{\circ}\text{C}$ . It is a very soft metal with a Mohs hardness of 1.25. Its melting temperature of 1000 K (727 °C, 1341 °F) is intermediate between those of the lighter strontium (1050 K) and heavier radium (973 K); however, its boiling point of 2170 K (1897 °C, 3447 °F) exceeds that of strontium (1655 K). The density ( $3.62 \text{ g}\cdot\text{cm}^{-3}$ ) is again intermediate between those of strontium ( $2.36 \text{ g}\cdot\text{cm}^{-3}$ ) and radium ( $\sim 5 \text{ g}\cdot\text{cm}^{-3}$ ).

### Chemical Reactivity

Barium is chemically similar to magnesium, calcium, and strontium, being even more reactive. It always exhibits the oxidation state of +2. Reactions with chalcogens are highly exothermic (release energy); the reaction with oxygen or air occurs at room temperature, and therefore barium is stored under oil or inert gas atmosphere.

Reactions with other nonmetals, such as carbon, nitrogen, phosphorus, silicon, and hydrogen, are generally exothermic and proceed upon heating. Reactions with water and alcohols are also very exothermic and release hydrogen gas:



Additionally, barium reacts with ammonia to form complexes such as Ba(NH<sub>3</sub>)<sub>6</sub>.

The metal is readily attacked by most acids. Sulfuric acid is a notable exception, as passivation stops the reaction by forming the insoluble barium sulfate. Barium combines with several metals, including aluminum, zinc, lead, and tin, forming intermetallic phases and alloys.

## Compounds

Selected alkaline earth and zinc salts densities,  
 $\text{g}\cdot\text{cm}^{-3}$

	$\text{O}^{2-}$	$\text{S}^{2-}$	$\text{F}^-$	$\text{Cl}^-$	$\text{SO}_2^{2-}$ 4	$\text{CO}_2^{2-}$ 3	$\text{O}_2^{2-}$ 2	$\text{H}^-$
$\text{Ca}^{2+}$ <sup>[9]</sup>	3.34	2.59	3.18	2.15	2.96	2.83	2.9	1.7
$\text{Sr}^{2+}$ <sup>[10]</sup>	5.1	3.7	4.24	3.05	3.96	3.5	4.78	3.26
$\text{Ba}^{2+}$ <sup>[11]</sup>	5.72	4.3	2.1	1.9	4.49	4.29	4.96	4.16
$\text{Zn}^{2+}$ <sup>[12]</sup>	5.6	4.09	4.9	2.09	3.8	4.4	1.57	—

Barium salts are typically white when solid and colorless when dissolved, as barium ions provide no specific coloring. They are also denser than their strontium or calcium analogs, except for the halides.

Barium hydroxide ("baryta") was known to alchemists who produced it by heating barium carbonate. Unlike calcium hydroxide, it absorbs very little  $\text{CO}_2$  in aqueous solutions and is therefore insensitive to atmospheric fluctuations. This property is used in calibrating pH equipment.

Volatile barium compounds burn with a green to pale green flame, which is an efficient test to detect a barium compound. The color results from spectral lines at 455.4, 493.4, 553.6, and 611.1 nm.

Organobarium compounds are a growing class of compounds: for example, dialkylbariums are known, as are alkylhalobariums.

## Isotopes of Barium

Barium occurs naturally on Earth as a mixture of seven primordial nuclides, barium-130, 132, and 134 through 138. The first two are thought to be radioactive: barium-130 should decay to xenon-130 via double beta plus decay, and barium-132 should similarly decay to xenon-132.

The corresponding half-lives should exceed the age of the Universe by at least thousand times. Their abundances are ~0.1% relative to that of natural barium. Their radioactivity is so weak that they pose no danger to life.

Out of the stable isotopes, barium-138 makes up 71.7% of all barium, and the lighter the isotope, the less it is abundant. In total, barium has about 50 known isotopes, ranging in mass between 114 and 153. The most stable metastable isotope is barium-133, which has a half-life of approximately 10.51 years, and five more isotopes have their half-lives longer than a day. Barium also has 10 meta states, out of which barium-133m1 is the most stable, having a half-life of about 39 hours.

## Biological Dangers and Precautions

Because of the high reactivity of the metal toxicological data are available only for compounds. Water-soluble barium compounds are poisonous. At low doses, barium ions act as a muscle stimulant, whereas higher doses affect the nervous system, causing cardiac irregularities, tremors, weakness, anxiety, dyspnea and paralysis. This may be due to the ability of  $\text{Ba}^{2+}$  to block potassium ion channels, which are critical to the proper function of the nervous system.

Other target organs for water-soluble barium compounds (i.e., barium ions) are eyes, immune system, heart, respiratory system, and skin. They affect the body strongly, causing, for example, blindness and sensitization.

Barium is not carcinogenic, and it does not bioaccumulate. However, inhaled dust containing insoluble barium compounds can accumulate in the lungs, causing a benign condition called baritosis. For comparison to the soluble poisons, the insoluble sulfate is nontoxic and is thus not classified as a dangerous good.

To avoid a potentially vigorous chemical reaction, barium metal is kept under argon or mineral oils. Contact with air is dangerous, as it may cause ignition. Moisture, friction, heat, sparks, flames, shocks, static electricity, reactions with oxidizers and acids should be avoided. Everything that may make contact with barium should be grounded.

Those who work with the metal should wear pre-cleaned non-sparking shoes, flame-resistant rubber clothes, rubber gloves, apron, goggles, and a gas mask; they are not allowed to smoke in the working area and must wash themselves after handling barium.

## Beryllium - Inorganic Contaminant 0.004 mg/L MCL

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for beryllium is 0.004 mg/L or 4 ppb. EPA has set this level of protection based on the best available science to prevent potential health problems. EPA has set an enforceable regulation for beryllium, called a maximum contaminant level (MCL), at 0.004 mg/L or 4 ppb.

MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies.



In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.

The Phase V Rule, the regulation for beryllium, became effective in 1994. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed beryllium as part of the Six Year Review and determined that the 0.004 mg/L or 4 ppb MCLG and 0.004 mg/L or 4 ppb MCL for beryllium are still protective of human health.

### How does Beryllium get into my Drinking Water?

Beryllium naturally enters surface water and ground water through the weathering of rocks and soils or from industrial wastewater discharges. The major source of environmental releases from human activities are coal and fuel oil combustion.

A federal law called the Emergency Planning and Community Right to Know Act (EPCRA) requires facilities in certain industries, which manufacture, process, or use significant amounts of toxic chemicals, to report annually on their releases of these chemicals. For more information on the uses and releases of chemicals in your state, contact the Community Right-to-Know Hotline: (800) 424-9346.

### **How will I know if Beryllium is in my Drinking Water?**

When routine monitoring indicates that beryllium levels are above the MCL, your water supplier must take steps to reduce the amount of beryllium so that it is below that level. Water suppliers must notify their customers as soon as practical, but no later than 30 days after the system learns of the violation. Additional actions, such as providing alternative drinking water supplies, may be required to prevent serious risks to public health.

**Beryllium** is the chemical element with the symbol **Be** and atomic number 4. Because any beryllium synthesized in stars is short-lived, it is a relatively rare element in both the universe and in the crust of the Earth. It is a divalent element which occurs naturally only in combination with other elements in minerals. Notable gemstones which contain beryllium include beryl (aquamarine, emerald) and chrysoberyl. As a free element it is a steel-gray, strong, lightweight and brittle alkaline earth metal.

Beryllium increases hardness and resistance to corrosion when alloyed to aluminum, cobalt, copper (notably beryllium copper), iron and nickel. In structural applications, high flexural rigidity, thermal stability, thermal conductivity and low density (1.85 times that of water) make beryllium a quality aerospace material for high-speed aircraft, missiles, space vehicles and communication satellites. Because of its low density and atomic mass, beryllium is relatively transparent to X-rays and other forms of ionizing radiation; therefore, it is the most common window material for X-ray equipment and in particle physics experiments. The high thermal conductivities of beryllium and beryllium oxide have led to their use in heat transport and heat sinking applications.

The commercial use of beryllium metal presents technical challenges due to the toxicity (especially by inhalation) of beryllium-containing dusts. Beryllium is corrosive to tissue, and can cause a chronic life-threatening allergic disease called berylliosis in some people. The element is not known to be necessary or useful for either plant or animal life

### **Characteristics**

#### **Physical Properties**

Beryllium is a steel gray and hard metal that is brittle at room temperature and has a close-packed hexagonal crystal structure. It has exceptional flexural rigidity (Young's modulus 287 GPa) and a reasonably high melting point. The modulus of elasticity of beryllium is approximately 50% greater than that of steel.

The combination of this modulus and a relatively low density results in an unusually fast sound conduction speed in beryllium – about 12.9 km/s at ambient conditions.

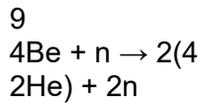
Other significant properties are high specific heat ( $1925 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ ) and thermal conductivity ( $216 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ), which make beryllium the metal with the best heat dissipation characteristics per unit weight. In combination with the relatively low coefficient of linear thermal expansion ( $11.4 \times 10^{-6} \text{ K}^{-1}$ ), these characteristics result in a unique stability under conditions of thermal loading.

#### **Nuclear Properties**

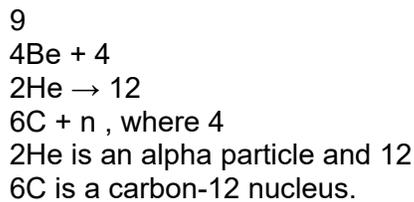
Natural beryllium, save for slight contamination by cosmogenic radioisotopes, is essentially beryllium-9, which has a nuclear spin of  $3/2^-$ . Beryllium has a large scattering cross section for high-energy neutrons, about 6 barns for energies above  $\sim 0.01 \text{ MeV}$ . Therefore, it works as a neutron reflector and neutron moderator, effectively slowing the neutrons to the thermal energy range of below 0.03 eV, where the total cross section is at least an order of magnitude lower – exact value strongly depends on the purity and size of the crystallites in the material.

The single primordial beryllium isotope  ${}^9\text{Be}$  also undergoes a (n,2n) neutron reaction with neutron energies over about 1.9 MeV, to produce  ${}^8\text{Be}$ , which almost immediately breaks into two alpha particles. Thus, for high-energy neutrons beryllium is a neutron multiplier, releasing more neutrons than it absorbs.

This nuclear reaction is:



Neutrons are liberated when beryllium nuclei are struck by energetic alpha particles producing the nuclear reaction



Beryllium also releases neutrons under bombardment by gamma rays. Thus, natural beryllium bombarded either by alphas or gammas from a suitable radioisotope is a key component of most radioisotope-powered nuclear reaction neutron sources for the laboratory production of free neutrons.

As a metal, beryllium is transparent to most wavelengths of X-rays and gamma rays, making it useful for the output windows of X-ray tubes and other such apparatus.

### Isotopes and Nucleosynthesis

Both stable and unstable isotopes of beryllium are created in stars, but these do not last long. It is believed that most of the stable beryllium in the universe was originally created in the interstellar medium when cosmic rays induced fission in heavier elements found in interstellar gas and dust. Primordial beryllium contains only one stable isotope,  ${}^9\text{Be}$ , and therefore beryllium is a monoisotopic element.

Plot showing variations in solar activity, including variation in  ${}^{10}\text{Be}$  concentration. Note that the beryllium scale is inverted, so increases on this scale indicate lower  ${}^{10}\text{Be}$  levels

Radioactive cosmogenic  ${}^{10}\text{Be}$  is produced in the atmosphere of the Earth by the cosmic ray spallation of oxygen.  ${}^{10}\text{Be}$  accumulates at the soil surface, where its relatively long half-life (1.36 million years) permits a long residence time before decaying to boron-10. Thus,  ${}^{10}\text{Be}$  and its daughter products are used to examine natural soil erosion, soil formation and the development of lateritic soils, and as a proxy for measurement of the variations in solar activity and the age of ice cores.

The production of  ${}^{10}\text{Be}$  is inversely proportional to solar activity, because increased solar wind during periods of high solar activity decreases the flux of galactic cosmic rays that reach the Earth. Nuclear explosions also form  ${}^{10}\text{Be}$  by the reaction of fast neutrons with  ${}^{13}\text{C}$  in the carbon dioxide in air.

This is one of the indicators of past activity at nuclear weapon test sites. The isotope  $^7\text{Be}$  (half-life 53 days) is also cosmogenic, and shows an atmospheric abundance linked to sunspots, much like  $^{10}\text{Be}$ .

$^8\text{Be}$  has a very short half-life of about  $7 \times 10^{-17}$  s that contributes to its significant cosmological role, as elements heavier than beryllium could not have been produced by nuclear fusion in the Big Bang. This is due to the lack of sufficient time during the Big Bang's nucleosynthesis phase to produce carbon by the fusion of  $^4\text{He}$  nuclei and the very low concentrations of available beryllium-8.

The British astronomer Sir Fred Hoyle first showed that the energy levels of  $^8\text{Be}$  and  $^{12}\text{C}$  allow carbon production by the so-called triple-alpha process in helium-fueled stars where more nucleosynthesis time is available. This process allows carbon to be produced in stars, but not in the Big Bang. Star-created carbon (the basis of carbon-based life) is thus a component in the elements in the gas and dust ejected by AGB stars and supernovae (see also Big Bang nucleosynthesis), as well as the creation of all other elements with atomic numbers larger than that of carbon.

The innermost electrons of beryllium may contribute to chemical bonding. Therefore, when  $^7\text{Be}$  decays by electron capture, it does so by taking electrons from atomic orbitals that may participate in bonding. This makes its decay rate dependent to a measurable degree upon its electron configuration – a rare occurrence in nuclear decay.

The shortest-lived known isotope of beryllium is  $^{13}\text{Be}$  which decays through neutron emission. It has a half-life of  $2.7 \times 10^{-21}$  s.  $^6\text{Be}$  is also very short-lived with a half-life of  $5.0 \times 10^{-21}$  s. The exotic isotopes  $^{11}\text{Be}$  and  $^{14}\text{Be}$  are known to exhibit a nuclear halo. This phenomenon can be understood as the nuclei of  $^{11}\text{Be}$  and  $^{14}\text{Be}$  have, respectively, 1 and 4 neutrons orbiting substantially outside the classical Fermi 'water drop' model of the nucleus.

### Occurrence

Beryllium has a concentration of 2 to 6 parts per million (ppm) in the Earth's crust. The Sun has a concentration of 0.1 parts per billion (ppb) of beryllium, similar to that of rhenium. It is most concentrated in the soils, 6 ppm, and is found in 0.2 parts per trillion (ppt) of sea water.

Trace amounts of  $^9\text{Be}$  are found in the Earth's atmosphere. In sea water, beryllium is exceedingly rare, more so than even scandium, comprising only 0.0006 ppb by weight. In stream water, however, beryllium is more abundant with 0.1 ppb by weight.

Beryllium is found in over 100 minerals, but most are uncommon to rare. The more common beryllium containing minerals include: bertrandite ( $\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$ ), beryl ( $\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18}$ ), chrysoberyl ( $\text{Al}_2\text{BeO}_4$ ) and phenakite ( $\text{Be}_2\text{SiO}_4$ ). Precious forms of beryl are aquamarine, bixbite and emerald. The green color in gem-quality forms of beryl comes from varying amounts of chromium (about 2% for emerald).

The two main ores of beryllium, beryl and bertrandite, are found in Argentina, Brazil, India, Madagascar, Russia and the United States. Total world reserves of beryllium ore are greater than 400,000 tons.

## Production

The extraction of beryllium from its compounds is a difficult process due to its high affinity for oxygen at elevated temperatures, and its ability to reduce water when its oxide film is removed. The United States, China and Kazakhstan are the only three countries involved in the industrial scale extraction of beryllium.

Beryllium is most-commonly extracted from beryl, which is either sintered using an extraction agent or melted into a soluble mixture. The sintering process involves mixing beryl with sodium fluorosilicate and soda at 770°C to form sodium fluoroberyllate, aluminum oxide and silicon dioxide. Beryllium hydroxide is precipitated from a solution of sodium fluoroberyllate and sodium hydroxide in water. Extraction of beryllium using the melt method involves grinding beryl into a powder and heating it to 1650°C. The melt is quickly cooled with water and then reheated 250 to 300°C in concentrated sulfuric acid, mostly yielding beryllium sulfate and aluminum sulfate.

Aqueous ammonia is then used to remove the aluminum and sulfur, leaving beryllium hydroxide.

Beryllium hydroxide created using either the sinter or melt method is then converted into beryllium fluoride or beryllium chloride. To form the fluoride, aqueous ammonium hydrogen fluoride is added to beryllium hydroxide to yield a precipitate of ammonium tetrafluoroberyllate, which is heated to 1000°C to form beryllium fluoride.

Heating the fluoride to 900°C with magnesium forms finely divided beryllium and additional heating to 1300°C creates the compact metal. Heating beryllium hydroxide forms the oxide which becomes beryllium chloride when mixed with carbon and chloride. Electrolysis of molten beryllium chloride is then used to obtain the metal.

## Chemical Properties

Beryllium's chemical behavior is largely a result of its small atomic and ionic radii. It thus has very high ionization potentials and strong polarization while bonded to other atoms, which is why all of its compounds are covalent. It is more chemically similar to aluminum than its close neighbors in the periodic table due to having a similar charge-to-radius ratio. An oxide layer forms around beryllium that prevents further reactions with air unless heated above 1000°C.

Once ignited, beryllium burns brilliantly forming a mixture of beryllium oxide and beryllium nitride. Beryllium dissolves readily in non-oxidizing acids, such as HCl and diluted H<sub>2</sub>SO<sub>4</sub>, but not in nitric acid or water as this forms the oxide. This behavior is similar to that of aluminum metal. Beryllium also dissolves in alkali solutions.

The beryllium atom has the electronic configuration [He] 2s<sup>2</sup>. The two valence electrons give beryllium a +2 oxidation state and thus the ability to form two covalent bonds; the only evidence of lower valence of beryllium is in the solubility of the metal in BeCl<sub>2</sub>. Due to the octet rule, atoms tend to seek a valence of 8 in order to resemble a noble gas. Beryllium tries to achieve a coordination number of 4 because its two covalent bonds fill half of this octet. A coordination of 4 allows beryllium compounds, such as the fluoride or chloride, to form polymers.

This characteristic is employed in analytical techniques using EDTA as a ligand. EDTA preferentially forms octahedral complexes – thus absorbing other cations such as Al<sup>3+</sup> which might interfere – for example, in the solvent extraction of a complex formed between Be<sup>2+</sup> and acetylacetonate. Beryllium(II) readily forms complexes with strong donating ligands such as phosphine oxides and arsine oxides. There have been extensive studies of these complexes which show the stability of the O-Be bond.

Solutions of beryllium salts, e.g. beryllium sulfate and beryllium nitrate, are acidic because of hydrolysis of the  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$  ion.



Other products of hydrolysis include the trimeric ion  $[\text{Be}_3(\text{OH})_3(\text{H}_2\text{O})_6]^{3+}$ . Beryllium hydroxide,  $\text{Be}(\text{OH})_2$ , is insoluble even in acidic solutions with pH less than 6, that is at biological pH. It is amphoteric and dissolves in strongly alkaline solutions.

Beryllium forms binary compounds with many non-metals. Anhydrous halides are known for F, Cl, Br and I.  $\text{BeF}_2$  has a silica-like structure with corner-shared  $\text{BeF}_4$  tetrahedra.  $\text{BeCl}_2$  and  $\text{BeBr}_2$  have chain structures with edge-shared tetrahedra. All beryllium halides have a linear monomeric molecular structure in the gas phase.

Beryllium difluoride,  $\text{BeF}_2$ , is different than the other difluorides. In general, beryllium has a tendency to bond covalently, much more so than the other alkaline earths and its fluoride is partially covalent (although still more ionic than its other halides).

$\text{BeF}_2$  has many similarities to  $\text{SiO}_2$  (quartz) a mostly covalently bonded network solid.  $\text{BeF}_2$  has tetrahedrally coordinated metal and forms glasses (is difficult to crystallize). When crystalline, beryllium fluoride has the same room temperature crystal structure as quartz and shares many higher temperatures structures also. Beryllium difluoride is very soluble in water, unlike the other alkaline earths. (Although they are strongly ionic, they do not dissolve because of the especially strong lattice energy of the fluorite structure.) However,  $\text{BeF}_2$  has much lower electrical conductivity when in solution or when molten than would be expected if it were fully ionic.

### **Beryllium Oxide**

Beryllium oxide,  $\text{BeO}$ , is a white refractory solid, which has the wurtzite crystal structure and a thermal conductivity as high as in some metals.  $\text{BeO}$  is amphoteric. Salts of beryllium can be produced by treating  $\text{Be}(\text{OH})_2$  with acid. Beryllium sulfide, selenide and telluride are known, all having the zincblende structure.

### **Beryllium Nitride**

Beryllium nitride,  $\text{Be}_3\text{N}_2$  is a high-melting-point compound which is readily hydrolyzed. Beryllium azide,  $\text{BeN}_6$  is known and beryllium phosphide,  $\text{Be}_3\text{P}_2$  has a similar structure to  $\text{Be}_3\text{N}_2$ . Basic beryllium nitrate and basic beryllium acetate have similar tetrahedral structures with four beryllium atoms coordinated to a central oxide ion. A number of beryllium borides are known, such as  $\text{Be}_5\text{B}$ ,  $\text{Be}_4\text{B}$ ,  $\text{Be}_2\text{B}$ ,  $\text{BeB}_2$ ,  $\text{BeB}_6$  and  $\text{BeB}_{12}$ . Beryllium carbide,  $\text{Be}_2\text{C}$ , is a refractory brick-red compound that reacts with water to give methane. No beryllium silicide has been identified.

Approximately 35 micrograms of beryllium is found in the human body, but this amount is not considered harmful. Beryllium is chemically similar to magnesium and therefore can displace it from enzymes, which causes them to malfunction.

Chronic berylliosis is a pulmonary and systemic granulomatous disease caused by inhalation of dust or fumes contaminated with beryllium; either large amounts over a short time or small amounts over a long time can lead to this ailment. Symptoms of the disease can take up to 5 years to develop; about a third of patients with it die and the survivors are left disabled. The International Agency for Research on Cancer (IARC) lists beryllium and beryllium compounds as Category 1 carcinogens.

Acute beryllium disease in the form of chemical pneumonitis was first reported in Europe in 1933 and in the United States in 1943. A survey found that about 5% of workers in plants manufacturing fluorescent lamps in 1949 in the United States had beryllium-related lung diseases. Chronic berylliosis resembles sarcoidosis in many respects, and the differential diagnosis is often difficult. It killed some early workers in nuclear weapons design, such as Herbert L. Anderson.

Early researchers tasted beryllium and its various compounds for sweetness in order to verify its presence. Modern diagnostic equipment no longer necessitates this highly risky procedure and no attempt should be made to ingest this highly toxic substance. Beryllium and its compounds should be handled with great care and special precautions must be taken when carrying out any activity which could result in the release of beryllium dust (lung cancer is a possible result of prolonged exposure to beryllium laden dust).

Although the use of beryllium compounds in fluorescent lighting tubes was discontinued in 1949, potential for exposure to beryllium exists in the nuclear and aerospace industries and in the refining of beryllium metal and melting of beryllium-containing alloys, the manufacturing of electronic devices, and the handling of other beryllium-containing material.

A successful test for beryllium in air and on surfaces has been recently developed and published as an international voluntary consensus standard ASTM D7202. The procedure uses dilute ammonium bifluoride for dissolution and fluorescence detection with beryllium bound to sulfonated hydroxybenzoquinoline, allowing up to 100 times more sensitive detection than the recommended limit for beryllium concentration in the workplace.

Fluorescence increases with increasing beryllium concentration. The new procedure has been successfully tested on a variety of surfaces and is effective for the dissolution and ultratrace detection of refractory beryllium oxide and siliceous beryllium (ASTM D7458).



## Cadmium - Inorganic Contaminant 0.005 mg/L MCL

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for cadmium is 0.005 mg/L or 5 ppb. EPA has set this level of protection based on the best available science to prevent potential health problems. EPA has set an enforceable regulation for cadmium, called a maximum contaminant level (MCL), at 0.005 mg/L or 5 ppb. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.



The Phase II Rule, the regulation for cadmium, became effective in 1992. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed cadmium as part of the Six Year Review and determined that the 0.005 mg/L or 5 ppb MCLG and 0.005 mg/L or 5 ppb MCL for cadmium are still protective of human health.

### How does cadmium get into my drinking water?

The major sources of cadmium in drinking water are corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints.

A federal law called the Emergency Planning and Community Right to Know Act (EPCRA) requires facilities in certain industries, which manufacture, process, or use significant amounts of toxic chemicals, to report annually on their releases of these chemicals. For more information on the uses and releases of chemicals in your state, contact the Community Right-to-Know Hotline: (800) 424-9346.

### How will I know if cadmium is in my drinking water?

When routine monitoring indicates that cadmium levels are above the MCL, your water supplier must take steps to reduce the amount of cadmium so that it is below that level. Water suppliers must notify their customers as soon as practical, but no later than 30 days after the system learns of the violation. Additional actions, such as providing alternative drinking water supplies, may be required to prevent serious risks to public health.

If your water comes from a household well, check with your health department or local water systems that use ground water for information on contaminants of concern in your area.

### How will cadmium be removed from my drinking water?

The following treatment method(s) have proven to be effective for removing cadmium to below 0.005 mg/L or 5 ppb: coagulation/filtration, ion exchange, lime softening, and reverse osmosis.

### Cadmium Explained

Cadmium is a chemical element with the symbol **Cd** and atomic number 48. This soft, bluish-white metal is chemically similar to the two other stable metals in group 12, zinc and mercury. Like zinc, it prefers oxidation state +2 in most of its compounds and like mercury it shows a low melting point compared to transition metals. Cadmium and its congeners are not always considered transition metals, in that they do not have partly filled d or f electron shells in the elemental or common oxidation states. The average concentration of cadmium in the Earth's crust is between 0.1 and 0.5 parts per million (ppm). It was discovered in 1817 simultaneously by Stromeyer and Hermann, both in Germany, as an impurity in zinc carbonate.

Cadmium occurs as a minor component in most zinc ores and therefore is a byproduct of zinc production. It was used for a long time as a pigment and for corrosion resistant plating on steel while cadmium compounds were used to stabilize plastic.

With the exception of its use in nickel–cadmium batteries and cadmium telluride solar panels, the use of cadmium is generally decreasing. These declines have been due to competing technologies, cadmium's toxicity in certain forms and concentration and resulting regulations. Although cadmium has no known biological function in higher organisms, a cadmium-dependent carbonic anhydrase has been found in marine diatoms.

### Characteristics

#### Physical Properties

Cadmium is a soft, malleable, ductile, bluish-white divalent metal. It is similar in many respects to zinc but forms complex compounds. Unlike other metals, cadmium is resistant to corrosion and as a result it is used as a protective layer when deposited on other metals. As a bulk metal, cadmium is insoluble in water and is not flammable; however, in its powdered form it may burn and release toxic fumes.

#### Chemical Properties

Although cadmium usually has an oxidation state of +2, it also exists in the +1 state. Cadmium and its congeners are not always considered transition metals, in that they do not have partly filled d or f electron shells in the elemental or common oxidation states. Cadmium burns in air to form brown amorphous cadmium oxide (CdO); the crystalline form of this compound is a dark red which changes color when heated, similar to zinc oxide.

Hydrochloric acid, sulfuric acid and nitric acid dissolve cadmium by forming cadmium chloride (CdCl<sub>2</sub>), cadmium sulfate (CdSO<sub>4</sub>), or cadmium nitrate (Cd(NO<sub>3</sub>)<sub>2</sub>). The oxidation state +1 can be reached by dissolving cadmium in a mixture of cadmium chloride and aluminum chloride, forming the Cd<sub>2</sub><sup>2+</sup> cation, which is similar to the Hg<sub>2</sub><sup>2+</sup> cation in mercury(I) chloride.



## Isotopes

Naturally occurring cadmium is composed of 8 isotopes. Two of them are naturally radioactive, and three are expected to decay but have not been experimentally confirmed to do so. The two natural radioactive isotopes are  $^{113}\text{Cd}$  (beta decay, half-life is  $7.7 \times 10^{15}$  years) and  $^{116}\text{Cd}$  (two-neutrino double beta decay, half-life is  $2.9 \times 10^{19}$  years). The other three are  $^{106}\text{Cd}$ ,  $^{108}\text{Cd}$  (both double electron capture), and  $^{114}\text{Cd}$  (double beta decay); only lower limits on their half-life times have been set. At least three isotopes –  $^{110}\text{Cd}$ ,  $^{111}\text{Cd}$ , and  $^{112}\text{Cd}$  – are stable.

Among the isotopes that do not occur naturally, the most long-lived are  $^{109}\text{Cd}$  with a half-life of 462.6 days, and  $^{115}\text{Cd}$  with a half-life of 53.46 hours. All of the remaining radioactive isotopes have half-lives that are less than 2.5 hours, and the majority of these have half-lives that are less than 5 minutes. Cadmium has 8 known meta states, with the most stable being  $^{113\text{m}}\text{Cd}$  ( $t_{1/2} = 14.1$  years),  $^{115\text{m}}\text{Cd}$  ( $t_{1/2} = 44.6$  days), and  $^{117\text{m}}\text{Cd}$  ( $t_{1/2} = 3.36$  hours).

The known isotopes of cadmium range in atomic mass from 94.950 u ( $^{95}\text{Cd}$ ) to 131.946 u ( $^{132}\text{Cd}$ ). For isotopes lighter than 112 u, the primary decay mode is electron capture and the dominant decay product is element 47 (silver).

Heavier isotopes decay mostly through beta emission producing element 49 (indium).

One isotope of cadmium,  $^{113}\text{Cd}$ , absorbs neutrons with very high probability if they have an energy below the *cadmium cut-off* and transmits them otherwise. The cadmium cut-off is about 0.5 eV. Neutrons with energy below the cut-off are deemed slow neutrons, distinguishing them from intermediate and fast neutrons.

Cadmium is created via the long s-process in low-medium mass stars with masses of 0.6 to 10 solar masses, which lasts thousands of years. It requires a silver atom to capture a neutron and then undergo beta decay.

Cadmium makes up about 0.1 ppm of the Earth's crust. Compared with the more abundant 65 ppm zinc, cadmium is rare. No significant deposits of cadmium-containing ores are known. Greenockite (CdS), the only cadmium mineral of importance, is nearly always associated with sphalerite (ZnS).

This association is caused by the geochemical similarity between zinc and cadmium which makes geological separation unlikely. As a consequence, cadmium is produced mainly as a byproduct from mining, smelting, and refining sulfidic ores of zinc, and, to a lesser degree, lead and copper.

Small amounts of cadmium, about 10% of consumption, are produced from secondary sources, mainly from dust generated by recycling iron and steel scrap. Production in the United States began in 1907, but it was not until after World War I that cadmium came into wide use. One place where metallic cadmium can be found is the Vilyuy River basin in Siberia.

Rocks mined to produce phosphate fertilizers contain varying amounts of cadmium, leading to a cadmium concentration of up to 300 mg/kg in the produced phosphate fertilizers and thus in the high cadmium content in agricultural soils. Coal can contain significant amounts of cadmium, which ends up mostly in the flue dust.



## Chromium- Inorganic Contaminant 0.1 mg/L MCL

The Safe Drinking Water Act requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based on possible health risks from exposure over a lifetime, are called maximum contaminant level goals (MCLG).

EPA sets enforceable standards for drinking water contaminants based on the best available science to prevent potential health problems. In most cases, the enforceable standard is known as a maximum contaminant level (MCL), the maximum permissible level of a contaminant in water which is delivered to any user of a public water system. MCLs are set as close to the health goals as possible after considering costs, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies.

The national primary drinking water regulation that established the MCL for total chromium was promulgated in 1991. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed total chromium as part of the second six-year review that was announced in March 2010.



The Agency noted in March 2010 that it had initiated a reassessment of the health risks associated with chromium exposure and that the Agency did not believe it was appropriate to revise the national primary drinking water regulation while that effort was in process. In 2008, EPA began a rigorous and comprehensive review of chromium-6 health effects based on new science. When this human health assessment is finalized EPA will carefully review the conclusions and consider all relevant information to determine if the current chromium standard should be revised

Ensuring safe drinking water for all Americans is a top priority for EPA. EPA has an enforceable drinking water standard of 0.1 milligrams per liter (mg/L) for total chromium, which includes chromium-6 and chromium-3. This standard was established in 1991 and was based on the best available science at the time which indicated that some people who use water containing chromium in excess of the drinking water standard over many years could experience allergic dermatitis (skin reactions).

EPA regularly re-evaluates drinking water standards and, based on new science on chromium-6, had begun a rigorous and comprehensive review of its health effects in 2008. In September 2010, EPA released a draft of that scientific assessment for public comment. When this human health assessment is finalized, EPA will carefully review the conclusions and consider all relevant information to determine if a new drinking water standard for chromium-6 or a revision to the current total chromium standard is warranted.

Chromium is an odorless and tasteless metallic element. Chromium is found naturally in rocks, plants, soil and volcanic dust, humans and animals. The most common forms of chromium that occur in natural waters in the environment are trivalent chromium (chromium-3), and hexavalent chromium (chromium-6).

Chromium-3 is an essential human dietary element and occurs naturally in many vegetables, fruits, meats, grains and yeast. Chromium-6 occurs naturally in the environment from the erosion of natural chromium deposits but it can also be produced by industrial processes. There are demonstrated instances of chromium being released to the environment by leakage, poor storage, or inadequate industrial waste disposal practices.

### **What are some uses for Chromium?**

Metallic chromium is used mainly for making steel and other alloys. Chromium compounds in either the chromium-3 or chromium-6 forms are used for chrome plating, dyes and pigments, leather and wood preservation.

### **What are Chromium's Health Effects?**

Chromium-3 is a nutritionally essential element in humans and is often added to vitamins as a dietary supplement. Chromium-3 has relatively low toxicity and would be a concern in drinking water only at very high levels of contamination; Chromium-6 is more toxic and poses potential health risks. People who use water containing total chromium in excess of the maximum contaminant level (MCL) over many years could experience allergic dermatitis.

EPA proposed to classify chromium-6 as likely to be carcinogenic to humans when ingested. The Agency continues to work towards completing the human health assessment and making a final determination about the carcinogenicity of chromium-6. When the assessment is completed, EPA will determine whether the drinking water standard for total chromium needs to be revised.

### **What are EPA's drinking water regulations for Chromium?**

The Safe Drinking Water Act requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based on possible health risks from exposure over a lifetime are called maximum contaminant level goals (MCLG).

The MCLG for total chromium is 0.1 mg/L or 100 parts per billion (ppb). EPA has set this level of protection based on the best available science at the time the rule was promulgated. EPA has set an enforceable regulation for total chromium, called a maximum contaminant level (MCL), at 0.1 mg/L or 100 ppb. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies.

In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation. States may set more stringent drinking water MCLGs and MCLs for total chromium than EPA.

### **Why are Chromium-6 and Chromium-3 covered in the same Standard?**

Chromium-6 and chromium-3 are covered under the total chromium drinking water standard because these forms of chromium can convert back and forth in water and in the human body, depending on environmental conditions.

Measuring just one form may not capture all of the chromium that is present. In order to ensure that the greatest potential risk is addressed, EPA's regulation assumes that a measurement of total chromium is 100 percent chromium-6, the more toxic form.

### **How often does the EPA update the Total Chromium Drinking Water Standard?**

The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed total chromium as part of the second six-year review that was announced in March 2010. The Agency noted in March 2010 that it had initiated a reassessment of the health risks associated with chromium exposure and that the Agency did not believe it was appropriate to revise the national primary drinking water regulation while that effort was in process.

In 2008, EPA began a rigorous and comprehensive review of chromium-6 health effects based on new science. When this human health assessment is finalized EPA will carefully review the conclusions and consider all relevant information to determine if the current chromium standard should be revised.

## **Chromium Explained**

### **Chromium Description**

Chromium is a chemical element which has the symbol **Cr** and atomic number 24. It is the first element in Group 6. It is a steely-gray, lustrous, hard metal that takes a high polish and has a high melting point. It is also odorless, tasteless, and malleable. The name of the element is derived from the Greek word "chrōma" (χρῶμα), meaning color, because many of its compounds are intensely colored.

Chromium oxide was used by the Chinese in the Qin dynasty over 2,000 years ago to coat metal weapons found with the Terracotta Army. Chromium was discovered as an element after it came to the attention of the western world in the red crystalline mineral crocoite (lead(II) chromate), discovered in 1761 and initially used as a pigment. Louis Nicolas Vauquelin first isolated chromium metal from this mineral in 1797.

Since Vauquelin's first production of metallic chromium, small amounts of native (free) chromium metal have been discovered in rare minerals, but these are not used commercially. Instead, nearly all chromium is commercially extracted from the single commercially viable ore chromite, which is iron chromium oxide ( $\text{FeCr}_2\text{O}_4$ ). Chromite is also now the chief source of chromium for chromium pigments. Chromium metal and ferrochromium alloy are commercially produced from chromite by silicothermic or aluminothermic reactions, or by roasting and leaching processes.

Chromium metal has proven of high value due to its high corrosion resistance and hardness. A major development was the discovery that steel could be made highly resistant to corrosion and discoloration by adding metallic chromium to form stainless steel. This application, along with chrome plating (electroplating with chromium) currently comprise 85% of the commercial use for the element, with applications for chromium compounds forming the remainder.

Trivalent chromium (Cr(III)) ion is possibly required in trace amounts for sugar and lipid metabolism, although the issue remains in debate. In larger amounts and in different forms, chromium can be toxic and carcinogenic. The most prominent example of toxic chromium is hexavalent chromium (Cr(VI)). Abandoned chromium production sites often require environmental cleanup.

## Characteristics

### Physical

Chromium is remarkable for its magnetic properties: it is the only elemental solid which shows antiferromagnetic ordering at room temperature (and below). Above 38 °C, it transforms into a paramagnetic state.

### Passivation

Chromium metal left standing in air is passivated by oxygen, forming a thin protective oxide surface layer. This layer is a spinel structure only a few atoms thick. It is very dense, and prevents the diffusion of oxygen into the underlying material. This barrier is in contrast to iron or plain carbon steels, where the oxygen migrates into the underlying material and causes rusting.

The passivation can be enhanced by short contact with oxidizing acids like nitric acid. Passivated chromium is stable against acids. The opposite effect can be achieved by treatment with a strong reducing agent that destroys the protective oxide layer on the metal. Chromium metal treated in this way readily dissolves in weak acids.

Chromium, unlike metals such as iron and nickel, does not suffer from hydrogen embrittlement. However, it does suffer from nitrogen embrittlement, reacting with nitrogen from air and forming brittle nitrides at the high temperatures necessary to work the metal parts.

### Occurrence

Chromium is the 24th most abundant element in Earth's crust with an average concentration of 100 ppm. Chromium compounds are found in the environment, due to erosion of chromium-containing rocks and can be distributed by volcanic eruptions. The concentrations range in soil is between 1 and 3000 mg/kg, in sea water 5 to 800 µg/liter, and in rivers and lakes 26 µg/liter to 5.2 mg/liter. Chromium is mined as chromite ( $\text{FeCr}_2\text{O}_4$ ) ore. About two-fifths of the chromite ores and concentrates in the world are produced in South Africa, while Kazakhstan, India, Russia, and Turkey are also substantial producers. Untapped chromite deposits are plentiful, but geographically concentrated in Kazakhstan and southern Africa.

Although rare, deposits of native chromium exist. The Udachnaya Pipe in Russia produces samples of the native metal. This mine is a kimberlite pipe, rich in diamonds, and the reducing environment helped produce both elemental chromium and diamond.

The relation between Cr(III) and Cr(VI) strongly depends on pH and oxidative properties of the location, but in most cases, the Cr(III) is the dominating species, although in some areas the ground water can contain up to 39 µg/liter of total chromium of which 30 µg/liter is present as Cr(VI).

### Isotopes

Naturally occurring chromium is composed of three stable isotopes;  $^{52}\text{Cr}$ ,  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$  with  $^{52}\text{Cr}$  being the most abundant (83.789% natural abundance). 19 radioisotopes have been characterized with the most stable being  $^{50}\text{Cr}$  with a half-life of (more than)  $1.8 \times 10^{17}$  years, and  $^{51}\text{Cr}$  with a half-life of 27.7 days. All of the remaining radioactive isotopes have half-lives that are less than 24 hours and the majority of these have half-lives that are less than 1 minute. This element also has 2 meta states.

$^{53}\text{Cr}$  is the radiogenic decay product of  $^{53}\text{Mn}$ . Chromium isotopic contents are typically combined with manganese isotopic contents and have found application in isotope geology.

Mn-Cr isotope ratios reinforce the evidence from  $^{26}\text{Al}$  and  $^{107}\text{Pd}$  for the early history of the solar system. Variations in  $^{53}\text{Cr}/^{52}\text{Cr}$  and Mn/Cr ratios from several meteorites indicate an initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio that suggests Mn-Cr isotopic composition must result from in-situ decay of  $^{53}\text{Mn}$  in differentiated planetary bodies. Hence  $^{53}\text{Cr}$  provides additional evidence for nucleosynthetic processes immediately before coalescence of the solar system.

The isotopes of chromium range in atomic mass from 43 u ( $^{43}\text{Cr}$ ) to 67 u ( $^{67}\text{Cr}$ ). The primary decay mode before the most abundant stable isotope,  $^{52}\text{Cr}$ , is electron capture and the primary mode after is beta decay.  $^{53}\text{Cr}$  has been posited as a proxy for atmospheric oxygen concentration

### Chromium (III)

A large number of chromium(III) compounds are known. Chromium(III) can be obtained by dissolving elemental chromium in acids like hydrochloric acid or sulfuric acid. The  $\text{Cr}^{3+}$  ion has a similar radius (63 pm) to the  $\text{Al}^{3+}$  ion (radius 50 pm), so they can replace each other in some compounds, such as in chrome alum and alum. When a trace amount of  $\text{Cr}^{3+}$  replaces  $\text{Al}^{3+}$  in corundum (aluminum oxide,  $\text{Al}_2\text{O}_3$ ), the red-colored ruby is formed.

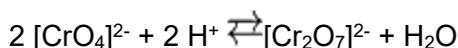
Chromium(III) ions tend to form octahedral complexes. The colors of these complexes is determined by the ligands attached to the Cr center. The commercially available chromium(III) chloride hydrate is the dark green complex  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}$ . Closely related compounds have different colors: pale green  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2$  and the violet  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ .

If water-free green chromium(III) chloride is dissolved in water then the green solution turns violet after some time, due to the substitution of water by chloride in the inner coordination sphere. This kind of reaction is also observed with solutions of chrome alum and other water-soluble chromium(III) salts.

Chromium(III) hydroxide ( $\text{Cr}(\text{OH})_3$ ) is amphoteric, dissolving in acidic solutions to form  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , and in basic solutions to form  $[\text{Cr}(\text{OH})_6]^{3-}$ . It is dehydrated by heating to form the green chromium(III) oxide ( $\text{Cr}_2\text{O}_3$ ), which is the stable oxide with a crystal structure identical to that of corundum.

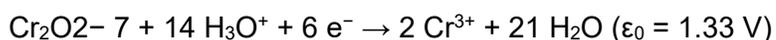
### Chromium(VI)

Chromium(VI) compounds are powerful oxidants at low or neutral pH. Most important are chromate anion ( $\text{CrO}_4^{2-}$ ) and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) anions, which exist in equilibrium:



Chromium(VI) halides are known also and include the hexafluoride  $\text{CrF}_6$  and chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ). Sodium chromate is produced industrially by the oxidative roasting of chromite ore with calcium or sodium carbonate. The dominant species is therefore, by the law of mass action, determined by the pH of the solution. The change in equilibrium is visible by a change from yellow (chromate) to orange (dichromate), such as when an acid is added to a neutral solution of potassium chromate. At yet lower pH values, further condensation to more complex oxyanions of chromium is possible.

Both the chromate and dichromate anions are strong oxidizing reagents at low pH:  
Sodium chromate ( $\text{Na}_2\text{CrO}_4$ )



They are, however, only moderately oxidizing at high pH:



Chromium(VI) compounds in solution can be detected by adding an acidic hydrogen peroxide solution. The unstable dark blue chromium(VI) peroxide ( $\text{CrO}_5$ ) is formed, which can be stabilized as an ether adduct  $\text{CrO}_5 \cdot \text{OR}_2$ .

Chromic acid has the hypothetical formula  $\text{H}_2\text{CrO}_4$ . It is a vaguely described chemical, despite many well-defined chromates and dichromates are known. The dark red chromium(VI) oxide  $\text{CrO}_3$ , the acid anhydride of chromic acid, is sold industrially as "chromic acid". It can be produced by mixing sulfuric acid with dichromate, and is a strong oxidizing agent.

### Chromium(V) and chromium(IV)

The oxidation state +5 is only realized in few compounds but are intermediates in many reactions involving oxidations by chromate. The only binary compound is the volatile chromium(V) fluoride ( $\text{CrF}_5$ ). This red solid has a melting point of  $30^\circ\text{C}$  and a boiling point of  $117^\circ\text{C}$ . It can be synthesized by treating chromium metal with fluorine at  $400^\circ\text{C}$  and 200 bar pressure. The peroxochromate(V) is another example of the +5 oxidation state. Potassium peroxochromate ( $\text{K}_3[\text{Cr}(\text{O}_2)_4]$ ) is made by reacting potassium chromate with hydrogen peroxide at low temperatures. This red brown compound is stable at room temperature but decomposes spontaneously at  $150\text{--}170^\circ\text{C}$ .

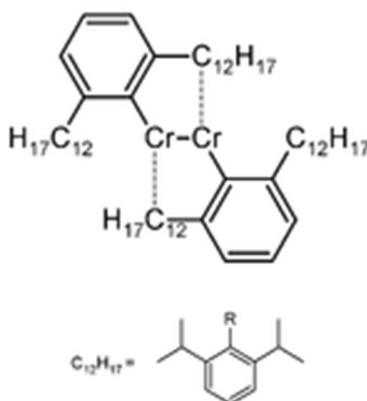
Compounds of chromium(IV) (in the +4 oxidation state) are slightly more common than those of chromium(V). The tetrahalides,  $\text{CrF}_4$ ,  $\text{CrCl}_4$ , and  $\text{CrBr}_4$ , can be produced by treating the trihalides ( $\text{CrX}_3$ ) with the corresponding halogen at elevated temperatures. Such compounds are susceptible to disproportionation reactions and are not stable in water.

### Chromium(II)

Many chromium(II) compounds are known, including the water-stable chromium(II) chloride,  $\text{CrCl}_2$ , which can be made by reduction of chromium(III) chloride with zinc. The resulting bright blue solution is only stable at neutral pH. Many chromous carboxylates are also known, most famously, the red chromous acetate ( $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ ), which features a quadruple bond.

### Chromium(I)

Most Cr(I) compounds are obtained by oxidation of electron-rich, octahedral Cr(0) complexes. Other Cr(I) complexes contain cyclopentadienyl ligands. As verified by X-ray diffraction, a Cr-Cr quintuple bond (length  $183.51(4) \text{ pm}$ ) has also been described. Extremely bulky monodentate ligands stabilize this compound by shielding the quintuple bond from further reactions.



Chromium compound determined experimentally to contain a Cr-Cr quintuple bond

### **Chromium(0)**

Many chromium(0) compounds are known. Most are derivatives of chromium hexacarbonyl or bis(benzene)chromium.

### **What are EPA's Drinking Water Regulations for Chromium (total)?**

EPA has a drinking water standard of 0.1 milligrams per liter (mg/L) or 100 parts per billion (ppb) for total chromium, which includes all forms of chromium including chromium-6. Water systems are required to test for total chromium. The current standard is based on potential adverse dermatological effects over many years, such as allergic dermatitis (skin reactions). EPA regularly re-evaluates drinking water standards and, based on new science on chromium-6, began a rigorous and comprehensive review of its health effects in 2008.

### **Is Total Chromium or Chromium-6 in Drinking Water a Health Concern?**

The current federal drinking water standard for total chromium is 0.1 mg/L or 100 ppb. Chromium-6 and chromium-3 are covered under the total chromium drinking water standard because these forms of chromium can convert back and forth in water and in the human body, depending on environmental conditions. Measuring just one form may not capture all of the chromium that is present. In order to ensure that the greatest potential risk is addressed, EPA's regulation assumes that a measurement of total chromium is 100 percent chromium-6, the more toxic form. If tap water from a public water system exceeds this federal standard, consumers will be notified.

The MCL for total chromium was established in 1991 and is based on the best available science at the time which indicated that continued exposure to chromium-6 could result in allergic dermatitis (skin reactions). EPA is now reviewing data from a 2008 long-term animal study by the Department of Health and Human Service's National Toxicology Program, which suggested that chromium-6 may be a human carcinogen if ingested. When the review is completed, EPA will consider this and other information to determine whether the drinking water standard for total chromium needs to be revised.

### **If EPA decides to revise the Regulation that includes Chromium-6 in Drinking Water, what is the process the agency will follow?**

Prior to EPA making any decisions about revising the chromium drinking water regulation, EPA must issue its final human health assessment for chromium-6. EPA will carefully review the final assessment and consider all other relevant information to determine if a new drinking water regulation for chromium-6 or a revision to the current total chromium standard is warranted.

### **How does Chromium get into my Drinking Water?**

The most common forms of chromium that occur in natural waters in the environment are chromium-3 and chromium-6. Chromium-3 and chromium-6 occur naturally in the environment, and are present in water from the erosion of chromium deposits found in rocks and soils. Chromium-6 is also produced by industrial processes and manufacturing activities including discharges from steel and pulp mills among others. At many locations, chromium compounds have been released to the environment via leakage, poor storage, or improper disposal practices. Chromium compounds are very persistent in water as sediments.

A federal law called the Emergency Planning and Community Right to Know Act requires facilities in certain industries, which manufacture, process, or use significant amounts of toxic chemicals, to report annually on their releases of these chemicals.

For more information on the uses and releases of chemicals in your state, contact the community right-to-know hotline at (800) 424-9346.

### **How will I know if there is Chromium in my Drinking Water?**

Your public water system's annual water quality report will provide information if total chromium is detected in the drinking water it delivers. The water quality report is sent to customers by July 1 of each year and may also be found on your public water system's website. Some water utilities have conducted monitoring specifically for chromium-6. Contact your public water system to find out if this information is available.

Consumers served by private wells can have their water tested by a state certified laboratory. You can find information on how to sample for chromium-6 and where to send samples by contacting your state water laboratory certification officer.

### **What should I do if I am concerned about the Presence of Chromium-6 in my Drinking Water while EPA is reviewing the Science and the Regulation?**

If you remain concerned after finding out more about the chromium-6 levels in your drinking water, you may consider taking additional steps.

### **Can home treatment devices remove chromium-6?**

Some home treatment devices are certified by organizations to remove chromium-6. Two certification organizations are: NSF International and the Water Quality Association. These certification programs are based on current drinking water standards and home treatment devices are only certified to remove chromium-6 to either 50 or 100 parts per billion.

Contact the device's manufacturer for specific information about how effective the product is, given your water and treatment goal. Your public water system's water quality report and your water system's staff can help you understand the characteristics of your water.

If you choose to use a home treatment device, it is very important to follow the manufacturer's operation and maintenance instructions carefully in order to make sure the device works properly.

Consumers should be aware that the current EPA drinking water standard for chromium requires that public water systems provide drinking water that does not exceed a total chromium concentration of 100 ppb.

### **Can I avoid exposure to chromium-6 if I only Drink Bottled Water? (Is there Chromium-6 in bottled water?)**

The Food and Drug Administration (FDA) establishes standards for bottled water and has adopted EPA's total chromium standard of 100 ppb. Contact bottled water manufacturers for specific information about levels of chromium-6 in their products.

### **How do I learn more about my Drinking Water?**

EPA strongly encourages people to learn more about their drinking water, and to support local efforts to provide safe drinking water. Your water bill or telephone book's government listings are a good starting point for local information. Check your water system provider's website or contact your water provider. EPA requires all community water systems to prepare and deliver an annual consumer confidence report, sometimes called a water quality report, to their customers by July 1 of each year.

## Copper - Inorganic Contaminant 1.3 mg/L MCLG

### What are Copper's Health Effects?

Some people who drink water containing copper in excess of the action level may, with short term exposure, experience gastrointestinal distress, and with long-term exposure may experience liver or kidney damage. People with Wilson's Disease should consult their personal doctor if the amount of copper in their water exceeds the action level.

This health effects language is not intended to catalog all possible health effects for copper. Rather, it is intended to inform consumers of some of the possible health effects associated with copper in drinking water when the rule was finalized.



### What are EPA's Drinking Water Regulations for Copper?

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for copper is 1.3 mg/L or 1.3 ppm. EPA has set this level of protection based on the best available science to prevent potential health problems.

For most contaminants, EPA sets an enforceable regulation called a maximum contaminant level (MCL) based on the MCLG. MCLs are set as close to the MCLGs as feasible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies.

However, because copper contamination of drinking water often results from corrosion of the plumbing materials belonging to water system customers, EPA established a treatment technique rather than an MCL for copper.

A treatment technique is an enforceable procedure or level of technological performance which water systems must follow to ensure control of a contaminant. The treatment technique regulation for copper (referred to as the Lead and Copper rule) requires water systems to control the corrosivity of the water.

The regulation also requires systems to collect tap samples from sites served by the system that are more likely to have plumbing materials containing lead. If more than 10 percent of tap water samples exceed the copper action level of 1.3 milligrams per Liter (mg/L), water systems must take additional steps to reduce corrosiveness.

EPA promulgated the Lead and Copper Rule in 1991, and revised the regulation in 2000 and in 2007. States may set a more stringent regulation for copper in drinking water than EPA.

### **How does Copper get into my Drinking Water?**

The major sources of copper in drinking water are corrosion of household plumbing systems; and erosion of natural deposits. Copper enters the water (“leaches”) through contact with the plumbing. Copper leaches into water through corrosion – a dissolving or wearing away of metal caused by a chemical reaction between water and your plumbing.

Copper can leach into water primarily from pipes, but fixtures and faucets (brass), and fittings can also be a source. The amount of copper in your water also depends on the types and amounts of minerals in the water, how long the water stays in the pipes, the amount of wear in the pipes, the water’s acidity and its temperature.

### **How will I know if Copper is in my Drinking Water?**

If you are concerned about copper in your drinking water, have the water tested for copper by a certified laboratory. (Lists are available from your state or local drinking water authority.) Since you cannot see, taste, or smell copper dissolved in water, testing is the only sure way of telling whether there are harmful quantities of lead in your drinking water. You should be particularly suspicious if your home has copper pipes.

If you see signs of corrosion (frequent leaks, rust-colored water, stained dishes or laundry, or if your non-plastic plumbing is less than five years old. Your water supplier may have useful information, including whether the service connector used in your home or area is made of copper. Testing is especially important in high-rise buildings where flushing might not work.

If your water comes from a household well, check with your health department or local water systems that use ground water for information on contaminants of concern in your area.

### **How will Copper be removed from my Drinking Water?**

The following treatment method(s) have proven to be effective for removing copper to below the action level of 1.3 mg/L or 1.3 ppm: corrosion control.

### **How do I learn more about my Drinking Water?**

EPA strongly encourages people to learn more about their drinking water, and to support local efforts to protect the supply of safe drinking water and upgrade the community water system. Your water bill or telephone book’s government listings are a good starting point for local information.

Contact your water utility. EPA requires all community water systems to prepare and deliver an annual consumer confidence report (CCR) (sometimes called a water quality report) for their customers by July 1 of each year. If your water provider is not a community water system, or if you have a private water supply, request a copy from a nearby community water system.

### **Copper Explained**

**Copper** is a chemical element with the symbol **Cu** (from Latin: *cuprum*) and atomic number 29. It is a ductile metal with very high thermal and electrical conductivity. Pure copper is soft and malleable; a freshly exposed surface has a reddish-orange color. It is used as a conductor of heat and electricity, a building material, and a constituent of various metal alloys.

The metal and its alloys have been used for thousands of years. In the Roman era, copper was principally mined on Cyprus, hence the origin of the name of the metal as *cuprium* (metal of Cyprus), later shortened to *cuprum*.

Its compounds are commonly encountered as copper(II) salts, which often impart blue or green colors to minerals such as turquoise and have been widely used historically as pigments.

Architectural structures built with copper corrode to give green verdigris (or patina). Decorative art prominently features copper, both by itself and as part of pigments.

Copper(II) ions are water-soluble, where they function at low concentration as bacteriostatic substances, fungicides, and wood preservatives. In sufficient amounts, they are poisonous to higher organisms; at lower concentrations it is an essential trace nutrient to all higher plant and animal life. The main areas where copper is found in animals are liver, muscle and bone.

## Characteristics

### Physical

Copper, silver and gold are in group 11 of the periodic table, and they share certain attributes: they have one s-orbital electron on top of a filled d-electron shell and are characterized by high ductility and electrical conductivity. The filled d-shells in these elements do not contribute much to the interatomic interactions, which are dominated by the s-electrons through metallic bonds. Contrary to metals with incomplete d-shells, metallic bonds in copper are lacking a covalent character and are relatively weak. This explains the low hardness and high ductility of single crystals of copper. At the macroscopic scale, introduction of extended defects to the crystal lattice, such as grain boundaries, hinders flow of the material under applied stress thereby increasing its hardness. For this reason, copper is usually supplied in a fine-grained polycrystalline form, which has greater strength than monocrystalline forms.

The low hardness of copper partly explains its high electrical ( $59.6 \times 10^6$  S/m) and thus also high thermal conductivity, which are the second highest among pure metals at room temperature. This is because the resistivity to electron transport in metals at room temperature mostly originates from scattering of electrons on thermal vibrations of the lattice, which are relatively weak for a soft metal. The maximum permissible current density of copper in open air is approximately  $3.1 \times 10^6$  A/m<sup>2</sup> of cross-sectional area, above which it begins to heat excessively. As with other metals, if copper is placed against another metal, galvanic corrosion will occur.

Together with caesium and gold (both yellow), copper is one of only three elemental metals with a natural color other than gray or silver. Pure copper is orange-red and acquires a reddish tarnish when exposed to air. The characteristic color of copper results from the electronic transitions between the filled 3d and half-empty 4s atomic shells – the energy difference between these shells is such that it corresponds to orange light. The same mechanism accounts for the yellow color of gold and caesium.

### Chemical

Copper forms a rich variety of compounds with oxidation states +1 and +2, which are often called *cuprous* and *cupric*, respectively. It does not react with water, but it slowly reacts with atmospheric oxygen forming a layer of brown-black copper oxide. In contrast to the oxidation of iron by wet air, this oxide layer stops the further, bulk corrosion. A green layer of verdigris (copper carbonate) can often be seen on old copper constructions, such as the Statue of Liberty, the largest copper statue in the world built using repoussé and chasing. Hydrogen sulfides and sulfides react with copper to form various copper sulfides on the surface. In the latter case, the copper corrodes, as is seen when copper is exposed to air containing sulfur compounds.

Oxygen-containing ammonia solutions give water-soluble complexes with copper, as do oxygen and hydrochloric acid to form copper chlorides and acidified hydrogen peroxide to form copper(II) salts. Copper(II) chloride and copper comproportionate to form copper(I) chloride.

## Isotopes

There are 29 isotopes of copper.  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  are stable, with  $^{63}\text{Cu}$  comprising approximately 69% of naturally occurring copper; they both have a spin of 3/2. The other isotopes are radioactive, with the most stable being  $^{67}\text{Cu}$  with a half-life of 61.83 hours. Seven metastable isotopes have been characterized, with  $^{68\text{m}}\text{Cu}$  the longest-lived with a half-life of 3.8 minutes. Isotopes with a mass number above 64 decay by  $\beta^-$ , whereas those with a mass number below 64 decay by  $\beta^+$ .  $^{64}\text{Cu}$ , which has a half-life of 12.7 hours, decays both ways.

$^{62}\text{Cu}$  and  $^{64}\text{Cu}$  have significant applications.  $^{64}\text{Cu}$  is a radiocontrast for X-ray imaging, and complexed with a chelate can be used for treating cancer.  $^{62}\text{Cu}$  is used in  $^{62}\text{Cu}$ -PTSM that is a radioactive tracer for positron emission tomography.

## Occurrence

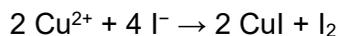
Copper can be found as either native copper or as part of minerals. Native copper is a polycrystal, with the largest described single crystal measuring 4.4×3.2×3.2 cm. The largest mass of elemental copper weighed 420 tons and was found in 1857 on the Keweenaw Peninsula in Michigan, US. There are many examples of copper-containing minerals: chalcopyrite and chalcocite are copper sulfides, azurite and malachite are copper carbonates and cuprite is a copper oxide. Copper is present in the Earth's crust at a concentration of about 50 parts per million (ppm), and is also synthesized in massive stars.

## Compounds

### Binary Compounds

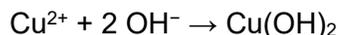
As for other elements, the simplest compounds of copper are binary compounds, i.e. those containing only two elements. The principal ones are the oxides, sulfides and halides. Both cuprous and cupric oxides are known. Among the numerous copper sulfides, important examples include copper(I) sulfide and copper(II) sulfide.

The cuprous halides with chlorine, bromine, and iodine are known, as are the cupric halides with fluorine, chlorine, and bromine. Attempts to prepare copper(II) iodide give cuprous iodide and iodine.

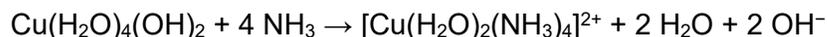


### Coordination Chemistry

Copper, like all metals, forms coordination complexes with ligands. In aqueous solution, copper(II) exists as  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . This complex exhibits the fastest water exchange rate (speed of water ligands attaching and detaching) for any transition metal aquo complex. Adding aqueous sodium hydroxide causes the precipitation of light blue solid copper(II) hydroxide. A simplified equation is:



Aqueous ammonia results in the same precipitate. Upon adding excess ammonia, the precipitate dissolves, forming tetraamminecopper(II):



Many other oxyanions form complexes; these include copper(II) acetate, copper(II) nitrate, and copper(II) carbonate. Copper(II) sulfate forms a blue crystalline pentahydrate, which is the most familiar copper compound in the laboratory. It is used in a fungicide called the Bordeaux mixture.

Polyols, compounds containing more than one alcohol functional group, generally interact with cupric salts. For example, copper salts are used to test for reducing sugars. Specifically, using Benedict's reagent and Fehling's solution the presence of the sugar is signaled by a color change from blue Cu(II) to reddish copper(I) oxide. Schweizer's reagent and related complexes with ethylenediamine and other amines dissolve cellulose. Amino acids form very stable chelate complexes with copper(II). Many wet-chemical tests for copper ions exist, one involving potassium ferrocyanide, which gives a brown precipitate with copper(II) salts.

### Organocopper Chemistry

Compounds that contain a carbon-copper bond are known as organocopper compounds. They are very reactive towards oxygen to form copper(I) oxide and have many uses in chemistry. They are synthesized by treating copper(I) compounds with Grignard reagents, terminal alkynes or organolithium reagents; in particular, the last reaction described produces a Gilman reagent. These can undergo substitution with alkyl halides to form coupling products; as such, they are important in the field of organic synthesis.

Copper(I) acetylide is highly shock-sensitive but is an intermediate in reactions such as the Cadiot-Chodkiewicz coupling and the Sonogashira coupling. Conjugate addition to enones and carbocupration of alkynes can also be achieved with organocopper compounds. Copper(I) forms a variety of weak complexes with alkenes and carbon monoxide, especially in the presence of amine ligands.

### Copper (III) and Copper (IV)

Copper(III) is most characteristically found in oxides. A simple example is potassium cuprate,  $\text{KCuO}_2$ , a blue-black solid. The best studied copper(III) compounds are the cuprate superconductors. Yttrium barium copper oxide ( $\text{YBa}_2\text{Cu}_3\text{O}_7$ ) consists of both Cu(II) and Cu(III) centers. Like oxide, fluoride is a highly basic anion and is known to stabilize metal ions in high oxidation states. Indeed, both copper(III) and even copper(IV) fluorides are known,  $\text{K}_3\text{CuF}_6$  and  $\text{Cs}_2\text{CuF}_6$ , respectively.

Some copper proteins form oxo complexes, which also feature copper(III). With di- and tripeptides, purple-colored copper(III) complexes are stabilized by the deprotonated amide ligands.

Complexes of copper(III) are also observed as intermediates in reactions of organocopper compounds.

### Biological Role

Rich sources of copper include oysters, beef and lamb liver, Brazil nuts, blackstrap molasses, cocoa, and black pepper. Good sources include lobster, nuts and sunflower seeds, green olives, avocados, and wheat bran.

Copper proteins have diverse roles in biological electron transport and oxygen transportation, processes that exploit the easy interconversion of Cu(I) and Cu(II). The biological role for copper commenced with the appearance of oxygen in earth's atmosphere. The protein hemocyanin is the oxygen carrier in most mollusks and some arthropods such as the horseshoe crab (*Limulus polyphemus*).

Because hemocyanin is blue, these organisms have blue blood, not the red blood found in organisms that rely on hemoglobin for this purpose. Structurally related to hemocyanin are the laccases and tyrosinases. Instead of reversibly binding oxygen, these proteins hydroxylate substrates, illustrated by their role in the formation of lacquers.

Copper is also a component of other proteins associated with the processing of oxygen. In cytochrome c oxidase, which is required for aerobic respiration, copper and iron cooperate in the reduction of oxygen. Copper is also found in many superoxide dismutases, proteins that catalyze the decomposition of superoxides, by converting it (by disproportionation) to oxygen and hydrogen peroxide:



Several copper proteins, such as the "blue copper proteins", do not interact directly with substrates, hence they are not enzymes. These proteins relay electrons by the process called electron transfer.

Photosynthesis functions by an elaborate electron transport chain within the thylakoid membrane. A central "link" in this chain is plastocyanin, a blue copper protein.

### **Dietary Needs**

Copper is an essential trace element in plants and animals, but not some microorganisms. The human body contains copper at a level of about 1.4 to 2.1 mg per kg of body mass. Stated differently, the RDA for copper in normal healthy adults is quoted as 0.97 mg/day and as 3.0 mg/day. Copper is absorbed in the gut, then transported to the liver bound to albumin. After processing in the liver, copper is distributed to other tissues in a second phase.

Copper transport here involves the protein ceruloplasmin, which carries the majority of copper in blood. Ceruloplasmin also carries copper that is excreted in milk, and is particularly well-absorbed as a copper source. Copper in the body normally undergoes enterohepatic circulation (about 5 mg a day, vs. about 1 mg per day absorbed in the diet and excreted from the body), and the body is able to excrete some excess copper, if needed, via bile, which carries some copper out of the liver that is not then reabsorbed by the intestine.

### **Copper-based Disorders**

Because of its role in facilitating iron uptake, copper deficiency can produce anemia-like symptoms, neutropenia, bone abnormalities, hypopigmentation, impaired growth, increased incidence of infections, osteoporosis, hyperthyroidism, and abnormalities in glucose and cholesterol metabolism. Conversely, Wilson's disease causes an accumulation of copper in body tissues.

Severe deficiency can be found by testing for low plasma or serum copper levels, low ceruloplasmin, and low red blood cell superoxide dismutase levels; these are not sensitive to marginal copper status. The "cytochrome c oxidase activity of leucocytes and platelets" has been stated as another factor in deficiency, but the results have not been confirmed by replication.

### **Copper Toxicity**

Gram quantities of various copper salts have been taken in suicide attempts and produced acute copper toxicity in humans, possibly due to redox cycling and the generation of reactive oxygen species that damage DNA. Corresponding amounts of copper salts (30 mg/kg) are toxic in animals. A minimum dietary value for healthy growth in rabbits has been reported to be at least 3 ppm in the diet. However, higher concentrations of copper (100 ppm, 200 ppm, or 500 ppm) in the diet of rabbits may favorably influence feed conversion efficiency, growth rates, and carcass dressing percentages.

Chronic copper toxicity does not normally occur in humans because of transport systems that regulate absorption and excretion. Autosomal recessive mutations in copper transport proteins can disable these systems, leading to Wilson's disease with copper accumulation and cirrhosis of the liver in persons who have inherited two defective genes.

## Cyanide - Inorganic Contaminant 0.2 mg/L MCL

Cyanide is a carbon-nitrogen chemical unit which combines with many organic and inorganic compounds.

### Uses for Cyanide.

The most commonly used form, hydrogen cyanide, is mainly used to make compounds and other synthetic fibers and resins.

### What are Cyanide's Health Effects?

Some people who drink water containing cyanide well in excess of the maximum contaminant level (MCL) for many years could experience nerve damage or problems with their thyroid.

This health effects language is not intended to catalog all possible health effects for cyanide. Rather, it is intended to inform consumers of some of the possible health effects associated with cyanide in drinking water when the rule was finalized.



### What are EPA's Drinking Water Regulations for Cyanide?

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for cyanide is 0.2 mg/L or 200 ppb. EPA has set this level of protection based on the best available science to prevent potential health problems. EPA has set an enforceable regulation for cyanide, called a maximum contaminant level (MCL), at 0.2 mg/L or 200 ppb.

MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.

The Phase V Rule, the regulation for cyanide, became effective in 1994. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate.

EPA reviewed cyanide as part of the Six Year Review and determined that the 0.2 mg/L or 200 ppb MCLG and 0.2 mg/L or 200 ppb MCL for cyanide are still protective of human health. States may set more stringent drinking water MCLGs and MCLs for cyanide than EPA.

### How does Cyanide get into my Drinking Water?

The major source of cyanide in drinking water is discharge from industrial chemical factories.

A federal law called the Emergency Planning and Community Right to Know Act (EPCRA) requires facilities in certain industries, which manufacture, process, or use significant amounts of toxic chemicals, to report annually on their releases of these chemicals. For more information on the uses and releases of chemicals in your state, contact the Community Right-to-Know Hotline: (800) 424-9346.

### **How will I know if Cyanide is in my Drinking Water?**

When routine monitoring indicates that cyanide levels are above the MCL, your water supplier must take steps to reduce the amount of cyanide so that it is below that level. Water suppliers must notify their customers as soon as practical, but no later than 30 days after the system learns of the violation. Additional actions, such as providing alternative drinking water supplies, may be required to prevent serious risks to public health.

If your water comes from a household well, check with your health department or local water systems that use ground water for information on contaminants of concern in your area.

### **How will Cyanide be Removed from my Drinking Water?**

The following treatment method(s) have proven to be effective for removing cyanide to below 0.2 mg/L or 200 ppb: granular activated carbon in combination with packed tower aeration.

### **How do I learn more about my Drinking Water?**

EPA strongly encourages people to learn more about their drinking water, and to support local efforts to protect the supply of safe drinking water and upgrade the community water system. Your water bill or telephone book's government listings are a good starting point for local information.

Contact your water utility. EPA requires all community water systems to prepare and deliver an annual consumer confidence report (CCR) (sometimes called a water quality report) for their customers by July 1 of each year. If your water provider is not a community water system, or if you have a private water supply, request a copy from a nearby community water system.

## **Cyanide Explained**

A **cyanide** is a chemical compound that contains the **cyano group**,  $-C\equiv N$ , which consists of a carbon atom triple-bonded to a nitrogen atom. Cyanides most commonly refer to salts of the anion  $CN^-$ , which is isoelectronic with carbon monoxide and with molecular nitrogen. Most cyanides are highly toxic.

### **Nomenclature and Etymology**

In IUPAC nomenclature, organic compounds that have a  $-C\equiv N$  functional group are called nitriles. Thus, nitriles are organic compounds. An example of a nitrile is  $CH_3CN$ , acetonitrile, also known as methyl cyanide. Nitriles usually do not release cyanide ions. A functional group with a hydroxyl and cyanide bonded to the same carbon is called cyanohydrin. Unlike nitriles, cyanohydrins do release hydrogen cyanide. In inorganic chemistry, salts containing the  $C\equiv N^-$  ion are referred to as **cyanides**.

### **Occurrence and Reactions**

Cyanides are produced by certain bacteria, fungi, and algae and are found in a number of plants. Cyanides are found, although in small amounts, in certain seeds and fruit stones, e.g., those of apple, mango, peach, and bitter almonds. In plants, cyanides are usually bound to sugar molecules in the form of cyanogenic glycosides and defend the plant against herbivores.

Cassava roots (also called manioc), an important potato-like food grown in tropical countries (and the base from which tapioca is made), also contain cyanogenic glycosides.

## Interstellar Medium

The cyanide radical  $\text{CN}\cdot$  has been identified in interstellar space. The cyanide radical (called cyanogen) is used to measure the temperature of interstellar gas clouds.

## Pyrolysis and Combustion Product

Hydrogen cyanide is produced by the combustion or pyrolysis of certain materials under oxygen-deficient conditions. For example, it can be detected in the exhaust of internal combustion engines and tobacco smoke. Certain plastics, especially those derived from acrylonitrile, release hydrogen cyanide when heated or burnt.

## Coordination Chemistry

The cyanide anion is a ligand for many transition metals. The high affinities of metals for this anion can be attributed to its negative charge, compactness, and ability to engage in  $\pi$ -bonding.

### Well-known complexes include:

- hexacyanides  $[\text{M}(\text{CN})_6]^{3-}$  ( $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$ ), which are octahedral in shape;
- the tetracyanides,  $[\text{M}(\text{CN})_4]^{2-}$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ), which are square planar in their geometry;
- the dicyanides  $[\text{M}(\text{CN})_2]^-$  ( $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$ ), which are linear in geometry.

The dye Prussian blue was first accidentally made around 1706, by heating substances containing iron and carbon and nitrogen. Prussian blue consists of an iron-containing compound called "ferrocyanide" ( $[\text{Fe}(\text{CN})_6]^{4-}$ ) meaning "blue substance with iron", from Latin *ferrum* = "iron" and Greek *kyanos* = "(dark) blue". Prussian blue is the deep-blue pigment used in the making of blueprints.

The enzymes called hydrogenases contain cyanide ligands attached to iron in their active sites. The biosynthesis of cyanide in the  $[\text{NiFe}]$ -hydrogenases proceeds from carbamoylphosphate, which converts to cysteinyl thiocyanate, the  $\text{CN}^-$  donor.

## Organic Derivatives

Because of the cyanide anion's high nucleophilicity, cyano groups are readily introduced into organic molecules by displacement of a halide group (e.g., the chloride on methyl chloride). In general, organic cyanides are called nitriles. Thus,  $\text{CH}_3\text{CN}$  can be called methyl cyanide but more commonly is referred to as acetonitrile. In organic synthesis, cyanide is a C-1 synthon; i.e., it can be used to lengthen a carbon chain by one, while retaining the ability to be functionalized.

$\text{RX} + \text{CN}^- \rightarrow \text{RCN} + \text{X}^-$  (nucleophilic substitution) followed by

1.  $\text{RCN} + 2 \text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{NH}_3$  (hydrolysis under reflux with mineral acid catalyst), or
2.  $2 \text{RCN} + \text{LiAlH}_4 + (\text{second step}) 4 \text{H}_2\text{O} \rightarrow 2 \text{RCH}_2\text{NH}_2 + \text{LiAl}(\text{OH})_4$  (under reflux in dry ether, followed by addition of  $\text{H}_2\text{O}$ )

## Manufacture

The principal process used to manufacture cyanides is the Andrussov process in which gaseous hydrogen cyanide is produced from methane and ammonia in the presence of oxygen and a platinum catalyst.



Gaseous hydrogen cyanide may be dissolved in aqueous sodium hydroxide solution to produce sodium cyanide.

## **Toxicity**

Many cyanides are highly toxic. The cyanide anion is an inhibitor of the enzyme cytochrome c oxidase (also known as aa<sub>3</sub>) in the fourth complex of the electron transport chain (found in the membrane of the mitochondria of eukaryotic cells). It attaches to the iron within this protein. The binding of cyanide to this cytochrome prevents transport of electrons from cytochrome c oxidase to oxygen. As a result, the electron transport chain is disrupted, meaning that the cell can no longer aerobically produce ATP for energy. Tissues that depend highly on aerobic respiration, such as the central nervous system and the heart, are particularly affected. This is an example of histotoxic hypoxia.

The most hazardous compound is hydrogen cyanide, which is a gas at ambient temperatures and pressure and can therefore be inhaled. For this reason, an air respirator supplied by an external oxygen source must be worn when working with hydrogen cyanide. Hydrogen cyanide is produced when a solution containing a labile cyanide is made acidic, because HCN is a weak acid. Alkaline solutions are safer to use because they do not evolve hydrogen cyanide gas. Hydrogen cyanide may be produced in the combustion of polyurethanes; for this reason, polyurethanes are not recommended for use in domestic and aircraft furniture. Oral ingestion of a small quantity of solid cyanide or a cyanide solution as little as 200 mg, or to airborne cyanide of 270 ppm is sufficient to cause death within minutes.

Organic nitriles do not readily release cyanide ions, and so have low toxicities. By contrast, compounds such as trimethylsilyl cyanide (CH<sub>3</sub>)<sub>3</sub>SiCN readily release HCN or the cyanide ion upon contact with water.

## **Antidote**

Hydroxocobalamin reacts with cyanide to form cyanocobalamin, which can be safely eliminated by the kidneys. This method has the advantage of avoiding the formation of methemoglobin.

An older cyanide antidote kit included administration of three substances: amyl nitrite pearls (administered by inhalation), sodium nitrite, and sodium thiosulfate (administered by infusion). The goal of the antidote was to generate a large pool of ferric iron (Fe<sup>3+</sup>) to compete with cyanide cytochrome a<sub>3</sub> (so that cyanide will bind to the antidote rather than the enzyme).

The nitrites oxidize hemoglobin to methemoglobin, which competes with cytochrome oxidase for the cyanide ion. Cyanmethemoglobin is formed and the cytochrome oxidase enzyme is restored. The major mechanism to remove the cyanide from the body is by enzymatic conversion to thiocyanate by the mitochondrial enzyme rhodanese. Thiocyanate is a relatively non-toxic molecule and is excreted by the kidneys. To accelerate this detoxification, sodium thiosulfate is administered to provide a sulfur donor for rhodanese, needed in order to produce thiocyanate.

## **Sensitivity**

Minimum risk levels (MRLs) may not protect for delayed health effects or health effects acquired following repeated sublethal exposure, such as hypersensitivity, asthma, or bronchitis. MRLs may be revised after sufficient data accumulates (Toxicological Profile for Cyanide, U.S. Department of Health and Human Services, 2006).

## **Chemical Tests for Cyanide**

### **Prussian Blue**

Iron (II) sulfate is added to a solution suspected of containing cyanide, such as the filtrate from the sodium fusion test. The resulting mixture is acidified with mineral acid. The formation of Prussian blue is a positive result for cyanide.

### **Para-Benzoquinone in DMSO**

A solution of *para*-benzoquinone in DMSO reacts with inorganic cyanide to form a cyanophenol, which is fluorescent. Illumination with a UV light gives a green/blue glow if the test is positive.

### **Copper and an Aromatic Amine**

As used by fumigators to detect hydrogen cyanide, copper (II) salt and an aromatic amine such as benzidine is added to the sample; as an alternative to benzidine an alternative amine di-(4,4-*bis*-dimethylaminophenyl) methane can be used. A positive test gives a blue color. Copper (I) cyanide is poorly soluble.

By sequestering the copper(I) the copper(II) is rendered a stronger oxidant. The copper, in a cyanide facilitated oxidation, converts the amine into a colored compound. The Nernst equation explains this process. Another good example of such chemistry is the way in which the saturated calomel reference electrode (SCE) works. The copper, in a cyanide-facilitated oxidation, converts the amine into a colored compound.

### **Pyridine-Barbituric Acid Colorimetry**

A sample containing inorganic cyanide is purged with air from a boiling acid solution into a basic absorber solution. The cyanide salt absorbed in the basic solution is buffered at pH 4.5 and then reacted with chlorine to form cyanogen chloride. The cyanogen chloride formed couples pyridine with barbituric acid to form a strongly colored red dye that is proportional to the cyanide concentration.

This colorimetric method following distillation is the basis for most regulatory methods (for instance EPA 335.4) used to analyze cyanide in water, wastewater, and contaminated soils.

Distillation followed by colorimetric methods, however, have been found to be prone to interferences from thiocyanate, nitrate, thiosulfate, sulfite, and sulfide that can result in both positive and negative bias. It has been recommended by the USEPA (MUR March 12, 2007) that samples containing these compounds be analyzed by Gas-Diffusion Flow Injection Analysis — Amperometry.

### **Gas Diffusion Flow Injection Analysis — Amperometry**

Instead of distilling, the sample is injected into an acidic stream where the HCN formed is passed under a hydrophobic gas diffusion membrane that selectively allows only HCN to pass through. The HCN that passes through the membrane is absorbed into a basic carrier solution that transports the CN to an amperometric detector that accurately measures cyanide concentration with high sensitivity.

Sample pretreatment determined by acid reagents, ligands, or preliminary UV irradiation allow cyanide speciation of free cyanide, available cyanide, and total cyanide respectively. The relative simplicity of these flow injection analysis methods limit the interference experienced by the high heat of distillation and also prove to be cost effective since time consuming distillations are not required.



## Fluoride - Inorganic Contaminant 4.0 mg/L MCL

Fluoride compounds are salts that form when the element, fluorine, combines with minerals in soil or rocks.

### Uses for Fluoride.

Many communities add fluoride to their drinking water to promote dental health.

### What are Fluoride's Health Effects?

Exposure to excessive consumption of fluoride over a lifetime may lead to increased likelihood of bone fractures in adults, and may result in effects on bone leading to pain and tenderness.

Children aged 8 years and younger exposed to excessive amounts of fluoride have an increased chance of developing pits in the tooth enamel, along with a range of cosmetic effects to teeth.



This health effects language is not intended to catalog all possible health effects for fluoride. Rather, it is intended to inform consumers of some of the possible health effects associated with fluoride in drinking water.

### What are EPA's Drinking Water Regulations for Fluoride?

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for fluoride is 4.0 mg/L or 4.0 ppm. EPA has set this level of protection based on the best available science to prevent potential health problems. EPA has set an enforceable regulation for fluoride, called a maximum contaminant level (MCL), at 4.0 mg/L or 4.0 ppm.

MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.

EPA has also set a secondary standard (SMCL) for fluoride at 2.0 mg/L or 2.0 ppm. Secondary standards are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. EPA recommends secondary standards to water systems but does not require systems to comply. However, states may choose to adopt them as enforceable standards.

Tooth discoloration and/or pitting is caused by excess fluoride exposures during the formative period prior to eruption of the teeth in children. The secondary standard of 2.0 mg/L is intended as a guideline for an upper bound level in areas which have high levels of naturally occurring fluoride. The level of the SMCL was set based upon a balancing of the beneficial effects of protection from tooth decay and the undesirable effects of excessive exposures leading to discoloration. Fluoride is voluntarily added to some drinking water systems as a public health measure for reducing the incidence of cavities among the treated population.

The decision to fluoridate a water supply is made by the State or local municipality, and is not mandated by EPA or any other Federal entity. The Centers for Disease Control and Prevention (CDC) provides recommendations about the optimal levels of fluoride in drinking water in order to prevent tooth decay. Information about CDC's recommendations can be found at: <http://www.cdc.gov/fluoridation/>

States may set more stringent drinking water MCLGs and MCLs for fluoride than EPA.

The drinking water standards are currently under review. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. In 2003 and as part of the first Six Year Review, EPA reviewed the drinking water standard for fluoride and found that new health and exposure data were available on orally ingested fluoride. EPA requested that the National Research Council (NRC) of the National Academies of Science (NAS) conduct a review of this data and in 2006, the NRC published their evaluation in a report entitled, Fluoride in Drinking Water:

A Scientific Review of EPA's Standards. The NRC recommended that EPA update its fluoride risk assessment to include new data on health risks and better estimates of total exposure.

In March 2010 and as part of the second Six Year Review, the Agency indicated that the Office of Water was in the process of developing its health and exposure assessments to address the NRC's recommendations. The Agency finalized the risk and exposure assessments for fluoride in January 2011 and announced its intent to review the drinking water regulations for fluoride to determine whether revisions are appropriate.

### **How does Fluoride get into my Drinking Water?**

Some fluoride compounds, such as sodium fluoride and fluorosilicates, dissolve easily into ground water as it moves through gaps and pore spaces between rocks. Most water supplies contain some naturally occurring fluoride. Fluoride also enters drinking water in discharge from fertilizer or aluminum factories. Also, many communities add fluoride to their drinking water to promote dental health.

A federal law called the Emergency Planning and Community Right to Know Act (EPCRA) requires facilities in certain industries, which manufacture, process, or use significant amounts of toxic chemicals, to report annually on their releases of these chemicals. For more information on the uses and releases of chemicals in your state, contact the Community Right-to-Know Hotline: (800) 424-9346.

### **How will I know if Fluoride is in my Drinking Water?**

When routine monitoring indicates that fluoride levels are above the MCL, your water supplier must take steps to reduce the amount of fluoride so that it is below that level. Water suppliers must notify their customers as soon as practical, but no later than 30 days after the system learns of the violation. Additional actions, such as providing alternative drinking water supplies, may be required to prevent serious risks to public health.

If your water comes from a household or private well, check with your health department or local water systems that use ground water for information on contaminants of concern in your area.

### **How will Fluoride be removed from my Drinking Water?**

The following treatment method(s) have proven to be effective for removing fluoride to below 4.0 mg/L or 4.0 ppm: distillation or reverse osmosis.

### **How do I learn more about my Drinking Water?**

EPA strongly encourages people to learn more about their drinking water, and to support local efforts to protect the supply of safe drinking water and upgrade the community water system. Your water bill or telephone book's government listings are a good starting point for local information.

Contact your water utility. EPA requires all community water systems to prepare and deliver an annual consumer confidence report (CCR) (sometimes called a water quality report) for their customers by July 1 of each year. If your water provider is not a community water system, or if you have a private water supply, request a copy from a nearby community water system.

## **Fluoride Explained**

**Fluoride** is the anion  $F^-$ , the reduced form of fluorine when as an ion and when bonded to another element. Inorganic fluorine containing compounds are called fluorides. Fluoride, like other halides, is a monovalent ion ( $-1$  charge). Its compounds often have properties that are distinct relative to other halides. Structurally, and to some extent chemically, the fluoride ion resembles the hydroxide ion.

### **Occurrence**

Solutions of inorganic fluorides in water contain  $F^-$  and bifluoride  $HF_2^-$ . Few inorganic fluorides are soluble in water without undergoing significant hydrolysis. In terms of its reactivity, fluoride differs significantly from chloride and other halides, and is more strongly solvated due to its smaller radius/charge ratio. Its closest chemical relative is hydroxide. When relatively unsolvated, fluoride anions are called "naked". Naked fluoride is a very strong Lewis base. The presence of fluoride and its compounds can be detected by  $F$  NMR spectroscopy.

### **Natural Occurrence**

Many fluoride minerals are known, but of paramount commercial importance are fluorite and fluorapatite.

Fluoride is usually found naturally in low concentration in drinking water and foods. The concentration in seawater averages 1.3 parts per million (ppm). Fresh water supplies generally contain between 0.01–0.3 ppm, whereas the ocean contains between 1.2 and 1.5 ppm. In some locations, the fresh water contains dangerously high levels of fluoride, leading to serious health problems.

## Applications

Fluorides are pervasive in modern technology. Hydrofluoric acid is the fluoride synthesized on the largest scale. It is produced by treating fluoride minerals with sulfuric acid. Hydrofluoric acid and its anhydrous form hydrogen fluoride are used in the production of fluorocarbons and aluminum fluorides. Hydrofluoric acid has a variety of specialized applications, including its ability to dissolve glass.

## Inorganic Chemicals

Fluoride salts are used in the manufacture of many inorganic chemicals, many of which contain fluoride covalently bonded to the metal or nonmetal in question. Some examples of these are:

- Cryolite ( $\text{Na}_3\text{AlF}_6$ ) is a pesticide that can leave fluoride on agricultural commodities. Cryolite was originally utilized in the preparation of aluminum.
- Sulfuryl fluoride ( $\text{SO}_2\text{F}_2$ ) is used as a pesticide and fumigant on agricultural crops. In 2010, the United States Environmental Protection Agency proposed to withdraw the use of sulfuryl fluoride on food. Sulfuryl fluoride releases fluoride when metabolized.
- Sulfur hexafluoride is an inert, nontoxic insulator gas that is used in electrical transformers and as a tracer gas in indoor air quality investigations.
- Uranium hexafluoride, although not ionic, is prepared from fluoride reagents. It is utilized in the separation of isotopes of uranium between the fissile isotope U-235 and the non-fissile isotope U-238 in preparation of nuclear reactor fuel and atomic bombs. This is due to the volatility of fluorides of uranium.

## Organic Chemicals

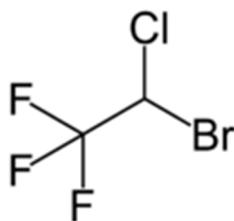
Fluoride reagents are significant in synthetic organic chemistry. Organofluorine chemistry has produced many useful compounds over the last 50 years. Included in this area are polytetrafluoroethylene (Teflon), polychlorotrifluoroethylene (moisture barriers), efavirenz (pharmaceutical used for treatment of HIV), fluoxetine (an antidepressant), 5-fluorouracil (an anticancer drug), hydrochlorofluorocarbons and hydrofluorocarbons (refrigerants, blowing agents and propellants).

Due to the affinity of silicon for fluoride, and the ability of silicon to expand its coordination number, silyl ether protecting groups can be easily removed by the fluoride sources such as sodium fluoride and tetra-n-butylammonium fluoride (TBAF). This is quite useful for organic synthesis and the production of fine chemicals. The Si-F linkage is one of the strongest single bonds. In contrast, other silyl halides are easily hydrolyzed.

## Cavity Prevention

Fluoride-containing compounds are used in topical and systemic fluoride therapy for preventing tooth decay. They are used for water fluoridation and in many products associated with oral hygiene. Originally, sodium fluoride was used to fluoridate water; hexafluorosilicic acid ( $\text{H}_2\text{SiF}_6$ ) and its salt sodium hexafluorosilicate ( $\text{Na}_2\text{SiF}_6$ ) are more commonly used additives, especially in the United States.

The fluoridation of water is known to prevent tooth decay and is considered by the U.S. Centers for Disease Control and Prevention as "one of 10 great public health achievements of the 20th century". In some countries where large, centralized water systems are uncommon, fluoride is delivered to the populace by fluoridating table salt. Fluoridation of water has its critics (see Water fluoridation controversy).



Structure of halothane.

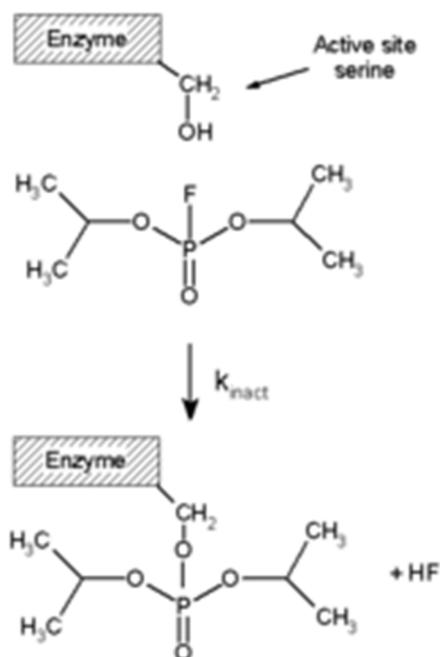
### Biomedical Applications

Positron emission tomography is commonly carried out using fluoride-containing pharmaceuticals such as fluorodeoxyglucose, which is labeled with the radioactive isotope fluorine-18, which emits positrons when it decays into  $^{18}\text{O}$ .

Numerous drugs contain fluorine including antipsychotics such as fluphenazine, HIV protease inhibitors such as tipranavir, antibiotics such as ofloxacin and trovafloxacin, and anesthetics such as halothane. Fluorine is incorporated in the drug structures to reduce drug metabolism, as the strong C-F bond resists deactivation in the liver by cytochrome P450 oxidases.

Fluoride salts are commonly used to inhibit the activity of phosphatases, such as serine/threonine phosphatases. Fluoride mimics the nucleophilic hydroxyl ion in these enzymes' active sites. Beryllium fluoride and aluminum fluoride are also used as phosphatase inhibitors, since these compounds are structural mimics of the phosphate group and can act as analogues of the transition state of the reaction.

### Toxicology



Reaction of the irreversible inhibitor diisopropylfluorophosphate with a serine protease. Fluoride-containing compounds are so diverse that it is not possible to generalize on their toxicity, which depends on their reactivity and structure, and in the case of salts, their solubility and ability to release fluoride ions.

Soluble fluoride salts, of which sodium fluoride is the most common, are mildly toxic but have resulted in both accidental and suicidal deaths from acute poisoning. While the minimum fatal dose in humans is not known, the lethal dose for most adult humans is estimated at 5 to 10 g (which is equivalent to 32 to 64 mg/kg elemental fluoride/kg body weight). However, a case of a fatal poisoning of an adult with 4 grams of sodium fluoride is documented, while a dose of 120 g sodium fluoride has been survived.

A toxic dose that may lead to adverse health effects is estimated at 3 to 5 mg/kg of elemental fluoride. For Sodium fluorosilicate ( $\text{Na}_2\text{SiF}_6$ ), the median lethal dose ( $\text{LD}_{50}$ ) orally in rats is 0.125 g/kg, corresponding to 12.5 g for a 100 kg adult.

The fatal period ranges from 5 min to 12 hours. The mechanism of toxicity involves the combination of the fluoride anion with the calcium ions in the blood to form insoluble calcium fluoride, resulting in hypocalcemia; calcium is indispensable for the function of the nervous system, and the condition can be fatal.

Treatment may involve oral administration of dilute calcium hydroxide or calcium chloride to prevent further absorption, and injection of calcium gluconate to increase the calcium levels in the blood. Hydrogen fluoride is more dangerous than salts such as NaF because it is corrosive and volatile, and can result in fatal exposure through inhalation or upon contact with the skin; calcium gluconate gel is the usual antidote.

In the higher doses used to treat osteoporosis, sodium fluoride can cause pain in the legs and incomplete stress fractures when the doses are too high; it also irritates the stomach, sometimes so severely as to cause ulcers.

Slow-release and enteric-coated versions of sodium fluoride do not have gastric side effects in any significant way, and have milder and less frequent complications in the bones. In the lower doses used for water fluoridation, the only clear adverse effect is dental fluorosis, which can alter the appearance of children's teeth during tooth development; this is mostly mild and is unlikely to represent any real effect on aesthetic appearance or on public health.

## Lead- Inorganic Contaminant 0.015 Action Level

The United States Environmental Protection Agency (EPA) regulates lead in drinking water to protect public health. Lead may cause health problems if present in public or private water supplies in amounts greater than the drinking water standard set by EPA.

### What is Lead?

Lead is a toxic metal that was used for many years in products found in and around homes. Even at low levels, lead may cause a range of health effects including behavioral problems and learning disabilities. Children six years old and under are most at risk because this is when the brain is developing. The primary source of lead exposure for most children is lead-based paint in older homes. Lead in drinking water can add to that exposure.



### Uses for Lead

Lead is sometimes used in household plumbing materials or in water service lines used to bring water from the main to the home. A prohibition on lead in plumbing materials has been in effect since 1986. The lead ban, which was included in the 1986 Amendments of the Safe Drinking Water Act, states that only “lead free” pipe, solder, or flux may be used in the installation or repair of (1) public water systems, or (2) any plumbing in a residential or non-residential facility providing water for human consumption, which is connected to a public water system. But even “lead free” plumbing may contain traces of lead. The term “lead free” means that solders and flux may not contain more than 0.2 percent lead, and that pipes and pipe fittings may not contain more than 8.0 percent lead. Faucets and other end use devices must be tested and certified against the ANSI – NSF Standard 61 to be considered lead free.

### What are Lead’s Health Effects?

Infants and children who drink water containing lead in excess of the action level could experience delays in their physical or mental development. Children could show slight deficits in attention span and learning abilities. Adults who drink this water over many years could develop kidney problems or high blood pressure.

This health effects language is not intended to catalog all possible health effects for lead. Rather, it is intended to inform consumers of the most significant and probable health effects, associated with lead in drinking water.

### What are EPA’s Drinking Water Regulations for Lead?

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur with an adequate margin of safety. These non-enforceable health goals, based solely on possible health risks are called maximum contaminant level goals (MCLG) The MCLG for lead is zero.

EPA has set this level based on the best available science which shows there is no safe level of exposure to lead.

For most contaminants, EPA sets an enforceable regulation called a maximum contaminant level (MCL) based on the MCLG.

MCLs are set as close to the MCLGs as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. However, because lead contamination of drinking water often results from corrosion of the plumbing materials belonging to water system customers, EPA established a treatment technique rather than an MCL for lead.

A treatment technique is an enforceable procedure or level of technological performance which water systems must follow to ensure control of a contaminant. The treatment technique regulation for lead (referred to as the Lead and Copper rule) requires water systems to control the corrosivity of the water. The regulation also requires systems to collect tap samples from sites served by the system that are more likely to have plumbing materials containing lead.

If more than 10% of tap water samples exceed the lead action level of 15 parts per billion, then water systems are required to take additional actions including:

- Taking further steps optimize their corrosion control treatment (for water systems serving 50,000 people that have not fully optimized their corrosion control) .
- Educating the public about lead in drinking water and actions consumers can take to reduce their exposure to lead.
- Replacing the portions of lead service lines (lines that connect distribution mains to customers) under the water system's control.

EPA promulgated the Lead and Copper Rule in 1991 and revised the regulation in 2000 and 2007. States may set more stringent drinking water regulations than EPA.

### **How does Lead get into my Drinking Water?**

The major sources of lead in drinking water are corrosion of household plumbing systems; and erosion of natural deposits. Lead enters the water (“leaches”) through contact with the plumbing. Lead leaches into water through corrosion – a dissolving or wearing away of metal caused by a chemical reaction between water and your plumbing.

Lead can leach into water from pipes, solder, fixtures and faucets (brass), and fittings. The amount of lead in your water also depends on the types and amounts of minerals in the water, how long the water stays in the pipes, the amount of wear in the pipes, the water's acidity and its temperature.

Although the main sources of exposure to lead are ingesting paint chips and inhaling dust, EPA estimates that 10 to 20 percent of human exposure to lead may come from lead in drinking water. Infants who consume mostly mixed formula can receive 40 to 60 percent of their exposure to lead from drinking water.

### **How will I know if Lead is in my Drinking Water?**

Have your water tested for lead. A list of certified laboratory of labs are available from your state or local drinking water authority. Testing costs between \$20 and \$100. Since you cannot see, taste, or smell lead dissolved in water, testing is the only sure way of telling whether there are harmful quantities of lead in your drinking water. You should be particularly suspicious if your home has lead pipes (lead is a dull gray metal that is soft enough to be easily scratched with a house key) or if you see signs of corrosion (frequent leaks, rust-colored water). Your water supplier may have useful information, including whether the service connector used in your home or area is made of lead. Testing is especially important in high-rise buildings where flushing might not work.

If your water comes from a household well, check with your health department or local water systems that use ground water for information on contaminants of concern in your area.

### **How can I Reduce Lead in Drinking Water at Home?**

Flush your pipes before drinking, and only use cold water for consumption. The more time water has been sitting in your home's pipes, the more lead it may contain. Anytime the water in a particular faucet has not been used for six hours or longer, "flush" your cold-water pipes by running the water until it becomes as cold as it will get.

This could take as little as five to thirty seconds if there has been recent heavy water use such as showering or toilet flushing. Otherwise, it could take two minutes or longer. Your water utility will inform you if longer flushing times are needed to respond to local conditions.

Use only water from the cold-water tap for drinking, cooking, and especially for making baby formula. Hot water is likely to contain higher levels of lead. The two actions recommended above are very important to the health of your family. They will probably be effective in reducing lead levels because most of the lead in household water usually comes from the plumbing in your house, not from the local water supply.

### **Should I be concerned about Lead in Drinking water in my child's school or child care facility?**

Children spend a significant part of their days at school or in a child care facility. The faucets that provide water used for consumption, including drinking, cooking lunch, and preparing juice and infant formula, should be tested.

### **How do I learn more about my Drinking Water?**

EPA strongly encourages people to learn more about their drinking water, and to support local efforts to protect and upgrade the supply of safe drinking water. Your water bill or telephone book's government listings are a good starting point for local information.

Contact your water utility. EPA requires all community water systems to prepare and deliver an annual consumer confidence report (CCR) (sometimes called a water quality report) for their customers by July 1 of each year. If your water provider is not a community water system, or if you have a private water supply, request a copy from a nearby community water system.

### **Lead Explained**

**Lead** is a chemical element in the carbon group with symbol **Pb** (from Latin: *plumbum*) and atomic number 82. Lead is a soft, malleable poor metal. It is also counted as one of the heavy metals. Metallic lead has a bluish-white color after being freshly cut, but it soon tarnishes to a dull grayish color when exposed to air. Lead has a shiny chrome-silver luster when it is melted into a liquid.

Lead is used in building construction, lead-acid batteries, bullets and shot, weights, as part of solders, pewters, fusible alloys, and as a radiation shield. Lead has the highest atomic number of all of the stable elements, although the next higher element, bismuth, has a half-life that is so long (much longer than the age of the universe) that it can be considered stable. Its four stable isotopes have 82 protons, a magic number in the nuclear shell model of atomic nuclei.

Lead, at certain contact degrees, is a poisonous substance to animals, including humans. It damages the nervous system and causes brain disorders. Excessive lead also causes blood disorders in mammals. Like the element mercury, another heavy metal, lead is a neurotoxin that accumulates both in soft tissues and the bones. Lead poisoning has been documented from ancient Rome, ancient Greece, and ancient China.

## Characteristics

Lead is a bright and silvery metal with a very slight shade of blue in a dry atmosphere. Upon contact with air, it begins to tarnish by forming a complex mixture of compounds depending on the conditions. The color of the compounds can vary. The tarnish layer can contain significant amounts of carbonates and hydroxycarbonates. It has a few characteristic properties: high density, softness, ductility and malleability, poor electrical conductivity compared to other metals, high resistance to corrosion, and ability to react with organic chemicals.

Various traces of other metals change its properties significantly: the addition of small amounts of antimony or copper increases hardness and improves the corrosion reflection from sulfuric acid for lead. A few other metals also improve only hardness and fight metal fatigue, such as cadmium, tin, or tellurium; metals like sodium or calcium also have this ability, but they weaken the chemical stability. Finally, zinc and bismuth simply impair the corrosion resistance (0.1% bismuth content is the industrial usage threshold). In return, lead impurities mostly worsen the quality of industrial materials, although there are exceptions: for example, small amounts of lead improve the ductility of steel.

Lead has only one common allotrope, which is face-centered cubic, with the lead–lead distance being 349 pm. At 327.5 °C (621.5 °F), lead melts; the melting point is above that of tin (232 °C, 449.5 °F), but significantly below that of germanium (938 °C, 1721 °F).<sup>[6]</sup> The boiling point of lead is 1749 °C (3180 °F), which is below those of both tin (2602 °C, 4716 °F) and germanium (2833 °C, 5131 °F). Densities increase down the group: the Ge and Sn values (5.23 and 7.29 g•cm<sup>-3</sup>, respectively) are significantly below that of lead: 11.32 g•cm<sup>-3</sup>.

A lead atom has 82 electrons, having an electronic configuration of [Xe]4f<sup>14</sup>5d<sup>10</sup>6s<sup>2</sup>6p<sup>2</sup>. In its compounds, lead (unlike the other group 14 elements) most commonly loses its two and not four outermost electrons, becoming lead(II) ions, Pb<sup>2+</sup>. Such unusual behavior is rationalized by considering the inert pair effect, which occurs because of the stabilization of the 6s-orbital due to relativistic effects, which are stronger closer to the bottom of the periodic table. Tin shows a weaker such effect: tin(II) is still a reducer.

The figures for electrode potential show that lead is only slightly easier to oxidize than hydrogen. Lead thus can dissolve in acids, but this is often impossible due to specific problems (such as the formation of insoluble salts). Powdered lead burns with a bluish-white flame. As with many metals, finely divided powdered lead exhibits pyrophoricity. Toxic fumes are released when lead is burned.

## Isotopes

Lead occurs naturally on Earth exclusively in the form of four isotopes: lead-204, -206, -207, and -208. All four can be radioactive as the hypothetical alpha decay of any would be exothermic, but the lower half-life limit has been put only for lead-204: over 1.4×10<sup>17</sup> years. This effect is, however, so weak that natural lead poses no radiation hazard.

Three isotopes are also found in three of the four major decay chains: lead-206, -207 and -208 are final decay products of uranium-238, uranium-235, and thorium-232, respectively. Since the amounts of them in nature depend also on other elements' presence, the isotopic composition of natural lead varies by sample: in particular, the relative amount of lead-206 varies between 20.84% and 27.78%.

Aside from the stable ones, thirty-four radioisotopes have been synthesized: they have mass numbers of 178–215. Lead-205 is the most stable radioisotope of lead, with a half-life of over 10<sup>7</sup> years. 47 nuclear isomers (long-lived excited nuclear states), corresponding to 24 lead isotopes, have been characterized. The most long-lived isomer is lead-204m2 (half-life of about 1.1 hours).

## Chemical Reactivity

Lead is classified as a post-transition metal and is also a member of the carbon group. Lead only forms a protective oxide layer although finely powdered highly purified lead can ignite in air. Melted lead is oxidized in air to lead monoxide. All chalcogens oxidize lead upon heating.

Fluorine does not oxidize cold lead. Hot lead can be oxidized, but the formation of a protective halide layer lowers the intensity of the reaction above 100 °C (210 °F). The reaction with chlorine is similar: thanks to the chloride layer, lead persistence against chlorine surpasses those of copper or steel up to 300 °C (570 °F).

Water in the presence of oxygen attacks lead to start an accelerating reaction. The presence of carbonates or sulfates results in the formation of insoluble lead salts, which protect the metal from corrosion. So does carbon dioxide, as the insoluble lead carbonate is formed; however, an excess of the gas leads to the formation of the soluble bicarbonate; this makes the use of lead pipes dangerous. Lead dissolves in organic acids (in the presence of oxygen) and concentrated ( $\geq 80\%$ ) sulfuric acid thanks to complexation; however, it is only weakly affected by hydrochloric acid and is stable against hydrofluoric acid, as the corresponding halides are weakly soluble. Lead also dissolves in quite concentrated alkalis ( $\geq 10\%$ ) because of the amphoteric character and solubility of plumbites.

## Compounds

Lead compounds exist mainly in two main oxidation states, +2 and +4. The former is more common. Inorganic lead(IV) compounds are typically strong oxidants or exist only in highly acidic solutions.

## Oxides and Sulfides

Three oxides are known: lead(II) oxide or lead monoxide (PbO), lead tetroxide (Pb<sub>3</sub>O<sub>4</sub>) (sometimes called "minimum"), and lead dioxide (PbO<sub>2</sub>). The monoxide exists as two allotropes:  $\alpha$ -PbO and  $\beta$ -PbO, both with layer structure and tetracoordinated lead.

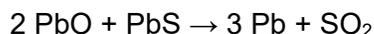
The alpha polymorph is red-colored and has the Pb–O distance of 230 pm; the beta polymorph is yellow-colored and has the Pb–O distance of 221 and 249 pm (due to asymmetry). Both polymorphs can exist under standard conditions (beta with small ( $10^{-5}$  relative) impurities, such as Si, Ge, Mo, etc.). PbO reacts with acids to form salts, and with alkalis to give plumbites, [Pb(OH)<sub>3</sub>]<sup>-</sup> or [Pb(OH)<sub>4</sub>]<sup>2-</sup>. The monoxide oxidizes in air to trilead tetroxide, which at 550 °C (1020 °F) degrades back into PbO.

The dioxide may be prepared by, for example, halogenization of lead(II) salts. Regardless the polymorph, it has a black-brown color. The alpha allotrope is rhombohedral, and the beta allotrope is tetragonal. Both allotropes are black-brown in color and always contain some water, which cannot be removed, as heating also causes decomposition (to PbO and Pb<sub>3</sub>O<sub>4</sub>).

The dioxide is a powerful oxidizer: it can oxidize hydrochloric and sulfuric acids. It does not react with alkaline solution, but reacts with solid alkalis to give hydroxyplumbates, or with basic oxides to give plumbates.

Reaction of lead salts with hydrogen sulfide yields lead monosulfide. The solid has the rocksalt-like simple cubic structure, which it keeps up to the melting point, 1114 °C (2037 °F). When heated in air, it oxidizes to the sulfate and then the monoxide. Lead monosulfide is almost insoluble in water, weak acids, and (NH<sub>4</sub>)<sub>2</sub>S/(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub> solution is the key for separation of lead from analytical groups I to III ions, tin, arsenic, and antimony.

However, it dissolves in nitric and hydrochloric acids, to give elemental sulfur and hydrogen sulfide, respectively. Upon heating under high pressures with sulfur, it gives the disulfide. In the compound, the lead atoms are linked octahedrally with the sulfur atoms. It is also a semiconductor. A mixture of the monoxide and the monosulfide when heated forms the metal.



### Halides and Other Salts

Heating lead carbonate with hydrogen fluoride yields the hydrofluoride, which decomposes to the difluoride when it melts. This white crystalline powder is more soluble than the diiodide, but less than the dibromide and the dichloride. The tetrafluoride, a yellow crystalline powder, is unstable.

Other dihalides are obtained upon heating lead(II) salts with the halides of other metals; lead dihalides precipitate to give white orthorhombic crystals (diiodide forms yellow hexagonal crystals). They can also be obtained by direct reaction of their constituent elements at temperature exceeding melting points of dihalides. Their solubility increases with temperature; adding more halides first decreases the solubility, but then increases due to complexation, with the maximum coordination number being 6.

The complexation depends on halide ion numbers, atomic number of the alkali metal, the halide of which is added, temperature and solution ionic strength. The tetrachloride is obtained upon dissolving the dioxide in hydrochloric acid; to prevent the exothermic decomposition, it is kept under concentrated sulfuric acid. The tetrabromide may not, and the tetraiodide definitely does not exist. The diastatide has also been prepared.

The metal is not attacked by sulfuric or hydrochloric acids. It dissolves in nitric acid with the evolution of nitric oxide gas to form dissolved  $\text{Pb}(\text{NO}_3)_2$ . It is a well-soluble solid in water; it is thus a key to receive the precipitates of halides, sulfate, chromate, carbonate, and basic carbonate  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$  salts of lead.

### Organolead

The best-known compounds are the two simplest plumbane derivatives: tetramethyllead (TML) and tetraethyllead (TEL). The homologs of these, as well as hexaethyldilead (HEDL), are of lesser stability. The tetralkyl derivatives contain lead(IV), where the Pb–C bonds are covalent. They thus resemble typical organic compounds.

Lead readily forms an equimolar alloy with sodium metal that reacts with alkyl halides to form organometallic compounds of lead such as tetraethyllead. The Pb–C bond energies in TML and TEL are only 167 and 145 kJ/mol; the compounds thus decompose upon heating, with first signs of TEL composition seen at 100 °C (210 °F).

The pyrolysis yields of elemental lead and alkyl radicals; their interreaction causes the synthesis of HEDL. TML and TEL also decompose upon sunlight or UV light. In presence of chlorine, the alkyls begin to be replaced with chlorides; the  $\text{R}_2\text{PbCl}_2$  in the presence of HCl (a by-product of the previous reaction) leads to the complete mineralization to give  $\text{PbCl}_2$ . Reaction with bromine follows the same principle.

## Applications

### Elemental Form

Contrary to popular belief, pencil leads in wooden pencils have never been made from lead. The term comes from the Roman stylus, called the *penicillus*, a small brush used for painting. When the pencil originated as a wrapped graphite writing tool, the particular type of graphite being used was named *plumbago* (lit. *act for lead*, or *lead mockup*).

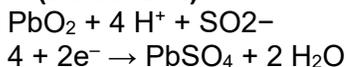
Lead is used in applications where its low melting point, ductility and high density are advantageous. The low melting point makes casting of lead easy, and therefore small arms ammunition and shotgun pellets can be cast with minimal technical equipment. It is also inexpensive and denser than other common metals.

Because of its high density and resistance from corrosion, lead is used for the ballast keel of sailboats. Its high density allows it to counterbalance the heeling effect of wind on the sails while at the same time occupying a small volume and thus offering the least underwater resistance.

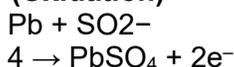
For the same reason it is used in scuba diving weight belts to counteract the diver's natural buoyancy and that of his equipment. It does not have the weight-to-volume ratio of many heavy metals, but its low cost increases its use in these and other applications.

More than half of the US lead production (at least 1.15 million tons in 2000) is used for automobiles, mostly as electrodes in the lead–acid battery, used extensively as a car battery.

### Cathode (Reduction)



### Anode (Oxidation)



Lead is used as electrodes in the process of electrolysis. It is used in solder for electronics, although this usage is being phased out by some countries to reduce the amount of environmentally hazardous waste, and in high voltage power cables as sheathing material to prevent water diffusion into insulation. Lead is one of three metals used in the Oddy test for museum materials, helping detect organic acids, aldehydes, and acidic gases. It is also used as shielding from radiation (e.g., in X-ray rooms). Molten lead is used as a coolant (e.g., for lead cooled fast reactors).

Lead is added to brass to reduce machine tool wear. In the form of strips, or tape, lead is used for the customization of tennis rackets. Tennis rackets of the past sometimes had lead added to them by the manufacturer to increase weight. It is also used to form glazing bars for stained glass or other multi-lit windows. The practice has become less common, not for danger but for stylistic reasons.

Lead, or *sheet-lead*, is used as a sound deadening layer in some areas in wall, floor and ceiling design in sound studios where levels of airborne and mechanically produced sound are targeted for reduction or virtual elimination. It is the traditional base metal of organ pipes, mixed with varying amounts of tin to control the tone of the pipe.

## Compounds

Lead compounds are used as a coloring element in ceramic glazes, notably in the colors red and yellow. Lead is frequently used in polyvinyl chloride (PVC) plastic, which coats electrical cords.

Lead is used in some candles to treat the wick to ensure a longer, more even burn. Because of the dangers, European and North American manufacturers use more expensive alternatives such as zinc.

Lead glass is composed of 12–28% lead oxide. It changes the optical characteristics of the glass and reduces the transmission of radiation.

Some artists using oil-based paints continue to use lead carbonate white, citing its properties in comparison with the alternatives. Tetra-ethyl lead is used as an anti-knock additive for aviation fuel in piston-driven aircraft. Lead-based semiconductors, such as lead telluride, lead selenide and lead antimonide are finding applications in photovoltaic (solar energy) cells and infrared detectors.

### **Former Applications**

Lead pigments were used in lead paint for white as well as yellow, orange, and red. Most uses have been discontinued due to the dangers of lead poisoning. Beginning April 22, 2010, US federal law requires that contractors performing renovation, repair, and painting projects that disturb more than six square feet of paint in homes, child care facilities, and schools built before 1978 must be certified and trained to follow specific work practices to prevent lead contamination.

Lead chromate is still in industrial use. Lead carbonate (white) is the traditional pigment for the priming medium for oil painting, but it has been largely displaced by the zinc and titanium oxide pigments. It was also quickly replaced in water-based painting mediums. Lead carbonate white was used by the Japanese geisha and in the West for face-whitening make-up, which was detrimental to health. Lead is the hot metal that was used in hot metal typesetting. It was used for plumbing (hence the name) as well as a preservative for food and drink in Ancient Rome.

Until the early 1970s, lead was used for joining cast iron water pipes and used as a material for small diameter water pipes.

Tetraethyllead was used in leaded fuels to reduce engine knocking, but this practice has been phased out across many countries of the world in efforts to reduce toxic pollution that affected humans and the environment.

Lead was used to make bullets for slings. Lead was used for shotgun pellets in the US until about 1992 when it was outlawed (for waterfowl hunting only) and replaced by non-toxic shot, primarily steel pellets. In the Netherlands, the use of lead shot for hunting and sport shooting was banned in 1993, which caused a large drop in lead emission, from 230 tons in 1990 to 47.5 tons in 1995, two years after the ban.

Lead was a component of the paint used on children's toys – now restricted in the United States and across Europe (ROHS Directive). Lead was used in car body filler, which was used in many custom cars in the 1940s–60s. Hence the term Leadsled.

Lead is a superconductor with a transition temperature of 7.2 K, and therefore IBM tried to make a Josephson effect computer out of a lead alloy.

Lead was also used in pesticides before the 1950s, when fruit orchards were treated especially against the codling moth. A lead cylinder attached to a long line was used by sailors for the vital navigational task of determining water depth by *heaving the lead* at regular intervals. A soft tallow insert at its base allowed the nature of the sea bed to be determined, further aiding position finding.

## Health Effects

Lead is a highly poisonous metal (regardless if inhaled or swallowed), affecting almost every organ and system in the body. The main target for lead toxicity is the nervous system, both in adults and children. Long-term exposure of adults can result in decreased performance in some tests that measure functions of the nervous system. Long-term exposure to lead or its salts (especially soluble salts or the strong oxidant  $\text{PbO}_2$ ) can cause nephropathy, and colic-like abdominal pains. It may also cause weakness in fingers, wrists, or ankles. Lead exposure also causes small increases in blood pressure, particularly in middle-aged and older people and can cause anemia. Exposure to high lead levels can severely damage the brain and kidneys in adults or children and ultimately cause death. In pregnant women, high levels of exposure to lead may cause miscarriage.

Chronic, high-level exposure have shown to reduce fertility in males. Lead also damages nervous connections (especially in young children) and cause blood and brain disorders. Lead poisoning typically results from ingestion of food or water contaminated with lead; but may also occur after accidental ingestion of contaminated soil, dust, or lead-based paint. It is rapidly absorbed into the bloodstream and is believed to have adverse effects on the central nervous system, the cardiovascular system, kidneys, and the immune system.

The component limit of lead ( $1.0 \mu\text{g/g}$ ) is a test benchmark for pharmaceuticals, representing the maximum daily intake an individual should have. However, even at this low level, a prolonged intake can be hazardous to human beings. The treatment for lead poisoning consists of dimercaprol and succimer.

The concern about lead's role in cognitive deficits in children has brought about widespread reduction in its use (lead exposure has been linked to learning disabilities). Most cases of adult elevated blood lead levels are workplace-related. High blood levels are associated with delayed puberty in girls. Lead has been shown many times to permanently reduce the cognitive capacity of children at extremely low levels of exposure.

During the 20th century, the use of lead in paint pigments was sharply reduced because of the danger of lead poisoning, especially to children. By the mid-1980s, a significant shift in lead end-use patterns had taken place. Much of this shift was a result of the U.S. lead consumers' compliance with environmental regulations that significantly reduced or eliminated the use of lead in non-battery products, including gasoline, paints, solders, and water systems. Lead use is being further curtailed by the European Union's RoHS directive. Lead may still be found in harmful quantities in stoneware, vinyl (such as that used for tubing and the insulation of electrical cords), and Chinese brass. Older houses may still contain substantial amounts of lead paint. White lead paint has been withdrawn from sale in industrialized countries, but the yellow lead chromate is still in use. Old paint should not be stripped by sanding, as this produces inhalable dust.

Lead salts used in pottery glazes have on occasion caused poisoning, when acidic drinks, such as fruit juices, have leached lead ions out of the glaze. It has been suggested that what was known as "Devon colic" arose from the use of lead-lined presses to extract apple juice in the manufacture of cider. Lead is considered to be particularly harmful for women's ability to reproduce. Lead(II) acetate (also known as *sugar of lead*) was used in the Roman Empire as a sweetener for wine, and some consider this to be the cause of the dementia that affected many of the Roman Emperors and even be a partial reason for the Roman Empire's fall.

## Biochemistry of Poisoning

In the human body, lead inhibits porphobilinogen synthase and ferrochelatase, preventing both porphobilinogen formation and the incorporation of iron into protoporphyrin IX, the final step in heme synthesis. This causes ineffective heme synthesis and subsequent microcytic anemia. At lower levels, it acts as a calcium analog, interfering with ion channels during nerve conduction.

This is one of the mechanisms by which it interferes with cognition. Acute lead poisoning is treated using disodium calcium edetate: the calcium chelate of the disodium salt of ethylene-diamine-tetracetic acid (EDTA). This chelating agent has a greater affinity for lead than for calcium and so the lead chelate is formed by exchange. This is then excreted in the urine leaving behind harmless calcium. According to the Agency for Toxic Substance and Disease Registry, a small amount of ingested lead (1%) will store itself in bones, and the rest will be excreted by an adult through urine and feces within a few weeks of exposure. However, only about 32% of lead will be excreted by a child.

### **Exposure**

Exposure to lead and lead chemicals can occur through inhalation, ingestion and dermal contact. Most exposure occurs through ingestion or inhalation; in the U.S. the skin exposure is unlikely as leaded gasoline additives are no longer used. Lead exposure is a global issue as lead mining and lead smelting are common in many countries.

Most countries have stopped using lead-containing gasoline by 2007. Lead exposure mostly occurs through ingestion.

Lead paint is the major source of lead exposure for children. As lead paint deteriorates, it peels, is pulverized into dust and then enters the body through hand-to-mouth contact or through contaminated food, water or alcohol. Ingesting certain home remedy medicines may also expose people to lead or lead compounds. Lead can be ingested through fruits and vegetables contaminated by high levels of lead in the soils they were grown in.

Soil is contaminated through particulate accumulation from lead in pipes, lead paint and residual emissions from leaded gasoline that was used before the Environment Protection Agency issue the regulation around 1980. The use of lead for water pipes is problematic in areas with soft or (and) acidic water. Hard water forms insoluble layers in the pipes while soft and acidic water dissolves the lead pipes.

Inhalation is the second major pathway of exposure, especially for workers in lead-related occupations. Almost all inhaled lead is absorbed into the body, the rate is 20–70% for ingested lead; children absorb more than adults. Dermal exposure may be significant for a narrow category of people working with organic lead compounds, but is of little concern for general population. The rate of skin absorption is also low for inorganic lead.

## Mercury - Inorganic Contaminant 0.002 mg/L MCL

EPA regulates mercury in drinking water to protect public health. Mercury may cause health problems if present in public or private water supplies in amounts greater than the drinking water standard set by EPA.

### What is Mercury?

Mercury is a liquid metal found in natural deposits such as ores containing other elements.

### Uses for Mercury

Electrical products such as dry-cell batteries, fluorescent light bulbs, switches, and other control equipment account for 50 percent of mercury used.

### What are Mercury's Health Effects?

Some people who drink water containing mercury well in excess of the maximum contaminant level (MCL) for many years could experience kidney damage.

This health effects language is not intended to catalog all possible health effects for mercury. Rather, it is intended to inform consumers of some of the possible health effects associated with mercury in drinking water when the rule was finalized.

### What are EPA's Drinking Water Regulations for Mercury?

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for mercury is 0.002 mg/L or 2 ppb. EPA has set this level of protection based on the best available science to prevent potential health problems. EPA has set an enforceable regulation for mercury, called a maximum contaminant level (MCL), at 0.002 mg/L or 2 ppb.

MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.

The Phase II Rule, the regulation for mercury, became effective in 1992. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate.

EPA reviewed mercury as part of the Six Year Review and determined that the 0.002 mg/L or 2 ppb MCLG and 0.002 mg/L or 2 ppb MCL for mercury are still protective of human health.

States may set more stringent drinking water MCLGs and MCLs for mercury than EPA.



### **How does Mercury get into my Drinking Water?**

The major sources of mercury in drinking water are erosion of natural deposits; discharge from refineries and factories; runoff from landfills; and runoff from croplands. A federal law called the Emergency Planning and Community Right to Know Act (EPCRA) requires facilities in certain industries, which manufacture, process, or use significant amounts of toxic chemicals, to report annually on their releases of these chemicals. For more information on the uses and releases of chemicals in your state, contact the Community Right-to-Know Hotline: (800) 424-9346.

### **How will I know if Mercury is in my Drinking Water?**

When routine monitoring indicates that mercury levels are above the MCL, your water supplier must take steps to reduce the amount of mercury so that it is below that level. Water suppliers must notify their customers as soon as practical, but no later than 30 days after the system learns of the violation. Additional actions, such as providing alternative drinking water supplies, may be required to prevent serious risks to public health. If your water comes from a household well, check with your health department or local water systems that use ground water for information on contaminants of concern in your area.

### **How will Mercury be removed from my Drinking Water?**

The following treatment method(s) have proven to be effective for removing mercury to below 0.002 mg/L or 2 ppb: coagulation/filtration, granular activated carbon, lime softening, and reverse osmosis.

### **How do I learn more about my Drinking Water?**

EPA strongly encourages people to learn more about their drinking water, and to support local efforts to protect the supply of safe drinking water and upgrade the community water system. Your water bill or telephone book's government listings are a good starting point for local information.

Contact your water utility. EPA requires all community water systems to prepare and deliver an annual consumer confidence report (CCR) (sometimes called a water quality report) for their customers by July 1 of each year. If your water provider is not a community water system, or if you have a private water supply, request a copy from a nearby community water system.

### **Mercury Explained**

**Mercury** is a chemical element with the symbol **Hg** and atomic number 80. It is also known as **quicksilver** or **hydrargyrum** (< Greek "hydr-" *water* and "argyros" *silver*). A heavy, silvery d-block element, mercury is the only metal that is liquid at standard conditions for temperature and pressure; the only other element that is liquid under these conditions is bromine, though metals such as caesium, gallium, and rubidium melt just above room temperature.

With a freezing point of  $-38.83\text{ }^{\circ}\text{C}$  and boiling point of  $356.73\text{ }^{\circ}\text{C}$ , mercury has one of the narrowest ranges of its liquid state of any metal.

Mercury occurs in deposits throughout the world mostly as cinnabar (mercuric sulfide). The red pigment vermilion is mostly obtained by reduction from cinnabar. Cinnabar is highly toxic by ingestion or inhalation of the dust. Mercury poisoning can also result from exposure to water-soluble forms of mercury (such as mercuric chloride or methylmercury), inhalation of mercury vapor, or eating seafood contaminated with mercury.

Mercury is used in thermometers, barometers, manometers, sphygmomanometers, float valves, mercury switches, and other devices though concerns about the element's toxicity have led to mercury thermometers and sphygmomanometers being largely phased out in clinical environments in favor of alcohol-filled, galinstan-filled, digital, or thermistor-based instruments. It remains in use in scientific research applications and in amalgam material for dental restoration. It is used in lighting: electricity passed through mercury vapor in a phosphor tube produces short-wave ultraviolet light which then causes the phosphor to fluoresce, making visible light.

### Physical Properties

Mercury is a heavy, silvery-white metal. As compared to other metals, it is a poor conductor of heat, but a fair conductor of electricity. Mercury has an exceptionally low melting temperature for a d-block metal. A complete explanation of this delves deep into the realm of quantum physics, but it can be summarized as follows: mercury has a unique electronic configuration where electrons fill up all the available 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d and 6s subshells.

As such configuration strongly resists removal of an electron; mercury behaves similarly to noble gas elements, which form weak bonds and thus easily melting solids. The stability of the 6s shell is due to the presence of a filled 4f shell. An f shell poorly screens the nuclear charge that increases the attractive Coulomb interaction of the 6s shell and the nucleus (see lanthanide contraction).

The absence of a filled inner *f* shell is the reason for the somewhat higher melting temperature of cadmium and zinc, although both these metals still melt easily and, in addition, have unusually low boiling points. On the other hand, gold, which is one space to the left of mercury on the periodic table, has atoms with one less 6s electron than mercury. Those electrons are more easily removed and are shared between the gold atoms forming relatively strong metallic bonds.

### Chemical Properties

Mercury does not react with most acids, such as dilute sulfuric acid, although oxidizing acids such as concentrated sulfuric acid and nitric acid or aqua regia dissolve it to give sulfate, nitrate, and chloride salts. Like silver, mercury reacts with atmospheric hydrogen sulfide. Mercury even reacts with solid sulfur flakes, which are used in mercury spill kits to absorb mercury vapors (spill kits also use activated carbon and powdered zinc).

### Amalgams

Mercury dissolves to form amalgams with gold, zinc and many other metals. Because iron is an exception, iron flasks have been traditionally used to trade mercury. Other metals that do not form amalgams with mercury include tantalum, tungsten and platinum. Sodium amalgam is a common reducing agent in organic synthesis, and is also used in high-pressure sodium lamps.

Mercury readily combines with aluminum to form a mercury-aluminum amalgam when the two pure metals come into contact. Since the amalgam destroys the aluminum oxide layer which protects metallic aluminum from oxidizing in-depth (as in iron rusting), even small amounts of mercury can seriously corrode aluminum. For this reason, mercury is not allowed aboard an aircraft under most circumstances because of the risk of it forming an amalgam with exposed aluminum parts in the aircraft.

### Isotopes

There are seven stable isotopes of mercury with  $^{202}\text{Hg}$  being the most abundant (29.86%). The longest-lived radioisotopes are  $^{194}\text{Hg}$  with a half-life of 444 years, and  $^{203}\text{Hg}$  with a half-life of 46.612 days. Most of the remaining radioisotopes have half-lives that are less than a day.  $^{199}\text{Hg}$  and  $^{201}\text{Hg}$  are the most often studied NMR-active nuclei, having spins of  $\frac{1}{2}$  and  $\frac{3}{2}$  respectively.

## History



The symbol for the planet Mercury (♿) has been used since ancient times to represent the element.

In China and Tibet, mercury use was thought to prolong life, heal fractures, and maintain generally good health, although it is now known that exposure to mercury leads to serious adverse health effects. The first emperor of China, Qín Shǐ Huáng Dì — allegedly buried in a tomb that contained rivers of flowing mercury on a model of the land he ruled, representative of the rivers of China — was killed by drinking a mercury and powdered jade mixture formulated by Qin alchemists (causing liver failure, mercury poisoning, and brain death) who intended to give him eternal life.

The ancient Greeks used mercury in ointments; the ancient Egyptians and the Romans used it in cosmetics which sometimes deformed the face. In Lamanai, once a major city of the Maya civilization, a pool of mercury was found under a marker in a Mesoamerican ballcourt. By 500 BC mercury was used to make amalgams (Medieval Latin *amalgama*, "alloy of mercury") with other metals.

Alchemists thought of mercury as the First Matter from which all metals were formed. They believed that different metals could be produced by varying the quality and quantity of sulfur contained within the mercury. The purest of these was gold, and mercury was called for in attempts at the transmutation of base (or impure) metals into gold, which was the goal of many alchemists.

Hg is the modern chemical symbol for mercury. It comes from *hydrargyrum*, a Latinized form of the Greek word ὕδραργυρος (*hydrargyros*), which is a compound word meaning "water-silver" (hydr = water, argyros = silver) — since it is liquid like water and shiny like silver. The element was named after the Roman god Mercury, known for speed and mobility. It is associated with the planet Mercury; the astrological symbol for the planet is also one of the alchemical symbols for the metal; the Sanskrit word for alchemy is *Rasavātam* which means "the way of mercury". Mercury is the only metal for which the alchemical planetary name became the common name.

The mines in Almadén (Spain), Monte Amiata (Italy), and Idrija (now Slovenia) dominated mercury production from the opening of the mine in Almadén 2500 years ago, until new deposits were found at the end of the 19th century.

## Chemistry

Mercury exists in two main oxidation states, I and II. Higher oxidation states are unimportant, but have been detected, e.g., mercury(IV) fluoride (HgF<sub>4</sub>) but only under extraordinary conditions.

### Compounds of Mercury (I)

Different from its lighter neighbors, cadmium and zinc, mercury forms simple stable compounds with metal-metal bonds. The mercury(I) compounds are diamagnetic and feature the dimeric cation, Hg<sub>2</sub><sup>2+</sup>.

Stable derivatives include the chloride and nitrate. Treatment of Hg(I) compounds complexation with strong ligands such as sulfide, cyanide, etc. induces disproportionation to  $\text{Hg}^{2+}$  and elemental mercury. Mercury(I) chloride, a colorless solid also known as calomel, is really the compound with the formula  $\text{Hg}_2\text{Cl}_2$ , with the connectivity Cl-Hg-Hg-Cl. It is a standard in electrochemistry. It reacts with chlorine to give mercuric chloride, which resists further oxidation.

Indicative of its tendency to bond to itself, mercury forms mercury polycations, which consist of linear chains of mercury centers, capped with a positive charge. One example is  $\text{Hg}_2^{3+}(\text{AsF}_6^-)_2$ .

### Compounds of Mercury (II)

Mercury(II) is the most common oxidation state and is the main one in nature as well. All four mercuric halides are known. The form tetrahedral complexes with other ligands but the halides adopt linear coordination geometry, somewhat like  $\text{Ag}^+$  does. Best known is mercury(II) chloride, an easily sublimating white solid.  $\text{HgCl}_2$  forms coordination complexes that are typically tetrahedral, e.g.  $\text{HgCl}_2\cdot 4\text{L}$ .

Mercury(II) oxide, the main oxide of mercury, arises when the metal is exposed to air for long periods at elevated temperatures. It reverts to the elements upon heating near  $400^\circ\text{C}$ , as was demonstrated by Priestly in an early synthesis of pure oxygen. Hydroxides of mercury are poorly characterized, as they are for its neighbors gold and silver.

Being a soft metal, mercury forms very stable derivatives with the heavier chalcogens. Preeminent is mercury(II) sulfide,  $\text{HgS}$ , which occurs in nature as the ore cinnabar and is the brilliant pigment vermilion. Like  $\text{ZnS}$ ,  $\text{HgS}$  crystallizes in two forms, the reddish cubic form and the black zinc blende form. Mercury(II) selenide ( $\text{HgSe}$ ) and mercury(II) telluride ( $\text{HgTe}$ ) are also known, these as well as various derivatives, e.g. mercury cadmium telluride and mercury zinc telluride being semiconductors useful as infrared detector materials.

Mercury(II) salts form a variety of complex derivatives with ammonia. These include Millon's base ( $\text{Hg}_2\text{N}^+$ ), the one-dimensional polymer (salts of  $\text{Hg}(\text{NH}_2)_n$ ), and "fusible white precipitate" or  $[\text{Hg}(\text{NH}_3)_2]\text{Cl}_2$ . Known as Nessler's reagent, potassium tetraiodomercurate(II) ( $\text{HgI}_2\cdot 4\text{K}^+$ ) is still occasionally used to test for ammonia owing to its tendency to form the deeply colored iodide salt of Millon's base.

### Higher Oxidation States

Oxidation states above +2 in a non-charged species are extremely rare, although a cyclic mercurinium(IV) cation, with three substituents, is an intermediate in oxymercuration reactions. In 2007, a report of synthesis of a mercury(IV) compound, mercury(IV) fluoride, was published. In the 1970s, there was a claim on synthesis of a mercury(III) compound, but it is now thought to be false.

### Organomercury Compounds

Organic mercury compounds are historically important but are of little industrial value in the western world. Mercury(II) salts are a rare examples of simple metal complexes that react directly with aromatic rings. Organomercury compounds are always divalent and usually two-coordinate and linear geometry. Unlike organocadmium and organozinc compounds, organomercury, . compounds do not react with water.

They usually have the formula  $\text{HgR}_2$ , which are often volatile, or  $\text{HgRX}$ , which are often solids, where R is aryl or alkyl and X is usually halide or acetate. Methylmercury, a generic term for compounds with the formula  $\text{CH}_3\text{HgX}$ , is a dangerous family of compounds that are often found in polluted water. They arise by a process known as biomethylation.

## Applications

Mercury is used primarily for the manufacture of industrial chemicals or for electrical and electronic applications. It is used in some thermometers, especially ones which are used to measure high temperatures. A still increasing amount is used as gaseous mercury in fluorescent lamps, while most of the other applications are slowly phased out due to health and safety regulations and is in some applications replaced with less toxic but considerably more expensive Galinstan alloy.

## Medicine

Mercury and its compounds have been used in medicine, although they are much less common today than they once were, now that the toxic effects of mercury and its compounds are more widely understood. The element mercury is an ingredient in dental amalgams. Thiomersal (called *Thimerosal* in the United States) is an organic compound used as a preservative in vaccines, though this use is in decline. Another mercury compound Merbromin (Mercurochrome) is a topical antiseptic used for minor cuts and scrapes is still in use in some countries.

Since the 1930s some vaccines have contained the preservative thiomersal, which is metabolized or degraded to ethyl mercury. Although it was widely speculated that this mercury-based preservative can cause or trigger autism in children, scientific studies showed no evidence supporting any such link. Nevertheless thiomersal has been removed from or reduced to trace amounts in all U.S. vaccines recommended for children 6 years of age and under, with the exception of inactivated influenza vaccine.

Mercury in the form of one of its common ores, cinnabar, is used in various traditional medicines, especially in traditional Chinese medicine. Review of its safety has found cinnabar can lead to significant mercury intoxication when heated, consumed in overdose or taken long term, and can have adverse effects at therapeutic doses, though this is typically reversible at therapeutic doses. Although this form of mercury appears less toxic than others, its use in traditional Chinese medicine has not yet been justified as the therapeutic basis for the use of cinnabar is not clear.

Today, the use of mercury in medicine has greatly declined in all respects, especially in developed countries. Thermometers and sphygmomanometers containing mercury were invented in the early 18th and late 19th centuries, respectively. In the early 21st century, their use is declining and has been banned in some countries, states and medical institutions.

In 2002, the U.S. Senate passed legislation to phase out the sale of non-prescription mercury thermometers. In 2003, Washington and Maine became the first states to ban mercury blood pressure devices. Mercury compounds are found in some over-the-counter drugs, including topical antiseptics, stimulant laxatives, diaper-rash ointment, eye drops, and nasal sprays.

The FDA has "inadequate data to establish general recognition of the safety and effectiveness", of the mercury ingredients in these products. Mercury is still used in some diuretics, although substitutes now exist for most therapeutic uses.

## Production of Chlorine and Caustic Soda

Chlorine is produced from sodium chloride (common salt, NaCl) using electrolysis to separate the metallic sodium from the chlorine gas. Usually the salt is dissolved in water to produce a brine. By-products of any such chloralkali process are hydrogen ( $H_2$ ) and sodium hydroxide (NaOH), which is commonly called caustic soda or lye. By far the largest use of mercury in the late 20th century was in the mercury cell process (also called the Castner-Kellner process) where metallic sodium is formed as an amalgam at a cathode made from mercury; this sodium is then reacted with water to produce sodium hydroxide. Many of the industrial mercury releases of the 20th century came from this process, although modern plants claimed to be safe in this regard.

After about 1985, all new chloralkali production facilities that were built in the United States used either membrane cell or diaphragm cell technologies to produce chlorine.

### **Laboratory Uses**

Some medical thermometers, especially those for high temperatures, are filled with mercury; however, they are gradually disappearing. In the United States, non-prescription sale of mercury fever thermometers has been banned since 2003.

Liquid mercury is a part of popular secondary reference electrode (called the calomel electrode) in electrochemistry as an alternative to the standard hydrogen electrode. The calomel electrode is used to work out the electrode potential of half cells. Last, but not least, the triple point of mercury,  $-38.8344\text{ }^{\circ}\text{C}$ , is a fixed point used as a temperature standard for the International Temperature Scale (ITS-90).

### **Toxicity and Safety**

Mercury and most of its compounds are extremely toxic and must be handled with care; in cases of spills involving mercury (such as from certain thermometers or fluorescent light bulbs), specific cleaning procedures are used to avoid exposure and contain the spill. Protocols call for physically merging smaller droplets on hard surfaces, combining them into a single larger pool for easier removal with an eyedropper, or for gently pushing the spill into a disposable container. Vacuum cleaners and brooms cause greater dispersal of the mercury and should not be used.

Afterwards, fine sulfur, zinc, or some other powder that readily forms an amalgam (alloy) with mercury at ordinary temperatures is sprinkled over the area before itself being collected and properly disposed of. Cleaning porous surfaces and clothing is not effective at removing all traces of mercury and it is therefore advised to discard these kinds of items should they be exposed to a mercury spill.

Mercury can be absorbed through the skin and mucous membranes and mercury vapors can be inhaled, so containers of mercury are securely sealed to avoid spills and evaporation.

Heating of mercury, or of compounds of mercury that may decompose when heated, is always carried out with adequate ventilation in order to avoid exposure to mercury vapor. The most toxic forms of mercury are its organic compounds, such as dimethylmercury and methylmercury. Inorganic compounds, such as cinnabar are also highly toxic by ingestion or inhalation. Mercury can cause both chronic and acute poisoning.

### **Releases in the Environment**

Amount of atmospheric mercury deposited at Wyoming's Upper Fremont Glacier over the last 270 years

Preindustrial deposition rates of mercury from the atmosphere may be about  $4\text{ ng}/(1\text{ L of ice deposit})$ . Although that can be considered a natural level of exposure, regional or global sources have significant effects. Volcanic eruptions can increase the atmospheric source by 4–6 times. Natural sources, such as volcanoes, are responsible for approximately half of atmospheric mercury emissions.

The human-generated half can be divided into the following estimated percentages:

- 65% from stationary combustion, of which coal-fired power plants are the largest aggregate source (40% of U.S. mercury emissions in 1999). This includes power plants fueled with gas where the mercury has not been removed. Emissions from coal combustion are

between one and two orders of magnitude higher than emissions from oil combustion, depending on the country.

- 11% from gold production. The three largest point sources for mercury emissions in the U.S. are the three largest gold mines. Hydrogeochemical release of mercury from gold-mine tailings has been accounted as a significant source of atmospheric mercury in eastern Canada.
- 6.8% from non-ferrous metal production, typically smelters.
- 6.4% from cement production.
- 3.0% from waste disposal, including municipal and hazardous waste, crematoria, and sewage sludge incineration.
- 3.0% from caustic soda production.
- 1.4% from pig iron and steel production.
- 1.1% from mercury production, mainly for batteries.
- 2.0% from other sources.

The above percentages are estimates of the global human-caused mercury emissions in 2000, excluding biomass burning, an important source in some regions.

Mercury also enters into the environment through the improper disposal (e.g., land filling, incineration) of certain products. Products containing mercury include: auto parts, batteries, fluorescent bulbs, medical products, thermometers, and thermostats.

Due to health concerns (see below), toxics use reduction efforts are cutting back or eliminating mercury in such products. For example, the amount of mercury sold in thermostats in the United States decreased from 14.5 tons in 2004 to 3.9 tons in 2007.

Most thermometers now use pigmented alcohol instead of mercury, and galinstan alloy thermometers are also an option.

Mercury thermometers are still occasionally used in the medical field because they are more accurate than alcohol thermometers, though both are commonly being replaced by electronic thermometers and less commonly by galinstan thermometers. Mercury thermometers are still widely used for certain scientific applications because of their greater accuracy and working range.

The United States Clean Air Act, passed in 1990, put mercury on a list of toxic pollutants that need to be controlled to the greatest possible extent.

Thus, industries that release high concentrations of mercury into the environment agreed to install maximum achievable control technologies (MACT). In March 2005 EPA rule added power plants to the list of sources that should be controlled and a national cap and trade rule was issued.

States were given until November 2006 to impose stricter controls, and several States are doing so. The rule was being subjected to legal challenges from several States in 2005 and decision was made in 2008. The Clean Air Mercury Rule was struck down by a Federal Appeals Court on February 8, 2008. The rule was deemed not sufficient to protect the health of persons living near coal-fired power plants. The court opinion cited the negative impact on human health from coal-fired power plants' mercury emissions documented in the EPA Study Report to Congress of 1998.

The EPA announced new rules for coal-fired power plants on December 22, 2011. Cement kilns that burn hazardous waste are held to a looser standard than are standard hazardous waste incinerators in the United States, and as a result are a disproportionate source of mercury pollution.

Historically, one of the largest releases was from the Colex plant, a lithium-isotope separation plant at Oak Ridge. The plant operated in the 1950s and 1960s. Records are incomplete and unclear, but government commissions have estimated that some two million pounds of mercury are unaccounted for.

A serious industrial disaster was the dumping of mercury compounds into Minamata Bay, Japan. It is estimated that over 3,000 people suffered various deformities, severe mercury poisoning symptoms or death from what became known as Minamata disease.

### **Occupational Exposure**

Due to the health effects of mercury exposure, industrial and commercial uses are regulated in many countries. The World Health Organization, OSHA, and NIOSH all treat mercury as an occupational hazard, and have established specific occupational exposure limits. Environmental releases and disposal of mercury are regulated in the U.S. primarily by the United States Environmental Protection Agency.

Case control studies have shown effects such as tremors, impaired cognitive skills, and sleep disturbance in workers with chronic exposure to mercury vapor even at low concentrations in the range 0.7–42  $\mu\text{g}/\text{m}^3$ . A study has shown that acute exposure (4 – 8 hours) to calculated elemental mercury levels of 1.1 to 44  $\text{mg}/\text{m}^3$  resulted in chest pain, dyspnea, cough, hemoptysis, impairment of pulmonary function, and evidence of interstitial pneumonitis. Acute exposure to mercury vapor has been shown to result in profound central nervous system effects, including psychotic reactions characterized by delirium, hallucinations, and suicidal tendency.

Occupational exposure has resulted in broad-ranging functional disturbance, including erethism, irritability, excitability, excessive shyness, and insomnia. With continuing exposure, a fine tremor develops and may escalate to violent muscular spasms. Tremor initially involves the hands and later spreads to the eyelids, lips, and tongue. Long-term, low-level exposure has been associated with more subtle symptoms of erethism, including fatigue, irritability, loss of memory, vivid dreams and depression.

### **Treatment**

Research on the treatment of mercury poisoning is limited. Currently available drugs for acute mercurial poisoning include chelators N-acetyl-D, L-penicillamine (NAP), British Anti-Lewisite (BAL), 2,3-dimercapto-1-propanesulfonic acid (DMPS), and dimercaptosuccinic acid (DMSA). In one small study including 11 construction workers exposed to elemental mercury, patients were treated with DMSA and NAP. Chelation therapy with both drugs resulted in the mobilization of a small fraction of the total estimated body mercury. DMSA was able to increase the excretion of mercury to a greater extent than NAP.

### **Fish**

Fish and shellfish have a natural tendency to concentrate mercury in their bodies, often in the form of methylmercury, a highly toxic organic compound of mercury. Species of fish that are high on the food chain, such as shark, swordfish, king mackerel, bluefin tuna, albacore tuna, and tilefish contain higher concentrations of mercury than others. As mercury and methylmercury are fat soluble, they primarily accumulate in the viscera, although they are also found throughout the muscle tissue. When this fish is consumed by a predator, the mercury level is accumulated. Since fish are less efficient at depurating than accumulating methylmercury, fish-tissue concentrations increase over time. Thus species that are high on the food chain amass body burdens of mercury that can be ten times higher than the species they consume. This process is called biomagnification. Mercury poisoning happened this way in Minamata, Japan, now called Minamata disease.

## **Regulations**

### **United States**

In the United States, the Environmental Protection Agency is charged with regulating and managing mercury contamination. Several laws give the EPA this authority, including the Clean Air Act, the Clean Water Act, the Resource Conservation and Recovery Act, and the Safe Drinking Water Act. Additionally, the Mercury-Containing and Rechargeable Battery Management Act, passed in 1996, phases out the use of mercury in batteries, and provides for the efficient and cost-effective disposal of many types of used batteries. North America contributed approximately 11% of the total global anthropogenic mercury emissions in 1995.

## Nitrate (Measured as Nitrogen) - Inorganic Contaminant 10 mg/L MCL

EPA regulates nitrate in drinking water to protect public health. Nitrate may cause health problems if present in public or private water supplies in amounts greater than the drinking water standard set by EPA.

### What is Nitrate?

Nitrates and nitrites are nitrogen-oxygen chemical units which combine with various organic and inorganic compounds.

### Uses for Nitrate

The greatest use of nitrates is as a fertilizer. Once taken into the body, nitrates are converted to nitrites.

### What are Nitrate's Health Effects?

Infants below six months who drink water containing nitrate in excess of the maximum contaminant level (MCL) could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue baby syndrome.



This health effects language is not intended to catalog all possible health effects for nitrate. Rather, it is intended to inform consumers of some of the possible health effects associated with nitrate in drinking water when the rule was finalized.

### What are EPA's Drinking Water Regulations for Nitrate?

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for nitrate is 10 mg/L or 10 ppm. EPA has set this level of protection based on the best available science to prevent potential health problems. EPA has set an enforceable regulation for nitrate, called a maximum contaminant level (MCL), at 10 mg/L or 10 ppm.

MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.

The Phase II Rule, the regulation for nitrate, became effective in 1992. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed nitrate as part of the Six Year Review and determined that the 10 mg/L or 10 ppm MCLG and 10 mg/L or 10 ppm MCL for nitrate are still protective of human health.

States may set more stringent drinking water MCLGs and MCLs for nitrate than EPA.

### **How does Nitrate get into my Drinking Water?**

The major sources of nitrates in drinking water are runoff from fertilizer use; leaking from septic tanks, sewage; and erosion of natural deposits.

A federal law called the Emergency Planning and Community Right to Know Act (EPCRA) requires facilities in certain industries, which manufacture, process, or use significant amounts of toxic chemicals, to report annually on their releases of these chemicals. For more information on the uses and releases of chemicals in your state, contact the Community Right-to-Know Hotline: (800) 424-9346.

### **How will I know if Nitrate is in my Drinking Water?**

When routine monitoring indicates that nitrate levels are above the MCL, your water supplier must take steps to reduce the amount of nitrate so that it is below that level. Water suppliers must notify their customers as soon as practical, but no later than 24 hours after the system learns of the violation. Additional actions, such as providing alternative drinking water supplies, may be required to prevent serious risks to public health.

If your water comes from a household well, check with your health department or local water systems that use ground water for information on contaminants of concern in your area.

### **How will nitrate be Removed from my Drinking Water?**

The following treatment method(s) have proven to be effective for removing nitrate to below 10 mg/L or 10 ppm: ion exchange, reverse osmosis, electrodialysis.

### **How do I learn more about my Drinking Water?**

EPA strongly encourages people to learn more about their drinking water, and to support local efforts to protect the supply of safe drinking water and upgrade the community water system. Your water bill or telephone book's government listings are a good starting point for local information.

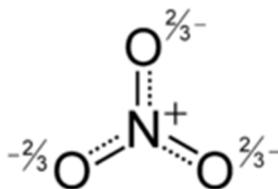
Contact your water utility. EPA requires all community water systems to prepare and deliver an annual consumer confidence report (CCR) (sometimes called a water quality report) for their customers by July 1 of each year. If your water provider is not a community water system, or if you have a private water supply, request a copy from a nearby community water system.

## **Nitrate Explained**

The **nitrate ion** is a polyatomic ion with the molecular formula  $\text{NO}_3^-$  and a molecular mass of 62.0049 g/mol.

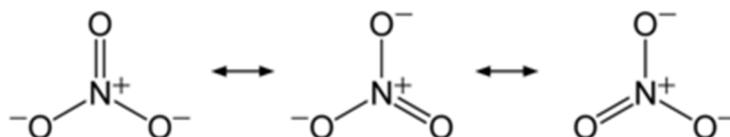
### **Structure**

It is the conjugate base of nitric acid, consisting of one central nitrogen atom surrounded by three identically bonded oxygen atoms in a trigonal planar arrangement. The nitrate ion carries a formal charge of -1. This results from a combination formal charge in which each of the three oxygens carries a  $-\frac{2}{3}$  charge, whereas the nitrogen carries a +1 charge, all these adding up to formal charge of the polyatomic nitrate ion.



The nitrate ion. The net charge of the whole ion is  $1^-$ .

This arrangement is commonly used as an example of resonance. Like the isoelectronic carbonate ion, the nitrate ion can be represented by resonance structures:



### Properties

Almost all inorganic nitrate salts are soluble in water at standard temperature and pressure. A common example of an inorganic nitrate salt is potassium nitrate (saltpeter).

In organic chemistry a nitrate (not to be confused with Nitro or Nitrite) is a relatively rare functional group with general chemical formula  $\text{RONO}_2$  where R stands for any organic residue. They are the esters of nitric acid and alcohols formed by **nitroxylation**. Examples are **methyl nitrate** formed by reaction of methanol and nitric acid, the nitrate of tartaric acid, and the inaccurately named nitroglycerin (which is actually an organic *nitrate* compound, not a *nitro* compound).

Like organic nitro compounds (see below) both organic and inorganic nitrates can be used as propellants and explosives. In these uses, the thermal decomposition of the nitrate yields molecular nitrogen  $\text{N}_2$  gas plus considerable chemical energy, due to the high strength of the bond in molecular nitrogen. Especially in inorganic nitrate reactions, oxidation from the nitrate oxygens is also an important energy-releasing process.

### Occurrence

Nitrate compounds are found naturally on earth as large deposits, particularly of Chile saltpeter a major source of sodium nitrate.

Nitrites are produced by a number of species of nitrifying bacteria, and the nitrate compounds for gunpowder (see this topic for more) were historically produced, in the absence of mineral nitrate sources, by means of various fermentation processes using urine and dung.

### Uses

Nitrates are mainly produced for use as fertilizers in agriculture because of their high solubility and biodegradability. The main nitrates are ammonium, sodium, potassium, and calcium salts. Several million kilograms are produced annually for this purpose.

### Other Uses

The second major application of nitrates as oxidizing agents, most notably in explosives where the rapid oxidation of carbon compounds liberates large volumes of gases (see Gunpowder for an example). Sodium nitrate is used to remove air bubbles from molten glass and some ceramics. Mixtures of the molten salt are used to harden some metals.

## Detection

Free nitrate ions in solution can be detected by a nitrate ion selective electrode. Such electrodes analogously to the pH selective electrode. This response is partially described by the Nernst equation.

## Toxicity/Toxicosis

**Nitrate toxicosis** can occur through enterohepatic metabolism of nitrate to nitrite being an intermediate. Nitrites oxidize the iron atoms in hemoglobin from ferrous iron (2+) to ferric iron (3+), rendering it unable to carry oxygen. This process can lead to generalized lack of oxygen in organ tissue and a dangerous condition called methemoglobinemia. Although nitrite converts to ammonia, if there is more nitrite than can be converted, the animal slowly suffers from a lack of oxygen.

## Human Health Effects

Humans are subject to nitrate toxicity, with infants being especially vulnerable to methemoglobinemia due to nitrate metabolizing triglycerides present at higher concentrations than at other stages of development. Methemoglobinemia in infants is known as blue baby syndrome. Although nitrates in drinking water were once thought to be a contributing factor, there are now significant scientific doubts as to whether there is a causal link.

Blue baby syndrome is now thought to be the product of a number of factors, which can include any factor which causes gastric upset, such as diarrheal infection, protein intolerance, heavy metal toxicity etc., with nitrates playing a minor role. Nitrates, if a factor in a specific case, would most often be ingested by infants in high nitrate drinking water. However, nitrate exposure may also occur if eating, for instance, vegetables containing high levels of nitrate. Lettuce may contain elevated nitrate under growth conditions such as reduced sunlight, undersupply of the essential micronutrients molybdenum (Mo) and iron (Fe), or high concentrations of nitrate due to reduced assimilation of nitrate in the plant.

High levels of nitrate fertilization also contribute to elevated levels of nitrate in the harvested plant.

Some adults can be more susceptible to the effects of nitrate than others. The methemoglobin reductase enzyme may be under-produced or absent in certain people that have an inherited mutation. Such individuals cannot break down methemoglobin as rapidly as those that do have the enzyme, leading to increased circulating levels of methemoglobin (the implication being that their blood is not as oxygen-rich). Those with insufficient stomach acid (including some vegetarians and vegans) may also be at risk. It is the increased consumption of green, leafy vegetables that typically accompany these types of diets may lead to increased nitrate intake. A wide variety of medical conditions, including food allergies, asthma, hepatitis, and gallstones may be linked with low stomach acid; these individuals may also be highly sensitive to the effects of nitrate.

Methemoglobinemia can be treated with methylene blue, which reduces ferric iron (3+) in affected blood cells back to ferrous iron (2+). Nitrate also is a by-product of septic systems. To be specific, it is a naturally occurring chemical that is left after the breakdown or decomposition of animal or human waste. Water quality may also be affected through ground water resources that have a high number of septic systems in a watershed. Septics leach down into ground water resources or aquifers and supply nearby bodies of water. Lakes that rely on ground water are often affected by nitrification through this process.

Nitrate in drinking water at levels above the national standard poses an immediate threat to young children. Excessive levels can result in a condition known as "blue baby syndrome". If untreated, the condition can be fatal. Boiling water contaminated with nitrate increases the nitrate concentration and the potential risk.





## Nitrite (Measured as Nitrogen) - Inorganic Contaminant 1 mg/L MCL

EPA regulates nitrite in drinking water to protect public health. Nitrite may cause health problems if present in public or private water supplies in amounts greater than the drinking water standard set by EPA.

### What is Nitrite?

Nitrates and nitrites are nitrogen-oxygen chemical units which combine with various organic and inorganic compounds.

### Uses for Nitrite

The greatest use of nitrates is as a fertilizer. Once taken into the body, nitrates are converted to nitrites.

### What are Nitrite's Health Effects?

Infants below six months who drink water containing nitrite in excess of the maximum contaminant level (MCL) could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue baby syndrome.



This health effects language is not intended to catalog all possible health effects for nitrite.

Rather, it is intended to inform consumers of some of the possible health effects associated with nitrite in drinking water when the rule was finalized.

### What are EPA's Drinking Water Regulations for Nitrite?

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for nitrite is 1 mg/L or 1 ppm. EPA has set this level of protection based on the best available science to prevent potential health problems. EPA has set an enforceable regulation for nitrite, called a maximum contaminant level (MCL), at 1 mg/L or 1 ppm.

MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.

The Phase II Rule, the regulation for nitrite, became effective in 1992. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed nitrite as part of the Six Year Review and determined that the 1 mg/L or 1 ppm MCLG and 1 mg/L or 1 ppm MCL for nitrite are still protective of human health. States may set more stringent drinking water MCLGs and MCLs for nitrite than EPA.

### **How does Nitrite get into my Drinking Water?**

The major sources of nitrite in drinking water are runoff from fertilizer use; leaching from septic tanks, sewage; and erosion of natural deposits.

A federal law called the Emergency Planning and Community Right to Know Act (EPCRA) requires facilities in certain industries, which manufacture, process, or use significant amounts of toxic chemicals, to report annually on their releases of these chemicals. For more information on the uses and releases of chemicals in your state, contact the Community Right-to-Know Hotline: (800) 424-9346.

### **How will I know if Nitrite is in my Drinking Water?**

When routine monitoring indicates that nitrite levels are above the MCL, your water supplier must take steps to reduce the amount of nitrite so that it is below that level. Water suppliers must notify their customers as soon as practical, but no later than 24 hours after the system learns of the violation. Additional actions, such as providing alternative drinking water supplies, may be required to prevent serious risks to public health.

If your water comes from a household well, check with your health department or local water systems that use ground water for information on contaminants of concern in your area.

### **How will Nitrite be removed from my Drinking Water?**

The following treatment method(s) have proven to be effective for removing nitrite to below 1 mg/L or 1 ppm: ion exchange, reverse osmosis.

### **How do I learn more about my Drinking Water?**

EPA strongly encourages people to learn more about their drinking water, and to support local efforts to protect the supply of safe drinking water and upgrade the community water system. Your water bill or telephone book's government listings are a good starting point for local information.

Contact your water utility. EPA requires all community water systems to prepare and deliver an annual consumer confidence report (CCR) (sometimes called a water quality report) for their customers by July 1 of each year. If your water provider is not a community water system, or if you have a private water supply, request a copy from a nearby community water system.

### **Nitrite Explained**

The **nitrite** ion, which has the chemical formula  $\text{NO}_2^-$ , is a symmetric anion with equal N-O bond lengths and a O-N-O bond angle of approximately  $120^\circ$ . Upon protonation, the unstable weak acid nitrous acid is produced.

Nitrite can be oxidized or reduced, with the product somewhat dependent on the oxidizing/reducing agent and its strength. The nitrite ion is an ambidentate ligand, and is known to bond to metal centers in at least five different ways.

Nitrite is also important in biochemistry as a source of the potent vasodilator nitric oxide. In organic chemistry the  $\text{NO}_2$  group is present in nitrous acid esters and nitro compounds. Nitrites are also used in the food production industry for curing meat.

## The Nitrite Ion

### Nitrite Salts

Sodium nitrite is made industrially by passing "nitrous fumes" into aqueous sodium hydroxide or sodium carbonate solution:



The product is purified by recrystallization. Alkali metal nitrites are thermally stable up to and beyond their melting point (441 °C for KNO<sub>2</sub>). Ammonium nitrite can be made from dinitrogen trioxide, N<sub>2</sub>O<sub>3</sub>, which is formally the anhydride of nitrous acid:



This compound may decompose explosively on heating. In organic chemistry nitrites are used in diazotization reactions.

### Structure

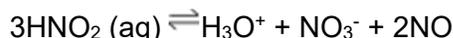
The nitrite ion has a symmetrical structure (C<sub>2v</sub> symmetry), with both N-O bonds having equal length. In valence bond theory, it is described as a resonance hybrid with equal contributions from two canonical forms that are mirror images of each other. In molecular orbital theory, there is a sigma bond between each oxygen atom and the nitrogen atom, and a delocalized pi bond made from the p orbitals on nitrogen and oxygen atoms which is perpendicular to the plane of the molecule. The negative charge of the ion is equally distributed on the two oxygen atoms. Both nitrogen and oxygen atoms carry a lone pair of electrons. Therefore, the nitrite ion is a Lewis base. Moreover, it can act as an ambidentate ligand towards a metal ion, donating a pair of electrons from either nitrogen or oxygen atoms.

### Acid-base Properties

In aqueous solution, nitrous acid is a weak acid:



Nitrous acid is also highly volatile - in the gas phase it exists predominantly as a *trans*-planar molecule. In solution, it is unstable with respect to the disproportionation reaction:



This reaction is slow at 0 °C. Addition of acid to a solution of a nitrite in the presence of a reducing agent, such as iron (II), is a way to make nitric oxide (NO) in the laboratory.

### Oxidation and reduction

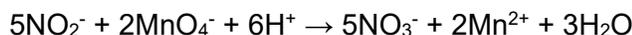
The formal oxidation state of the nitrogen atom in a nitrite is +3. This means that it can be either oxidized to oxidation states +4 and +5, or reduced to oxidation states as low as -3. Standard reduction potentials for reactions directly involving nitrous acid are shown in the table below:

Half-reaction	E <sup>0</sup> /V
$\text{NO}_3^- + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HNO}_2 + \text{H}_2\text{O}$	+0.94
$2\text{HNO}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{H}_2\text{N}_2\text{O}_2 + 2\text{H}_2\text{O}$	+0.86
$\text{N}_2\text{O}_4 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{HNO}_2$	+1.065
$2\text{HNO}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{N}_2\text{O} + 3\text{H}_2\text{O}$	+1.29

The data can be extended to include products in lower oxidation states. For example:



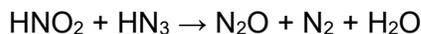
Oxidation reactions usually result in the formation of the nitrate ion, with nitrogen in oxidation state +5. For example, oxidation with permanganate ion can be used for quantitative analysis of nitrite (by titration):



The product of reduction reactions with nitrite ion are varied, depending on the reducing agent used and its strength. With sulfur dioxide, the products are NO and N<sub>2</sub>O; with tin (II), Sn<sup>2+</sup>, the product is hyponitrous acid, H<sub>2</sub>N<sub>2</sub>O<sub>2</sub>; reduction all the way to ammonia (NH<sub>3</sub>) occurs with hydrogen sulfide. With the hydrazinium cation, N<sub>2</sub>H<sub>5</sub><sup>+</sup>, hydrogen azide, HN<sub>3</sub>, an explosive compound, is produced:



which can also further react with nitrite:



This reaction is unusual in that it involves compounds with nitrogen in four different oxidation states.

### Coordination Complexes

The nitrite ion is known to form coordination complexes in at least five different ways.

1. When donation is from nitrogen to a metal center, the complex is known as a *nitro-* complex.
2. When donation is from one oxygen to a metal center, the complex is known as a *nitrito-* complex.
3. Both oxygen atoms may donate to a metal center, forming a chelate complex.
4. A nitrite ion can form an unsymmetrical bridge between two metal centers, donating through nitrogen to one metal, and through oxygen to the other.
5. A single oxygen atom can bridge to two metal centers.

Alfred Werner studied the nitro-nitrito isomerism (1 and 2) extensively. The red isomer of cobalt pentamine with nitrite is now known to be a nitrito complex, [Co(NH<sub>3</sub>)<sub>5</sub>(ONO)]<sup>2+</sup>; it is metastable and isomerizes to the yellow nitro complex [Co(NH<sub>3</sub>)<sub>5</sub>(NO<sub>2</sub>)]<sup>2+</sup>. An example of chelating nitrite (3) was found in [Cu(bipy)<sub>2</sub>(O<sub>2</sub>N)]NO<sub>3</sub> - "bipy" is the bidentate ligand 2,2'-bipyridyl, with the two bipy ligands occupying four coordination sites on the copper ion, so that the nitrite is forced to occupy two sites in order to achieve an octahedral environment around the copper ion.

### Nitrite in Biochemistry

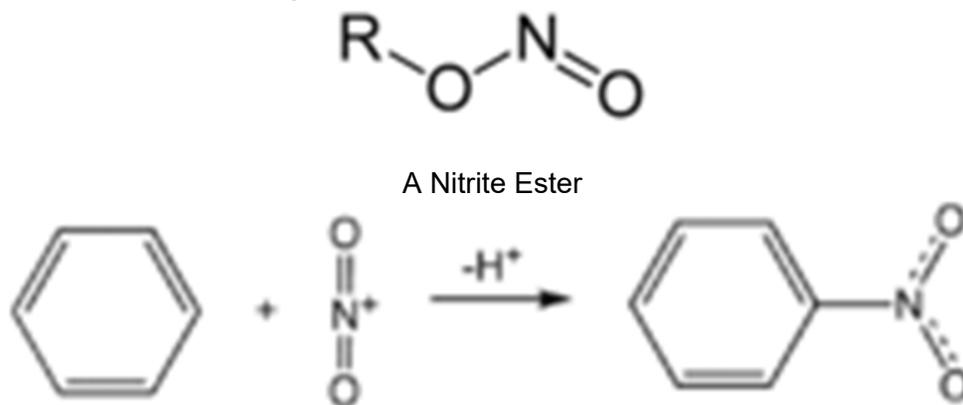
Sodium nitrite is used for the curing of meat because it prevents bacterial growth and, in a reaction with the meat's myoglobin, gives the product a desirable dark red color. Because of the relatively high toxicity of nitrite (the lethal dose in humans is about 22 milligrams per kilogram of body weight), the maximum allowed nitrite concentration in meat products is 200 ppm.

Under certain conditions - especially during cooking - nitrites in meat can react with degradation products of amino acids, forming nitrosamines, which are known carcinogens.

Nitrite is detected and analyzed by the Griess Reaction, involving the formation of a deep red-colored azo dye upon treatment of a  $\text{NO}_2^-$ -containing sample with sulfanilic acid and naphthyl-1-amine in the presence of acid. Nitrite can be reduced to nitric oxide or ammonia by many species of bacteria.

Under hypoxic conditions, nitrite may release nitric oxide, which causes potent vasodilation. Several mechanisms for nitrite conversion to NO have been described, including enzymatic reduction by xanthine oxidoreductase, nitrite reductase, and NO synthase (NOS), as well as nonenzymatic acidic disproportionation reactions.

### Organic Nitrites and Nitro Compounds



### Aromatic Nitration

In organic chemistry, nitrites are esters of nitrous acid and contain the nitrosoxy functional group. Nitro compounds contain the  $\text{C}-\text{NO}_2$  group. Nitrites have the general formula  $\text{RONO}$ , where R is an aryl or alkyl group.

Nitrobenzene is a simple example of a nitro compound. In aromatic nitration reactions a C-H bond is broken, leaving the two electrons on the carbon atom. These two electrons are added to the nitronium ion, reducing it to nitrite.



Here is a wastewater Inspector is utilizing the auto sampler's manual to help adjust the time and adjust for the correct flow for a composite sample. You can see that she is pouring off the pickle jar.

## Selenium- Inorganic Contaminant 0.05 mg/L MCL

Selenium (Se) is an essential element for human nutrition, with the majority of our intake coming from foods such as nuts, cereals, meat, fish, and eggs. The concentration of Selenium in drinking water is usually low, and comes from natural minerals. In soils, selenium often occurs in soluble forms such as selenate, which are leached into rivers very easily by runoff increasing the amount of selenium in groundwater. Selenium in water is also a by-product of copper mining / smelting. Selenium is also used in photoelectric devices because its electrical conductivity varies with light.

Naturally occurring selenium compounds have not been shown to be carcinogenic in animals. However, acute toxicity caused by high levels of selenium in water or other sources of intake has been observed in laboratory animals and in animals grazing in areas where high selenium levels exist in the soil. The US EPA has established the MCL for selenium in water at 0.05 mg/l.



### What are selenium's health effects?

Some people who drink water containing selenium well in excess of the maximum contaminant level (MCL) for many years could experience hair or fingernail losses, numbness in fingers or toes, or problems with their circulation.

This health effects language is not intended to catalog all possible health effects for selenium. Rather, it is intended to inform consumers of some of the possible health effects associated with selenium in drinking water when the rule was finalized.

### What are EPA's drinking water regulations for selenium?

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for selenium is 0.05 mg/L or 50 ppb. EPA has set this level of protection based on the best available science to prevent potential health problems.

EPA has set an enforceable regulation for selenium, called a maximum contaminant level (MCL), at 0.05 mg/L or 50 ppb.

MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.

The Phase II Rule, the regulation for selenium, became effective in 1992. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed selenium as part of the Six Year Review and determined that the 0.05 mg/L or 50 ppb MCLG and 0.05 mg/L or 50 ppb MCL for selenium are still protective of human health.

### **Selenium Water Treatment**

Selenium contamination of water systems may result whenever new agricultural runoff courses through normally dry undeveloped lands. If you have high levels of selenium in your water the following are recommended selenium water treatment options. Anion exchange can reduce the amount of selenium in drinking water by 60 - 95%. Reverse Osmosis Systems are excellent at removing selenium in drinking water.

Selenium shows borderline metalloid or nonmetal behavior. Its most stable form, the grey trigonal allotrope, is sometimes called 'metallic' selenium. This is because its electrical conductivity is several orders of magnitude greater than that of the red monoclinic form.

### **The metallic character of selenium is further shown by the following properties:**

- Its luster.
- Its crystalline structure, which is thought to include weakly 'metallic' interchain bonding.
- Its capacity, when molten, to be drawn into thin threads.
- Its reluctance to acquire 'the high positive oxidation numbers characteristic of nonmetals'.
- Its capacity to form cyclic polycations (such as  $\text{Se}_2^{+8}$ ) when dissolved in oleums (an attribute it shares with sulfur and tellurium).
- The existence of a hydrolyzed cationic salt in the form of trihydroxoselenium (IV) perchlorate  $[\text{Se}(\text{OH})_3]^+ \cdot \text{ClO}_4^-$ .

### **The Non-metallic Character of Selenium is shown by:**

- Its brittleness.
- Its electronic band structure, which is that of a semiconductor.
- The low electrical conductivity ( $\sim 10^{-9}$  to  $10^{-12} \text{ S}\cdot\text{cm}^{-1}$ ) of its highly purified form. This is comparable to or less than that of bromine ( $7.95 \times 10^{-12} \text{ S}\cdot\text{cm}^{-1}$ ), a nonmetal.
- Its relatively high electronegativity (2.55 revised Pauling scale).
- The retention of its semiconducting properties in liquid form.
- Its reaction chemistry, which is mainly that of its nonmetallic anionic forms  $\text{Se}^{2-}$ ,  $\text{SeO}_2^{3-}$  and  $\text{SeO}_2^{4-}$ .

### **Selenium Explained**

**Selenium** is a chemical element with symbol **Se** and atomic number 34. It is a nonmetal with properties that are intermediate between those of its periodic table column-adjacent chalcogen elements sulfur and tellurium. It rarely occurs in its elemental state in nature, or as pure ore compounds. Selenium (Greek *σελήνη* *selene* meaning "Moon") was discovered in 1817 by Jöns Jakob Berzelius, who noted the similarity of the new element to the previously-known tellurium (named for the Earth).

Selenium is found impurely in metal sulfide ores, where it partially replaces the sulfur. Commercially, selenium is produced as a byproduct in the refining of these ores, most often during copper production.

Minerals that are pure selenide or selenate compounds are known, but are rare. The chief commercial uses for selenium today are in glassmaking and in pigments.

Selenium is a semiconductor and is used in photocells. Uses in electronics, once important, have been mostly supplanted by silicon semiconductor devices. Selenium continues to be used in a few types of DC power surge protectors and one type of fluorescent quantum dot.

Selenium salts are toxic in large amounts, but trace amounts are necessary for cellular function in many organisms, including all animals. Selenium is a component of the antioxidant enzymes glutathione peroxidase and thioredoxin reductase (which indirectly reduce certain oxidized molecules in animals and some plants). It is also found in three deiodinase enzymes, which convert one thyroid hormone to another. Selenium requirements in plants differ by species, with some plants requiring relatively large amounts, and others apparently requiring none.

## Characteristics

### Physical Properties

Selenium exists in several allotropes that interconvert upon heating and cooling carried out at different temperatures and rates. As prepared in chemical reactions, selenium is usually amorphous, brick-red powder. When rapidly melted, it forms the black, vitreous form, which is usually sold industrially as beads. The structure of black selenium is irregular and complex and consists of polymeric rings with up to 1000 atoms per ring. Black Se is a brittle, lustrous solid that is slightly soluble in CS<sub>2</sub>. Upon heating, it softens at 50 °C and converts to gray selenium at 180 °C; the transformation temperature is reduced by presence of halogens and amines.

The red-colored  $\alpha$ ,  $\beta$  and  $\gamma$  forms are produced from solutions of black selenium by varying evaporation rates of the solvent (usually CS<sub>2</sub>). They all have relatively low, monoclinic crystal symmetries and contain nearly identical puckered Se<sub>8</sub> rings arranged in different fashions, as in sulfur. The packing is most dense in the  $\alpha$  form. In the Se<sub>8</sub> rings, the Se-Se distance is 233.5 pm and Se-Se-Se angle is 105.7 degrees. Other selenium allotropes may contain Se<sub>6</sub> or Se<sub>7</sub> rings.

The most stable and dense form of selenium has a gray color and hexagonal crystal lattice consisting of helical polymeric chains, wherein the Se-Se distance is 237.3 pm and Se-Se-Se angle is 130.1 degrees. The minimum distance between chains is 343.6 pm.

Gray Se is formed by mild heating of other allotropes, by slow cooling of molten Se, or by condensing Se vapors just below the melting point. Whereas other Se forms are insulators, gray Se is a semiconductor showing appreciable photoconductivity. Contrary to other allotropes, it is insoluble in CS<sub>2</sub>. It resists oxidation by air and is not attacked by non-oxidizing acids. With strong reducing agents, it forms polyselenides. Selenium does not exhibit the unusual changes in viscosity that sulfur undergoes when gradually heated.

### Isotopes

Selenium has six naturally occurring isotopes, five of which are stable: <sup>74</sup>Se, <sup>76</sup>Se, <sup>77</sup>Se, <sup>78</sup>Se, and <sup>80</sup>Se. The last three also occur as fission products, along with <sup>79</sup>Se, which has a half-life of 327,000 years.

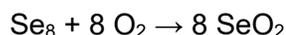
The final naturally occurring isotope, <sup>82</sup>Se, has a very long half-life (~10<sup>20</sup> yr, decaying via double beta decay to <sup>82</sup>Kr), which, for practical purposes, can be considered to be stable. Twenty-three other unstable isotopes have been characterized. See *also Selenium-79* for more information on recent changes in the measured half-life of this long-lived fission product, important for the dose calculations performed in the frame of the geological disposal of long-lived radioactive waste.

## Chemical Compounds

Selenium compounds commonly exist in the oxidation states -2, +2, +4, and +6.

## Chalcogen Compounds

Selenium forms two oxides: selenium dioxide (SeO<sub>2</sub>) and selenium trioxide (SeO<sub>3</sub>). Selenium dioxide is formed by the reaction of elemental selenium with oxygen:



It is a polymeric solid that forms monomeric SeO<sub>2</sub> molecules in the gas phase. It dissolves in water to form selenous acid, H<sub>2</sub>SeO<sub>3</sub>. Selenous acid can also be made directly by oxidizing elemental selenium with nitric acid:



Unlike sulfur, which forms a stable trioxide, selenium trioxide is thermodynamically unstable and decomposes to the dioxide above 185 °C:



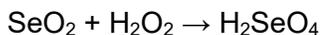
Selenium trioxide is produced in the laboratory by the reaction of anhydrous potassium selenate (K<sub>2</sub>SeO<sub>4</sub>) and sulfur trioxide (SO<sub>3</sub>).

Salts of selenous acid are called *selenites*. These include silver selenite (Ag<sub>2</sub>SeO<sub>3</sub>) and sodium selenite (Na<sub>2</sub>SeO<sub>3</sub>).

Hydrogen sulfide reacts with aqueous selenous acid to produce selenium disulfide:



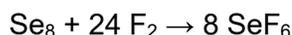
Selenium disulfide consists of 8-membered rings of a nearly statistical distribution of sulfur and selenium atoms. It has an approximate composition of SeS<sub>2</sub>, with individual rings varying in composition, such as Se<sub>4</sub>S<sub>4</sub> and Se<sub>2</sub>S<sub>6</sub>. Selenium disulfide has been used in shampoo as an anti-dandruff agent, an inhibitor in polymer chemistry, a glass dye, and a reducing agent in fireworks. Selenium trioxide may be synthesized by dehydrating selenic acid, H<sub>2</sub>SeO<sub>4</sub>, which is itself produced by the oxidation of selenium dioxide with hydrogen peroxide:



Hot, concentrated selenic acid is capable of dissolving gold, forming gold(III) selenate.

## Halogen Compounds

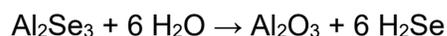
Iodides of selenium are not well known. The only stable chloride is selenium monochloride (Se<sub>2</sub>Cl<sub>2</sub>), which might be better known as selenium(I) chloride; the corresponding bromide is also known. These species are structurally analogous to the corresponding disulfur dichloride. Selenium dichloride is an important reagent in the preparation of selenium compounds (e.g. the preparation of Se<sub>7</sub>). It is prepared by treating selenium with sulfuryl chloride (SO<sub>2</sub>Cl<sub>2</sub>). Selenium reacts with fluorine to form selenium hexafluoride:



In comparison with its sulfur counterpart (sulfur hexafluoride), selenium hexafluoride (SeF<sub>6</sub>) is more reactive and is a toxic pulmonary irritant. Some of the selenium oxyhalides, such as selenium oxyfluoride (SeOF<sub>2</sub>) and selenium oxychloride (SeOCl<sub>2</sub>) have been used as specialty solvents.

### Selenides

Analogous to the behavior of other chalcogens, selenium forms a dihydride H<sub>2</sub>Se. It is a strongly odiferous, toxic, and colorless gas. It is more acidic than H<sub>2</sub>S. In solution it ionizes to HSe<sup>-</sup>. The selenide dianion Se<sup>2-</sup> forms a variety of compounds, including the minerals from which selenium is obtained commercially. Illustrative selenides include mercury selenide (HgSe), lead selenide (PbSe), zinc selenide (ZnSe), and copper indium gallium diselenide (Cu(Ga, In)Se<sub>2</sub>). These materials are semiconductors. With highly electropositive metals, such as aluminum, these selenides are prone to hydrolysis:

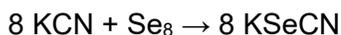


Alkali metal selenides react with selenium to form polyselenides, Se<sub>2-x</sub>, which exist as chains.

### Other Compounds

Tetraselenium tetranitride, Se<sub>4</sub>N<sub>4</sub>, is an explosive orange compound analogous to tetrasulfur tetranitride (S<sub>4</sub>N<sub>4</sub>). It can be synthesized by the reaction of selenium tetrachloride (SeCl<sub>4</sub>) with [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>N<sub>2</sub>Se.

Selenium reacts with cyanides to yield selenocyanates:



### Organoselenium Compounds

Selenium, especially in the II oxidation state, forms stable bonds to carbon, which are structurally analogous to the corresponding organosulfur compounds. Especially common are selenides (R<sub>2</sub>Se, analogues of thioethers), diselenides (R<sub>2</sub>Se<sub>2</sub>, analogues of disulfides), and selenols (RSeH, analogues of thiols). Representatives of selenides, diselenides, and selenols include respectively selenomethionine, diphenyldiselenide, and benzeneselenol.

The sulfoxide in sulfur chemistry is represented in selenium chemistry by the selenoxides (formula RSe(O)R), which are intermediates in organic synthesis, as illustrated by the selenoxide elimination reaction. Consistent with trends indicated by the double bond rule, selenoketones, R(C=Se)R, and selenaldehydes, R(C=Se)H, are rarely observed.

### History

Selenium (Greek σελήνη *selene* meaning "Moon") was discovered in 1817 by Jöns Jakob Berzelius and Johan Gottlieb Gahn. Both chemists owned a chemistry plant near Gripsholm, Sweden producing sulfuric acid by the lead chamber process.

The pyrite from the Falun mine created a red precipitate in the lead chambers which was presumed to be an arsenic compound, and so the pyrite's use to make acid was discontinued. Berzelius and Gahn wanted to use the pyrite and they also observed that the red precipitate gave off a smell like horseradish when burned. This smell was not typical of arsenic, but a similar odor was known from tellurium compounds. Hence, Berzelius's first letter to Alexander Marcet stated that this was a tellurium compound. However, the lack of tellurium compounds in the Falun mine minerals eventually led Berzelius to reanalyze the red precipitate, and in 1818 he wrote a second letter to Marcet describing a newly found element similar to sulfur and tellurium. Because of its similarity to tellurium, named for the Earth, Berzelius named the new element after the Moon.

In 1873, Willoughby Smith found that the electrical resistance of grey selenium was dependent on the ambient light. This led to its use as a cell for sensing light. The first of commercial products using selenium were developed by Werner Siemens in the mid-1870s. The selenium cell was used in the photophone developed by Alexander Graham Bell in 1879. Selenium transmits an electric current proportional to the amount of light falling on its surface. This phenomenon was used in the design of light meters and similar devices. Selenium's semiconductor properties found numerous other applications in electronics. The development of selenium rectifiers began during the early 1930s, and these replaced copper oxide rectifiers because of their superior efficiencies. These lasted in commercial applications until the 1970s, following which they were replaced with less expensive and even more efficient silicon rectifiers.

Selenium came to medical notice later because of its toxicity to human beings working in industries.

Selenium was also recognized as an important veterinary toxin, which is seen in animals that have eaten high-selenium plants. In 1954, the first hints of specific biological functions of selenium were discovered in microorganisms. Its essentiality for mammalian life was discovered in 1957. In the 1970s, it was shown to be present in two independent sets of enzymes. This was followed by the discovery of selenocysteine in proteins.

### **Occurrence**

Native (i.e., elemental) selenium is a rare mineral, which does not usually form good crystals, but, when it does, they are steep rhombohedra or tiny acicular (hair-like) crystals. Isolation of selenium is often complicated by the presence of other compounds and elements.

Selenium occurs naturally in a number of inorganic forms, including selenide-, selenate-, and selenite-containing minerals, but these minerals are rare. The common mineral selenite is *not* a selenium mineral, and contains no selenite ion, but is rather a type of gypsum (calcium sulfate hydrate) named like selenium for the moon well before the discovery of selenium. Selenium is most commonly found quite impurely, replacing a small part of the sulfur in sulfide ores of many metals.

In living systems, selenium is found in the amino acids selenomethionine, selenocysteine, and methylselenocysteine. In these compounds, selenium plays a role analogous to that of sulfur. Another naturally occurring organoselenium compound is dimethyl selenide.

Certain solids are selenium-rich, and selenium can be bioconcentrated by certain plants. In soils, selenium most often occurs in soluble forms such as selenate (analogous to sulfate), which are leached into rivers very easily by runoff. Ocean water contains significant amounts of selenium.

Anthropogenic sources of selenium include coal burning and the mining and smelting of sulfide ores.

### **Production**

Selenium is most commonly produced from selenide in many sulfide ores, such as those of copper, silver, or lead. Electrolytic metal refining is particularly conducive to producing selenium as a byproduct, and it is obtained from the anode mud of copper refineries. Another source was the mud from the lead chambers of sulfuric acid plants but this method to produce sulfuric acid is no longer used.

These muds can be processed by a number of means to obtain selenium. However, most elemental selenium comes as a byproduct of refining copper or producing sulfuric acid.

Since the invention of solvent extraction and electrowinning (SX/EW) for the production of copper this method takes an increasing share of the world wide copper production. This changes the availability of selenium because only a comparably small part of the selenium in the ore is leached together with the copper.

Industrial production of selenium usually involves the extraction of selenium dioxide from residues obtained during the purification of copper. Common production from the residue then begins by oxidation with sodium carbonate to produce selenium dioxide. The selenium dioxide is then mixed with water and the solution is acidified to form selenous acid (oxidation step). Selenous acid is bubbled with sulfur dioxide (reduction step) to give elemental selenium.

### **Toxicity**

Although selenium is an essential trace element, it is toxic if taken in excess. Exceeding the Tolerable Upper Intake Level of 400 micrograms per day can lead to selenosis. This 400 microgram ( $\mu\text{g}$ ) Tolerable Upper Intake Level is based primarily on a 1986 study of five Chinese patients who exhibited overt signs of selenosis and a follow up study on the same five people in 1992.

The 1992 study actually found the maximum safe dietary Se intake to be approximately 800 micrograms per day (15 micrograms per kilogram body weight), but suggested 400 micrograms per day to not only avoid toxicity, but also to avoid creating an imbalance of nutrients in the diet and to account for data from other countries.

In China, people who ingested corn grown in extremely selenium-rich stony coal (carbonaceous shale) have suffered from selenium toxicity. This coal was shown to have selenium content as high as 9.1%, the highest concentration in coal ever recorded in literature.

Symptoms of selenosis include a garlic odor on the breath, gastrointestinal disorders, hair loss, sloughing of nails, fatigue, irritability, and neurological damage. Extreme cases of selenosis can result in cirrhosis of the liver, pulmonary edema, and death. Elemental selenium and most metallic selenides have relatively low toxicities because of their low bioavailability.

By contrast, selenates and selenites are very toxic, having an oxidant mode of action similar to that of arsenic trioxide. The chronic toxic dose of selenite for humans is about 2400 to 3000 micrograms of selenium per day for a long time. Hydrogen selenide is an extremely toxic, corrosive gas. Selenium also occurs in organic compounds, such as dimethyl selenide, selenomethionine, selenocysteine and methylselenocysteine, all of which have high bioavailability and are toxic in large doses.

In fish and other wildlife, low levels of selenium cause deficiency while high levels cause toxicity. For example, in salmon, the optimal concentration of selenium in the fish tissue (whole body) is about 1 microgram selenium per gram of tissue (dry weight). At levels much below that concentration, young salmon die from selenium deficiency; much above that level they die from toxic excess.

hydrogen 1 <b>H</b> 1.0079																	helium 2 <b>He</b> 4.0026	
lithium 3 <b>Li</b> 6.941	beryllium 4 <b>Be</b> 9.0122											boron 5 <b>B</b> 10.811	carbon 6 <b>C</b> 12.011	nitrogen 7 <b>N</b> 14.007	oxygen 8 <b>O</b> 15.999	fluorine 9 <b>F</b> 18.998	neon 10 <b>Ne</b> 20.180	
sodium 11 <b>Na</b> 22.990	magnesium 12 <b>Mg</b> 24.305											aluminum 13 <b>Al</b> 26.982	silicon 14 <b>Si</b> 28.086	phosphorus 15 <b>P</b> 30.974	sulfur 16 <b>S</b> 32.065	chlorine 17 <b>Cl</b> 35.453	argon 18 <b>Ar</b> 39.948	
potassium 19 <b>K</b> 39.098	calcium 20 <b>Ca</b> 40.078	scandium 21 <b>Sc</b> 44.956	titanium 22 <b>Ti</b> 47.867	vanadium 23 <b>V</b> 50.942	chromium 24 <b>Cr</b> 51.996	manganese 25 <b>Mn</b> 54.938	iron 26 <b>Fe</b> 55.845	cobalt 27 <b>Co</b> 58.933	nickel 28 <b>Ni</b> 58.693	copper 29 <b>Cu</b> 63.546	zinc 30 <b>Zn</b> 65.39	gallium 31 <b>Ga</b> 69.723	germanium 32 <b>Ge</b> 72.61	arsenic 33 <b>As</b> 74.922	selenium 34 <b>Se</b> 78.96	bromine 35 <b>Br</b> 79.904	krypton 36 <b>Kr</b> 83.80	
rubidium 37 <b>Rb</b> 85.468	strontium 38 <b>Sr</b> 87.62	yttrium 39 <b>Y</b> 88.906	zirconium 40 <b>Zr</b> 91.224	niobium 41 <b>Nb</b> 92.906	molybdenum 42 <b>Mo</b> 95.94	technetium 43 <b>Tc</b> [98]	ruthenium 44 <b>Ru</b> 101.07	rhodium 45 <b>Rh</b> 102.91	palladium 46 <b>Pd</b> 106.42	silver 47 <b>Ag</b> 107.87	cadmium 48 <b>Cd</b> 112.41	indium 49 <b>In</b> 114.82	tin 50 <b>Sn</b> 118.71	antimony 51 <b>Sb</b> 121.76	tellurium 52 <b>Te</b> 127.60	iodine 53 <b>I</b> 126.90	xenon 54 <b>Xe</b> 131.29	
caesium 55 <b>Cs</b> 132.91	barium 56 <b>Ba</b> 137.33	57-70 *	lutetium 71 <b>Lu</b> 174.97	hafnium 72 <b>Hf</b> 178.49	tantalum 73 <b>Ta</b> 180.95	tungsten 74 <b>W</b> 183.84	rhenium 75 <b>Re</b> 186.21	osmium 76 <b>Os</b> 190.23	iridium 77 <b>Ir</b> 192.22	platinum 78 <b>Pt</b> 195.08	gold 79 <b>Au</b> 196.97	mercury 80 <b>Hg</b> 200.59	thallium 81 <b>Tl</b> 204.38	lead 82 <b>Pb</b> 207.2	bismuth 83 <b>Bi</b> 208.98	polonium 84 <b>Po</b> [209]	astatine 85 <b>At</b> [210]	radon 86 <b>Rn</b> [222]
francium 87 <b>Fr</b> [223]	radium 88 <b>Ra</b> [226]	89-102 **	lawrencium 103 <b>Lr</b> [262]	rutherfordium 104 <b>Rf</b> [261]	dubnium 105 <b>Db</b> [262]	seaborgium 106 <b>Sg</b> [266]	bohrium 107 <b>Bh</b> [264]	hassium 108 <b>Hs</b> [269]	meitnerium 109 <b>Mt</b> [268]	unnilium 110 <b>Uun</b> [271]	ununium 111 <b>Uuu</b> [272]	unbibium 112 <b>Uub</b> [277]	ununquadium 114 <b>Uuq</b> [289]					

\* Lanthanide series

lanthanum 57 <b>La</b> 138.91	cerium 58 <b>Ce</b> 140.12	praseodymium 59 <b>Pr</b> 140.91	neodymium 60 <b>Nd</b> 144.24	promethium 61 <b>Pm</b> [145]	samarium 62 <b>Sm</b> 150.36	europium 63 <b>Eu</b> 151.96	gadolinium 64 <b>Gd</b> 157.25	terbium 65 <b>Tb</b> 158.93	dysprosium 66 <b>Dy</b> 162.50	holmium 67 <b>Ho</b> 164.93	erbium 68 <b>Er</b> 167.26	thulium 69 <b>Tm</b> 168.93	ytterbium 70 <b>Yb</b> 173.04
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\*\* Actinide series

actinium 89 <b>Ac</b> [227]	thorium 90 <b>Th</b> 232.04	protactinium 91 <b>Pa</b> 231.04	uranium 92 <b>U</b> 238.03	neptunium 93 <b>Np</b> [237]	plutonium 94 <b>Pu</b> [244]	americium 95 <b>Am</b> [243]	curium 96 <b>Cm</b> [247]	berkelium 97 <b>Bk</b> [247]	californium 98 <b>Cf</b> [251]	einsteinium 99 <b>Es</b> [252]	fermium 100 <b>Fm</b> [257]	mendelevium 101 <b>Md</b> [258]	nobelium 102 <b>No</b> [259]
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## Thallium- Inorganic Contaminant 0.002 mg/L MCL

Thallium is a metal found in natural deposits such as ores containing other elements.

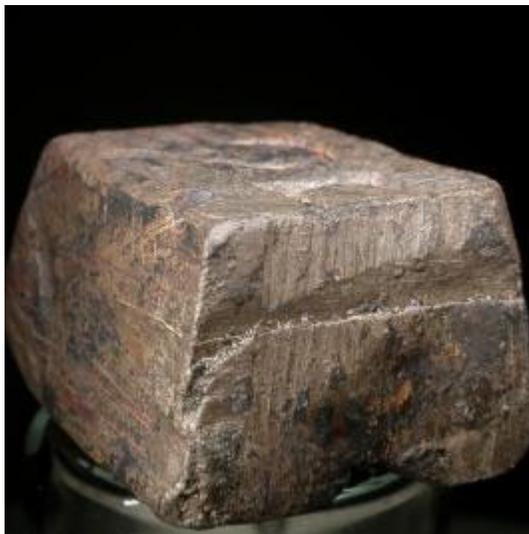
### Uses for Thallium.

The greatest use of thallium is in specialized electronic research equipment.

### What are Thallium's Health Effects?

Some people who drink water containing thallium well in excess of the maximum contaminant level (MCL) for many years could experience hair loss, changes in their blood, or problems with their kidneys, intestines, or liver problems.

This health effects language is not intended to catalog all possible health effects for thallium. Rather, it is intended to inform consumers of some of the possible health effects associated with thallium in drinking water when the rule was finalized.



### What are EPA's Drinking Water Regulations for Thallium?

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for thallium is 0.0005 mg/L or 0.5 ppb. EPA has set this level of protection based on the best available science to prevent potential health problems.

EPA has set an enforceable regulation for thallium, called a maximum contaminant level (MCL), at 0.002 mg/L or 2 ppb. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies.

The Phase V Rule, the regulation for thallium, became effective in 1994. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed thallium as part of the Six Year Review and determined that the 0.0005 mg/L or 0.5 ppb MCLG and 0.002 mg/L or 2 ppb MCL for thallium are still protective of human health. States may set more stringent drinking water MCLGs and MCLs for thallium than EPA.

### How does Thallium get into my Drinking Water?

The major sources of thallium in drinking water are leaching from ore-processing sites; and discharge from electronics, glass, and drug factories.

A federal law called the Emergency Planning and Community Right to Know Act (EPCRA) requires facilities in certain industries, which manufacture, process, or use significant amounts of toxic chemicals, to report annually on their releases of these chemicals.

For more information on the uses and releases of chemicals in your state, contact the Community Right-to-Know Hotline: (800) 424-9346.

### **How will I know if Thallium is in my Drinking Water?**

When routine monitoring indicates that thallium levels are above the MCL, your water supplier must take steps to reduce the amount of thallium so that it is below that level. Water suppliers must notify their customers as soon as practical, but no later than 30 days after the system learns of the violation. Additional actions, such as providing alternative drinking water supplies, may be required to prevent serious risks to public health.

### **How will Thallium be Removed from my Drinking Water?**

The following treatment method(s) have proven to be effective for removing thallium to below 0.002 mg/L or 2 ppb: activated alumina; ion exchange.

### **How do I learn more about my Drinking Water?**

EPA strongly encourages people to learn more about their drinking water, and to support local efforts to protect the supply of safe drinking water and upgrade the community water system. Your water bill or telephone book's government listings are a good starting point for local information.

Contact your water utility. EPA requires all community water systems to prepare and deliver an annual consumer confidence report (CCR) (sometimes called a water quality report) for their customers by July 1 of each year. If your water provider is not a community water system, or if you have a private water supply, request a copy from a nearby community water system.

## **Thallium Explained**

**Thallium** is a chemical element with symbol **Tl** and atomic number 81. This soft gray poor metal is not found free in nature. When isolated, it resembles tin, but discolors when exposed to air. Chemists William Crookes and Claude-Auguste Lamy discovered thallium independently in 1861, in residues of sulfuric acid production. Both used the newly developed method of flame spectroscopy, in which thallium produces a notable green spectral line. Thallium, from Greek *θαλλός*, *thallos*, meaning "a green shoot or twig," was named by Crookes. It was isolated by electrolysis a year later, by Lamy.

Thallium tends to oxidize to the +3 and +1 oxidation states as ionic salts. The +3 state resembles that of the other elements in thallium's group (boron, aluminum, gallium, indium). However, the +1 state, which is far more prominent in thallium than the elements above it, recalls the chemistry of alkali metals, and thallium(I) ions are found geologically mostly in potassium-based ores, and (when ingested) are handled in many ways like potassium ions ( $K^+$ ) by ion pumps in living cells.

Commercially, however, thallium is produced not from potassium ores, but as a byproduct from refining of heavy metal sulfide ores. Approximately 60–70% of thallium production is used in the electronics industry, and the remainder is used in the pharmaceutical industry and in glass manufacturing. It is also used in infrared detectors.

The radioisotope thallium-201 (as the soluble chloride  $TlCl$ ) is used in small, nontoxic amounts as an agent in a nuclear medicine scan, during one type of nuclear cardiac stress test. Soluble thallium salts (many of which are nearly tasteless) are highly toxic in quantity, and were historically used in rat poisons and insecticides.

Use of these compounds has been restricted or banned in many countries, because of their nonselective toxicity. Thallium poisoning notably results in hair loss. Because of its historic popularity as a murder weapon, thallium has gained notoriety as "the poisoner's poison" and "inheritance powder" (alongside arsenic).

### Characteristics

Thallium is extremely soft, malleable and sectile enough to be cut with a knife at room temperature. It has a metallic luster that, when exposed to air, quickly tarnishes to a bluish-gray tinge, resembling lead. It may be preserved by immersion in oil. A heavy layer of oxide builds up on thallium if left in air. In the presence of water, thallium hydroxide is formed. Sulfuric and nitric acid dissolve thallium rapidly to make the sulfate and nitrate salts, while hydrochloric acid forms an insoluble thallium(I) chloride layer. Its standard electrode potential is  $-0.34$ , slightly higher than the potential for iron (at  $-0.44$ ).

### Isotopes

Thallium has 25 isotopes which have atomic masses that range from 184 to 210.  $^{203}\text{Tl}$  and  $^{205}\text{Tl}$  are the only stable isotopes, and  $^{204}\text{Tl}$  is the most stable radioisotope, with a half-life of 3.78 years.

$^{202}\text{Tl}$  (half-life 12.23 days) can be made in a cyclotron, while  $^{204}\text{Tl}$  is made by the neutron activation of stable thallium in a nuclear reactor.

$^{201}\text{Tl}$  (half-life 73 hrs), decays by electron capture, emitting Hg X-rays ( $\sim 70$ – $80$  keV), and photons of 135 and 167 keV in 10% total abundance; therefore it has good imaging characteristics without excessive patient radiation dose. It is the most popular isotope used for thallium nuclear cardiac stress tests.

$^{208}\text{Tl}$  (half-life 3.05 minutes) is generated in the naturally-occurring thorium decay chain. Its prominent 2615 keV gamma ray is the dominant high-energy feature observed in natural background radiation.

### Chemistry

The two main oxidation states of thallium are +1 and +3. In the oxidation state +1 most compounds closely resemble the corresponding potassium or silver compounds (the ionic radius of thallium(I) is  $1.47$  Å while that of potassium is  $1.33$  Å and that of silver is  $1.26$  Å), which was the reason why thallium was sometimes considered to be an alkali metal in Europe (but not in England) in the years immediately following its discovery.

126 for example, the water-soluble and very basic thallium(I) hydroxide reacts with carbon dioxide forming water-soluble thallium carbonate. This carbonate is the only water soluble heavy metal carbonate. The similarity with silver compounds is observed with the halide, oxide, and sulfide compounds.

Thallium(I) bromide is a photosensitive yellow compound very similar to the silver bromide, while the black thallium(I) oxide and thallium(I) sulfide are very similar to the silver oxide and silver sulfide.

The compounds with oxidation state +3 resemble the corresponding aluminum (III) compounds. They are moderately strong oxidizing agents, as illustrated by the reduction potential of  $+0.72$  volts for  $\text{Tl}^{3+} + 3 \text{e}^- \rightarrow \text{Tl(s)}$ . The thallium(III) oxide is a black solid which decomposes above  $800$  °C, forming the thallium(I) oxide and oxygen.

## History

Thallium (Greek *θαλλός*, *thallos*, meaning "a green shoot or twig") was discovered by flame spectroscopy in 1861. The name comes from thallium's bright green spectral emission lines.

After the publication of the improved method of flame spectroscopy by Robert Bunsen and Gustav Kirchhoff and the discovery of caesium and rubidium in the years 1859 to 1860, flame spectroscopy became an approved method to determine the composition of minerals and chemical products.

William Crookes and Claude-Auguste Lamy both started to use the new method. William Crookes used it to make spectroscopic determinations for tellurium on selenium compounds deposited in the lead chamber of a sulfuric acid production plant near Tilkerode in the Harz mountains. He had obtained the samples for his research on selenium cyanide from August Hofmann years earlier. By 1862, Crookes was able to isolate small quantities of the new element and determine the properties of a few compounds. Claude-Auguste Lamy used a spectrometer that was similar to Crookes' to determine the composition of a selenium-containing substance which was deposited during the production of sulfuric acid from pyrite. He also noticed the new green line in the spectra and concluded that a new element was present. Lamy had received this material from the sulfuric acid plant of his friend Fréd Kuhlmann and this by-product was available in large quantities. Lamy started to isolate the new element from that source.

The fact that Lamy was able to work ample quantities of thallium enabled him to determine the properties of several compounds and in addition he prepared a small ingot of metallic thallium which he prepared by remelting thallium he had obtained by electrolysis of thallium salts.

As both scientists discovered thallium independently and a large part of the work, especially the isolation of the metallic thallium was done by Lamy, Crookes tried to secure his priority on the work. Lamy was awarded a medal at the International Exhibition in London 1862: *For the discovery of a new and abundant source of thallium* and after heavy protest Crookes also received a medal: *thallium, for the discovery of the new element*. The controversy between both scientists continued through 1862 and 1863. Most of the discussion ended after Crookes was elected Fellow of the Royal Society in June 1863.

The dominant use of thallium was the use as poison for rodents. After several accidents the use as poison was banned in the United States by the Presidential Executive Order 11643 in February 1972. In the subsequent years several other countries also banned the use.

## Occurrence and Production

Although thallium is a modestly abundant element in the Earth's crust, with a concentration estimated to be about 0.7 mg/kg, mostly in association with potassium-based minerals in clays, soils, and granites, thallium is not generally economically recoverable from these sources. The major source of thallium for practical purposes is the trace amount that is found in copper, lead, zinc, and other heavy-metal-sulfide ores.

Thallium is found in the minerals crookesite  $\text{TiCu}_7\text{Se}_4$ , hutchinsonite  $\text{TiPbAs}_5\text{S}_9$ , and lorandite  $\text{TiAs}_2$ . Thallium also occurs as a trace element in iron pyrite, and thallium is extracted as a by-product of roasting this mineral for the production of sulfuric acid.

Thallium can also be obtained from the smelting of lead and zinc ores. Manganese nodules found on the ocean floor also contain some thallium, but the collection of these nodules has been and continues to be prohibitively expensive.

There is also the potential for damaging the environment of the oceans. In addition, several other thallium minerals, containing 16% to 60% thallium, occur in nature as complexes of sulfides or selenides that primarily contain antimony, arsenic, copper, lead, and/or silver. However, these minerals are rare, and they have had no commercial importance as sources of thallium. The Allchar deposit in southern Macedonia was the only area where thallium was ever actively mined. This deposit still contains a loosely estimated 500 tons of thallium, and it is a source for several rare thallium minerals, for example lorandite.

The United States Geological Survey (USGS) estimates that the annual worldwide production of thallium is about 10 metric tons as a by-product from the smelting of copper, zinc, and lead ores. Thallium is either extracted from the dusts from the smelter flues or from residues such as slag that are collected at the end of the smelting process. The raw materials used for thallium production contain large amounts of other materials and therefore a purification is the first step.

The thallium is leached either by the use of a base or sulfuric acid from the material. The thallium is several times precipitated from the solution and to remove further impurities. At the end it is converted to thallium sulfate and the thallium is extracted by electrolysis on platinum or stainless steel plates.

The production of thallium decreased by about 33% in the period from 1995 to 2009 – from about 15 metric tons to about 10 tons. Since there are several small deposits or ores with relatively high thallium content, it would be possible to increase the production of it if a new application, such as a hypothetical thallium-containing high-temperature superconductor, becomes practical for widespread use outside of the laboratory.

## **Applications**

### **Historic Uses**

The odorless and tasteless thallium sulfate was once widely used as rat poison and ant killer. Since 1972 this use has been prohibited in the United States due to safety concerns. Many other countries followed this example in the following years. Thallium salts were used in the treatment of ringworm, other skin infections and to reduce the night sweating of tuberculosis patients. However this use has been limited due to their narrow therapeutic index, and the development of more-advanced medicines for these conditions.

### **Optics**

Thallium(I) bromide and thallium(I) iodide crystals have been used as infrared optical materials, because they are harder than other common infrared optics, and because they have transmission at significantly longer wavelengths. The trade name KRS-5 refers to this material.

Thallium(I) oxide has been used to manufacture glasses that have a high index of refraction. Combined with sulfur or selenium and arsenic, thallium has been used in the production of high-density glasses that have low melting points in the range of 125 and 150 °C. These glasses have room temperature properties that are similar to ordinary glasses and are durable, insoluble in water and have unique refractive indices.

### **Electronics**

Thallium(I) sulfide's electrical conductivity changes with exposure to infrared light therefore making this compound useful in photoresistors. Thallium selenide has been used in a bolometer for infrared detection. Doping selenium semiconductors with thallium improves their performance, and therefore it is used in trace amounts in selenium rectifiers. Another application of thallium doping is the sodium iodide crystals in gamma radiation detection devices.

In these, the sodium iodide crystals are doped with a small amount of thallium to improve their efficiency as scintillation generators. Some of the electrodes in dissolved oxygen analyzers contain thallium.

### **High-Temperature Superconductivity**

Research activity with thallium is ongoing to develop high-temperature superconducting materials for such applications as magnetic resonance imaging, storage of magnetic energy, magnetic propulsion, and electric power generation and transmission. The research in applications started after the discovery of the first thallium barium calcium copper oxide superconductor in 1988.

### **Other Uses**

A mercury-thallium alloy, which forms a eutectic at 8.5% thallium, is reported to freeze at  $-60\text{ }^{\circ}\text{C}$ , some  $20\text{ }^{\circ}\text{C}$  below the freezing point of mercury. This alloy is used in thermometers and low-temperature switches. In organic synthesis thallium(III) salts, as thallium trinitrate or triacetate, are useful reagents performing different transformations in aromatics, ketones, olefins, among others. Thallium is a constituent of the alloy in the anode plates in magnesium seawater batteries. Soluble thallium salts are added to gold plating baths to increase the speed of plating and to reduce grain size within the gold layer.

The saturated solution of equal parts of thallium(I) formate ( $\text{TI}(\text{CHO}_2)$ ) and thallium(I) malonate ( $\text{TI}(\text{C}_3\text{H}_3\text{O}_4)$ ) in water is known as Clerici solution. It is a mobile odorless liquid whose color changes from yellowish to clear upon reducing the concentration of the thallium salts.

With the density of  $4.25\text{ g/cm}^3$  at  $20\text{ }^{\circ}\text{C}$ , Clerici solution is one of the heaviest aqueous solutions known.

It was used in the 20th century for measuring density of minerals by the flotation method, but the use is discontinued due to the high toxicity and corrosiveness of the solution.

Thallium iodide is used as an additive to metal halide lamps, often together with one-two halides of other metals. It allows to optimize the lamp temperature and color rendering, and shift the spectral output to the green region, which is useful for underwater lighting.

### **Toxicity**

Thallium and its compounds are extremely toxic, and should be handled with great care. There are numerous recorded cases of fatal thallium poisoning. Contact with skin is dangerous, and adequate ventilation should be provided when melting this metal. Thallium(I) compounds have a high aqueous solubility and are readily absorbed through the skin. Exposure to them should not exceed  $0.1\text{ mg per m}^2$  of skin in an 8-hour time-weighted average (40-hour work week).

Thallium is a suspected human carcinogen. For a long time thallium compounds were easily available as rat poison. This fact and that it is water soluble and nearly tasteless led to frequent intoxications caused by accident or criminal intent.

### **Treatment and Internal Decontamination**

One of the main methods of removing thallium (both radioactive and normal) from humans is to use Prussian blue, which is a material which absorbs thallium. Up to  $20\text{ g}$  per day of Prussian blue is fed by mouth to the person, and it passes through their digestive system and comes out in the stool. Hemodialysis and hemoperfusion are also used to remove thallium from the blood serum. At later stage of the treatment additional potassium is used to mobilize thallium from the tissue.

## SOC Section



**Common water sampling bottles.**

SOC/VOC bottles are the smaller, thin bottles with the septum tops. Be careful not to get any air bubbles in the SOC/VOC bottles and this may take a few weeks to learn to collect a proper sample.

### **SOC Introduction**

Synthetic Organic Chemicals (SOCs) are organic (carbon based) chemicals that are less volatile than Volatile Organic Compounds (VOCs). SOCs are used as pesticides, defoliants, fuel additives and as ingredients for other organic compounds. They are all man made and do not naturally occur in the environment. Some of the more well-known SOCs are Atrazine, 2,4-D, Dioxin and Polychlorinated Biphenyls (PCBs).

SOCs most often enter the natural environment through application of pesticide (including runoff from areas where they are applied), as part of a legally discharged waste stream, improper or illegal waste disposal, accidental releases or as a byproduct of incineration. Some SOCs are very persistent in the environment, whether in soil or water.

SOCs are generally toxic and can have substantial health impacts from both acute (short-term) and chronic (long-term) exposure. Many are known carcinogens (cancer causing). EPA has set Maximum Contaminant Levels (MCL) for 30 SOC's under the Safe Drinking Water Act. The Safe Drinking Water Act requires that all water sources of all public water systems be periodically monitored for regulated SOC's. The monitoring frequency can be adjusted through a waiver if SOC's are not detected.

EPA established Maximum Contaminant Levels (MCL), Maximum Contaminant Level Goals (MCLG), monitoring requirements and best available technologies for removal for 65 chemical contaminants over a five year period as EPA gathered and analyzed occurrence and health effects data. This series of rules are known as the Chemical Phase Rules and they define regulations for three contaminant groups:

- Inorganic Chemicals (IOC),
- Synthetic Organic Chemicals (SOC), and
- Volatile Organic Chemicals (VOC).

The Chemical Phase rules provide public health protection through the reduction of chronic risks from:

- cancer;
- organ damage; and
- circulatory,
- nervous, and
- reproductive system disorders.

They also help to reduce the occurrence of Methemoglobinemia or "blue baby syndrome" from ingestion of elevated levels of nitrate or nitrite. All public water systems must monitor for Nitrate and Nitrite. Community water systems and Non-transient non-community water systems must also monitor for IOCs, SOC's, and VOC's.

This is a list of the organic chemicals—which include pesticides, industrial chemicals, and disinfection by-products—that are tested for in public water systems (those that provide water to the public), along with the maximum standard for the contaminant, and a brief description of the potential health effects associated with long-term consumption of elevated levels of the contaminants.

The federal standard for most contaminants is listed as a Maximum Contaminant Level (MCL), the lowest concentration at which that particular contaminant is believed to represent a potential health concern. Unless otherwise noted, the MCL is expressed as parts per billion (ppb). Also, because of technological limitations or other factors, it is not possible to test for some contaminants in a reliable fashion. Instead, public water systems are required to use specific Treatment Techniques (TT) that are designed to remove these particular contaminants from the water.

In addition to the chemicals listed, monitoring is done for approximately 60 organic chemicals for which MCL's have not been established. If unacceptable levels are found of these "unregulated" contaminants—based on established state health standards and an assessment of the risks they pose—the response is the same as if an MCL has been exceeded: the public water system must notify those served by the system.

Synthetic Organic Chemicals	MCL (ppb)	Potential Health Effects
Acrylamide	TT	Cancer, nervous system effects
Alachlor	2	Cancer
Aldicarb	3	Nervous system effects
Aldicarb sulfoxide	4	Nervous system effects
Aldicarb sulfone	2	Nervous system effects
Atrazine	3	Liver, kidney, lung, cardiovascular effects; possible carcinogen
Benzo(a)pyrene (PAHs)	0.2	Liver, kidney effects, possible carcinogen
Carbofuran	40	Nervous system, reproductive system effects
Chlordane	2	Cancer
2,4-D	70	Liver, kidney effects
Di(2-ethylhexyl) adipate	400	Reproductive effects
Di(2-ethylhexyl) phthalate	6	Cancer
Dibromochloro-propane (DBCP)	0.2	Cancer
Dinoseb	7	Thyroid, reproductive effects
Diquat	20	Ocular, liver, kidney effects
Endothall	100	Liver, kidney, gastrointestinal effects
Endrin	2	Liver, kidney effects
Epichlorohydrin	TT	Cancer
Ethylene dibromide (EDB)	0.05	Cancer
Glyphosate	700	Liver, kidney effects
Heptachlor	0.4	Cancer
Heptachlor epoxide	0.2	Cancer
Hexachlorobenzene	1	Cancer
Hexachlorocyclopentadiene (HEX)	50	Kidney, stomach effects

Lindane	0.2	Liver, kidney, nervous system, immune system, circulatory system effects
Methoxychlor	40	Developmental, liver, kidney, nervous system effects
Oxamyl (Vydate)	200	Kidney effects
Pentachlorophenol	1	Cancer
Picloram	500	Kidney, liver effects
Polychlorinated biphenyls (PCBs)	0.5	Cancer
Simazine	4	Body weight and blood effects, possible carcinogen
2,3,7,8-TCDD (Dioxin)	0.00003	Cancer
Toxaphene	3	Cancer
2,4,5-TP (Silvex)	50	Liver, kidney effects

Aldicarb, aldicarb sulfone, and aldicarb sulfoxide are considered regulated chemicals although their MCLs are stayed. Therefore PWS are not required to meet an MCL.

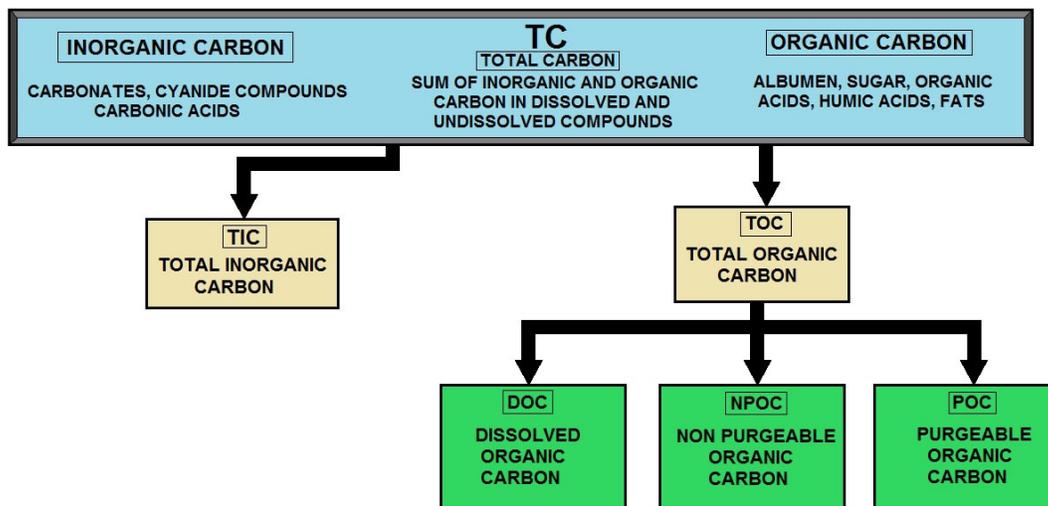
For each contaminant, EPA set a health goal, or Maximum Contaminant Level Goals (MCLG). This is the level at which a person could drink two liters of water containing the contaminant every day for 70 years without suffering any ill effects. This goal is not a legal limit with which water systems must comply; it is based solely on human health.

For known cancer-causing agents (Carcinogens), EPA set the health goal at zero, under the assumption that any exposure to the chemical could present a cancer risk.

The rules also set a legal limit, or Maximum Contaminant Level (MCL), for each contaminant. EPA sets Maximum Contaminant Level Goals (MCLG) as close to the health goal as possible, keeping in mind the technical and financial barriers that exist.

Except for contaminants regulated as Carcinogens, most legal limits and health goals are the same. Even when they are less strict than the health goals, the legal limits provide substantial public health protection.

# Volatile Organic Compounds (VOCs)



## TOTAL ORGANIC COMPOUNDS (CARBON)

### Definitions

**Volatile Organic Compounds (VOCs)** – “VOCs are ground-water contaminants of concern because of very large environmental releases, human toxicity, and a tendency for some compounds to persist in and migrate with ground-water to drinking-water supply well ... In general, VOCs have high vapor pressures, low-to-medium water solubilities, and low molecular weights.

Some VOCs may occur naturally in the environment, other compounds occur only as a result of manmade activities, and some compounds have both origins.” - Zogorski and others, 2006

**Volatile Organic Compounds (VOCs)** – “Volatile organic compounds released into the atmosphere by anthropogenic and natural emissions which are important because of their involvement in photochemical pollution.” - Lincoln and others, 1998

**Volatile Organic Compounds (VOCs)** – “Hydrocarbon compounds that have low boiling points, usually less than 100°C, and therefore evaporate readily. Some are gases at room temperature. Propane, benzene, and other components of gasoline are all volatile organic compounds.” - Art, 1993

**Volatile Organic Compounds (VOCs)** – “VOCs are organic compounds that can be isolated from the water phase of a sample by purging the water sample with inert gas, such as helium, and, subsequently, analyzed by gas chromatography. Many VOCs are human-made chemicals that are used and produced in the manufacture of paints, adhesives, petroleum products, pharmaceuticals, and refrigerants. They often are compounds of fuels, solvents, hydraulic fluids, paint thinners, and dry-cleaning agents commonly used in urban settings.

VOC contamination of drinking water supplies is a human-health concern because many are toxic and are known or suspected human carcinogens.” - U.S. Geological Survey, 2005

## **VOCs Explained**

**Volatile organic compounds** (VOCs) are organic chemicals that have a high vapor pressure at ordinary, room-temperature conditions. Their high vapor pressure results from a low boiling point, which causes large numbers of molecules to evaporate or sublime from the liquid or solid form of the compound and enter the surrounding air. An example is formaldehyde, with a boiling point of  $-19\text{ }^{\circ}\text{C}$  ( $-2\text{ }^{\circ}\text{F}$ ), slowly exiting paint and getting into the air.

VOCs are numerous, varied, and ubiquitous. They include both human-made and naturally occurring chemical compounds. Most scents or odors are of VOCs. VOCs play an important role in communication between plants. Some VOCs are dangerous to human health or cause harm to the environment. Anthropogenic VOCs are regulated by law, especially indoors, where concentrations are the highest.

Harmful VOCs are typically not acutely toxic, but instead have compounding long-term health effects. Because the concentrations are usually low and the symptoms slow to develop, research into VOCs and their effects is difficult.

## **Specific Components**

### **Paints and Coatings**

A major source of man-made VOCs are coatings, especially paints and protective coatings. Solvents are required to spread a protective or decorative film. Approximately 12 billion liters of paints are produced annually. Typical solvents are aliphatic hydrocarbons, ethyl acetate, glycol ethers, and acetone. Motivated by cost, environmental concerns, and regulation, the paint and coating industries are increasingly shifting toward aqueous solvents.

### **Chlorofluorocarbons and Chlorocarbons**

Chlorofluorocarbons, which are banned or highly regulated, were widely used cleaning products and refrigerants. Tetrachloroethene is used widely in dry cleaning and by industry. Industrial use of fossil fuels produces VOCs either directly as products (e.g., gasoline) or indirectly as byproducts (e.g., automobile exhaust).

### **Benzene**

One VOC that is a known human carcinogen is benzene, which is a chemical found in environmental tobacco smoke, stored fuels, and exhaust from cars in an attached garage. Benzene also has natural sources such as volcanoes and forest fires. It is frequently used to make other chemicals in the production of plastics, resins, and synthetic fibers. Benzene evaporates into the air quickly and the vapor of benzene is heavier than air allowing the compound to sink into low-lying areas.

Benzene has also been known to contaminate food and water and if digested can lead to vomiting, dizziness, sleepiness, rapid heartbeat, and at high levels, even death may occur.

### **Methylene Chloride**

Methylene chloride is another VOC that is highly dangerous to human health. It can be found in adhesive removers and aerosol spray paints and the chemical has been proven to cause cancer in animals. In the human body, methylene chloride is converted to carbon monoxide and a person will suffer the same symptoms as exposure to carbon monoxide.

If a product that contains methylene chloride needs to be used the best way to protect human health is to use the product outdoors. If it must be used indoors, proper ventilation is essential to keeping exposure levels down.

### **Perchloroethylene**

Perchloroethylene is a volatile organic compound that has been linked to causing cancer in animals. It is also suspected to cause many of the breathing related symptoms of exposure to VOC's. Perchloroethylene is used mostly in dry cleaning.

Studies show that people breathe in low levels of this VOC in homes where dry-cleaned clothes are stored and while wearing dry-cleaned clothing. While dry cleaners attempt to recapture perchloroethylene in the dry cleaning process to reuse it in an effort to save money, they can't recapture it all.

To avoid exposure to perchloroethylene, if a strong chemical odor is coming from clothing when picked up from the dry cleaner, do not accept them and request that less of the chemical be used as well as a complete drying of the garments

### **MTBE**

MTBE was banned in the US around 2004 in order to limit further contamination of drinking water aquifers primarily from leaking underground gasoline storage tanks where MTBE was used as an octane booster and oxygenated-additive.

### **Formaldehyde**

Many building materials such as paints, adhesives, wall boards, and ceiling tiles slowly emit formaldehyde, which irritates the mucous membranes and can make a person irritated and uncomfortable. Formaldehyde emissions from wood are in the range of 0.02 – 0.04 ppm. Relative humidity within an indoor environment can also affect the emissions of formaldehyde. High relative humidity and high temperatures allow more vaporization of formaldehyde from wood-materials.

### **Health Risks**

Respiratory, allergic, or immune effects in infants or children are associated with man-made VOCs and other indoor or outdoor air pollutants. Some VOCs, such as styrene and limonene, can react with nitrogen oxides or with ozone to produce new oxidation products and secondary aerosols, which can cause sensory irritation symptoms. Unspecified VOCs are important in the creation of smog.

### **Health effects include:**

Eye, nose, and throat irritation; headaches, loss of coordination, nausea; damage to liver, kidney, and central nervous system. Some organics can cause cancer in animals; some are suspected or known to cause cancer in humans. Key signs or symptoms associated with exposure to VOCs include conjunctival irritation, nose and throat discomfort, headache, allergic skin reaction, dyspnea, declines in serum cholinesterase levels, nausea, emesis, epistaxis, fatigue, dizziness.

The ability of organic chemicals to cause health effects varies greatly from those that are highly toxic, to those with no known health effects. As with other pollutants, the extent and nature of the health effect will depend on many factors including level of exposure and length of time exposed.

Eye and respiratory tract irritation, headaches, dizziness, visual disorders, and memory impairment are among the immediate symptoms that some people have experienced soon after exposure to some organics. At present, not much is known about what health effects occur from the levels of organics usually found in homes. Many organic compounds are known to cause cancer in animals; some are suspected of causing, or are known to cause, cancer in humans.

### **Reducing Exposure**

To reduce exposure to these toxins, one should buy products that contain Low-VOC's or No VOC's. Only the quantity which will soon be needed should be purchased, eliminating stockpiling of these chemicals.

Use products with VOC's in well ventilated areas. When designing homes and buildings, design teams can implement the best possible ventilation plans, call for the best mechanical systems available, and design assemblies to reduce the amount of infiltration into the building. These methods will help improve indoor air quality, but by themselves they cannot keep a building from becoming an unhealthy place to breathe.

While proper building ventilation is a key component to improving indoor air quality, it cannot do the job on its own. As stated earlier, awareness is the key component to improving air quality, when choosing building materials, furnishings, and decorations. When architects and engineers implement best practices in ventilation and mechanical systems, the owner must maintain good air quality levels thereafter.

### **Limit Values for VOC Emissions**

Limit values for VOC emissions into indoor air are published by e.g. AgBB, AFSSET, California Department of Public Health, and others.

### **Chemical Fingerprinting**

The exhaled human breath contains a few hundred volatile organic compounds and is used in breath analysis to serve as a VOC biomarker to test for diseases such as lung cancer.

One study has shown that "volatile organic compounds ... are mainly blood borne and therefore enable monitoring of different processes in the body." And it appears that VOC compounds in the body "may be either produced by metabolic processes or inhaled/absorbed from exogenous sources" such as environmental tobacco smoke. Research is still in the process to determine whether VOCs in the body are contributed by cellular processes or by the cancerous tumors in the lung or other organs.

<b>Volatile Organic Chemicals</b>	<b>MCL (ppb)</b>	<b>Potential Health Effects</b>
Benzene	5	Cancer
Carbon tetrachloride	5	Liver effects, cancer
Chlorobenzene	100	Liver, kidney, nervous system effects
o-Dichlorobenzene	600	Liver, kidney, blood cell effects
para-Dichlorobenzene	175	Kidney effects, possible carcinogen
1,2-Dichloroethane	5	Cancer
1,1-Dichloroethylene	7	Liver, kidney effects, possible carcinogen
cis-1,2-Dichloroethylene	70	Liver, kidney, nervous system, circulatory system effects
trans-1,2-Dichloroethylene	100	Liver, kidney, nervous system, circulatory system effects
1,2-Dichloropropane	5	Cancer
Ethylbenzene	700	Liver, kidney, nervous system effects
Methylene chloride	5	Cancer
Styrene	100	Liver, nervous systems effects, possible carcinogen
Tetrachloroethylene (PCE)	5	Cancer
Toluene	1,000	Liver, kidney, nervous system, circulatory system effects
Total trihalomethanes		
Chloroform		
Bromoform	100	Cancer
Bromodichloromethane		
Chlorodibromomethane		
1,2,4-Trichlorobenzene	70	Liver, kidney effects
1,1,1-Trichloroethane	200	Liver, nervous system effects
1,1,2-Trichloroethane	5	Kidney, liver effects, possible carcinogen
Trichloroethylene (TCE)	5	Cancer

Vinyl chloride	2	Nervous system, liver effects, cancer
Xylenes (total)	10,000	Liver, kidney, nervous system effects

Disinfection By-products	MCL (ppb)	Potential Health Effects
Bromate	10	Cancer
Chlorate	1,000	Anemia, nervous system effects
Haloacetic Acids (HAA5)*	60	Cancer
Total trihalomethanes (TTHMs)**	100	Cancer

\*Haloacetic acids consist of monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid.

\*\*Total trihalomethanes consist of chloroform, bromoform, bromodichloromethane, and chlorodibromomethane.

# Metalloid Section

# Periodic Table of the Elements

1 IA New Original	2 IIA	3	4	5	6	7	8	9	10	11	12	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 H Hydrogen 1.00784	2 He Helium 4.002602	3 Li Lithium 6.941	4 Be Beryllium 9.012182	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.0074	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797	11 Na Sodium 22.989770	12 Mg Magnesium 24.3050	13 Al Aluminum 26.9815386	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfur 32.06	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955912	22 Ti Titanium 47.887	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938044	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.409	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.9216	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.757	52 Te Tellurium 127.6	53 I Iodine 126.90547	54 Xe Xenon 131.29
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 to 71 Lanthanide series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.222	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98039	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 to 103 Actinide series	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (264)	108 Hs Hassium (265)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (271)	111 Rg Roentgenium (272)	112 Uub Ununbium (285)	113 Uut Ununtrium (288)	114 Uuq Ununquadium (289)	115 Uup Ununpentium (288)	116 Uuh Ununhexium (284)	117 Uus Ununseptium (286)	118 Uuo Ununoctium (289)

Atomic masses in parentheses are those of the most stable or common isotope.

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Note: The subgroup numbers 1-18 were adopted in 1954 by the International Union of Pure and Applied Chemistry. The names of elements 112-118 are the Latin equivalents of those numbers.

57 La Lanthanum 138.9055	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 151.964	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93032	68 Er Erbium 167.259	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
89 Ac Actinium (227)	90 Th Thorium 232.0381	91 Pa Protactinium 231.03888	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)



Germanium, left and Boron, right



## Metalloid Section

Drinking water contaminants that can cause health effects after continuous long-term exposure at levels greater than the maximum contaminant level (MCL) are considered “chronic” contaminants. Examples of chronic drinking water contaminants regulated by EPA include inorganic contaminants like arsenic, cadmium, and copper; organic contaminants such as pesticides and industrial chemicals; and radiological contaminants like radium and uranium.

If your water system has installed some form of inorganic contaminant or arsenic treatment, keep in mind that the treatment you installed may change the water quality in other ways. It might cause the water to react differently in the distribution system. Depending on the kind of treatment you’ve installed, consider what distribution system problems might result.

A change in the taste, odor or appearance of the water at customers’ taps may be the first indication of a problem. Some water quality parameters to consider monitoring, depending on your arsenic treatment technology, include iron, pH, manganese, alkalinity, and aluminum.

In contrast, “acute” contaminants can cause short-term health effects within hours or days of exposure. Microbes such as *E. coli* and *Cryptosporidium* are examples of contaminants that can cause an acute health risk. Some chronic-type contaminants can also fall in this category if they are present at high enough concentrations to cause immediate health effects. For example, nitrate levels over the MCL can cause “blue-baby” syndrome in children less than 6 months.

Arsenic, boron, silicon, germanium, antimony and tellurium are commonly classified as metalloids. One or more from among selenium, polonium or astatine are sometimes added to the list. Boron is sometimes excluded from the list, by itself or together with silicon. Tellurium is sometimes not regarded as a metalloid. The inclusion of antimony, polonium and astatine as metalloids has also been questioned.

A metalloid is a chemical element with properties that are in-between or a mixture of those of metals and nonmetals, and which is considered to be difficult to classify unambiguously as either a metal or a nonmetal. There is no standard definition of a metalloid nor is there agreement as to which elements are appropriately classified as such. Despite this lack of specificity the term continues to be used in the chemistry literature.

Some authors do not classify elements bordering the metal-nonmetal dividing line as metalloids noting that a binary classification can facilitate the establishment of some simple rules for determining bond types between metals and/or nonmetals. Other authors, in contrast, have suggested that classifying some elements as metalloids 'emphasizes that properties change gradually rather than abruptly as one moves across or down the periodic table.

Alternatively, some periodic tables distinguish elements that are metalloids in the absence of any formal dividing line between metals and nonmetals. Metalloids are instead shown as occurring in a diagonal fixed band or diffuse region, running from upper left to lower right, centered around arsenic.

The six elements commonly recognized as metalloids are boron, silicon, germanium, arsenic, antimony and tellurium. They are metallic-looking brittle solids, with intermediate to relatively good electrical conductivities, and each having the electronic band structure of either a semiconductor or a semimetal.

Chemically, they mostly behave as (weak) nonmetals, have intermediate ionization energy and electronegativity values, and form amphoteric or weakly acidic oxides. Being too brittle to have any structural uses, the metalloids and their compounds instead find common use in glasses, alloys and semiconductors. The electrical properties of silicon and germanium, in particular, enabled the establishment of the semiconductor industry in the 1950s and the development of solid state electronics from the early 60s onwards.

Other elements less commonly recognized as metalloids include carbon, aluminum, selenium, polonium and astatine. On a standard periodic table these elements, as well as the elements commonly recognized as metalloids, occur in or near a diagonal region of the p-block, having its main axis anchored by boron at one end and astatine at the other. Some periodic tables include a dividing line between metals and nonmetals and it is generally the elements adjacent to this line or, less frequently, one or more of the elements adjacent to those elements, which are identified as metalloids.

The term *metalloid* was first popularly used to refer to nonmetals. It's more recent meaning as a category of elements with intermediate or hybrid properties did not become widespread until the period 1940–1960. Metalloids are sometimes called semimetals, a practice which has been discouraged. This is because the term *semimetal* has a different meaning in physics, one which more specifically refers to the electronic band structure of a substance rather than the overall classification of a chemical element.

There is no universally agreed or rigorous definition of a metalloid. The feasibility of establishing a specific definition has also been questioned, noting anomalies can be found in several such attempted constructs. Classifying any particular element as a metalloid has been described as 'arbitrary'.

The generic definition set out at the start of this article is based on metalloid attributes consistently cited in the literature. Illustrative definitions and extracts include:

- 'In chemistry a metalloid is an element with properties intermediate between those of metals and nonmetals.'
- 'Between the metals and nonmetals in the periodic table we find elements...[that] share some of the characteristic properties of both the metals and nonmetals, making it difficult to place them in either of these two main categories.'
- 'Chemists sometimes use the name metalloid...for these elements which are difficult to classify one way or the other.'
- 'Because the traits distinguishing metals and nonmetals are qualitative in nature, some elements do not fall unambiguously in either category. These elements...are called metalloids...'

**More Broadly, Metalloids have also been referred to as:**

- 'elements that...are somewhat of a cross between metals and nonmetals' or
- 'weird in-between elements.'

The criterion that metalloids are difficult to unambiguously classify one way or the other is a key tenet. In contrast, elements such as sodium and potassium 'have metallic properties to a high degree' and fluorine, chlorine and oxygen 'are almost exclusively nonmetallic.'

Although most other elements have a mixture of metallic and nonmetallic properties most such elements can also be classified as either metals or nonmetals according to which set of properties are regarded as being more pronounced in them. It is only the elements at or near the margins, ordinarily those that are regarded as lacking a sufficiently clear preponderance of metallic or nonmetallic properties, which are classified as metalloids.

### **Which Elements are Metalloids?**

There is no universally agreed or rigorous definition of the term metalloid. So the answer to the question "Which elements are metalloids?" can vary, depending on the author and their inclusion criteria. Emsley, for example, recognized only four: germanium, arsenic, antimony and tellurium. James et al., on the other hand, listed twelve: boron, carbon, silicon, germanium, arsenic, selenium, antimony, tellurium, bismuth, polonium, ununpentium and livermorium. As of 2011 the list of metalloid lists recorded an average of just over seven elements classified as metalloids, per list of metalloids, based on a sample size of 194 lists.

The absence of a standardized division of the elements into metals, metalloids and nonmetals is not necessarily an issue. There is a more or less continuous progression from the metallic to the nonmetallic. A specified subset of this continuum can potentially serve its particular purpose as well as any other. In any event, individual metalloid classification arrangements tend to share common ground (as described above) with most variations occurring around the indistinct margins, as surveyed later.

### **How Are Chronic Contaminants Regulated?**

In 1974, Congress passed the Safe Drinking Water Act (SDWA) to give EPA the authority to set standards to ensure the safety of drinking water provided by public water systems. The SDWA, which was amended in 1986 and 1996, directs EPA to establish non-enforceable health goals called maximum contaminant level goals (MCLGs) which reflect the level at which no adverse health effects are expected from a particular contaminant.

Once an MCLG is established, EPA sets enforceable standards for contaminants called maximum contaminant levels (MCLs). MCLs are set as close to the health goals as possible considering cost, benefits, and the ability of public water systems to detect and remove contaminants using appropriate treatment technologies. When there is no reliable method to measure a contaminant that is economically and technically feasible, EPA develops a treatment technique requirement rather than an MCL. EPA continues to assess the occurrence of unregulated contaminants through the Unregulated Contaminant Monitoring Regulation (UCMR). Information about the UCMR can be found at <http://www.epa.gov/safewater/ucmr/>.

### **What Are Some Best Practices For Effective Communication About Chronic Contaminants?**

If you expect that your public water system will exceed EPA's standard for a contaminant or that the costs of compliance may require public funding, communicate early and often. The most effective communication efforts follow these simple steps:

- Provide simple, straightforward, *and consistent* messages;

- Describe potential adverse health effects and populations at risk;
- Describe actions you are taking to correct the situation and when you anticipate it will be resolved;
- Describe actions the consumer can take such as using alternate water supplies and when to seek medical help;
- Provide links to useful information resources such as EPA's Web site.
- Use graphics, photographs, maps, charts, and drawings to illustrate your messages;
- Assume that consumers will only read the top half of the notice or what can be read in ten seconds;
- Display important elements in bold and/or large type in the top half of the notice;
- Communicate in multiple languages to meet the needs of your non-English speaking consumers; and Include contact information for further information in *all* communications.

## Near Metalloids

The concept of a class of elements intermediate between metals and nonmetals is sometimes extended to include elements that most chemists, and related science professionals, would not ordinarily recognize as metalloids. In 1935, Fernelius and Robey allocated carbon, phosphorus, selenium, and iodine to such an intermediary class of elements, together with boron, silicon, arsenic, antimony, tellurium and polonium. They also included a placeholder for the missing element 85 (astatine), five years ahead of its synthesis in 1940.

They excluded germanium from their considerations as it was still then regarded as a poorly conducting metal. In 1954, Szabó & Lakatos counted beryllium and aluminum in their list of metalloids, as well as boron, silicon, germanium, arsenic, antimony, tellurium, polonium and astatine. In 1957, Sanderson recognized carbon, phosphorus, selenium, and iodine as part of an intermediary class of elements with 'certain metallic properties', together with boron, silicon, arsenic, tellurium, and astatine. Germanium, antimony and polonium were classified by him as metals. More recently, in 2007, Petty included carbon, phosphorus, selenium, tin and bismuth in his list of metalloids, as well as boron, silicon, germanium, arsenic, antimony, tellurium, polonium and astatine.

Elements such as these are occasionally called or described as, *near-metalloids*, or the like. They are located near the elements commonly recognized as metalloids, and usually classified as either metals or nonmetals. Metals falling into this loose category tend to show 'odd' packing structures, marked covalent chemistry (molecular or polymeric), and amphotericism.

Aluminum, tin and bismuth are examples. They are also referred to as (*chemically*) *weak metals*, *poor metals*, *post-transition metals*, or *semimetals* (in the aforementioned sense of metals with incomplete metallic character). These classification groupings generally cohabit the same periodic table territory but are not necessarily mutually inclusive.

Nonmetals in the 'near-metalloid' category include carbon, phosphorus, selenium and iodine. They exhibit metallic luster, semiconducting properties and bonding or valence bands with delocalized character.

This applies to their most thermodynamically stable forms under ambient conditions: carbon as graphite; phosphorus as black phosphorus; and selenium as grey selenium. These elements are alternatively described as being 'near metalloid', showing metalloid character, or having metalloid-like or some metalloid(al) or metallic properties.

### Allotropes

Some allotropes of the elements exhibit more pronounced metallic, metalloid or nonmetallic behavior than others. For example, the diamond allotrope of carbon is clearly nonmetallic. The graphite allotrope however displays limited electrical conductivity more characteristic of a metalloid. Phosphorus, selenium, tin, and bismuth also have allotropes that display borderline or either metallic or nonmetallic behavior.

### Categorization and Periodic Table Territory

Metalloids are generally regarded as a third category of chemical elements, alongside metals and nonmetals. They have been described as forming a (fuzzy) buffer zone between metals and nonmetals. The make-up and size of this zone depends on the classification criteria being used. Metalloids are sometimes grouped instead with metals, regarded as nonmetals or treated as a sub-category of same.

#### Metalloid Border

H								He
Li	Be		B	C	N	O	F	Ne
Na	Mg		Al	Si	P	S	Cl	Ar
K	Ca	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

Periodic table extract showing elements that have sometimes<sup>1</sup> been classified as metalloids:

Elements that appear commonly to rarely in the list of metalloid lists.

Elements that appear still less frequently.  
Outlying elements showing that the metalloid net is sometimes cast very widely. Although they do not appear in the list of metalloids lists, isolated references to their designation as metalloids can be found in the literature.

Metalloids cluster on either side of the **dividing line between metals and nonmetals**. This can be found, in varying configurations, on some periodic tables (see mini-example, right). Elements to the lower left of the line generally display increasing metallic behavior; elements to the upper right display increasing nonmetallic behavior.

When presented as a regular stair-step, elements with the highest critical temperature for their groups (Li, Be, Al, Ge, Sb, Po) lie just below the line.

The diagonal positioning of the metalloids represents somewhat of an exception to the phenomenon that elements with similar properties tend to occur in vertical columns. Going across a periodic table row, the nuclear charge increases with atomic number just as there is as a corresponding increase in electrons. The additional 'pull' on outer electrons with increasing nuclear charge generally outweighs the screening efficacy of having more electrons.

With some irregularities, atoms therefore become smaller, ionization energy increases, and there is a gradual change in character, across a period, from strongly metallic, to weakly metallic, to weakly nonmetallic, to strongly nonmetallic elements.

Going down a main group periodic table column, the effect of increasing nuclear charge is generally outweighed by the effect of additional electrons being further away from the nucleus. With some irregularities, atoms therefore become larger, ionization energy falls, and metallic character increases. The combined effect of these competing horizontal and vertical trends is that the location of the metal-nonmetal transition zone shifts to the right in going down a period.

A related effect can be seen in other diagonal similarities that occur between some elements and their lower right neighbors, such as lithium-magnesium, beryllium-aluminum, carbon-phosphorus, and nitrogen-sulfur.

### **Other Metalloids**

Given there is no agreed definition of a metalloid, some other elements are occasionally classified as such. These elements include hydrogen, beryllium, nitrogen, phosphorus, sulfur, zinc, gallium, tin, iodine, lead, bismuth and radon. The term metalloid has also been used to refer to:

- Elements that exhibit metallic luster and electrical conductivity, and that are also amphoteric. Arsenic, antimony, vanadium, chromium, molybdenum, tungsten, tin, lead and aluminum are examples.
- Elements that are otherwise sometimes referred to as poor metals.
- Nonmetallic elements (for example, nitrogen; carbon) that can form alloys with, or modify the properties of, metals.

### **Heavy Metals**

A heavy metal is a member of a loosely defined subset of elements that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides, and actinides. Many different definitions have been proposed—some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity. The term *heavy metal* has been called a "misinterpretation" in an IUPAC technical report due to the contradictory definitions and its lack of a "coherent scientific basis".

There is an alternative term *toxic metal*, for which no consensus of exact definition exists either. As discussed below, depending on context, heavy metal can include elements lighter than carbon and can exclude some of the heaviest metals. Heavy metals occur naturally in the ecosystem with large variations in concentration. In modern times, anthropogenic sources of heavy metals, i.e. pollution, have been introduced to the ecosystem. Waste-derived fuels are especially prone to contain heavy metals, so heavy metals are a concern in consideration of waste as fuel.

Motivations for controlling heavy metal concentrations in gas streams are diverse. Some of them are dangerous to health or to the environment (e.g. mercury, cadmium, lead, chromium), some may cause corrosion (e.g. zinc, lead), some are harmful in other ways (e.g. arsenic may pollute catalysts).

Within the European community the eleven elements of highest concern are arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin, and thallium, the emissions of which are regulated in waste incinerators.

Some of these elements are actually necessary for humans in minute amounts (cobalt, copper, chromium, manganese, nickel) while others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones, or teeth (nickel, cadmium, copper, chromium).

Heavy metal pollution can arise from many sources but most commonly arises from the purification of metals, e.g., the smelting of copper and the preparation of nuclear fuels. Electroplating is the primary source of chromium and cadmium.

Through precipitation of their compounds or by ion exchange into soils and muds, heavy metal pollutants can localize and lay dormant. Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation. Currently, plants or microorganisms are tentatively used to remove some heavy metals such as mercury.

Plants which exhibit hyper accumulation can be used to remove heavy metals from soils by concentrating them in their bio matter. Some treatment of mining tailings has occurred where the vegetation is then incinerated to recover the heavy metals. One of the largest problems associated with the persistence of heavy metals is the potential for bioaccumulation and biomagnification causing heavier exposure for some organisms than is present in the environment alone. Coastal fish (such as the smooth toadfish) and seabirds (such as the Atlantic Puffin) are often monitored for the presence of such contaminants.

Living organisms require varying amounts of "heavy metals". Iron, cobalt, copper, manganese, molybdenum, and zinc are required by humans. Excessive levels can be damaging to the organism.

Other heavy metals such as mercury, plutonium, and lead are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation over time in the bodies of animals can cause serious illness. Certain elements that are normally toxic are, for certain organisms or under certain conditions, beneficial. Examples include vanadium, tungsten, and even cadmium.

### **Toxic Metals**

Toxic metals are metals that form poisonous soluble compounds and have no biological role, i.e. are not essential minerals, or are in the wrong form. Often heavy metals are thought as synonymous, but lighter metals also have toxicity, such as beryllium, and not all heavy metals are particularly toxic, and some are essential, such as iron. The definition may also include trace elements when considered in abnormally high, toxic doses. A difference is that there is no beneficial dose for a toxic metal with no biological role.

Toxic metals sometimes imitate the action of an essential element in the body, interfering with the metabolic process to cause illness.

Many metals, particularly heavy metals are toxic, but some heavy metals are essential, and some, such as bismuth, have a low toxicity. Most often the definition includes at least cadmium, lead, mercury and the radioactive metals. Metalloids (arsenic, polonium) may be included in the definition.

Radioactive metals have both radiological toxicity and chemical toxicity. Metals in an oxidation state abnormal to the body may also become toxic: chromium (III) is an essential trace element, but chromium (VI) is a carcinogen.

Toxicity is a function of solubility. Insoluble compounds as well as the metallic forms often exhibit negligible toxicity. The toxicity of any metal depends on its ligands. In some cases, organometallic forms, such as dimethyl mercury and tetraethyl lead, can be extremely toxic. In other cases, organometallic derivatives are less toxic such as the cobaltocenium cation.

Decontamination for toxic metals is different from organic toxins: because toxic metals are elements, they cannot be destroyed. Toxic metals may be made insoluble or collected, possibly by the aid of chelating agents. Toxic metals can bioaccumulate in the body and in the food chain. Therefore, a common characteristic of toxic metals is the chronic nature of their toxicity. This is particularly notable with radioactive heavy metals such as thorium, which imitates calcium to the point of being incorporated into human bone, although similar health implications are found in lead or mercury poisoning. The exceptions to this are barium and aluminum, which can be removed efficiently by the kidneys.

## Toxic Heavy Metals

- Antimony (a metalloid)
- Arsenic is a metalloid
- Barium
- Beryllium
- Cadmium - cadmium poisoning
- Lead - lead poisoning
- Mercury - mercury poisoning
- Osmium
- Thallium
- Vanadium
- Radioactive metals:
  - Actinium
  - Thorium
  - Uranium
  - Radium
  - The transuraniums, such as plutonium, americium, etc.
  - Polonium
  - Radioactive isotopes of metallic elements not otherwise strongly toxic, e.g. cobalt-60 and strontium-90.

Aluminum has no biological role and its classification into toxic metals is controversial. Significant toxic effects and accumulation to tissues have been observed in renally impaired patients. However, individuals with healthy kidneys can be exposed to large amounts of aluminum with no ill effects. Thus, aluminum is not considered dangerous to persons with normal elimination capacity.

### **Trace Elements with Toxicity**

- Chromium as hexavalent Cr(VI)
- Nickel – nickel salts are carcinogenic
- Copper – copper toxicity
- Zinc - zinc toxicity
- Iron – iron poisoning
- Fluorine-fluoride poisoning

### **Nonmetals**

Some heavy nonmetals may be erroneously called "metals", because they have some metallic properties.

- Selenium – a nonmetal; essential element
- Tellurium

### **Atomic Spectrometry**

Atomic spectrometry converts each metal in the water sample to a particulate emission that can then be weighed. Extrapolations are made to determine each metal concentration in each water sample taken. The complicated analysis requires preserving the sample with acid, heating the sample to convert to a particulate emission and then identifying each metal and its weight.

A simple analogy is to capture the steam from a pot of water, separate every atom in the steam, identify each atom, weigh each atom and then apply these numbers back to the original volume of water contained in the pot. The result is an accurate picture of what is in the water.

### **Heavy Metals in Water**

High heavy metals concentrations can be naturally occurring. Every geologic formation contains a certain amount of heavy metal. Mine operations extract and process these metals in areas with the highest concentrations. Water in these areas may have high metal concentrations due to the combination of naturally occurring deposits and mine waste.

Water samples are usually taken randomly within a contaminated area and offsite to identify the source of contamination and the pathway it travels, into the drinkable groundwater system or away from potable water sources. Accurate determination of heavy metal contamination is important to identify cumulative risks to people drinking water derived from these areas.

### **Treating Heavy Metal Contamination in Water**

Heavy metal water contamination is a difficult expensive problem to address. Most cleanup activities use a pump and treat system where contaminated groundwater is pumped out of the ground, treated with activated carbon to remove contaminants and then replaced into the groundwater system. Because large volumes of water must be pumped and treated over long time periods, associated operation and maintenance systems are very expensive. There are some new technologies being developed that actually treat the water in the ground which operate more efficiently and quickly, decreasing costs.

If groundwater is contaminated with heavy metals, an alternative source of drinking water must be used to prevent harmful health effects, until the water is treated to meet standards protective of human health and the environment

## Health Significance of Metals in the Environment

The metallic elements can be categorized into two groups. The heavy metals are those having densities five times greater than water, and the light metals, those having lesser densities. Well-known examples of heavy metallic elements are iron, lead, and copper. Examples of light metals are sodium, magnesium, and potassium. Humans consume metallic elements through both water and food. Some metals such as sodium, potassium, magnesium, calcium, and iron are found in living tissue and are essential to human life—biological anomalies arise when they are depleted or removed. Probably less well known is that currently no less than six other heavy metals including molybdenum, manganese, cobalt, copper, and zinc, have been linked to human growth, development, achievement, and reproduction (Vahrenkamp, 1979; Friberg and others, 1979). Even these metals, however, can become toxic or aesthetically undesirable when their concentrations are too great. Several heavy metals, like cadmium, lead, and mercury, are highly toxic at relatively low concentrations, can accumulate in body tissues over long periods of time, and are nonessential for human health. Table 1 lists metals according to their toxicities.

No specific health guidelines for heavy metals associated with suspended or bed sediments have been established by the U.S. Environmental Protection Agency. This lack of national guidelines based on concise scientific criteria causes difficulty when evaluating the environmental effects of heavy metals in sediments. Several different criteria have been defined, primarily on the basis of observed effects on aquatic life (Lyman and others, 1987). Table 2 lists criteria for open-water disposal of polluted sediments that can be used for comparison purposes.

**Table 1.** Classification of naturally occurring metals according to their toxicity and availability in the hydrologic environment (from Wood, 1974)

[Metals that normally do not exist as dissolved species in natural waters or are very rare in crustal rocks are in italics]

Nontoxic		Low toxicity		Moderate to high toxicity			
Aluminum	Magnesium	Barium	<i>Praseodymium</i>	<i>Actinium</i>	Indium	Polonium	Uranium
Bismuth	Manganese	<i>Cerium</i>	<i>Promethium</i>	<i>Antimony</i>	<i>Iridium</i>	<i>Radium</i>	Vanadium
Calcium	Molybdenum	<i>Dysprosium</i>	<i>Rhenium</i>	Beryllium	Lead	<i>Ruthenium</i>	Zinc
Cesium	Potassium	<i>Erbium</i>	<i>Rhodium</i>	Boron	Mercury	Silver	<i>Zirconium</i>
Iron	Strontium	<i>Europium</i>	<i>Samarium</i>	Cadmium	Nickel	<i>Tantalum</i>	
Lithium	Rubidium	<i>Gadolinium</i>	Scandium	Chromium	<i>Niobium</i>	Thallium	
	Sodium	<i>Gallium</i>	<i>Terbium</i>	Cobalt	<i>Osmium</i>	Thorium	
		Germanium	Thulium	Copper	Palladium	<i>Titanium</i>	
		<i>Gold</i>	<i>Tin</i>	<i>Hafnium</i>	Platinum	<i>Tungsten</i>	
		<i>Holmium</i>	<i>Ytterbium</i>				
		<i>Neodymium</i>	Yttrium				

**Table 2.** U.S. Environmental Protection Agency maximum contaminant levels for heavy-metal concentrations in drinking water and water supporting aquatic life, and criteria for open-water disposal of polluted sediments

[ $\mu\text{g/L}$ , microgram per liter;  $\mu\text{g/g}$ , microgram per gram; >, greater than; <, less than; --, no guideline available]

	<b>Cadmium</b>	<b>Chromium</b>	<b>Copper</b>	<b>Lead</b>	<b>Mercury</b>	<b>Uranium</b>
Drinking water, in $\mu\text{g/L}$ <sup>1</sup>	5	100	<sup>2</sup> 1,000	15	2	<sup>3</sup> 20
Water supporting aquatic life, in $\mu\text{g/L}$ <sup>4</sup>	12	100	20	100	0.05	–
Natural sediments, nonpolluted, in $\mu\text{g/g}$ <sup>5</sup>	--	<25	<25	<40	<1	–
Natural sediments, moderately polluted, in $\mu\text{g/g}$ <sup>5</sup>	--	25 to 75	25 to 50	40 to 60	--	–
Natural sediments, heavily polluted, in $\mu\text{g/g}$ <sup>5</sup>	>6	>75	>50	>60	>1	–

<sup>1</sup>U.S. Environmental Protection Agency, 1992.

<sup>2</sup>Secondary maximum contaminant level based on esthetic water quality.

<sup>3</sup>Proposed maximum contaminant level.

<sup>4</sup>U.S. Environmental Protection Agency, 1982.

<sup>5</sup>Great Lakes Water Quality Board, Dredging Subcommittee, 1982.

## **Antimony - Inorganic Contaminant 0.006 mg/L MCL Metalloid See Antimony in IOC Section for more information**

**Antimony** is a toxic chemical element with symbol **Sb** and atomic number 51. A lustrous gray metalloid, it is found in nature mainly as the sulfide mineral stibnite ( $\text{Sb}_2\text{S}_3$ ). Antimony compounds have been known since ancient times and were used for cosmetics; metallic antimony was also known, but it was erroneously identified as lead. It was established to be an element around the 17th century.

For some time, China has been the largest producer of antimony and its compounds, with most production coming from the Xikuangshan Mine in Hunan. The industrial methods to produce antimony are roasting and subsequent carbothermal reduction or direct reduction of stibnite with iron.

### **What are EPA's drinking water regulations for antimony?**

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.



The MCLG for antimony is 0.006 mg/L or 6 ppb. EPA has set this level of protection based on the best available science to prevent potential health problems. EPA has set an enforceable regulation for antimony, called a maximum contaminant level (MCL), at 0.006 mg/L or 6 ppb. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.

The Phase V Rule, the regulation for antimony, became effective in 1994. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed antimony as part of the Six Year Review and determined that the 0.006 mg/L or 6 ppb MCLG and 0.006 mg/L or 6 ppb MCL for antimony are still protective of human health.

### **Applications**

The largest applications for metallic antimony are as alloying material for lead and tin and for lead antimony plates in lead-acid batteries. Alloying lead and tin with antimony improves the properties of the alloys which are used in solders, bullets and plain bearings. Antimony compounds are prominent additives for chlorine- and bromine-containing fire retardants found in many commercial and domestic products. An emerging application is the use of antimony in microelectronics.

Antimony is in the nitrogen group (group 15) and has an electronegativity of 2.05. As expected by periodic trends, it is more electronegative than tin or bismuth, and less electronegative than tellurium or arsenic. Antimony is stable in air at room temperature, but reacts with oxygen if heated to form antimony trioxide,  $\text{Sb}_2\text{O}_3$ . Antimony is a silvery, lustrous gray metal that has a Mohs scale hardness of 3. Therefore, pure antimony is not used to make hard objects: coins made of antimony were issued in China's Guizhou province in 1931, but because of their rapid wear, their minting was discontinued. Antimony is resistant to attack by acids.

Four allotropes of antimony are known, a stable metallic form and three metastable forms, explosive, black and yellow. Metallic antimony is a brittle, silver-white shiny metal. When molten antimony is slowly cooled, metallic antimony crystallizes in a trigonal cell, isomorphic with that of the gray allotrope of arsenic. A rare explosive form of antimony can be formed from the electrolysis of antimony (III) trichloride. When scratched with a sharp implement, an exothermic reaction occurs and white fumes are given off as metallic antimony is formed; when rubbed with a pestle in a mortar, a strong detonation occurs.

Black antimony is formed upon rapid cooling of vapor derived from metallic antimony. It has the same crystal structure as red phosphorus and black arsenic; it oxidizes in air and may ignite spontaneously. At 100 °C, it gradually transforms into the stable form. The yellow allotrope of antimony is the most unstable. It has only been generated by oxidation of stibine ( $\text{SbH}_3$ ) at -90 °C. Above this temperature and in ambient light, this metastable allotrope transforms into the more stable black allotrope.

Metallic antimony adopts a layered structure (space group  $R\bar{3}m$  No. 166) in which layers consist of fused ruffled six-membered rings. The nearest and next-nearest neighbors form a distorted octahedral complex, with the three atoms in the same double-layer being slightly closer than the three atoms in the next. This relatively close packing leads to a high density of 6.697 g/cm<sup>3</sup>, but the weak bonding between the layers leads to the low hardness and brittleness of antimony.

### Isotopes

Antimony exists as two stable isotopes,  $^{121}\text{Sb}$  with a natural abundance of 57.36% and  $^{123}\text{Sb}$  with a natural abundance of 42.64%. It also has 35 radioisotopes, of which the longest-lived is  $^{125}\text{Sb}$  with a half-life of 2.75 years. In addition, 29 metastable states have been characterized. The most stable of these is  $^{124}\text{Sb}$  with a half-life of 60.20 days, which has an application in some neutron sources. Isotopes that are lighter than the stable  $^{123}\text{Sb}$  tend to decay by  $\beta^+$  decay, and those that are heavier tend to decay by  $\beta^-$  decay, with some exceptions.

### Occurrence

The abundance of antimony in the Earth's crust is estimated at 0.2 to 0.5 parts per million, comparable to thallium at 0.5 parts per million and silver at 0.07 ppm. Even though this element is not abundant, it is found in over 100 mineral species. Antimony is sometimes found natively, but more frequently it is found in the sulfide stibnite ( $\text{Sb}_2\text{S}_3$ ) which is the predominant ore mineral.

## Astatine- Nonmetal or a Metalloid

Astatine may be a nonmetal or a metalloid. It is ordinarily classified as a nonmetal, but has some 'marked' metallic properties. Immediately following its production in 1940, early investigators considered it to be a metal. In 1949 it was called the most noble (difficult to reduce) nonmetal as well as being a relatively noble (difficult to oxidize) metal. In 1950 astatine was described as a halogen and (therefore) a reactive nonmetal.

In terms of metallic indicators:

- Samsonov observes that, '[L]ike typical metals, it is precipitated by hydrogen sulfide even from strongly acid solutions and is displaced in a free form from sulfate solutions; it is deposited on the cathode on electrolysis'.
- Rossler cites further indications of a tendency for astatine to behave like a (heavy) metal as: '...the formation of pseudohalide compounds...complexes of astatine cations...complex anions of trivalent astatine...as well as complexes with a variety of organic solvents'.
- Rao and Ganguly note that elements with an enthalpy of vaporization (EoV) greater than ~42 kJ/mol are metallic when liquid. Such elements include boron, silicon, germanium, antimony, selenium and tellurium. Vásáros & Berei give estimated values for the EoV of diatomic astatine, the lowest of these being 50 kJ/mol. On this basis astatine may also be metallic in the liquid state. Diatomic iodine, with an EoV of 41.71, falls just short of the threshold figure.
- Siekierski and Burgess contend or presume that astatine would be a metal if it could form a condensed phase.
- Champion et al. argue that astatine demonstrates cationic behavior, by way of stable  $\text{At}^+$  and  $\text{AtO}^+$  forms, in strongly acidic aqueous solutions.



### For Nonmetallic Indicators:

- Batsanov gives a calculated band gap energy for astatine of 0.7 eV. This is consistent with nonmetals (in physics) having separated valence and conduction bands and thereby being either semiconductors or insulators.
- It has the narrow liquid range ordinarily associated with nonmetals (mp 575 K, bp 610).
- Its chemistry in aqueous solution is predominately characterized by the formation of various anionic species.
- Most of its known compounds resemble those of iodine, which is halogen and a nonmetal. Such compounds include astatides ( $\text{XAt}$ ), astatates ( $\text{XAtO}_3$ ), and monovalent interhalogen compounds.

Restrepo et al. reported that astatine appeared to share more in common with polonium than it did with the established halogens. They did so on the basis of detailed comparative studies of the known and interpolated properties of 72 elements.



## **Arsenic- Inorganic Contaminant 0.010 mg/L MCL Metalloid See Arsenic in IOC Section for more information**

Arsenic is a chemical element with symbol **As** and the atomic number is 33. Arsenic occurs in many minerals, usually in conjunction with sulfur and metals, and also as a pure elemental crystal. It was first documented by Albertus Magnus in 1250. Arsenic is a metalloid. It can exist in various allotropes, although only the gray form has important use in industry.

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for arsenic is zero. EPA has set this level of protection based on the best available science to prevent potential health problems. Based on the MCLG, EPA has set an enforceable regulation for arsenic, called a maximum contaminant level (MCL), at 0.010 mg/L or 10 ppb. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies.



The Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring Final Rule, the regulation for arsenic, became effective in 2002. The Safe Drinking Water Act requires EPA to periodically review and revise contaminants, if appropriate, based on new scientific data. The regulation for arsenic will be included in a future review cycle.

The main uses of metallic arsenic is for strengthening alloys of copper and especially lead (for example, in car batteries). Arsenic is a common n-type dopant in semiconductor electronic devices, and the optoelectronic compound gallium arsenide is the most common semiconductor in use after doped silicon. Arsenic and its compounds, especially the trioxide, are used in the production of pesticides (treated wood products), herbicides, and insecticides. These applications are declining, however.

Arsenic is notoriously poisonous to multicellular life, although a few species of bacteria are able to use arsenic compounds as respiratory metabolites. Arsenic contamination of groundwater is a problem that affects millions of people across the world.

Arsenic, a naturally occurring element, is found throughout the environment; for most people, food is the major source of exposure. Acute (short-term) high-level inhalation exposure to arsenic dust or fumes has resulted in gastrointestinal effects (nausea, diarrhea, abdominal pain); central and peripheral nervous system disorders have occurred in workers acutely exposed to inorganic arsenic. Chronic (long-term) inhalation exposure

to inorganic arsenic in humans is associated with irritation of the skin and mucous membranes.

Chronic oral exposure has resulted in gastrointestinal effects, anemia, peripheral neuropathy, skin lesions, hyperpigmentation, and liver or kidney damage in humans. Inorganic arsenic exposure in humans, by the inhalation route, has been shown to be strongly associated with lung cancer, while ingestion of inorganic arsenic in humans has been linked to a form of skin cancer and also to bladder, liver, and lung cancer. EPA has classified inorganic arsenic as a Group A, human carcinogen.

### **Contamination of Groundwater**

Arsenic contamination of groundwater is often due to naturally occurring high concentrations of arsenic in deeper levels of groundwater. It is a high-profile problem due to the use of deep tubewells for water supply in the Ganges Delta, causing serious arsenic poisoning to large numbers of people. In addition, mining techniques such as hydraulic fracturing mobilize arsenic in groundwater and aquifers due to enhanced methane transport and resulting changes in redox conditions, and inject fluid containing additional arsenic.

A 2007 study found that over 137 million people in more than 70 countries are probably affected by arsenic poisoning of drinking water. Arsenic contamination of ground water is found in many countries throughout the world, including the USA.

Approximately 20 incidents of groundwater arsenic contamination have been reported from all over the world. Of these, four major incidents were in Asia, including locations in Thailand, Taiwan, and Mainland China. In South America, Argentina and Chile are affected. There are also many locations in the United States where the groundwater contains arsenic concentrations in excess of the Environmental Protection Agency standard of 10 parts per billion adopted in 2001. Millions of private wells have unknown arsenic levels, and in some areas of the US, over 20% of wells may contain levels that are not safe.

### **Arsine**

Arsine is a gas consisting of arsenic and hydrogen. It is extremely toxic to humans, with headaches, vomiting, and abdominal pains occurring within a few hours of exposure. EPA has not classified arsine for carcinogenicity.

Drinking water regulations require public water systems to monitor for arsenic at the entry point to the distribution system. There is no federal requirement for systems to monitor for arsenic within the distribution system. You may, however, want to test your distribution system water for arsenic to be sure that the water being delivered has arsenic levels below the MCL.

If you decide to monitor your distribution system, consider testing for arsenic at locations where the settling and accumulation of iron solids or pipe scales are likely (i.e., areas with cast iron pipe, ductile iron pipe, or galvanized iron pipe).

If your water system has installed some form of arsenic treatment, keep in mind that the treatment you installed may change the water quality in other ways. It might cause the water to react differently in the distribution system. Depending on the kind of treatment you've installed, consider what distribution system problems might result.

## Boron - Metalloid

Boron is a chemical element with chemical symbol **B** and atomic number 5. Because boron is produced entirely by cosmic ray spallation and not by stellar nucleosynthesis, it is a low-abundance element in both the solar system and the Earth's crust. Boron is concentrated on Earth by the water-solubility of its more common naturally occurring compounds, the borate minerals. These are mined industrially as evaporites, such as borax and kernite.

Chemically uncombined boron, which is classed as a metalloid, is not found naturally on Earth. Industrially, very pure boron is produced with difficulty, as boron tends to form refractory materials containing small amounts of carbon or other elements. Several allotropes of boron exist: amorphous boron is a brown powder and crystalline boron is black, extremely hard (about 9.5 on the Mohs scale), and a poor conductor at room temperature. Elemental boron is used as a dopant in the semiconductor industry.



The major industrial-scale uses of boron compounds are in sodium perborate bleaches, and the borax component of fiberglass insulation. Boron polymers and ceramics play specialized roles as high-strength lightweight structural and refractory materials. Boron compounds are used in silica-based glasses and ceramics to give them resistance to thermal shock. Boron-containing reagents are used for as intermediates in the synthesis of organic fine chemicals.

A few boron-containing organic pharmaceuticals are used, or are in study. Natural boron is composed of two stable isotopes, one of which (boron-10) has a number of uses as a neutron-capturing agent.

In biology, borates have low toxicity in mammals (similar to table salt), but are more toxic to arthropods and are used as insecticides. Boric acid is mildly antimicrobial, and a natural boron-containing organic antibiotic is known. Boron is essential to life. Small amounts of boron compounds play a strengthening role in the cell walls of all plants, making boron necessary in soils. Experiments indicate a role for boron as an ultratrace element in animals, but the nature of its role in animal physiology is unknown.

Boron compounds were known thousands of years ago. Borax was known from the deserts of western Tibet, where it received the name of *tincal*, derived from the Sanskrit. Borax glazes were used in China from AD300, and some tincal even reached the West, where the Persian alchemist Jābir ibn Hayyān seems to mention it in 700. Marco Polo brought some glazes back to Italy in the 13th century. Agricola, around 1600, reports the use of borax as a flux in metallurgy.

In 1777, boric acid was recognized in the hot springs (soffioni) near Florence, Italy, and became known as *sal sedativum*, with mainly medical uses.

The rare mineral is called sassolite, which is found at Sasso, Italy. Sasso was the main source of European borax from 1827 to 1872, at which date American sources replaced it. Boron compounds were relatively rarely used chemicals until the late 1800s when Francis Marion Smith's Pacific Coast Borax Company first popularized these compounds and made them in volume and hence cheap.

Boron was not recognized as an element until it was isolated by Sir Humphrey Davy and by Joseph Louis Gay-Lussac and Louis Jacques Thénard. In 1808 Davy observed that electric current sent through a solution of borates produced a brown precipitate on one of the electrodes. In his subsequent experiments he used potassium to reduce boric acid instead of electrolysis. He produced enough boron to confirm a new element and named the element *boracium*.

Gay-Lussac and Thénard used iron to reduce boric acid at high temperatures. They showed by oxidizing boron with air that boric acid is an oxidation product of boron. Jöns Jakob Berzelius identified boron as an element in 1824. Pure boron was arguably first produced by the American chemist Ezekiel Weintraub in 1909.

### **Chemical Compounds**

In its most familiar compounds, boron has the formal oxidation state III. These include oxides, sulfides, nitrides, and halides. The trihalides adopt a planar trigonal structure. These compounds are Lewis acids in that they readily form adducts with electron-pair donors, which are called Lewis bases. For example, fluoride ( $F^-$ ) and boron trifluoride ( $BF_3$ ) combined to give the tetrafluoroborate anion,  $BF_4^-$ . Boron trifluoride is used in the petrochemical industry as a catalyst. The halides react with water to form boric acid.

Boron is found in nature on Earth entirely as various oxides of B (III), often associated with other elements. The more than one hundred borates all feature boron in oxidation state +3. These minerals resemble silicates in some respect, although boron is often found not only in a tetrahedral coordination with oxygen, but also in a trigonal planar configuration. Unlike silicates, the boron minerals never feature boron with coordination number greater than four.

A typical motif is exemplified by the tetraborate anions of the common mineral borax. The formal negative charge of the tetrahedral borate centers is balanced by metal cations in the minerals, such as the sodium ( $Na^+$ ) in borax.

### **Boron Nitride**

The boron nitrides are notable for the variety of structures that they adopt. They adopt structures analogous to various allotropes of carbon, including graphite, diamond, and nanotubes. In the diamond-like structure called cubic boron nitride (tradename Borazon), boron atoms exist in the tetrahedral structure of carbons atoms in diamond, but one in every four B-N bonds can be viewed as a coordinate covalent bond, wherein two electrons are donated by the nitrogen atom which acts as the Lewis base to a bond to the Lewis acidic boron (III) center.

Cubic boron nitride, among other applications, is used as an abrasive, as it has a hardness comparable with diamond (the two substances are able to produce scratches on each other). In the BN compound analogue of graphite, hexagonal boron nitride (h-BN), the positively-charged boron and negatively-charged nitrogen atoms in each plane lie adjacent to the oppositely charged atom in the next plane.

Consequently graphite and h-BN have very different properties, although both are lubricants, as these planes slip past each other easily. However, h-BN is a relatively poor electrical and thermal conductor in the planar directions.

### **Organoboron Chemistry**

A large number of organoboron compounds are known and many are useful in organic synthesis. Organoboron (III) compounds are usually tetrahedral or trigonal planar, for example, tetraphenylborate ( $B(C_6H_5)_4^-$ ) vs triphenylborane ( $B(C_6H_5)_3$ ). Many are produced from hydroboration, which employs diborane ( $B_2H_6$ ).

### **Compounds of B(I) and B(II)**

Although these are not found on Earth naturally, boron forms a variety of stable compounds with formal oxidation state less than three. As for many covalent compounds, formal oxidation states are often of little meaning in boron hydrides and metal borides. The halides also form derivatives of B(I) and B(II). BF<sub>3</sub>, isoelectronic with N<sub>2</sub>, is not isolable in condensed form, but B<sub>2</sub>F<sub>4</sub> and B<sub>4</sub>Cl<sub>4</sub> are well characterized.

Binary metal-boron compounds, the metal borides, feature boron in oxidation state less than III. Illustrative is magnesium diboride (MgB<sub>2</sub>). Each boron atom has a formal -1 charge and magnesium is assigned a formal charge of 2+. In this material, the boron centers are trigonal planar, with an extra double bond for each boron, with the boron atoms forming sheets akin to the carbon in graphite. However, unlike the case with hexagonal boron nitride which by comparison lacks electrons in the plane of the covalent atoms, the delocalized electrons in the plane of magnesium diboride allow it to conduct electricity similar to isoelectronic graphite. In addition, in 2001 this material was found to be a high-temperature superconductor. Certain other metal borides find specialized applications as hard materials for cutting tools.

From the structural perspective, the most distinctive chemical compounds of boron are the hydrides. Included in this series are the cluster compounds dodecaborate ( $B_{12}H_{12}^{2-}$ ), decaborane ( $B_{10}H_{14}$ ), and the carboranes such as  $C_2B_{10}H_{12}$ . Characteristically such compounds feature boron with coordination numbers greater than four.

### **Isotopes**

Boron has two naturally occurring and stable isotopes, <sup>11</sup>B (80.1%) and <sup>10</sup>B (19.9%). The mass difference results in a wide range of δ<sup>11</sup>B values, which are defined as a fractional difference between the <sup>11</sup>B and <sup>10</sup>B and traditionally expressed in parts per thousand, in natural waters ranging from -16 to +59. There are 13 known isotopes of boron, the shortest-lived isotope is <sup>7</sup>B which decays through proton emission and alpha decay. It has a half-life of 3.5×10<sup>-22</sup> s. Isotopic fractionation of boron is controlled by the exchange reactions of the boron species B(OH)<sub>3</sub> and [B(OH)<sub>4</sub>]<sup>-</sup>.

Boron isotopes are also fractionated during mineral crystallization, during H<sub>2</sub>O phase changes in hydrothermal systems, and during hydrothermal alteration of rock. The latter effect results in preferential removal of the <sup>10</sup>B(OH)<sub>4</sub> ion onto clays.

It results in solutions enriched in  $^{11}\text{B}(\text{OH})_3$  and therefore may be responsible for the large  $^{11}\text{B}$  enrichment in seawater relative to both oceanic crust and continental crust; this difference may act as an isotopic signature. The exotic  $^{17}\text{B}$  exhibits a nuclear halo, i.e. its radius is appreciably larger than that predicted by the liquid drop model.

The  $^{10}\text{B}$  isotope is good at capturing thermal neutrons. Natural boron is about 20%  $^{10}\text{B}$  and 80%  $^{11}\text{B}$ . The nuclear industry enriches natural boron to nearly pure  $^{10}\text{B}$ . The less-valuable by-product, depleted boron, is nearly pure  $^{11}\text{B}$ .

### **Commercial Isotope Enrichment**

Because of its high neutron cross-section, boron-10 is often used to control fission in nuclear reactors as a neutron-capturing substance. Several industrial-scale enrichment processes have been developed, however only the fractionated vacuum distillation of the dimethyl ether adduct of boron trifluoride (DME- $\text{BF}_3$ ) and column chromatography of borates are being used.

### **Enriched Boron (boron-10)**

Is used in neutron capture therapy of cancer. In the latter ("boron neutron capture therapy" or BNCT), a compound containing  $^{10}\text{B}$  is incorporated into a pharmaceutical which is selectively taken up by a malignant tumor and tissues near it. The patient is then treated with a beam of either thermal neutrons, or else neutrons of low energy, at a relatively low neutron radiation dose. The neutrons, however, trigger energetic and short-range secondary alpha particle and lithium-7 heavy ion radiation that are products of the boron + neutron nuclear reaction, and this ion radiation additionally bombards the tumor, especially from inside the tumor cells.

In nuclear reactors,  $^{10}\text{B}$  is used for reactivity control and in emergency shutdown systems. It can serve either function in the form of borosilicate control rods or as boric acid. In pressurized water reactors, boric acid is added to the reactor coolant when the plant is shut down for refueling. It is then slowly filtered out over many months as fissile material is used up and the fuel becomes less reactive.

In future manned interplanetary spacecraft,  $^{10}\text{B}$  has a theoretical role as structural material (as boron fibers or BN nanotube material) which would also serve a special role in the radiation shield. One of the difficulties in dealing with cosmic rays, which are mostly high energy protons, is that some secondary radiation from interaction of cosmic rays and spacecraft materials is high energy spallation neutrons. Such neutrons can be moderated by materials high in light elements such as polyethylene, but the moderated neutrons continue to be a radiation hazard unless actively absorbed in the shielding. Among light elements that absorb thermal neutrons,  $^6\text{Li}$  and  $^{10}\text{B}$  appear as potential spacecraft structural materials which serve both for mechanical reinforcement and radiation protection.

### **Depleted Boron (boron-11)**

Cosmic radiation will produce secondary neutrons if it hits spacecraft structures. Those neutrons will be captured in  $^{10}\text{B}$ , if it is present in the spacecraft's semiconductors, producing a gamma ray, an alpha particle, and a lithium ion. These resultant decay products may then irradiate nearby semiconductor 'chip' structures, causing data loss (bit flipping, or single event upset).

In radiation hardened semiconductor designs, one countermeasure is to use **depleted boron** which is greatly enriched in  $^{11}\text{B}$  and contains almost no  $^{10}\text{B}$ .  $^{11}\text{B}$  is largely immune to radiation damage. Depleted boron is a by-product of the nuclear industry.

$^{11}\text{B}$  is also a candidate as a fuel for aneutronic fusion. When struck by a proton with energy of about 500 keV, it produces three alpha particles and 8.7 MeV of energy. Most other fusion reactions involving hydrogen and helium produce penetrating neutron radiation, which weakens reactor structures and induces long term radioactivity thereby endangering operating personnel. Whereas, the alpha particles from  $^{11}\text{B}$  fusion can be turned directly into electric power, and all radiation stops as soon as the reactor is turned off.

### **Applications**

Nearly all boron ore extracted from the Earth is destined for refinement into boric acid and sodium tetraborate pentahydrate. In the United States, 70% of the boron is used for the production of glass and ceramics.

### **Glass and Ceramics**

Borosilicate glass, which is typically 12–15%  $\text{B}_2\text{O}_3$ , 80%  $\text{SiO}_2$ , and 2%  $\text{Al}_2\text{O}_3$ , has a low coefficient of thermal expansion giving it a good resistance to thermal shock. Duran and Pyrex are two major brand names for this glass, used both in laboratory glassware and in consumer cookware and bakeware, chiefly for this resistance.

Boron filaments are high-strength, lightweight materials that are used chiefly for advanced aerospace structures as a component of composite materials, as well as limited production consumer and sporting goods such as golf clubs and fishing rods. The fibers can be produced by chemical vapor deposition of boron on a tungsten filament.

Boron fibers and sub-millimeter sized crystalline boron springs are produced by laser-assisted chemical vapor deposition. Translation of the focused laser beam allows producing even complex helical structures. Such structures show good mechanical properties (elastic modulus 450 GPa, fracture strain 3.7%, fracture stress 17 GPa) and can be applied as reinforcement of ceramics or in micromechanical systems.

### **Detergent Formulations and Bleaching Agents**

Borax is used in various household laundry and cleaning products, including the well-known "20 Mule Team Borax" laundry booster and "Boraxo" powdered hand soap. It is also present in some tooth bleaching formulas. Sodium perborate serves as a source of active oxygen in many detergents, laundry detergents, cleaning products, and laundry bleaches. However, despite its name, "Borateem" laundry bleach no longer contains any boron compounds, using sodium percarbonate instead as a bleaching agent.

### **Insecticides**

Boric acid is used as an insecticide, notably against ants, fleas, and cockroaches.

### **Semiconductors**

Boron is a useful dopant for such semiconductors as silicon, germanium, and silicon carbide. Having one fewer valence electron than the host atom, it donates a hole resulting in p-type conductivity. Traditional method of introducing boron into semiconductors is via its atomic diffusion at high temperatures. This process uses either solid ( $\text{B}_2\text{O}_3$ ), liquid ( $\text{BBr}_3$ ), or gaseous boron sources ( $\text{B}_2\text{H}_6$  or  $\text{BF}_3$ ).

However, after 1970s, it was mostly replaced by ion implantation, which relies mostly on  $\text{BF}_3$  as a boron source. Boron trichloride gas is also an important chemical in semiconductor industry, however not for doping but rather for plasma etching of metals and their oxides. Triethylborane is also injected into vapor deposition reactors as a boron source. Examples are the plasma deposition of boron-containing hard carbon films, silicon nitride-boron nitride films, and for doping of diamond film with boron.

### **Magnets**

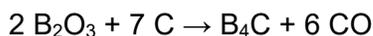
Boron is a component of neodymium magnets ( $\text{Nd}_2\text{Fe}_{14}\text{B}$ ), which are the strongest type of permanent magnet. They are found in a variety of domestic and professional electromechanical and electronic devices, such as magnetic resonance imaging (MRI), various motors and actuators, computer HDDs, CD and DVD players, mobile phones, timer switches, speakers, and so on.

### **High-Hardness and Abrasive Compounds**

Several boron compounds are known for their extreme hardness and toughness. Boron carbide and cubic boron nitride powders are widely used as abrasives. Metal borides are used for coating tools through chemical vapor deposition or physical vapor deposition. Implantation of boron ions into metals and alloys, through ion implantation or ion beam deposition, results in a spectacular increase in surface resistance and microhardness. Laser alloying has also been successfully used for the same purpose. These borides are an alternative to diamond coated tools, and their (treated) surfaces have similar properties to those of the bulk boride.

### **Boron Carbide**

Boron carbide is a ceramic material which is obtained by decomposing  $\text{B}_2\text{O}_3$  with carbon in the electric furnace:



Boron carbide's structure is only approximately  $\text{B}_4\text{C}$ , and it shows a clear depletion of carbon from this suggested stoichiometric ratio. This is due to its very complex structure. The substance can be seen with empirical formula  $\text{B}_{12}\text{C}_3$  (i.e., with  $\text{B}_{12}$  dodecahedra being a motif), but with less carbon as the suggested  $\text{C}_3$  units are replaced with B-C chains, and there are smaller ( $\text{B}_6$ ) octahedra present as well. (See the article for structural analysis).

The repeating polymer plus semi-crystalline structure of boron carbide gives it great structural strength per weight. It is used in tank armor, bulletproof vests, and numerous other structural applications.

Boron carbide's ability to absorb neutrons without forming long-lived radionuclides (especially when doped with extra boron-10) makes the material attractive as an absorbent for neutron radiation arising in nuclear power plants. Nuclear applications of boron carbide include shielding, control rods and shut-down pellets. Within control rods, boron carbide is often powdered, to increase its surface area.

### **Other Super Hard Boron Compounds**

- Heterodiamond (also called BCN);
- Boron nitride. This material is isoelectronic to carbon. Similar to carbon, it has both hexagonal (soft graphite-like h-BN) and cubic (hard, diamond-like c-BN) forms. h-BN is used as a high temperature component and lubricant. c-BN, also known

- under commercial name borazon, is a superior abrasive. Its hardness is only slightly smaller, but chemical stability is superior to that of diamond.
- Rhenium diboride can be produced at ambient pressures, but is rather expensive because of rhenium. The hardness of  $\text{ReB}_2$  exhibits considerable anisotropy because of its hexagonal layered structure. Its value is comparable to that of tungsten carbide, silicon carbide, titanium diboride or zirconium diboride.
  - $\text{AlMgB}_{14}$  +  $\text{TiB}_2$  composites possess high hardness and wear resistance and are used in either bulk form or as coatings for components exposed to high temperatures and wear loads.

### Shielding in Nuclear Reactors

Boron shielding is used as a control for nuclear reactors, taking advantage of its high cross-section for neutron capture.

### Other Nonmedical Uses

- Because of its distinctive green flame, amorphous boron is used in pyrotechnic flares.
- Starch and casein-based adhesives contain sodium tetraborate decahydrate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ )
- Some anti-corrosion systems contain borax.
- Sodium borates are used as a flux for soldering silver and gold and with ammonium chloride for welding ferrous metals. They are also fire retarding additives to plastics and rubber articles.
- Boric acid (also known as orthoboric acid)  $\text{H}_3\text{BO}_3$  is used in the production of textile fiberglass and flat panel displays and in many PVAc and PVOH based adhesives.
- Triethylborane is a substance which ignites the JP-7 fuel of the Pratt & Whitney J58 turbojet/ramjet engines powering the Lockheed SR-71 Blackbird. It was also used to ignite the F-1 Engines on the Saturn V Rocket utilized by NASA's Apollo and Skylab programs from 1967 until 1973. Triethylborane is suitable for this because of its pyrophoric properties, especially the fact that it burns with a very high temperature. Triethylborane is an industrial initiator in radical reactions, where it is effective even at low temperatures.

### Pharmaceutical and Biological Applications

**Boric acid** has antiseptic, antifungal, and antiviral properties and for these reasons is applied as a water clarifier in swimming pool water treatment. Mild solutions of boric acid have been used as eye antiseptics.

**Bortezomib (Velcade)**. Boron appears as an active element in its first-approved organic pharmaceutical in the novel pharmaceutical bortezomib, a new class of drug called the proteasome inhibitors, which are active in myeloma and one form of lymphoma (it is currently in experimental trials against other types of lymphoma). The boron atom in bortezomib binds the catalytic site of the 26S proteasome with high affinity and specificity.

- A number of potential boronated pharmaceuticals using boron-10, have been prepared for use in boron neutron capture therapy (BNCT).
- Some boron compounds show promise in treating arthritis, though none have as yet been generally approved for the purpose.

### **Research Areas**

Magnesium diboride is an important superconducting material with the transition temperature of 39 K.  $\text{MgB}_2$  wires are produced with the powder-in-tube process and applied in superconducting magnets. Amorphous boron is used as a melting point depressant in nickel-chromium braze alloys.

Hexagonal boron nitride forms atomically thin layers, which have been used to enhance the electron mobility in graphene devices. It also forms nanotubular structures (BNNTs), which have with high strength, high chemical stability, and high thermal conductivity, among its list of desirable properties.

### **Natural Biological Role**

There is a boron-containing natural antibiotic, boromycin, isolated from streptomyces. Boron is an essential plant nutrient, required primarily for maintaining the integrity of cell walls. Conversely, high soil concentrations of  $> 1.0$  ppm can cause marginal and tip necrosis in leaves as well as poor overall growth performance. Levels as low as 0.8 ppm can cause these same symptoms to appear in plants particularly sensitive to boron in the soil.

Nearly all plants, even those somewhat tolerant of boron in the soil, will show at least some symptoms of boron toxicity when boron content in the soil is greater than 1.8 ppm. When this content exceeds 2.0 ppm, few plants will perform well and some may not survive. When boron levels in plant tissue exceed 200 ppm symptoms of boron toxicity are likely to appear. As an ultratrace element, boron is necessary for the optimal health of rats, although it is necessary in such small amounts that ultra purified foods and dust filtration of air is necessary to induce boron deficiency, which manifest as poor coat or hair quality. Presumably, boron is necessary to other mammals.

No deficiency syndrome in humans has been described. Small amounts of boron occur widely in the diet, and the amounts needed in the diet would, by analogy with rodent studies, be very small. The exact physiological role of boron in the animal kingdom is poorly understood.

Boron occurs in all foods produced from plants. Since 1989 its nutritional value has been argued. It is thought that boron plays several biochemical roles in animals, including humans. The U.S. Department of agriculture conducted an experiment in which postmenopausal women took 3 mg of boron a day. The results showed that supplemental boron reduced excretion of calcium by 44%, and activated estrogen and vitamin D, suggesting a possible role in the suppression of osteoporosis. However, whether these effects were conventionally nutritional, or medicinal, could not be determined. The U.S. National Institutes of Health states that "Total daily boron intake in normal human diets ranges from 2.1–4.3 mg boron/day."

Congenital endothelial dystrophy type 2, a rare form of corneal dystrophy, is linked to mutations in SLC4A11 gene that encodes a transporter reportedly regulating the intracellular concentration of boron.

### **Analytical Quantification**

For determination of boron content in food or materials the colorimetric curcumin method is used. Boron has to be transferred to boric acid or borates and on reaction with curcumin in acidic solution, a red colored boron-chelate complex, rosocyanine, is formed.

## Germanium- Metalloid

Germanium looks like a metal. It has a bright, shiny, silvery color. But it is brittle and breaks apart rather easily, which metals normally do not do. It has a melting point of 937.4°C (1,719°F) and a boiling point of 2,830°C (5,130°F). It conducts an electric current poorly. Substances of this kind are called semiconductors. Semiconductors conduct an electric current, but not nearly as well as metals like silver, copper, and aluminum.

The ability of semiconductors to conduct electricity depends greatly on the presence of small amounts of impurities. The addition of an impurity to a semiconductor is called doping. Doping a semiconductor has significant effects on its ability to conduct an electric current.

Germanium is a chemical element with symbol Ge and atomic number 32. It is a lustrous, hard, grayish-white metalloid in the carbon group, chemically similar to its group neighbor's tin and silicon.



Purified germanium is a semiconductor, with an appearance most similar to elemental silicon. Like silicon, germanium naturally reacts and forms complexes with oxygen in nature. Unlike silicon, it is too reactive to be found naturally on Earth in the free (native) state.

Because very few minerals contain it in high concentration, germanium was discovered comparatively late in the history of chemistry.

Germanium ranks near fiftieth in relative abundance of the elements in the Earth's crust. In 1869, Dmitri Mendeleev predicted its existence and some of its properties based on its position on his periodic table and called the element ekasilicon.

Nearly two decades later, in 1886, Clemens Winkler found the new element along with silver and sulfur, in a rare mineral called argyrodite. Although the new element somewhat resembled arsenic and antimony in appearance, its combining ratios in the new element's compounds agreed with Mendeleev's predictions for a predicted relative of silicon.

Winkler named the element after his country, Germany. Today, germanium is mined primarily from sphalerite (the primary ore of zinc), though germanium is also recovered commercially from silver, lead, and copper ores.

Germanium "metal" (isolated germanium) is used as semiconductor in transistors and various other electronic devices. Historically the first decade of semiconductor electronics were entirely based on germanium, although its production for such use today is a small fraction (2%) of that of ultra-high purity silicon, which has largely replaced it.

Germanium's major end uses in the present are fiber-optic systems and infrared optics. It is used in solar cell applications. Germanium compounds are used for polymerization catalysts. Germanium is finding a new use in nanowires. Germanium forms a large number of organometallic compounds, such as tetraethylgermane, which are useful in chemistry.

Germanium is not thought to be an essential element for any living organism. Some complexed organic germanium compounds are being investigated as possible pharmaceuticals but none has had success. Similar to silicon and aluminum, natural germanium compounds, which tend to be insoluble in water, have little oral toxicity. However, synthetic soluble germanium salts are nephrotoxic, and synthetic chemically reactive germanium compounds with halogens and hydrogen are irritants and toxins.

In his report on *The Periodic Law of the Chemical Elements*, in 1869, the Russian chemist Dmitri Ivanovich Mendeleev predicted the existence of several unknown chemical elements, including one that would fill a gap in the carbon family in his Periodic Table of the Elements, located between silicon and tin. Because of its position in his Periodic Table, Mendeleev called it *ekasilicon (Es)*, and he estimated its atomic weight as about 72.0.

In mid-1885, at a mine near Freiberg, Saxony, a new mineral was discovered and named *argyrodite*, because of its high silver content. The chemist Clemens Winkler analyzed this new mineral, which proved to be a combination of silver, sulfur, and a new element. Winkler was able to isolate this new element and found it somewhat similar to antimony, in 1886.

Before Winkler published his results on the new element, he decided that he would name his element *neptunium*, since the recent discovery of planet Neptune in 1846 had been preceded by mathematical predictions of its existence. However, the name "neptunium" had already been given to another chemical element (though not the element that today bears the name neptunium, which was discovered in 1940), so instead, Winkler named the new element *germanium* (from the Latin word, *Germania*, for Germany) in honor of his homeland. Argyrodite proved empirically to be  $\text{Ag}_8\text{GeS}_6$ .

Because this new element showed some similarities with the elements arsenic and antimony, its proper place in the periodic table was under consideration, but its similarities with Dmitri Mendeleev's predicted element "ekasilicon" confirmed that it belonged in this place on the periodic table. With further material from 500 kg of ore from the mines in Saxony, Winkler confirmed the chemical properties of the new element in 1887. He also determined an atomic weight of 72.32 by analyzing pure germanium tetrachloride ( $\text{GeCl}_4$ ), while Lecoq de Boisbaudran deduced 72.3 by a comparison of the lines in the spark spectrum of the element.

Winkler was able to prepare several new compounds of germanium, including its fluorides, chlorides, sulfides, germanium dioxide, and tetraethylgermane ( $\text{Ge}(\text{C}_2\text{H}_5)_4$ ), the first organogermane.

The physical data from these compounds — which corresponded well with Mendeleev's predictions — made the discovery an important confirmation of Mendeleev's idea of element periodicity.

Until the late 1930s, germanium was thought to be a poorly conducting metal. Germanium did not become economically significant until after 1945, when its properties as a semiconductor were recognized as being very useful in electronics.

However, during World War II, small amounts of germanium had begun to be used in some special electronic devices, mostly diodes. Its first major use was the point-contact Schottky diodes for radar pulse detection during the War. The first silicon-germanium alloys were obtained in 1955. Before 1945, only a few hundred kilograms of germanium were produced in smelters each year, but by the end of the 1950s, the annual worldwide production had reached 40 metric tons.

The development of the germanium transistor in 1948 opened the door to countless applications of solid state electronics. From 1950 through the early 1970s, this area provided an increasing market for germanium, but then high-purity silicon began replacing germanium in transistors, diodes, and rectifiers. For example, the company that became Fairchild Semiconductor was founded in 1957 with the express purpose of producing silicon transistors. Silicon has superior electrical properties, but it requires far higher purity, and this purity could not be commercially achieved in the early years of semiconductor electronics.

Meanwhile, the demand for germanium for use in fiber optics communication networks, infrared night vision systems, and polymerization catalysts increased dramatically. These end uses represented 85% of worldwide germanium consumption in 2000. The U.S. government even designated germanium as a strategic and critical material, calling for a 146 ton (132 t) supply in the national defense stockpile in 1987. Germanium differs from silicon in that the supply for germanium is limited by the availability of exploitable sources, while the supply of silicon is only limited by production capacity since silicon comes from ordinary sand or quartz.

### **Characteristics**

Under standard conditions germanium is a brittle, silvery-white, semi-metallic element. This form constitutes an allotrope technically known as  *$\alpha$ -germanium*, which has a metallic luster and a diamond cubic crystal structure, the same as diamond. At pressures above 120 kbar, a different allotrope known as  *$\beta$ -germanium* forms, which has the same structure as  $\beta$ -tin. Along with silicon, gallium, bismuth, antimony, and water, it is one of the few substances that expands as it solidifies (i.e. freezes) from its molten state.

Germanium is a semiconductor. Zone refining techniques have led to the production of crystalline germanium for semiconductors that has an impurity of only one part in  $10^{10}$ , making it one of the purest materials ever obtained. The first metallic material discovered (in 2005) to become a superconductor in the presence of an extremely strong electromagnetic field was an alloy of germanium with uranium and rhodium.

Pure germanium is known to spontaneously extrude very long screw dislocations. They are one of the primary reasons for the failure of older diodes and transistors made from germanium; depending on what they eventually touch, they may lead to an electrical short.

## Chemistry

Germanium is not thought to be essential to the health of plants or animals. Some of its compounds present a hazard to human health, however. For example, germanium chloride and germanium fluoride ( $\text{GeF}_4$ ) are a liquid and gas, respectively that can be very irritating to the eyes, skin, lungs, and throat.

250 °C. Germanium is insoluble in dilute acids and alkalis but dissolves slowly in concentrated sulfuric acid and reacts violently with molten alkalis to produce germanates ( $[\text{GeO}]^{2-3}$ ). Germanium occurs mostly in the oxidation state +4 although many compounds are known with the oxidation state of +2. Other oxidation states are rare, such as +3 found in compounds such as  $\text{Ge}_2\text{Cl}_6$ , and +3 and +1 observed on the surface of oxides, or negative oxidation states in germanes, such as -4 in  $\text{GeH}_4$ .

Germanium cluster anions (Zintl ions) such as  $\text{Ge}_4^{2-}$ ,  $\text{Ge}_9^{4-}$ ,  $\text{Ge}_9^{2-}$ ,  $[(\text{Ge}_9)_2]^{6-}$  have been prepared by the extraction from alloys containing alkali metals and germanium in liquid ammonia in the presence of ethylenediamine or a cryptand. The oxidation states of the element in these ions are not integers—similar to the ozonides  $\text{O}_3^-$ .

Two oxides of germanium are known: germanium dioxide ( $\text{GeO}_2$ , germania) and germanium monoxide, ( $\text{GeO}$ ). The dioxide,  $\text{GeO}_2$  can be obtained by roasting germanium disulfide ( $\text{GeS}_2$ ), and is a white powder that is only slightly soluble in water but reacts with alkalis to form germanates. The monoxide, germanous oxide, can be obtained by the high temperature reaction of  $\text{GeO}_2$  with Ge metal. The dioxide (and the related oxides and germanates) exhibits the unusual property of having a high refractive index for visible light, but transparency to infrared light. Bismuth germanate,  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ , (BGO) is used as a scintillator.

Binary compounds with other chalcogens are also known, such as the disulfide ( $\text{GeS}_2$ ), diselenide ( $\text{GeSe}_2$ ), and the monosulfide ( $\text{GeS}$ ), selenide ( $\text{GeSe}$ ), and telluride ( $\text{GeTe}$ ).  $\text{GeS}_2$  forms as a white precipitate when hydrogen sulfide is passed through strongly acid solutions containing Ge(IV) The disulfide is appreciably soluble in water and in solutions of caustic alkalis or alkaline sulfides. Nevertheless, it is not soluble in acidic water, which allowed Winkler to discover the element.

By heating the disulfide in a current of hydrogen, the monosulfide ( $\text{GeS}$ ) is formed, which sublimes in thin plates of a dark color and metallic luster, and is soluble in solutions of the caustic alkalis. Upon melting with alkaline carbonates and sulfur, germanium compounds form salts known as thiogermanates.

Four tetrahalides are known. Under normal conditions  $\text{GeI}_4$  is a solid,  $\text{GeF}_4$  a gas and the others volatile liquids. For example, germanium tetrachloride,  $\text{GeCl}_4$ , is obtained as a colorless fuming liquid boiling at 83.1 °C by heating the metal with chlorine. All the tetrahalides are readily hydrolyzed to hydrated germanium dioxide.  $\text{GeCl}_4$  is used in the production of organogermanium compounds. All four dihalides are known and in contrast to the tetrahalides are polymeric solids. Additionally  $\text{Ge}_2\text{Cl}_6$  and some higher compounds of formula  $\text{Ge}_n\text{Cl}_{2n+2}$  are known. The unusual compound  $\text{Ge}_6\text{Cl}_{16}$  has been prepared that contains the  $\text{Ge}_5\text{Cl}_{12}$  unit with a neopentane structure.

Germane ( $\text{GeH}_4$ ) is a compound similar in structure to methane. Polygermanes—compounds that are similar to alkanes—with formula  $\text{Ge}_n\text{H}_{2n+2}$  containing up to five germanium atoms are known.

The germanes are less volatile and less reactive than their corresponding silicon analogues.  $\text{GeH}_4$  reacts with alkali metals in liquid ammonia to form white crystalline  $\text{MGeH}_3$  which contain the  $\text{GeH}_3^-$  anion. The germanium hydrohalides with one, two and three halogen atoms are colorless reactive liquids.

The first organogermanium compound was synthesized by Winkler in 1887; the reaction of germanium tetrachloride with diethylzinc yielded tetraethylgermane ( $\text{Ge}(\text{C}_2\text{H}_5)_4$ ). Organogermanes of the type  $\text{R}_4\text{Ge}$  (where R is an alkyl) such as tetramethylgermane ( $\text{Ge}(\text{CH}_3)_4$ ) and tetraethylgermane are accessed through the cheapest available germanium precursor germanium tetrachloride and alkyl nucleophiles.

Organic germanium hydrides such as isobutylgermane ( $(\text{CH}_3)_2\text{CHCH}_2\text{GeH}_3$ ) were found to be less hazardous and may be used as a liquid substitute for toxic germane gas in semiconductor applications. Many germanium reactive intermediates are known: germyl free radicals, germynes (similar to carbenes), and germynes (similar to carbynes). The organogermanium compound 2-carboxyethylgermasquioxane was first reported in the 1970s, and for a while was used as a dietary supplement and thought to possibly have anti-tumor qualities.

### Applications

The major end uses for germanium in 2007, worldwide, were estimated to be: 35% for fiber-optic systems, 30% infrared optics, 15% for polymerization catalysts, and 15% for electronics and solar electric applications. The remaining 5% went into other uses such as phosphors, metallurgy, and chemotherapy.

### Optics

The most notable physical characteristics of germania ( $\text{GeO}_2$ ) are its high index of refraction and its low optical dispersion. These make it especially useful for wide-angle camera lenses, microscopy, and for the core part of optical fibers. It also replaced titania as the silica dopant for silica fiber, eliminating the need for subsequent heat treatment, which made the fibers brittle.

At the end of 2002 the fiber optics industry accounted for 60% of the annual germanium use in the United States, but this use accounts for less than 10% of worldwide consumption.  $\text{GeSbTe}$  is a phase change material used for its optic properties, such as in rewritable DVDs.

Because germanium is transparent in the infrared it is a very important infrared optical material, that can be readily cut and polished into lenses and windows. It is especially used as the front optic in thermal imaging cameras working in the 8 to 14 micron wavelength range for passive thermal imaging and for hot-spot detection in military, night vision system in cars, and firefighting applications. It is therefore used in infrared spectrometers and other optical equipment which require extremely sensitive infrared detectors.

The material has a very high refractive index (4.0) and so needs to be anti-reflection coated. Particularly, a very hard special antireflection coating of diamond-like carbon (DLC), refractive index 2.0, is a good match and produces a diamond-hard surface that can withstand much environmental rough treatment.

## Electronics

Silicon-germanium alloys are rapidly becoming an important semiconductor material, for use in high-speed integrated circuits. Circuits utilizing the properties of Si-SiGe junctions can be much faster than those using silicon alone. Silicon-germanium is beginning to replace gallium arsenide (GaAs) in wireless communications devices. The SiGe chips, with high-speed properties, can be made with low-cost, well-established production techniques of the silicon chip industry.

The recent rise in energy cost has improved the economics of solar panels, a potential major new use of germanium. Germanium is the substrate of the wafers for high-efficiency multijunction photovoltaic cells for space applications.

Because germanium and gallium arsenide have very similar lattice constants, germanium substrates can be used to make gallium arsenide solar cells. The Mars Exploration Rovers and several satellites use triple junction gallium arsenide on germanium cells.

Germanium-on-insulator substrates are seen as a potential replacement for silicon on miniaturized chips. Other uses in electronics include phosphors in fluorescent lamps, and germanium-base solid-state light-emitting diodes (LEDs). Germanium transistors are still used in some effects pedals by musicians who wish to reproduce the distinctive tonal character of the "fuzz"-tone from the early rock and roll era.

## Other Uses

Germanium dioxide is also used in catalysts for polymerization in the production of polyethylene terephthalate (PET). The high brilliance of the produced polyester is especially used for PET bottles marketed in Japan. However, in the United States, no germanium is used for polymerization catalysts. Due to the similarity between silica ( $\text{SiO}_2$ ) and germanium dioxide ( $\text{GeO}_2$ ), the silica stationary phase in some gas chromatography columns can be replaced by  $\text{GeO}_2$ .

In recent years, germanium has seen increasing use in precious metal alloys. In sterling silver alloys, for instance, it has been found to reduce firescale, increase tarnish resistance, and increase the alloy's response to precipitation hardening. A tarnish-proof sterling silver alloy, trademarked Argentium, requires 1.2% germanium.

High purity germanium single crystal detectors can precisely identify radiation sources—for example in airport security. Germanium is useful for monochromators for beamlines used in single crystal neutron scattering and synchrotron X-ray diffraction. The reflectivity has advantages over silicon in neutron and high energy X-ray applications. Crystals of high purity germanium are used in detectors for gamma spectroscopy and the search for dark matter.

## Dietary Supplements, Pharmaceutical Development, and Health Hazard

Germanium is not thought to be essential to the health of plants or animals. Germanium in the environment has little or no health impact. This is primarily because it usually occurs only as a trace element in ores and carbonaceous materials, and is used in very small quantities that are not likely to be ingested, in its various industrial and electronic applications. For similar reasons, germanium in end-uses has little impact on the environment as a biohazard. Some reactive intermediate compounds of germanium are poisonous (see precautions, below).

## Polonium- Metalloid

Polonium is a chemical element with the symbol **Po** and atomic number 84, discovered in 1898 by Marie and Pierre Curie. A rare and highly radioactive element with no stable isotopes, polonium is chemically similar to bismuth and tellurium, and it occurs in uranium ores. Applications of polonium are few, and include heaters in space probes, antistatic devices, and sources of neutrons and alpha particles. Because of its position in the periodic table, polonium is sometimes referred to as a metalloid, however others note that on the basis of its properties and behavior it is "unambiguously a metal".

### Polonium is 'distinctly metallic' in some ways, or shows metallic character by way of:

- The metallic conductivity of both of its allotropic forms.
- The presence of the rose-colored  $\text{Po}^{2+}$  cation in aqueous solution.
- The many salts it forms.
- The predominating basicity of polonium dioxide.
- The highly reducing conditions required for the formation of the  $\text{Po}^{2-}$  anion in aqueous solution.



### However, polonium shows nonmetallic character in that:

- Its halides have properties generally characteristic of nonmetal halides (being volatile, easily hydrolyzed, and soluble in organic solvents).
- Many metal polonides, obtained by heating the elements together at 500–1,000 °C, and containing the  $\text{Po}^{2-}$  anion, are also known.

### Toxicity Overview

Polonium is highly dangerous and has no biological role. By mass, polonium-210 is around 250,000 times more toxic than hydrogen cyanide (the actual  $\text{LD}_{50}$  for  $^{210}\text{Po}$  is less than 1 microgram for an average adult (see below) compared with about 250 milligrams for hydrogen cyanide).

The main hazard is its intense radioactivity (as an alpha emitter), which makes it very difficult to handle safely. Even in microgram amounts, handling  $^{210}\text{Po}$  is extremely dangerous, requiring specialized equipment (a negative pressure alpha glove box equipped with high performance filters), adequate monitoring, and strict handling procedures to avoid any contamination.

Alpha particles emitted by polonium will damage organic tissue easily if polonium is ingested, inhaled, or absorbed, although they do not penetrate the epidermis and hence are not hazardous as long as the alpha particles remain outside of the body.

Meanwhile, wearing chemically resistant and "intact" gloves is a mandatory precaution to avoid transcutaneous diffusion of polonium directly through the skin. Polonium delivered in concentrated nitric acid can easily diffuse through inadequate gloves (e.g., latex gloves) or the acid may damage the gloves.

### **Acute Effects**

The median lethal dose (LD<sub>50</sub>) for acute radiation exposure is generally about 4.5 Sv. The committed effective dose equivalent <sup>210</sup>Po is 0.51 μSv/Bq if ingested, and 2.5 μSv/Bq if inhaled. Since <sup>210</sup>Po has an activity of 166 TBq per gram (4,500 Ci/g) (1 gram produces 166×10<sup>12</sup> decays per second), a fatal 4.5 Sv (J/kg) dose can be caused by ingesting 8.8 MBq (238 microcuries, μCi), about 50 nanograms (ng), or inhaling 1.8 MBq (48 μCi), about 10 ng. One gram of <sup>210</sup>Po could thus in theory poison 20 million people of whom 10 million would die.

The actual toxicity of <sup>210</sup>Po is lower than these estimates, because radiation exposure that is spread out over several weeks (the biological half-life of polonium in humans is 30 to 50 days) is somewhat less damaging than an instantaneous dose. It has been estimated that a median lethal dose of <sup>210</sup>Po is 0.015 GBq (0.4 mCi), or 0.089 micrograms, still an extremely small amount.

### **Long Term (Chronic) Effects**

In addition to the acute effects, radiation exposure (both internal and external) carries a long-term risk of death from cancer of 5–10% per Sv. The general population is exposed to small amounts of polonium as a radon daughter in indoor air; the isotopes <sup>214</sup>Po and <sup>218</sup>Po are thought to cause the majority of the estimated 15,000–22,000 lung cancer deaths in the US every year that have been attributed to indoor radon. Tobacco smoking causes additional exposure to polonium.

### **Regulatory Exposure Limits and Handling**

The maximum allowable body burden for ingested <sup>210</sup>Po is only 1.1 kBq (30 nCi), which is equivalent to a particle massing only 6.8 picograms. The maximum permissible workplace concentration of airborne <sup>210</sup>Po is about 10 Bq/m<sup>3</sup> (3 × 10<sup>-10</sup> μCi/cm<sup>3</sup>). The target organs for polonium in humans are the spleen and liver. As the spleen (150 g) and the liver (1.3 to 3 kg) are much smaller than the rest of the body, if the polonium is concentrated in these vital organs, it is a greater threat to life than the dose which would be suffered (on average) by the whole body if it were spread evenly throughout the body, in the same way as caesium or tritium (as T<sub>2</sub>O).

<sup>210</sup>Po is widely used in industry, and readily available with little regulation or restriction. In the US, a tracking system run by the Nuclear Regulatory Commission will be implemented in 2007 to register purchases of more than 16 curies (590 GBq) of polonium-210 (enough to make up 5,000 lethal doses). The IAEA "is said to be considering tighter regulations... There is talk that it might tighten the polonium reporting requirement by a factor of 10, to 1.6 curies (59 GBq)."

Polonium and its compounds must be handled in a glove box, which is further enclosed in another box, maintained at a slightly lower pressure than the glove box to prevent the radioactive materials from leaking out. Gloves made of natural rubber do not provide sufficient protection against the radiation from polonium; surgical gloves are necessary. Neoprene gloves shield radiation from polonium better than natural rubber.

### **Well-known Poisoning Cases**

Notably, the murder of Alexander Litvinenko, a Russian dissident, in 2006 was announced as due to  $^{210}\text{Po}$  poisoning (see Alexander Litvinenko poisoning). According to Prof. Nick Priest of Middlesex University, an environmental toxicologist and radiation expert, speaking on Sky News on December 2, Litvinenko was probably the first person ever to die of the acute  $\alpha$ -radiation effects of  $^{210}\text{Po}$ . However, according to William Dunkerley, a senior fellow at the American University in Moscow, the London coroner has yet to rule that polonium was actually the cause of Litvinenko's death, or that he was even a victim of homicide. It has also been suggested that Irène Joliot-Curie was the first person to die from the radiation effects of polonium. She was accidentally exposed to polonium in 1946 when a sealed capsule of the element exploded on her laboratory bench. In 1956 she died from leukemia.

### **Treatment**

It has been suggested that chelation agents such as British Anti-Lewisite (dimercaprol) can be used to decontaminate humans. In one experiment, rats were given a fatal dose of 1.45 MBq/kg (8.7 ng/kg) of  $^{210}\text{Po}$ ; all untreated rats were dead after 44 days, but 90% of the rats treated with the chelation agent HOEtTTC remained alive after 5 months.

### **Commercial Products Containing Polonium**

Some anti-static brushes contain up to 500 microcuries (20 MBq) of  $^{210}\text{Po}$  as a source of charged particles for neutralizing static electricity. In USA, the devices with no more than 500  $\mu\text{Ci}$  of (sealed)  $^{210}\text{Po}$  per unit can be bought in any amount under a "general license", which means that a buyer need not be registered by any authorities.

Tiny amounts of such radioisotopes are sometimes used in the laboratory and for teaching purposes—typically of the order of 4–40 kBq (0.1–1.0  $\mu\text{Ci}$ ), in the form of sealed sources, with the polonium deposited on a substrate or in a resin or polymer matrix—are often exempt from licensing by the NRC and similar authorities as they are not considered hazardous. Small amounts of  $^{210}\text{Po}$  are manufactured for sale to the public in the United States as 'needle sources' for laboratory experimentation, and are retailed by scientific supply companies.

The actual polonium is a layer of plating which in turn is plated with a material such as gold. This allows the alpha radiation (used in experiments such as cloud chambers) while preventing the polonium from being released and presenting a toxic hazard. According to United Nuclear, they typically sell between four and eight sources per year.

### **Occurrence in Humans and the Biosphere**

Polonium-210 is widespread in the biosphere, including in human tissues, because of its position in the uranium-238 decay chain.

Natural uranium-238 in the Earth's crust decays to through a series of solid radioactive intermediates including radium-226 to the radioactive gas radon-222, some of which, during its 3.6-day half-life, diffuses into the atmosphere.

There it decays through several more steps to Polonium-210, much of which, during its 138-day half-life, is washed back down to the Earth's surface, thus entering the biosphere, before finally decaying to stable lead-206.

As early as the 1920s Lacassagne, using polonium provided by his colleague Marie Curie, showed that the element has a very specific pattern of uptake in rabbit tissues, with high concentrations particularly in liver, kidney and testes. More recent evidence suggests that this behavior results from polonium substituting for sulfur in S-containing amino-acids or related molecules and that similar patterns of distribution occur in human tissues. Polonium is indeed an element naturally present in all humans, contributing appreciably to natural background dose, with wide geographical and cultural variations, and particularly high levels in arctic residents, for example.

## Silicon- Metalloid

Silicon is a tetravalent metalloid, is a chemical element with the symbol **Si** and atomic number 14. It is less reactive than its chemical analog carbon, the nonmetal directly above it in the periodic table, but more reactive than germanium, the metalloid directly below it in the table. Controversy about silicon's character dates to its discovery: silicon was first prepared and characterized in pure form in 1824, and given the name silicium (from Latin: *silicis*, flints), with an **-ium** word-ending to suggest a metal, a name which the element retains in several non-English languages. However, its final English name, suggested in 1831, reflects the more physically similar elements carbon and boron.

Silicon is the eighth most common element in the universe by mass, but very rarely occurs as the pure free element in nature. It is most widely distributed in dusts, sands, planetoids, and planets as various forms of silicon dioxide (silica) or silicates.

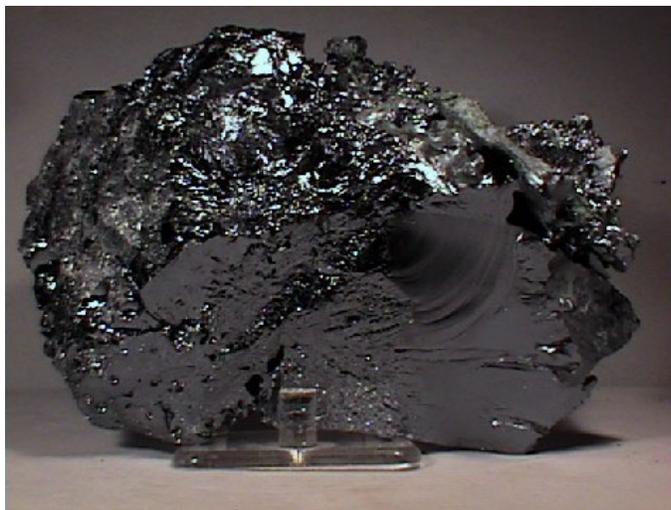
Over 90% of the Earth's crust is composed of silicate minerals, making silicon the second most abundant element in the Earth's crust (about 28% by mass) after oxygen.

Most silicon is used commercially without being separated, and indeed often with little processing of compounds from nature. These include direct industrial building-use of clays, silica sand and stone. Silica is used in ceramic brick. Silicate goes into Portland cement for mortar and stucco, and when combined with silica sand and gravel, to make concrete. Silicates are also in whiteware ceramics such as porcelain, and in traditional quartz-based soda-lime glass. More modern silicon compounds such as silicon carbide form abrasives and high-strength ceramics. Silicon is the basis of the ubiquitous synthetic silicon-based polymers called silicones.

Elemental silicon also has a large impact on the modern world economy. Although most free silicon is used in the steel refining, aluminum-casting, and fine chemical industries (often to make fumed silica), the relatively small portion of very highly purified silicon that is used in semiconductor electronics (< 10%) is perhaps even more critical. Because of wide use of silicon in integrated circuits, the basis of most computers, a great deal of modern technology depends on it.

Silicon is an essential element in biology, although only tiny traces of it appear to be required by animals, however various sea sponges as well as microorganisms like diatoms need silicon in order to have structure. It is much more important to the metabolism of plants, particularly many grasses, and silicic acid (a type of silica) forms the basis of the striking array of protective shells of the microscopic diatoms.

Silicon is a solid at room temperature, with relatively high melting and boiling points of approximately 1,400 and 2,800 degrees Celsius respectively. Interestingly, silicon has a greater density in a liquid state than a solid state.



Therefore, it does not contract when it freezes like most substances, but expands, similar to how ice is less dense than water and has less mass per unit of volume than liquid water. With a relatively high thermal conductivity of  $149 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ , silicon conducts heat well and as a result is not often used to insulate hot objects.

In its crystalline form, pure silicon has a gray color and a metallic luster. Like germanium, silicon is rather strong, very brittle, and prone to chipping. Silicon, like carbon and germanium, crystallizes in a diamond cubic crystal structure, with a lattice spacing of approximately  $0.5430710 \text{ nm}$  ( $5.430710 \text{ \AA}$ ).

The outer electron orbital of silicon, like that of carbon, has four valence electrons. The 1s, 2s, 2p and 3s subshells are completely filled while the 3p subshell contains two electrons out of a possible six.

Silicon is a semiconductor. It has a negative temperature coefficient of resistance, since the number of free charge carriers increases with temperature. The electrical resistance of single crystal silicon significantly changes under the application of mechanical stress due to the piezoresistive effect.

### Isotopes of Silicon

Naturally occurring silicon is composed of three stable isotopes, silicon-28, silicon-29, and silicon-30, with silicon-28 being the most abundant (92% natural abundance). Out of these, only silicon-29 is of use in NMR and EPR spectroscopy. Twenty radioisotopes have been characterized, with the most stable being silicon-32 with a half-life of 170 years, and silicon-31 with a half-life of 157.3 minutes. All of the remaining radioactive isotopes have half-lives that are less than seven seconds, and the majority of these have half-lives that are less than one tenth of a second. Silicon does not have any known nuclear isomers.

The isotopes of silicon range in mass number from 22 to 44. The most common decay mode of six isotopes with mass numbers lower than the most abundant stable isotope, silicon-28, is Beta Positive  $\beta^+$ , primarily forming aluminum isotopes (13 protons) as decay products. The most common decay mode(s) for 16 isotopes with mass numbers higher than silicon-28 is beta negative  $\beta^-$ , primarily forming phosphorus isotopes (15 protons) as decay products.

### Occurrence

Measured by mass, silicon makes up 27.7% of the Earth's crust and is the second most abundant element in the crust, with only oxygen having a greater abundance. Silicon is usually found in the form of complex silicate minerals, and less often as silicon dioxide (**silica**, a major component of common sand). Pure silicon crystals are very rarely found in nature.

The silicate minerals—various minerals containing silicon, oxygen and reactive metals—account for 90% of the mass of the Earth's crust. This is due to the fact that at the high temperatures characteristic of the formation of the inner solar system, silicon and oxygen have a great affinity for each other, forming networks of silicon and oxygen in chemical compounds of very low volatility. Since oxygen and silicon were the most common non-gaseous and non-metallic elements in the debris from supernova dust which formed the protoplanetary disk in the formation and evolution of the Solar System, they formed many complex silicates which accreted into larger rocky planetesimals that formed the terrestrial planets.

Here, the reduced silicate mineral matrix entrapped the metals reactive enough to be oxidized (aluminum, calcium, sodium, potassium and magnesium). After loss of volatile gases, as well as carbon and sulfur via reaction with hydrogen, this silicate mixture of elements formed most of the Earth's crust. These silicates were of relatively low density with respect to iron, nickel, and other metals non-reactive to oxygen and thus a residuum of uncombined iron and nickel sank to the planet's core, leaving a thick mantle consisting mostly of magnesium and iron silicates above.

Examples of silicate minerals in the crust include those in the pyroxene, amphibole, mica, and feldspar groups. These minerals occur in clay and various types of rock such as granite and sandstone.

Silica occurs in minerals consisting of very pure silicon dioxide in different crystalline forms, quartz, agate amethyst, rock crystal, chalcedony, flint, jasper, and opal. The crystals have the empirical formula of silicon dioxide, but do not consist of separate silicon dioxide molecules in the manner of solid carbon dioxide. Rather, silica is structurally a network-solid consisting of silicon and oxygen in three-dimensional crystals, like diamond. Less pure silica forms the natural glass obsidian. Biogenic silica occurs in the structure of diatoms, radiolaria and siliceous sponges.

Silicon is also a principal component of many meteorites, and is a component of tektites, a silicate mineral of possibly lunar origin, or (if Earth-derived) which has been subjected to unusual temperatures and pressures, possibly from meteorite strike.

## **Production**

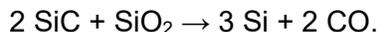
### **Alloys**

Ferrosilicon, an iron-silicon alloy that contains varying ratios of elemental silicon and iron, accounts for about 80% of the world's production of elemental silicon, with China, the leading supplier of elemental silicon, providing 4.6 million tons (or 2/3 of the world output) of silicon, most of which is in the form of ferrosilicon. It is followed by Russia (610,000 t), Norway (330,000 t), Brazil (240,000 t) and the United States (170,000 t). Ferrosilicon is primarily used by the steel industry (see below). Aluminum-silicon alloys are heavily used in the aluminum alloy casting industry, where silicon is the single most important additive to aluminum to improve its casting properties. Since cast aluminum is widely used in the automobile industry, this use of silicon is thus the single largest industrial use of "metallurgical grade" pure silicon (as this purified silicon is added to pure aluminum, whereas ferrosilicon is never purified before being added to steel).

### **Metallurgical Grade**

Elemental silicon not alloyed with significant quantities of other elements, and usually > 95%, is often referred to loosely as silicon metal. It makes up about 20% of the world total elemental silicon production, with less than 1 to 2% of total elemental silicon (5–10% of metallurgical grade silicon) ever purified to higher grades for use in electronics. Metallurgical grade silicon is commercially prepared by the reaction of high-purity silica with wood, charcoal, and coal in an electric arc furnace using carbon electrodes. At temperatures over 1,900 °C (3,450 °F), the carbon in the aforementioned materials and the silicon undergo the chemical reaction  $\text{SiO}_2 + 2 \text{C} \rightarrow \text{Si} + 2 \text{CO}$ . Liquid silicon collects in the bottom of the furnace, which is then drained and cooled.

The silicon produced this manner is called *metallurgical grade silicon* and is at least 98% pure. Using this method, silicon carbide (SiC) may also form from an excess of carbon in one or both of the following ways:  $\text{SiO}_2 + \text{C} \rightarrow \text{SiO} + \text{CO}$  or  $\text{SiO} + 2 \text{C} \rightarrow \text{SiC} + \text{CO}$ . However, provided the concentration of  $\text{SiO}_2$  is kept high, the silicon carbide can be eliminated by the chemical reaction



As noted above, metallurgical grade silicon "metal" has its primary use in the aluminum casting industry to make aluminum-silicon alloy parts. The remainder (about 45%) is used by the chemical industry, where it is primarily employed to make fumed silica.

### **Electronic Grade**

The use of silicon in semiconductor devices demands a much greater purity than afforded by metallurgical grade silicon. Very pure silicon (>99.9%) can be extracted directly from solid silica or other silicon compounds by molten salt electrolysis. This method, known as early as 1854 (see also FFC Cambridge process), has the potential to directly produce solar-grade silicon without any carbon dioxide emission at much lower energy consumption.

Solar grade silicon cannot be used for semiconductors, where purity must be extreme to properly control the process. Bulk silicon wafers used at the beginning of the integrated circuit making process must first be refined to "nine nines" purity (99.999999%), a process which requires repeated applications of refining technology.

The majority of silicon crystals grown for device production are produced by the Czochralski process, (CZ-Si) since it is the cheapest method available and it is capable of producing large size crystals. However, single crystals grown by the Czochralski process contain impurities because the crucible containing the melt often dissolves. Historically, a number of methods have been used to produce ultra-high-purity silicon.

Early silicon purification techniques were based on the fact that if silicon is melted and re-solidified, the last parts of the mass to solidify contain most of the impurities. The earliest method of silicon purification, first described in 1919 and used on a limited basis to make radar components during World War II, involved crushing metallurgical grade silicon and then partially dissolving the silicon powder in an acid.

When crushed, the silicon cracked so that the weaker impurity-rich regions were on the outside of the resulting grains of silicon. As a result, the impurity-rich silicon was the first to be dissolved when treated with acid, leaving behind a more pure product.

In zone melting, also called zone refining, the first silicon purification method to be widely used industrially, rods of metallurgical grade silicon are heated to melt at one end. Then, the heater is slowly moved down the length of the rod, keeping a small length of the rod molten as the silicon cools and re-solidifies behind it.

Since most impurities tend to remain in the molten region rather than re-solidify, when the process is complete, most of the impurities in the rod will have been moved into the end that was the last to be melted. This end is then cut off and discarded, and the process repeated if a still higher purity is desired.

At one time, DuPont produced ultra-pure silicon by reacting silicon tetrachloride with high-purity zinc vapors at 950 °C, producing silicon by  $\text{SiCl}_4 + 2 \text{Zn} \rightarrow \text{Si} + 2 \text{ZnCl}_2$ . However, this technique was plagued with practical problems (such as the zinc chloride byproduct solidifying and clogging lines) and was eventually abandoned in favor of the Siemens process. In the *Siemens process*, high-purity silicon rods are exposed to trichlorosilane at 1150 °C. The trichlorosilane gas decomposes and deposits additional silicon onto the rods, enlarging them because  $2 \text{HSiCl}_3 \rightarrow \text{Si} + 2 \text{HCl} + \text{SiCl}_4$ . Silicon produced from this and similar processes is called *polycrystalline silicon*. Polycrystalline silicon typically has impurity levels of less than one part per billion.

In 2006 REC announced construction of a plant based on *fluidized bed* (FB) technology using silane:  $3 \text{SiCl}_4 + \text{Si} + 2 \text{H}_2 \rightarrow 4 \text{HSiCl}_3$ ,  $4 \text{HSiCl}_3 \rightarrow 3 \text{SiCl}_4 + \text{SiH}_4$ ,  $\text{SiH}_4 \rightarrow \text{Si} + 2 \text{H}_2$ . The advantage of fluid bed technology is that processes can be run continuously, yielding higher yields than Siemens Process, which is a batch process.

Today, silicon is purified by converting it to a silicon compound that can be more easily purified by distillation than in its original state, and then converting that silicon compound back into pure silicon. Trichlorosilane is the silicon compound most commonly used as the intermediate, although silicon tetrachloride and silane are also used. When these gases are blown over silicon at high temperature, they decompose to high-purity silicon.

In addition, there is the *Schumacher process*, which utilizes tribromosilane in place of trichlorosilane and fluid bed technology. It requires lower deposition temperatures, lower capital costs to build facilities and operate, no hazardous polymers nor explosive material, and produces no amorphous silicon dust waste, all of which are drawbacks of the Siemens process. However, there are yet to be any major factories built using this process.

## Compounds

- Silicon forms binary compounds called silicides with many metallic elements whose properties range from reactive compounds, e.g. magnesium silicide,  $\text{Mg}_2\text{Si}$  through high melting refractory compounds such as molybdenum disilicide,  $\text{MoSi}_2$ .
- Silicon carbide,  $\text{SiC}$  (carborundum) is a hard, high melting solid and a well-known abrasive. It may also be sintered into a type of high-strength ceramic used in armor.
- Silane,  $\text{SiH}_4$ , is a pyrophoric gas with a similar tetrahedral structure to methane,  $\text{CH}_4$ . When pure, it does not react with pure water or dilute acids; however, even small amounts of alkali impurities from the laboratory glass can result in a rapid hydrolysis. There is a range of catenated silicon hydrides that form a homologous series of compounds,  $\text{Si}_n\text{H}_{2n+2}$  where  $n = 2-8$  (analogous to the alkanes). These are all readily hydrolyzed and are thermally unstable, particularly the heavier members.
- Disilenes contain a silicon-silicon double bond (analogous to the alkenes) and are generally highly reactive requiring large substituent groups to stabilize them. A disilyne with a silicon-silicon triple bond was first isolated in 2004; although as the compound is non-linear, the bonding is dissimilar to that in alkynes.
- Tetrahalides,  $\text{SiX}_4$ , are formed with all the halogens. Silicon tetrachloride, for example, reacts with water, unlike its carbon analogue, carbon tetrachloride. Silicon dihalides are formed by the high temperature reaction of tetrahalides and silicon; with a structure analogous to a carbene they are reactive compounds. Silicon difluoride condenses to form a polymeric compound,  $(\text{SiF}_2)_n$ .
- Silicon dioxide is a high melting solid with a number of crystal forms; the most familiar of which is the mineral quartz. In quartz each silicon atom is surrounded

by four oxygen atoms that bridge to other silicon atoms to form a three dimensional lattice. Silica is soluble in water at high temperatures forming a range of compounds called *monosilicic acid*,  $\text{Si}(\text{OH})_4$ .

- Under the right conditions monosilicic acid readily polymerizes to form more complex silicic acids, ranging from the simplest condensate, disilicic acid ( $\text{H}_6\text{Si}_2\text{O}_7$ ) to linear, ribbon, layer and lattice structures which form the basis of the many silicate minerals and are called *polysilicic acids*  $\{\text{Si}_x(\text{OH})_{4-2x}\}_n$ .
- With oxides of other elements the high temperature reaction of silicon dioxide can give a wide range of glasses with various properties. Examples include soda lime glass, borosilicate glass and lead crystal glass.
- Silicon sulfide,  $\text{SiS}_2$  is a polymeric solid (unlike its carbon analogue the liquid  $\text{CS}_2$ ).
- Silicon forms a nitride,  $\text{Si}_3\text{N}_4$  which is a ceramic. Silatranes, a group of tricyclic compounds containing five-coordinate silicon, may have physiological properties.
- Many transition metal complexes containing a metal-silicon bond are now known, which include complexes containing  $\text{SiH}_n\text{X}_{3-n}$  ligands,  $\text{SiX}_3$  ligands, and  $\text{Si}(\text{OR})_3$  ligands.
- Silicones are large group of polymeric compounds with an (Si-O-Si) backbone. An example is the silicone oil PDMS (polydimethylsiloxane). These polymers can be crosslinked to produce resins and elastomers.
- Many organosilicon compounds are known which contain a silicon-carbon single bond. Many of these are based on a central tetrahedral silicon atom, and some are optically active when central chirality exists. Long chain polymers containing a silicon backbone are known, such as polydimethylsilylene  $(\text{SiMe}_2)_n$ . Polycarbosilane,  $[(\text{SiMe}_2)_2\text{CH}_2]_n$  with a backbone containing a repeating -Si-Si-C unit, is a precursor in the production of silicon carbide fibers.

## History

Attention was first drawn to quartz as the possible oxide of a fundamental chemical element by Antoine Lavoisier, in 1787. In 1811, Gay-Lussac and Thénard are thought to have prepared impure amorphous silicon, through the heating of recently isolated potassium metal with silicon tetrafluoride, but they did not purify and characterize the product, nor identify it as a new element.

In 1824, Berzelius prepared amorphous silicon using approximately the same method as Gay-Lussac (potassium metal and potassium fluorosilicate), but purifying the product to a brown powder by repeatedly washing it. He named the product *silicium* from the Latin *silex*, *silicis* for flint, flints, and adding the "-ium" ending because he believed it was a metal.

As a result, he is usually given credit for the element's discovery. Silicon was given its present name in 1831 by Scottish chemist Thomas Thomson. He retained part of Berzelius's name but added "-on" because he believed silicon a nonmetal more similar to boron and carbon.

Silicon in its more common crystalline form was not prepared until 31 years later, by Deville. By electrolyzing impure sodium-aluminum chloride containing approximately 10% silicon, he was able to obtain a slightly impure allotrope of silicon in 1854. Later, more cost-effective methods have been developed to isolate silicon in several allotrope forms, the most recent being silicene.

## Tellurium- Metalloid

Tellurium is a chemical element with symbol Te and atomic number 52. A brittle, mildly toxic, rare, silver-white metalloid which looks similar to tin, tellurium is chemically related to selenium and sulfur. It is occasionally found in native form, as elemental crystals.

Tellurium is far more common in the universe as a whole than it is on Earth. Its extreme rarity in the Earth's crust, comparable to that of platinum, is partly due to its high atomic number, but also due to its formation of a volatile hydride which caused the element to be lost to space as a gas during the hot nebular formation of the planet.

Tellurium was discovered in Transylvania (today part of Romania) in 1782 by Franz-Joseph Müller von Reichenstein in a mineral containing tellurium and gold. Martin Heinrich Klaproth named the new element in 1798 after the Latin word for "earth", *tellus*. Gold telluride minerals are the most notable natural gold compounds.



However, they are not a commercially significant source of tellurium itself, which is normally extracted as a by-product of copper and lead production.

Commercially, the primary use of tellurium is in alloys, foremost in steel and copper to improve machinability. Applications in solar panels and as a semiconductor material also consume a considerable fraction of tellurium production.

Tellurium has no biological function, although fungi can incorporate it in place of sulfur and selenium into amino acids such as tellurocysteine and telluromethionine. In humans, tellurium is partly metabolized into dimethyl telluride,  $(\text{CH}_3)_2\text{Te}$ , a gas with a garlic-like odor which is exhaled in the breath of victims of tellurium toxicity or exposure.

### Characteristics

#### Physical Properties

When crystalline, tellurium is silvery-white and when it is in pure state it has a metallic luster. It is a brittle and easily pulverized metalloid. Amorphous tellurium is found by precipitating it from a solution of tellurous or telluric acid ( $\text{Te}(\text{OH})_6$ ).

Tellurium is a semiconductor that shows a greater electrical conductivity in certain directions which depends on atomic alignment; the conductivity increases slightly when exposed to light (photoconductivity). When in its molten state, tellurium is corrosive to copper, iron and stainless steel.

#### Chemical Properties

Tellurium adopts a polymeric structure, consisting of zig-zag chains of Te atoms. This gray material resists oxidation by air and is nonvolatile.

## Isotopes

Naturally occurring tellurium has eight isotopes. Five of those isotopes,  $^{122}\text{Te}$ ,  $^{123}\text{Te}$ ,  $^{124}\text{Te}$ ,  $^{125}\text{Te}$  and  $^{126}\text{Te}$ , are stable. The other three,  $^{120}\text{Te}$ ,  $^{128}\text{Te}$  and  $^{130}\text{Te}$ , have been observed to be radioactive.

The stable isotopes make up only 33.2% of the naturally occurring tellurium; this is possible due to the long half-lives of the unstable isotopes. They are in the range from  $10^{13}$  to  $2.2 \times 10^{24}$  years (for  $^{128}\text{Te}$ ). This makes  $^{128}\text{Te}$  the isotope with the longest half-life among all radionuclides, which is approximately 160 trillion ( $10^{12}$ ) times the age of known universe.

There are 38 known nuclear isomers of tellurium with atomic masses that range from 105 to 142. Tellurium is among the lightest elements known to undergo alpha decay, with isotopes  $^{106}\text{Te}$  to  $^{110}\text{Te}$  being able to undergo this mode of decay.<sup>[6]</sup> The atomic mass of tellurium ( $127.60 \text{ g}\cdot\text{mol}^{-1}$ ) exceeds that of the following element iodine ( $126.90 \text{ g}\cdot\text{mol}^{-1}$ ).

## Occurrence

With an abundance in the Earth's crust comparable to that of platinum, tellurium is one of the rarest stable solid elements in the Earth's crust. Its abundance is about  $1 \mu\text{g}/\text{kg}$ . In comparison, even the rarest of the lanthanides have crustal abundances of  $500 \mu\text{g}/\text{kg}$  (see Abundance of the chemical elements).

The extreme rarity of tellurium in the Earth's crust is not a reflection of its cosmic abundance, which is in fact greater than that of rubidium, even though rubidium is ten thousand times more abundant in the Earth's crust. The extraordinarily low abundance of tellurium on Earth is rather thought to be due to conditions in the Earth's formation, when the stable form of certain elements, in the absence of oxygen and water, was controlled by the reductive power of free hydrogen.

Under this scenario, certain elements such as tellurium which form volatile hydrides were severely depleted during the formation of the Earth's crust, through evaporation of these hydrides. Tellurium and selenium are the heavy elements most depleted in the Earth's crust by this process.

Tellurium is sometimes found in its native (i.e., elemental) form, but is more often found as the tellurides of gold such as calaverite and krennerite (two different polymorphs of  $\text{AuTe}_2$ ), petzite,  $\text{Ag}_3\text{AuTe}_2$ , and sylvanite,  $\text{AgAuTe}_4$ . The city of Telluride, Colorado was named in hope of a strike of gold telluride (which never materialized, though gold metal ore was found).

Gold itself is usually found uncombined, but when found naturally as a chemical compound, it is most often combined with tellurium (a few rare non-telluride gold compounds such as the antimonide aurostibite,  $\text{AuSb}_2$ , and bismuthide maldonite,  $\text{Au}_2\text{Bi}$ , are also known).

Although tellurium is found with gold more often than in uncombined form, it is found even more often combined with elements other than gold, as tellurides more common metals (e.g. melonite,  $\text{NiTe}_2$ ). Natural tellurite and tellurate minerals also occur, formed by oxidation of tellurides near the Earth's surface.

In contrast to selenium, tellurium is not in general able to replace sulfur in its minerals, due to the large difference in ion radius of sulfur and tellurium. In consequence, many common sulfide minerals contain considerable amounts of selenium, but only traces of tellurium.

In the gold rush of 1893, diggers in Kalgoorlie discarded a pyritic material which got in their way as they searched for pure gold. The Kalgoorlie waste was thus used to fill in potholes or as part of sidewalks.

Three years passed before it was realized that this waste was calaverite, a telluride of gold that had not been recognized. This led to a second gold rush in 1896 which included mining the streets.

### Production

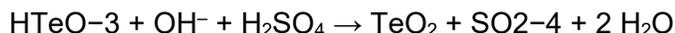
The principal source of tellurium is from anode sludges produced during the electrolytic refining of blister copper. It is a component of dusts from blast furnace refining of lead. Treatment of 500 tons of copper ore typically yields one pound (0.45 kg) of tellurium. Tellurium is produced mainly in the United States, Peru, Japan and Canada.

For the year 2009 the British Geological Survey gives the following numbers: United States 50 t, Peru 7 t, Japan 40 t and Canada 16 t. The anode sludges contain the selenides and tellurides of the noble metals in compounds with the formula  $M_2Se$  or  $M_2Te$  ( $M = Cu, Ag, Au$ ). At temperatures of 500 °C the anode sludges are roasted with sodium carbonate under air.

The metal ions are reduced to the metals, while the telluride is converted to sodium tellurite.



Tellurites can be leached from the mixture with water and are normally present as hydrotellurites  $HTeO_3^-$  in solution. Selenites are also formed during this process, but they can be separated by adding sulfuric acid. The hydrotellurites are converted into the insoluble tellurium dioxide while the selenites stay in solution.



The reduction to the metal is done either by electrolysis or by reacting the tellurium dioxide with sulfur dioxide in sulfuric acid.



Commercial-grade tellurium is usually marketed as 200-mesh powder but is also available as slabs, ingots, sticks, or lumps. The year-end price for tellurium in 2000 was US\$14 per pound. In recent years, the tellurium price was driven up by increased demand and limited supply, reaching as high as US\$100 per pound in 2006.

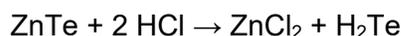
Despite an expected doubling in production due to improved extraction methods, the United States Department of Energy (DoE) anticipates a supply shortfall of tellurium by 2025.

## Compounds

Tellurium belongs to the same chemical family as oxygen, sulfur, selenium and polonium: the chalcogen family. Tellurium and selenium compounds are similar. It exhibits the oxidation states -2, +2, +4 and +6, with the +4 state being most common.

## Tellurides

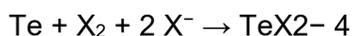
Reduction of Te metal produces the tellurides and polytellurides,  $\text{Te}_n^{2-}$ . The -2 oxidation state is exhibited in binary compounds with many metals, such as zinc telluride,  $\text{ZnTe}$ , formed by heating tellurium with zinc. Decomposition of  $\text{ZnTe}$  with hydrochloric acid yields hydrogen telluride ( $\text{H}_2\text{Te}$ ), a highly unstable analogue of the other chalcogen hydrides,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$ :



$\text{H}_2\text{Te}$  is unstable, whereas salts of its conjugate base  $[\text{TeH}]^-$  are stable.

## Halides

The +2 oxidation state is exhibited by the dihalides,  $\text{TeCl}_2$ ,  $\text{TeBr}_2$  and  $\text{TeI}_2$ . The dihalides have not been obtained in pure form, although they are known decomposition products of the tetrahalides in organic solvents, and their derived tetrahalotellurates are well-characterized:



where X is Cl, Br, or I. These anions are square planar in geometry. Polynuclear anionic species also exist, such as the dark brown  $\text{Te}_2\text{I}_2^{6-}$ , and the black  $\text{Te}_4\text{I}_4^{14-}$ .

Fluorine forms two halides with tellurium: the mixed-valence  $\text{Te}_2\text{F}_4$  and  $\text{TeF}_6$ . In the +6 oxidation state, the  $-\text{OTeF}_5$  structural group occurs in a number of compounds such as  $\text{HOTeF}_5$ ,  $\text{B}(\text{OTeF}_5)_3$ ,  $\text{Xe}(\text{OTeF}_5)_2$ ,  $\text{Te}(\text{OTeF}_5)_4$  and  $\text{Te}(\text{OTeF}_5)_6$ . The square antiprismatic anion  $\text{TeF}_2^{8-}$  is also attested. The other halogens do not form halides with tellurium in the +6 oxidation state, but only tetrahalides ( $\text{TeCl}_4$ ,  $\text{TeBr}_4$  and  $\text{TeI}_4$ ) in the +4 state, and other lower halides ( $\text{Te}_3\text{Cl}_2$ ,  $\text{Te}_2\text{Cl}_2$ ,  $\text{Te}_2\text{Br}_2$ ,  $\text{Te}_2\text{I}$  and two forms of  $\text{TeI}$ ). In the +4 oxidation state, halotellurate anions are known, such as  $\text{TeCl}_2^{6-}$  and  $\text{Te}_2\text{Cl}_2^{10-}$ .

Halotellurium cations are also attested, including  $\text{TeI}^{3+}$ , found in  $\text{TeI}_3\text{AsF}_6$ .

## Oxocompounds

Tellurium monoxide was first reported in 1883 as a black amorphous solid formed by the heat decomposition of  $\text{TeSO}_3$  in vacuum, disproportionating into tellurium dioxide,  $\text{TeO}_2$  and elemental tellurium upon heating.

Since then, however, some doubt has been cast on its existence in the solid phase, although it is known as a vapor phase fragment; the black solid may be merely an equimolar mixture of elemental tellurium and tellurium dioxide.

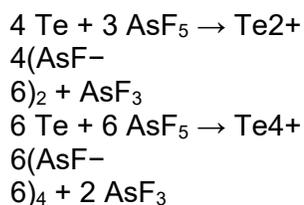
Tellurium dioxide is formed by heating tellurium in air, causing it to burn with a blue flame. Tellurium trioxide,  $\beta\text{-TeO}_3$ , is obtained by thermal decomposition of  $\text{Te}(\text{OH})_6$ . The other two forms of trioxide reported in the literature, the  $\alpha$ - and  $\gamma$ - forms, were found not to be

true oxides of tellurium in the +6 oxidation state, but a mixture of  $\text{Te}^{4+}$ ,  $\text{OH}^-$  and  $\text{O}^{2-}$ . Tellurium also exhibits mixed-valence oxides,  $\text{Te}_2\text{O}_5$  and  $\text{Te}_4\text{O}_9$ .

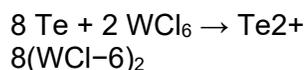
The tellurium oxides and hydrated oxides form a series of acids, including tellurous acid ( $\text{H}_2\text{TeO}_3$ ), orthotelluric acid ( $\text{Te}(\text{OH})_6$ ) and metatelluric acid ( $(\text{H}_2\text{TeO}_4)_n$ ). The two forms of telluric acid form *tellurate* salts containing the  $\text{TeO}_2-4$  and  $\text{TeO}_6-6$  anions, respectively. Tellurous acid forms *tellurite* salts containing the anion  $\text{TeO}_2-3$ . Other tellurium cations include  $\text{TeF}_2+8$ , which consists of two fused tellurium rings and the polymeric  $\text{TeF}_2+7$ .

### Zintl cations

When tellurium is treated with concentrated sulfuric acid, it forms red solutions containing the Zintl ion,  $\text{Te}_2+4$ . The oxidation of tellurium by  $\text{AsF}_5$  in liquid  $\text{SO}_2$  also produces this square planar cation, as well as with the trigonal prismatic, yellow-orange  $\text{Te}_4+6$ :



Other tellurium Zintl cations include the polymeric  $\text{Te}_2+7$  and the blue-black  $\text{Te}_2+8$ , which consists of two fused 5-membered tellurium rings. The latter cation is formed by the reaction of tellurium with tungsten hexachloride:



Interchalcogen cations also exist, such as  $\text{Te}_2\text{Se}_2+6$  (distorted cubic geometry) and  $\text{Te}_2\text{Se}_2+8$ . These are formed by oxidizing mixtures of tellurium and selenium with  $\text{AsF}_5$  or  $\text{SbF}_5$ .

### Organotellurium compounds

Tellurium does not readily form analogues of alcohols and thiols, with the functional group  $-\text{TeH}$  and are called tellurols. The  $-\text{TeH}$  functional group is also attributed to using the prefix *tellanyl-*. Like  $\text{H}_2\text{Te}$ , these species are unstable with respect to loss of hydrogen. Telluraethers ( $\text{R-Te-R}$ ) are more stable as are telluroxides.

### History

from the mines in Zlatna, near what is now Sibiu, Transylvania. This ore was known as "Faczebajer weißes blättriges Golderz" (white leafy gold ore from Faczebaja) or *antimonialischer Goldkies* (antimonic gold pyrite), and, according to Anton von Rupprecht, was *Spießglaskönig* (*argent molybdique*), containing native antimony. In 1782 Franz-Joseph Müller von Reichenstein, who was then serving as the Austrian chief inspector of mines in Transylvania, concluded that the ore did not contain antimony, but that it was bismuth sulfide.

The following year, he reported that this was erroneous and that the ore contained mostly gold and an unknown metal very similar to antimony. After a thorough investigation which lasted for three years and consisted of more than fifty tests, Müller determined the specific gravity of the mineral and noted the radish-like odor of the white smoke which passed off

when the new metal was heated, the red color which the metal imparts to sulfuric acid, and the black precipitate which this solution gives when diluted with water. Nevertheless, he was not able to identify this metal and gave it the names *aurum paradoxium* and *metallum problematicum*, as it did not show the properties predicted for the expected antimony.

In 1789, another Hungarian scientist, Pál Kitaibel, also discovered the element independently in an ore from Deutsch-Pilsen which had been regarded as argentiferous molybdenite, but later he gave the credit to Müller. In 1798, it was named by Martin Heinrich Klaproth who earlier isolated it from the mineral calaverite. The 1960s brought growth in thermoelectric applications for tellurium (as bismuth telluride), as well as its use in free-machining steel, which became the dominant use.

## **Applications**

### **Metallurgy**

The largest consumer of tellurium is metallurgy, where it is used in iron, copper and lead alloys. When added to stainless steel and copper it makes these metals more machinable. It is alloyed into cast iron for promoting chill for spectroscopic purposes, as the presence of electrically conductive free graphite tends to deleteriously affect spark emission testing results. In lead it improves strength and durability and decreases the corrosive action of sulfuric acid.

### **Semiconductor and electronics industry uses**

Tellurium is used in cadmium telluride (CdTe) solar panels. National Renewable Energy Laboratory lab tests using this material achieved some of the highest efficiencies for solar cell electric power generation. Massive commercial production of CdTe solar panels by First Solar in recent years has significantly increased tellurium demand. If some of the cadmium in CdTe is replaced by zinc then (Cd,Zn)Te is formed which is used in solid-state X-ray detectors.

Alloyed with both cadmium and mercury, to form mercury cadmium telluride, an infrared sensitive semiconductor material is formed.

Organotellurium compounds such as dimethyl telluride, diethyl telluride, diisopropyl telluride, diallyl telluride and methyl allyl telluride are used as precursors for metalorganic vapor phase epitaxy growth of II-VI compound semiconductors. Diisopropyl telluride (DIPTe) is employed as the preferred precursor for achieving the low-temperature growth of CdHgTe by MOVPE. For these processes highest purity metalorganics of both selenium and tellurium are used. The compounds for semiconductor industry and are prepared by adduct purification.

Tellurium as a tellurium suboxide is used in the media layer of several types of rewritable optical discs, including ReWritable Compact Discs (CD-RW), ReWritable Digital Video Discs (DVD-RW) and ReWritable Blu-ray Discs.

Tellurium is used in the new phase change memory chips developed by Intel. Bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) and lead telluride are working elements of thermoelectric devices. Lead telluride is used in far-infrared detectors.

### Other Uses

- Used to color ceramics.
- The strong increase in optical refraction upon the addition of selenides and tellurides into glass is used in the production of glass fibers for telecommunications. These chalcogenide glasses are widely used.
- Mixtures of selenium and tellurium are used with barium peroxide as oxidizer in the delay powder of electric blasting caps.
- Organic tellurides have been employed as initiators for living radical polymerization and electron-rich mono- and di-tellurides possess antioxidant activity.
- Rubber can be vulcanized with tellurium instead of sulfur or selenium. The rubber produced in this way shows improved heat resistance.
- Tellurite agar is used to identify member of the corynebacterium genus, most typically *Corynebacterium diphtheriae*, the pathogen responsible for diphtheria.



## Allotropes Section

Allotropy or allotropism is the property of some chemical elements to exist in two or more different forms, known as allotropes of these elements. Allotropes are different structural modifications of an element; the atoms of the element are bonded together in a different manner.

For example, the allotropes of carbon include diamond (where the carbon atoms are bonded together in a tetrahedral lattice arrangement), graphite (where the carbon atoms are bonded together in sheets of a hexagonal lattice), graphene (single sheets of graphite), and fullerenes (where the carbon atoms are bonded together in spherical, tubular, or ellipsoidal formations).

The term allotropy is used for elements only, not for compounds. The more general term, used for any crystalline material, is polymorphism. Allotropy refers only to different forms of an element within the same phase (i.e. different solid, liquid or gas forms); the changes of state between solid, liquid and gas in themselves are not considered allotropy.

For some elements, allotropes have different molecular formulae which can persist in different phases – for example, two allotropes of oxygen (dioxygen, O<sub>2</sub> and ozone, O<sub>3</sub>), can both exist in the solid, liquid and gaseous states.

Conversely, some elements do not maintain distinct allotropes in different phases – for example phosphorus has numerous solid allotropes, which all revert to the same P<sub>4</sub> form when melted to the liquid state.

The concept of allotropy was originally proposed in 1841 by the Swedish scientist Baron Jöns Jakob Berzelius (1779–1848). The term is derived from the Greek *ἀλλοτροπία* (*allotropia*; variability, changeableness).

After the acceptance of Avogadro's hypothesis in 1860 it was understood that elements could exist as polyatomic molecules, and the two allotropes of oxygen were recognized as O<sub>2</sub> and O<sub>3</sub>. In the early 20th century it was recognized that other cases such as carbon were due to differences in crystal structure.

By 1912, Ostwald noted that the allotropy of elements is just a special case of the phenomenon of polymorphism known for compounds, and proposed that the terms allotrope and allotropy be abandoned and replaced by polymorph and polymorphism. Although many other chemists have repeated this advice, IUPAC and most chemistry texts still favor the usage of allotrope and allotropy for elements only.

### List of Allotropes

Typically, elements capable of variable coordination number and/or oxidation states tend to exhibit greater numbers of allotropic forms. Another contributing factor is the ability of an element to catenate. Allotropes are typically more noticeable in non-metals (excluding the halogens and the noble gases) and metalloids. Nevertheless, metals tend to have many allotropes.



Cerium, left, Dysprosium, right.

**Examples of allotropes include:**

**Non-metals**

<b>Element</b>	<b>Allotropes</b>
Carbon	<ul style="list-style-type: none"> <li>• Diamond - an extremely hard, transparent crystal, with the carbon atoms arranged in a tetrahedral lattice. A poor electrical conductor. An excellent thermal conductor.</li> <li>• Lonsdaleite - also called hexagonal diamond.</li> <li>• Graphite - a soft, black, flaky solid, a moderate electrical conductor. The C atoms are bonded in flat hexagonal lattices (graphene), which are then layered in sheets.</li> <li>• Linear acetylenic carbon (Carbyne)</li> <li>• Amorphous carbon</li> <li>• Fullerenes, including Buckminsterfullerene, aka "buckyballs", such as C<sub>60</sub>.</li> <li>• Carbon nanotubes - allotropes of carbon with a cylindrical nanostructure.</li> </ul>
Phosphorus:	<ul style="list-style-type: none"> <li>• White phosphorus - crystalline solid P<sub>4</sub></li> <li>• Red phosphorus - polymeric solid</li> <li>• Scarlet phosphorus</li> <li>• Violet phosphorus</li> <li>• Black phosphorus - semiconductor, analogous to graphite</li> <li>• Diphosphorus</li> </ul>
Oxygen:	<ul style="list-style-type: none"> <li>• dioxygen, O<sub>2</sub> - colorless (faint blue)</li> <li>• Ozone, O<sub>3</sub> - blue</li> <li>• Tetraoxygen, O<sub>4</sub> - metastable</li> <li>• Octaoxygen, O<sub>8</sub> - red</li> </ul>
Sulfur:	<ul style="list-style-type: none"> <li>• Sulfur has a large number of allotropes, second only to carbon</li> </ul>
Selenium:	<ul style="list-style-type: none"> <li>• "Red selenium," cyclo-Se<sub>8</sub></li> <li>• Gray selenium, polymeric Se</li> <li>• Black selenium</li> </ul>

## Metalloids

Element	Allotropes
Boron:	<ul style="list-style-type: none"><li>• Amorphous boron - brown powder - B<sub>12</sub> regular icosahedra</li><li>• α-rhombohedral boron</li><li>• β-rhombohedral boron</li><li>• γ-orthorhombic boron</li><li>• α-tetragonal boron</li><li>• β-tetragonal boron</li><li>• High-pressure superconducting phase</li></ul>
Silicon:	<ul style="list-style-type: none"><li>• Amorphous silicon</li><li>• crystalline silicon, Diamond cubic structure</li></ul>
Arsenic:	<ul style="list-style-type: none"><li>• Yellow arsenic - molecular non-metallic As<sub>4</sub>, with the same structure of white phosphorus</li><li>• Gray arsenic, polymeric As (metalloid)</li><li>• Black arsenic - molecular and non-metallic, with the same structure of red phosphorus</li></ul>
Germanium:	<ul style="list-style-type: none"><li>• α-germanium – semi-metallic, with the same structure of diamond</li><li>• β-germanium - metallic, with the same structure of beta-tin</li></ul>
Antimony:	<ul style="list-style-type: none"><li>• blue-white antimony - the stable form (metalloid)</li><li>• yellow antimony (non-metallic)</li><li>• black antimony (non-metallic)</li><li>• explosive antimony</li></ul>
Polonium:	<ul style="list-style-type: none"><li>• α-polonium - simple cubic (metallic)</li><li>• β-polonium - rhombohedral (metallic)</li></ul>

## Metals

Among the metallic elements that occur in nature in significant quantities (up to U, without Tc and Pm), 27 are allotropic at ambient pressure: Li, Be, Na, Ca, Ti, Mn, Fe, Co, Sr, Y, Zr, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Yb, Hf, Ta, Th, Pa and U. Some phase transitions between allotropic forms of technologically-relevant metals are those of Ti at 882°C, Fe at 912°C and 1394°C, Co at 422°C, Zr at 863°C, Sn at 13°C and U at 668°C and 776°C.

## Element Allotropes

- Tin:
- grey tin (alpha tin)
  - white tin (beta tin)
  - rhombic tin (gamma tin)
  - sigma tin
- Iron:
- ferrite (alpha iron) - forms below 770°C (the Curie point,  $T_C$ ); the iron becomes magnetic in its alpha form; BCC
  - beta - forms below 912°C; BCC crystal structure
  - gamma - forms below 1,394°C; FCC crystal structure
  - delta - forms from cooling down molten iron below 1,538°C; BCC crystal structure
  - epsilon - forms at high pressures

## Lanthanides and Actinides

- Cerium, samarium, terbium, dysprosium and ytterbium have three allotropes.
- Praseodymium, neodymium, gadolinium and terbium have two allotropes.
- Plutonium has six distinct solid allotropes under "normal" pressures. Their densities vary within a ratio of some 4:3, which vastly complicates all kinds of work with the metal (particularly casting, machining, and storage). A seventh plutonium allotrope exists at very high pressures. The transuranium metals Np, Am, and Cm are also allotropic.
- Promethium, americium, berkelium and californium have 3 allotropes each.

hydrogen 1 H 1.0079																	helium 2 He 4.0026	
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180	
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948	
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80	
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29	
cesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 **	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]	ununquadium 114 Uuq [289]					

\* Lanthanide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

\*\* Actinide series

## Allotropes Described

### Aluminum- Post-transition Metal

Aluminum is ordinarily classified as a metal, given its luster, malleability and ductility, high electrical and thermal conductivity and close-packed crystalline structure.

It does however have some properties that are unusual for a metal. Taken together, these properties are sometimes used as a basis to classify aluminum as a metalloid:

- Its crystalline structure shows some evidence of directional bonding.
- Although it forms an  $\text{Al}^{3+}$  cation in some compounds, it bonds covalently in most others.
- Its oxide is amphoteric, and a conditional glass-former.
- it forms anionic aluminates, such behavior being considered nonmetallic in character.



Stott labels aluminum as weak metal. It has the physical properties of a good metal but some of the chemical properties of a nonmetal. Steele notes the somewhat paradoxical chemical behavior of aluminum.

It resembles a weak metal with its amphoteric oxide and the covalent character of many of its compounds. Yet it is also a strongly electropositive metal, with a high negative electrode potential.

The notion of aluminum as a metalloid is sometimes disputed given it has many metallic properties. Aluminum is therefore argued to be an exception to the mnemonic that elements adjacent to the metal-nonmetal dividing line are metalloids.

### Aluminum Sulfate

Aluminum sulfate, alternatively spelt either aluminum or sulfate, is a chemical compound with the formula  $\text{Al}_2(\text{SO}_4)_3$ .

Aluminum sulfate is mainly used as a flocculating agent in the purification of drinking water and wastewater treatment plants, and in paper manufacturing.

Aluminum sulfate is sometimes referred to as a type of alum. Alums are a class of related compounds typified by  $\text{AB}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . The anhydrous form occurs naturally as a rare mineral millosevichite, found e.g. in volcanic environments and on burning coal-mining waste dumps.

Aluminum sulfate is rarely, if ever, encountered as the anhydrous salt. It forms a number of different hydrates, of which the hexadecahydrate  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  and octadecahydrate  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  are the most common. The heptadecahydrate, whose formula can be written as  $[\text{Al}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ , occurs naturally as the mineral alunogen.

The compound decomposes to  $\gamma$ -alumina and sulfur trioxide when heated between 580 and 900 °C. It combines with water forming hydrated salts of various compositions.

Aluminum sulfate reacts with sodium bicarbonate to which foam stabilizer has been added, producing carbon dioxide for fire-extinguishing foams:



The carbon dioxide is trapped by the foam stabilizer and creates a thick foam which will float on top of hydrocarbon fuels and seal off access to atmospheric oxygen, smothering the fire. Chemical foam was unsuitable for use on polar solvents such as alcohol, as the fuel would mix with and break down the foam blanket. The carbon dioxide generated also served to propel the foam out of the container, be it a portable fire extinguisher or fixed installation using hoses. Chemical foam is considered obsolete in the United States and has been replaced by synthetic mechanical foams, such as AFFF which have a longer shelf life, are more effective, and more versatile, although some countries such as Japan and India continue to use it

### **Using Activated Alumina or Enhanced Coagulation with Alum**

If you plan on using activated alumina or enhanced coagulation with alum to treat your water, consider testing the water periodically for aluminum in the distribution system. While not a concern in terms of health effects, aluminum concentrations as low as 0.05 mg/L can result in customer complaints about particles or color in their water.

### **Reducing pH During Treatment**

Some arsenic treatment technologies require the pH to be reduced as a treatment step. If your system has adopted one of these techniques, be sure your pH is raised to a level that will not cause corrosion problems in your pipes. If you already have a corrosion control program in place, review whether you will need to adjust your corrosion chemical dose in response to any change in your water quality resulting from the installation of arsenic treatment. Keep in mind that adjusting the pH upward for lead and copper control may also cause arsenic to be released from scale on pipes and components.

### **Installing a Treatment Technology that Uses Iron**

If you have installed an arsenic removal treatment technology that uses iron, you should **not** see elevated levels of iron in the water entering the distribution system if the treatment technology is being operated properly. However, if the treatment technology has been recently installed and operational adjustments are still being made, you may see elevated iron levels after treatment.

You may also see elevated iron levels if you are blending with iron-rich water. In these cases, keep in mind that arsenic adsorbs onto iron, and the iron may deposit in your pipes and storage tanks. This arsenic-rich iron could dislodge and be re-suspended in the water when flows increase. If this happens, consumers may receive pulses of water containing high levels of arsenic and iron, and should be warned not to consume the water if it appears rusty in color.

Researchers found that chlorinating the water caused the formation of ferri-hydroxide solids. The minimal arsenic present in the groundwater was being concentrated as it absorbed onto the solids. Copper oxide particulates also formed and were released. To some extent, the polyphosphates served a useful role by keeping iron in solution and counteracting the tendency for the iron oxides to form, but additional steps were needed. For six months the system alternated their chlorination schedule: on for one day then off two days.

## Calcium- Post-Transition Metal

**Calcium** is the chemical element with symbol **Ca** and atomic number 20. Calcium is a soft gray alkaline earth metal, and is the fifth-most-abundant element by mass in the Earth's crust. Calcium is also the fifth-most-abundant dissolved ion in seawater by both molarity and mass, after sodium, chloride, magnesium, and sulfate.

Calcium is essential for living organisms, in particular in cell physiology, where movement of the calcium ion  $\text{Ca}^{2+}$  into and out of the cytoplasm functions as a signal for many cellular processes. As a major material used in mineralization of bone, teeth and shells calcium is the most abundant metal by mass in many animals.

In chemical terms, calcium is reactive and soft for a metal (though harder than lead, it can be cut with a knife with difficulty). It is a silvery metallic element that must be extracted by electrolysis from a fused salt like calcium chloride.

Once produced, it rapidly forms a gray-white oxide and nitride coating when exposed to air. In bulk form (typically as chips or "turnings"), the metal is somewhat difficult to ignite, more so even than magnesium chips; but, when lit, the metal burns in air with a brilliant high-intensity orange-red light.



Calcium metal reacts with water, evolving hydrogen gas at a rate rapid enough to be noticeable, but not fast enough at room temperature to generate much heat. In powdered form, however, the reaction with water is extremely rapid, as the increased surface area of the powder accelerates the reaction with the water.

Part of the slowness of the calcium-water reaction results from the metal being partly protected by insoluble white calcium hydroxide. In water solutions of acids, where this salt is soluble, calcium reacts vigorously.

Calcium, with a density of  $1.55 \text{ g/cm}^3$ , is the lightest of the alkaline earth metals; magnesium (specific gravity 1.74) and beryllium (1.84) are more dense, although lighter in atomic mass. From strontium onward, the alkali earth metals become more dense with increasing atomic mass. It has two allotropes.

Calcium has a higher electrical resistivity than copper or aluminum, yet weight-for-weight, due to its much lower density, it is a rather better conductor than either. However, its use in terrestrial applications is usually limited by its high reactivity with air.

Calcium salts are colorless from any contribution of the calcium, and ionic solutions of calcium ( $\text{Ca}^{2+}$ ) are colorless as well.

As with magnesium salts and other alkaline earth metal salts, calcium salts are often quite soluble in water. Notable exceptions include the hydroxide, the sulfate (unusual for sulfate salts), the carbonate and the phosphates. With the exception of the sulfate, even the insoluble ones listed are in general more soluble than its transition metal counterparts.

When in solution, the calcium ion to the human taste varies remarkably, being reported as mildly salty, sour, "mineral like" or even "soothing." It is apparent that many animals can taste, or develop a taste, for calcium, and use this sense to detect the mineral in salt licks or other sources. In human nutrition, soluble calcium salts may be added to tart juices without much effect to the average palate.

Calcium is the fifth-most-abundant element by mass in the human body, where it is a common cellular ionic messenger with many functions, and serves also as a structural element in bone. It is the relatively high-atomic-number calcium in the skeleton that causes bone to be radio-opaque.

Of the human body's solid components after drying and burning of organics (as for example, after cremation), about a third of the total "mineral" mass remaining, is the approximately one kilogram of calcium that composes the average skeleton (the remainder being mostly phosphorus and oxygen).

Calcium, combined with phosphate to form hydroxylapatite, is the mineral portion of human and animal bones and teeth. The mineral portion of some corals can also be transformed into hydroxylapatite.

Calcium hydroxide (slaked lime) is used in many chemical refinery processes and is made by heating limestone at high temperature (above  $825\text{ }^{\circ}\text{C}$ ) and then carefully adding water to it. When lime is mixed with sand, it hardens into a mortar and is turned into plaster by carbon dioxide uptake. Mixed with other compounds, lime forms an important part of Portland cement.

Calcium carbonate ( $\text{CaCO}_3$ ) is one of the common compounds of calcium. It is heated to form quicklime ( $\text{CaO}$ ), which is then added to water ( $\text{H}_2\text{O}$ ). This forms another material known as slaked lime ( $\text{Ca}(\text{OH})_2$ ), which is an inexpensive base material used throughout the chemical industry. Chalk, marble, and limestone are all forms of calcium carbonate.

When water percolates through limestone or other soluble carbonate rocks, it partially dissolves the rock and causes cave formation and characteristic stalactites and stalagmites and also forms hard water.

Other important calcium compounds are calcium nitrate, calcium sulfide, calcium chloride, calcium carbide, calcium cyanamide and calcium hypochlorite. A few calcium compounds in the oxidation state +1 have also been investigated recently.

## Isotopes

Calcium has four stable isotopes ( $^{40}\text{Ca}$ ,  $^{42}\text{Ca}$ ,  $^{43}\text{Ca}$  and  $^{44}\text{Ca}$ ), plus two more isotopes ( $^{46}\text{Ca}$  and  $^{48}\text{Ca}$ ) that have such long half-lives that for all practical purposes they also can be considered stable. The 20% range in relative mass among naturally occurring calcium isotopes is greater than for any element except hydrogen and helium. Calcium also has a cosmogenic isotope, radioactive  $^{41}\text{Ca}$ , which has a half-life of 103,000 years. Unlike cosmogenic isotopes that are produced in the atmosphere,  $^{41}\text{Ca}$  is produced by neutron activation of  $^{40}\text{Ca}$ . Most of its production is in the upper meter or so of the soil column, where the cosmogenic neutron flux is still sufficiently strong.  $^{41}\text{Ca}$  has received much attention in stellar studies because it decays to  $^{41}\text{K}$ , a critical indicator of solar-system anomalies.

Ninety-seven percent of naturally occurring calcium is in the form of  $^{40}\text{Ca}$ .  $^{40}\text{Ca}$  is one of the daughter products of  $^{40}\text{K}$  decay, along with  $^{40}\text{Ar}$ . While K-Ar dating has been used extensively in the geological sciences, the prevalence of  $^{40}\text{Ca}$  in nature has impeded its use in dating. Techniques using mass spectrometry and a double spike isotope dilution have been used for K-Ca age dating.

The most abundant isotope,  $^{40}\text{Ca}$ , has a nucleus of 20 protons and 20 neutrons. This is the heaviest stable isotope of any element that has equal numbers of protons and neutrons. In supernova explosions, calcium is formed from the reaction of carbon with various numbers of alpha particles (helium nuclei), until the most common calcium isotope (containing 10 helium nuclei) has been synthesized.

## Isotope Fractionation

As with the isotopes of other elements, a variety of processes fractionate, or alter the relative abundance of, calcium isotopes. The best studied of these processes is the mass dependent fractionation of calcium isotopes that accompanies the precipitation of calcium minerals, such as calcite, aragonite and apatite, from solution.

Isotopically light calcium is preferentially incorporated into minerals, leaving the solution from which the mineral precipitated enriched in isotopically heavy calcium. At room temperature the magnitude of this fractionation is roughly 0.25‰ (0.025%) per atomic mass unit (AMU). Mass-dependent differences in calcium isotope composition conventionally are expressed the ratio of two isotopes (usually  $^{44}\text{Ca}/^{40}\text{Ca}$ ) in a sample compared to the same ratio in a standard reference material.  $^{44}\text{Ca}/^{40}\text{Ca}$  varies by about 1% among common earth materials.

Calcium isotope fractionation during mineral formation has led to several applications of calcium isotopes. In particular, the 1997 observation by Skulan and DePaolo that calcium minerals are isotopically lighter than the solutions from which the minerals precipitate is the basis of analogous applications in medicine and in paleoceanography.

In animals with skeletons mineralized with calcium the calcium isotopic composition of soft tissues reflects the relative rate of formation and dissolution of skeletal mineral. In humans changes in the calcium isotopic composition of urine have been shown to be related to changes in bone mineral balance. When the rate of bone formation exceeds the rate of bone resorption, soft tissue  $^{44}\text{Ca}/^{40}\text{Ca}$  rises. Soft tissue  $^{44}\text{Ca}/^{40}\text{Ca}$  falls when bone resorption exceeds bone formation.

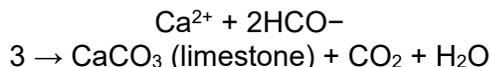
Because of this relationship, calcium isotopic measurements of urine or blood may be useful in the early detection of metabolic bone diseases like osteoporosis.

A similar system exists in the ocean, where seawater  $^{44}\text{Ca}/^{40}\text{Ca}$  tends to rise when the rate of removal of  $\text{Ca}^{2+}$  from seawater by mineral precipitation exceeds the input of new calcium into the ocean, and fall when calcium input exceeds mineral precipitation. It follows that rising  $^{44}\text{Ca}/^{40}\text{Ca}$  corresponds to falling seawater  $\text{Ca}^{2+}$  concentration, and falling  $^{44}\text{Ca}/^{40}\text{Ca}$  corresponds to rising seawater  $\text{Ca}^{2+}$  concentration. In 1997 Skulan and DePaolo presented the first evidence of change in seawater  $^{44}\text{Ca}/^{40}\text{Ca}$  over geologic time, along with a theoretical explanation of these changes. More recent papers have confirmed this observation, demonstrating that seawater  $\text{Ca}^{2+}$  concentration is not constant, and that the ocean probably never is in “steady state” with respect to its calcium input and output.

### Geochemical Cycling

Calcium provides an important link between tectonics, climate and the carbon cycle. In the simplest terms, uplift of mountains exposes Ca-bearing rocks to chemical weathering and releases  $\text{Ca}^{2+}$  into surface water. This  $\text{Ca}^{2+}$  eventually is transported to the ocean where it reacts with dissolved  $\text{CO}_2$  to form limestone. Some of this limestone settles to the sea floor where it is incorporated into new rocks. Dissolved  $\text{CO}_2$ , along with carbonate and bicarbonate ions, are referred to as dissolved inorganic carbon (DIC).

The actual reaction is more complicated and involves the bicarbonate ion ( $\text{HCO}_3^-$ ) that forms when  $\text{CO}_2$  reacts with water at seawater pH:



Note that at ocean pH most of the  $\text{CO}_2$  produced in this reaction is immediately converted back into  $\text{HCO}_3^-$ . The reaction results in a net transport of one molecule of  $\text{CO}_2$  from the ocean/atmosphere into the lithosphere.

The result is that each  $\text{Ca}^{2+}$  ion released by chemical weathering ultimately removes one  $\text{CO}_2$  molecule from the surficial system (atmosphere, ocean, soils and living organisms), storing it in carbonate rocks where it is likely to stay for hundreds of millions of years.

The weathering of calcium from rocks thus scrubs  $\text{CO}_2$  from the ocean and atmosphere, exerting a strong long-term effect on climate. Analogous cycles involving magnesium, and to a much smaller extent strontium and barium, have the same effect.

As the weathering of limestone ( $\text{CaCO}_3$ ) liberates equimolar amounts of  $\text{Ca}^{2+}$  and  $\text{CO}_2$ , it has no net effect on the  $\text{CO}_2$  content of the atmosphere and ocean. The weathering of silicate rocks like granite, on the other hand, is a net  $\text{CO}_2$  sink because it produces abundant  $\text{Ca}^{2+}$  but very little  $\text{CO}_2$ .

## History

Lime as building material was used since prehistoric times going as far back as 7000 to 14000 BC. The first dated lime kiln dates back to 2500 BC and was found in Khafajah Mesopotamia. Calcium (from Latin *calx*, genitive *calcis*, meaning "lime") was known as early as the first century when the Ancient Romans prepared lime as calcium oxide. Literature dating back to 975 AD notes that plaster of paris (calcium sulfate), is useful for setting broken bones. It was not isolated until 1808 in England when Sir Humphry Davy electrolyzed a mixture of lime and mercuric oxide. Davy was trying to isolate calcium; when he heard that Swedish chemist Jöns Jakob Berzelius and Pontin prepared calcium amalgam by electrolyzing lime in mercury, he tried it himself.

He worked with electrolysis throughout his life and also discovered/isolated sodium, potassium, magnesium, boron and barium. Calcium metal was not available in large scale until the beginning of the 20th century.

## Occurrence

Calcium is not naturally found in its elemental state. Calcium occurs most commonly in sedimentary rocks in the minerals calcite, dolomite and gypsum. It also occurs in igneous and metamorphic rocks chiefly in the silicate minerals: plagioclases, amphiboles, pyroxenes and garnets.

## Applications

Calcium is used

- as a reducing agent in the extraction of other metals, such as uranium, zirconium, and thorium.
- as a deoxidizer, desulfurizer, or decarbonizer for various ferrous and nonferrous alloys.
- as an alloying agent used in the production of aluminum, beryllium, copper, lead, and magnesium alloys.
- in the making of cements and mortars to be used in construction.
- in the making of cheese, where calcium ions influence the activity of rennin in bringing about the coagulation of milk.

## Calcium Compounds

- Calcium carbonate ( $\text{CaCO}_3$ ) is used in manufacturing cement and mortar, lime, limestone (usually used in the steel industry) and aids in production in the glass industry. It also has chemical and optical uses as mineral specimens in toothpastes, for example.
- Calcium hydroxide solution ( $\text{Ca(OH)}_2$ ) (also known as limewater) is used to detect the presence of carbon dioxide by being bubbled through a solution. It turns cloudy where  $\text{CO}_2$  is present.
- Calcium arsenate ( $\text{Ca}_3(\text{AsO}_4)_2$ ) is used in insecticides.
- Calcium carbide ( $\text{CaC}_2$ ) is used to make acetylene gas (for use in acetylene torches for welding) and in the manufacturing of plastics.
- Calcium chloride ( $\text{CaCl}_2$ ) is used in ice removal and dust control on dirt roads, in conditioner for concrete, as an additive in canned tomatoes, and to provide body for automobile tires.
- Calcium cyclamate ( $\text{Ca}(\text{C}_6\text{H}_{11}\text{NHSO}_3)_2$ ) was used as a sweetening agent but is no longer permitted for use because of suspected cancer-causing properties.
- Calcium gluconate ( $\text{Ca}(\text{C}_6\text{H}_{11}\text{O}_7)_2$ ) is used as a food additive and in vitamin pills.

- Calcium hypochlorite ( $\text{Ca}(\text{OCl})_2$ ) is used as a swimming pool disinfectant, as a bleaching agent, as an ingredient in deodorant, and in algaecide and fungicide.
- Calcium permanganate ( $\text{Ca}(\text{MnO}_4)_2$ ) is used in liquid rocket propellant, textile production, as a water sterilizing agent and in dental procedures.
- Calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ) is used as a supplement for animal feed, fertilizer, in commercial production for dough and yeast products, in the manufacture of glass, and in dental products.
- Calcium phosphide ( $\text{Ca}_3\text{P}_2$ ) is used in fireworks, rodenticide, torpedoes and flares.
- Calcium stearate ( $\text{Ca}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$ ) is used in the manufacture of wax crayons, cements, certain kinds of plastics and cosmetics, as a food additive, in the production of water resistant materials and in the production of paints.
- Calcium sulfate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is used as common blackboard chalk, as well as, in its hemihydrate form better known as Plaster of Paris.
- Calcium tungstate ( $\text{CaWO}_4$ ) is used in luminous paints, fluorescent lights and in X-ray studies.
- Hydroxylapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ), but is usually written  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  makes up seventy percent of bone. Also carbonated-calcium deficient hydroxylapatite is the main mineral of which dental enamel and dentin are comprised.

### Hazards and Toxicity

- Compared with other metals, the calcium ion and most calcium compounds have low toxicity. This is not surprising given the very high natural abundance of calcium compounds in the environment and in organisms. Calcium poses few serious environmental problems, with kidney stones the most common side-effect in clinical studies. Acute calcium poisoning is rare, and difficult to achieve unless calcium compounds are administered intravenously. For example, the oral median lethal dose ( $\text{LD}_{50}$ ) for rats for calcium carbonate and calcium chloride are 6.45 and 1.4 g/kg, respectively.
- Calcium metal is hazardous because of its sometimes-violent reactions with water and acids. Calcium metal is found in some drain cleaners, where it functions to generate heat and calcium hydroxide that saponifies the fats and liquefies the proteins (e.g., hair) that block drains. When swallowed calcium metal has the same effect on the mouth, esophagus and stomach, and can be fatal.
- Excessive consumption of calcium carbonate antacids/dietary supplements (such as Tums) over a period of weeks or months can cause milk-alkali syndrome, with symptoms ranging from hypercalcemia to potentially fatal renal failure. What constitutes “excessive” consumption is not well known and, it is presumed, varies a great deal from person to person. Persons consuming more than 10 grams/day of  $\text{CaCO}_3$  (=4 g Ca) are at risk of developing milk-alkali syndrome, but the condition has been reported in at least one person consuming only 2.5 grams/day of  $\text{CaCO}_3$  (=1 g Ca), an amount usually considered moderate and safe.
- Oral calcium supplements diminish the absorption of thyroxine when taken within four to six hours of each other. Thus, people taking both calcium and thyroxine run the risk of inadequate thyroid hormone replacement and thence hypothyroidism if they take them simultaneously or near-simultaneously

### Sources of Hardness

Water's hardness is determined by the concentration of multivalent cations in the water. Multivalent cations are cations (positively charged metal complexes) with a charge greater than 1+. Usually, the cations have the charge of 2+. Common cations found in hard water include  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .

These ions enter a water supply by leaching from minerals within an aquifer. Common calcium-containing minerals are calcite and gypsum. A common magnesium mineral is dolomite (which also contains calcium). Rainwater and distilled water are soft, because they also contain few ions.

The following equilibrium reaction describes the dissolving/formation of calcium carbonate scales:



Calcium carbonate scales formed in water-heating systems are called limescale. Calcium and magnesium ions can sometimes be removed by water softeners.

### **Temporary hardness**

Temporary hardness is a type of water hardness caused by the presence of dissolved bicarbonate minerals (calcium bicarbonate and magnesium bicarbonate). When dissolved, these minerals yield calcium and magnesium cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and carbonate and bicarbonate anions ( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ).

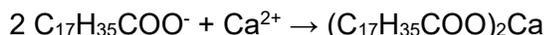
The presence of the metal cations makes the water hard. However, unlike the permanent hardness caused by sulfate and chloride compounds, this "temporary" hardness can be reduced either by boiling the water, or by the addition of lime (calcium hydroxide) through the softening process of lime softening. Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon cooling.

### **Permanent Hardness**

Permanent hardness is hardness (mineral content) that cannot be removed by boiling. When this is the case, it is usually caused by the presence of calcium and magnesium sulfates and/or chlorides in the water, which become more soluble as the temperature increases. Despite the name, the hardness of the water can be easily removed using a water softener, or ion exchange column.

### **Effects of Hard Water**

With hard water, soap solutions form a white precipitate (soap scum) instead of producing lather. This effect arises because the  $2+$  ions destroy the surfactant properties of the soap by forming a solid precipitate (the soap scum). A major component of such scum is calcium stearate, which arises from sodium stearate, the main component of soap:



Hardness can thus be defined as the soap-consuming capacity of a water sample, or the capacity of precipitation of soap as a characteristic property of water that prevents the lathering of soap. Synthetic detergents do not form such scums.

Hard water also forms deposits that clog plumbing. These deposits, called "scale", are composed mainly of calcium carbonate ( $\text{CaCO}_3$ ), magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ), and calcium sulfate ( $\text{CaSO}_4$ ). Calcium and magnesium carbonates tend to be deposited as off-white solids on the surfaces of pipes and the surfaces of heat exchangers.

This precipitation (formation of an insoluble solid) is principally caused by thermal decomposition of bi-carbonate ions but also happens to some extent even in the absence of such ions.

The resulting build-up of scale restricts the flow of water in pipes. In boilers, the deposits impair the flow of heat into water, reducing the heating efficiency and allowing the metal boiler components to overheat. In a pressurized system, this overheating can lead to failure of the boiler. The damage caused by calcium carbonate deposits varies depending on the crystalline form, for example, calcite or aragonite.

The presence of ions in an electrolyte, in this case, hard water, can also lead to galvanic corrosion, in which one metal will preferentially corrode when in contact with another type of metal, when both are in contact with an electrolyte. The softening of hard water by ion exchange does not increase its corrosivity *per se*. Similarly, where lead plumbing is in use, softened water does not substantially increase plumbo-solvency.

In swimming pools, hard water is manifested by a turbid, or cloudy (milky), appearance to the water. Calcium and magnesium hydroxides are both soluble in water. The solubility of the hydroxides of the alkaline-earth metals to which calcium and magnesium belong (group 2 of the periodic table) increases moving down the column.

Aqueous solutions of these metal hydroxides absorb carbon dioxide from the air, forming the insoluble carbonates, giving rise to the turbidity. This often results from the alkalinity (the hydroxide concentration) being excessively high ( $\text{pH} > 7.6$ ). Hence, a common solution to the problem is to, while maintaining the chlorine concentration at the proper level, raise the acidity (lower the pH) by the addition of hydrochloric acid, the optimum value being in the range of 7.2 to 7.6.

### **Softening**

For the reasons discussed above, it is often desirable to soften hard water. Most detergents contain ingredients that counteract the effects of hard water on the surfactants. For this reason, water softening is often unnecessary. Where softening is practiced, it is often recommended to soften only the water sent to domestic hot water systems so as to prevent or delay inefficiencies and damage due to scale formation in water heaters. A common method for water softening involves the use of ion exchange resins, which replace ions like  $\text{Ca}^{2+}$  by twice the number of monocations such as sodium or potassium ions.

### **Health Considerations**

The World Health Organization says that "there does not appear to be any convincing evidence that water hardness causes adverse health effects in humans".

Some studies have shown a weak inverse relationship between water hardness and cardiovascular disease in men, up to a level of 170 mg calcium carbonate per liter of water. The World Health Organization has reviewed the evidence and concluded the data were inadequate to allow for a recommendation for a level of hardness.

Recommendations have been made for the maximum and minimum levels of calcium (40–80 ppm) and magnesium (20–30 ppm) in drinking water, and a total hardness expressed as the sum of the calcium and magnesium concentrations of 2–4 mmol/L.

Other studies have shown weak correlations between cardiovascular health and water hardness.

Some studies correlate domestic hard water usage with increased eczema in children. The Softened-Water Eczema Trial (SWET), a multicenter randomized controlled trial of ion-exchange softeners for treating childhood eczema, was undertaken in 2008. However, no meaningful difference in symptom relief was found between children with access to a home water softener and those without.

### Measurement

Hardness can be quantified by instrumental analysis. The total water hardness is the sum of the molar concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , in mol/L or mmol/L units. Although water hardness usually measures only the total concentrations of calcium and magnesium (the two most prevalent divalent metal ions), iron, aluminum, and manganese can also be present at elevated levels in some locations. The presence of iron characteristically confers a brownish (rust-like) colour to the calcification, instead of white (the color of most of the other compounds).

Water hardness is often not expressed as a molar concentration, but rather in various units, such as degrees of general hardness (dGH), German degrees ( $^{\circ}\text{dH}$ ), parts per million (ppm, mg/L, or American degrees), grains per gallon (gpg), English degrees ( $^{\circ}\text{e}$ , e, or  $^{\circ}\text{Clark}$ ), or French degrees ( $^{\circ}\text{f}$ ). The table below shows conversion factors between the various units.

#### Hardness unit conversion.

	mmol/L	ppm, mg/L	dGH, $^{\circ}\text{dH}$	gpg	$^{\circ}\text{e}$ , $^{\circ}\text{Clark}$	$^{\circ}\text{f}$
mmol/L	1	0.009991	0.1783	0.171	0.1424	0.09991
ppm, mg/L	100.1	1	17.85	17.12	14.25	10
dGH, $^{\circ}\text{dH}$	5.608	0.05603	1	0.9591	0.7986	0.5603
gpg	5.847	0.05842	1.043	1	0.8327	0.5842
$^{\circ}\text{e}$ , $^{\circ}\text{Clark}$	7.022	0.07016	1.252	1.201	1	0.7016
$^{\circ}\text{f}$	10.01	0.1	1.785	1.712	1.425	1

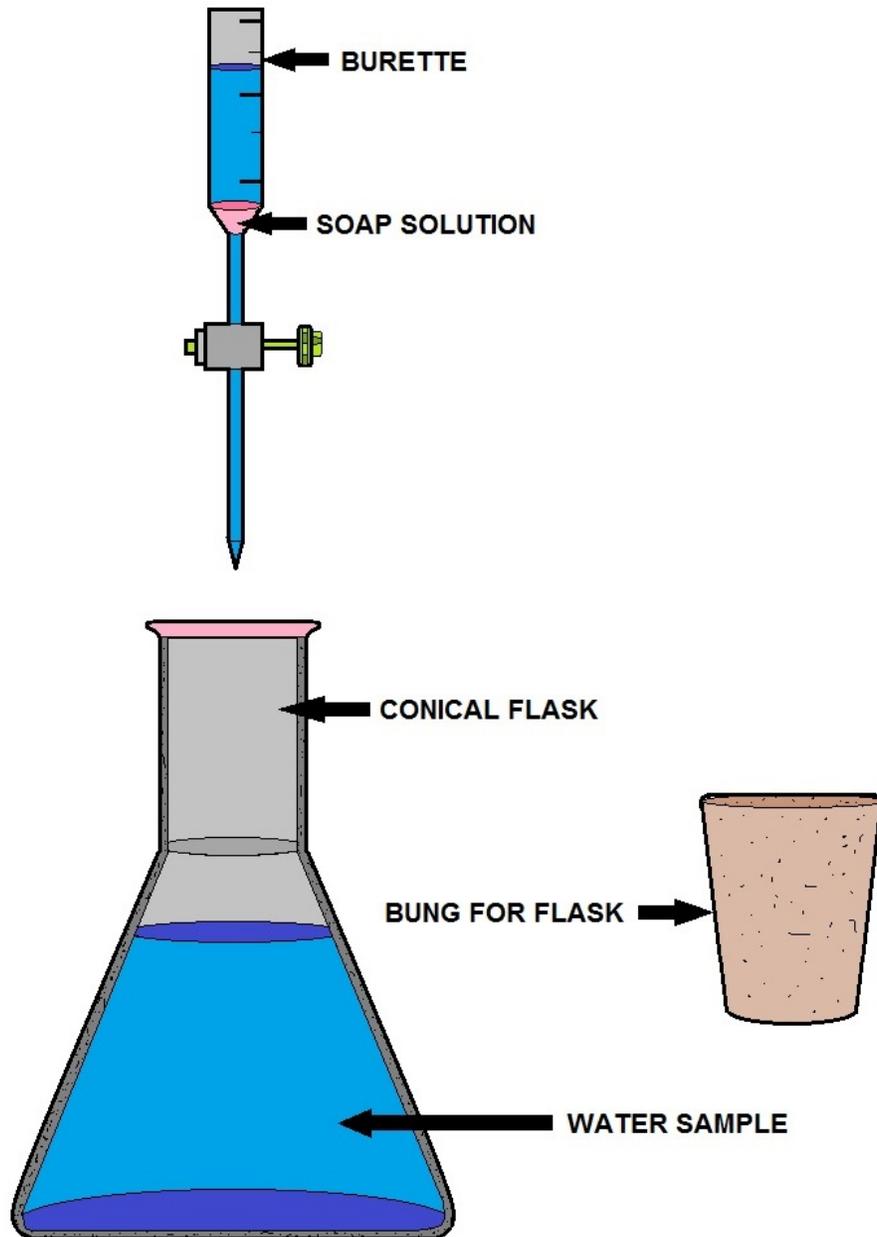
For example: 1 mmol/L = 100.1 ppm and 1 ppm = 0.056 dGH.

The various alternative units represent an equivalent mass of calcium oxide (CaO) or calcium carbonate ( $\text{CaCO}_3$ ) that, when dissolved in a unit volume of pure water, would result in the same total molar concentration of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . The different conversion factors arise from the fact that equivalent masses of calcium oxide and calcium carbonates differ, and that different mass and volume units are used.

#### The units are as follows:

- *Parts per million (ppm)* is usually defined as 1 mg/L  $\text{CaCO}_3$  (the definition used below). It is equivalent to **mg/L** without chemical compound specified, and to **American Degree**.
- *Grains per Gallon (gpg)* is defined as 1 grain (64.8 mg) of calcium carbonate per U.S. gallon (3.79 liters), or 17.118 ppm.
- a *mmol/L* is equivalent to 100.09 mg/L  $\text{CaCO}_3$  or 40.08 mg/L  $\text{Ca}^{2+}$ .
- A *degree of General Hardness (dGH or 'German degree ( $^{\circ}\text{dH}$ , *deutsche Härte*)'* is defined as 10 mg/L CaO or 17.848 ppm.

- A *Clark degree* ( $^{\circ}\text{Clark}$ ) or *English degrees* ( $^{\circ}\text{e}$  or  $e$ ) is defined as one grain (64.8 mg) of  $\text{CaCO}_3$  per Imperial gallon (4.55 liters) of water, equivalent to 14.254 ppm.
- A *French degree* ( $^{\circ}\text{F}$  or  $f$ ) is defined as 10 mg/L  $\text{CaCO}_3$ , equivalent to 10 ppm. The lowercase  $f$  is often used to prevent confusion with degrees Fahrenheit.



## TESTING FOR THE HARDNESS OF WATER

## Hard/Soft Classification

Because it is the precise mixture of minerals dissolved in the water, together with the water's pH and temperature, that determines the behavior of the hardness, a single-number scale does not adequately describe hardness.

However, the United States Geological Survey uses the following classification into hard and soft water.

Classification	hardness in mg/L	hardness in mmol/L	hardness in dGH/°dH
Soft	0–60	0.3-3.00	
Moderately hard	61–120	0.61–1.20	3.72-6.75
Hard	121–180	1.21–1.80	6.78–10.08
Very hard	≥ 181	≥ 1.81	≥ 10.14

### Indices

Several indices are used to describe the behavior of calcium carbonate in water, oil, or gas mixtures.

#### Langelier Saturation Index (LSI)

The Langelier Saturation Index (sometimes Langelier Stability Index) is a calculated number used to predict the calcium carbonate stability of water. It indicates whether the water will precipitate, dissolve, or be in equilibrium with calcium carbonate. In 1936, Wilfred Langelier developed a method for predicting the pH at which water is saturated in calcium carbonate (called pHs).

The LSI is expressed as the difference between the actual system pH and the saturation pH:

$$\text{LSI} = \text{pH (measured)} - \text{pHs}$$

- For LSI > 0, water is super saturated and tends to precipitate a scale layer of CaCO<sub>3</sub>.
- For LSI = 0, water is saturated (in equilibrium) with CaCO<sub>3</sub>. A scale layer of CaCO<sub>3</sub> is neither precipitated nor dissolved.
- For LSI < 0, water is under saturated and tends to dissolve solid CaCO<sub>3</sub>.

If the actual pH of the water is below the calculated saturation pH, the LSI is negative and the water has a very limited scaling potential. If the actual pH exceeds pHs, the LSI is positive, and being supersaturated with CaCO<sub>3</sub>, the water has a tendency to form scale. At increasing positive index values, the scaling potential increases.

In practice, water with an LSI between -0.5 and +0.5 will not display enhanced mineral dissolving or scale forming properties. Water with an LSI below -0.5 tends to exhibit noticeably increased dissolving abilities while water with an LSI above +0.5 tends to exhibit noticeably increased scale forming properties.

It is also worth noting that the LSI is temperature sensitive. The LSI becomes more positive as the water temperature increases. This has particular implications in situations where well water is used.

The temperature of the water when it first exits the well is often significantly lower than the temperature inside the building served by the well or at the laboratory where the LSI measurement is made. This increase in temperature can cause scaling, especially in cases such as hot water heaters. Conversely, systems that reduce water temperature will have less scaling.

### **Ryznar Stability Index (RSI)**

The Ryznar stability index (RSI) uses a database of scale thickness measurements in municipal water systems to predict the effect of water chemistry.

Ryznar saturation index (RSI) was developed from empirical observations of corrosion rates and film formation in steel mains. It is defined as:

$$\text{RSI} = 2 \text{ pHs} - \text{pH (measured)}$$

- For  $6,5 < \text{RSI} < 7$  water is considered to be approximately at saturation equilibrium with calcium carbonate
- For  $\text{RSI} > 8$  water is under saturated and, therefore, would tend to dissolve any existing solid  $\text{CaCO}_3$
- For  $\text{RSI} < 6,5$  water tends to be scale forming

### **Puckorius Scaling Index (PSI)**

The Puckorius Scaling Index (PSI) uses slightly different parameters to quantify the relationship between the saturation state of the water and the amount of limescale deposited.

### **Other Indices**

Other indices include the Larson-Skold Index, the Stiff-Davis Index, and the Oddo-Tomson Index.

### **Hard Water in the United States**

More than 85% of American homes have hard water. The softest waters occur in parts of the New England, South Atlantic-Gulf, Pacific Northwest, and Hawaii regions. Moderately hard waters are common in many of the rivers of the Tennessee, Great Lakes, and Alaska regions. Hard and very hard waters are found in some of the streams in most of the regions throughout the country. The hardest waters (greater than 1,000 ppm) are in streams in Texas, New Mexico, Kansas, Arizona, and southern California.

## Carbon-Allotrope

Carbon is ordinarily classified as a nonmetal although it has some metallic properties and is occasionally classified as a metalloid. Where applicable, properties listed below are for hexagonal graphitic carbon, the most thermodynamically stable form of carbon under ambient conditions.

### In terms of the Metallic Character of Carbon:

- It has a lustrous appearance.
- It shows good electrical conductivity.
- It has a positive temperature coefficient of electrical resistivity, in the direction of its planes, that is, its conductivity decreases with increasing temperature (behaving in this way as a metal).
- It has the electronic band structure of a semimetal.
- The various allotropes of carbon, including graphite, are capable of accepting foreign atoms or compounds into their structures via substitution, intercalation or doping (interstitial or intrastitial) with the resulting materials being referred to as 'carbon alloys'.
- It can form ionic salts, including a sulphate, perchlorate, nitrate, hydrogen selenate, and hydrogen phosphate.
- In organic chemistry, carbon can form complex cations—termed *carbocations*—in which the positive charge is on the carbon atom; examples are  $\text{CH}_3^+$ ,  $\text{CH}_5^+$ , and their derivatives.



### In terms of the Nonmetallic Character of Carbon:

- It is brittle.
- It behaves as a semiconductor, perpendicular to the direction of its planes.
- Most of its chemistry is nonmetallic.
- It has relatively high ionization energy.
- It has a relatively high electronegativity, compared to most metals.
- Its oxide  $\text{CO}_2$  forms a medium-strength *carbonic acid*  $\text{H}_2\text{CO}_3$ .

### Carbon Filtering

Carbon filtering is a method of filtering that uses a piece of activated carbon to remove contaminants and impurities, utilizing chemical adsorption.

Each piece of carbon is designed to provide a large section of surface area, in order to allow contaminants, the most possible exposure to the filter media. One pound (450 g) of activated carbon contains a surface area of approximately 100 acres (40 Hectares). This carbon is generally activated with a positive charge and is designed to attract negatively

charged water contaminants. Carbon filtering is commonly used for water purification, but is also used in air purifiers.

Carbon filters are most effective at removing chlorine, sediment, and volatile organic compounds (VOCs) from water. They are not effective at removing minerals, salts, and dissolved inorganic compounds.

Typical particle sizes that can be removed by carbon filters range from 0.5 to 50 micrometers. The particle size will be used as part of the filter description. The efficacy of a carbon filter is also based upon the flow rate regulation. When the water is allowed to flow through the filter at a slower rate, the contaminants are exposed to the filter media for a longer amount of time.

In certain regions, the treatment of the water intended for potable purposes is not necessary throughout the whole of the year. The presence of taste, odor and toxins is dependent largely on the biological action in areas where lake or reservoir supply is common. It is therefore often more cost-effective to use temporary or intermittent dosing of activated carbon into the water only during times when treatment is required. During these times, the use of Powdered Activated Carbon (PAC) is preferred as no costly fixed bed filtration equipment is required. The PAC can be dosed directly to existing flocculent tanks at a prescribed rate to achieve the level of removal of taste, odor and toxins as required.

Following dosing of PAC, the activated carbon is removed as part of the flocculation process, or subsequently filtered mechanically. The water is then disinfected for supply to the distribution network.

Nonmetals in the 'near-metalloid' category include carbon, phosphorus, selenium and iodine. They exhibit metallic luster, semiconducting properties and bonding or valence bands with delocalized character.

This applies to their most thermodynamically stable forms under ambient conditions: carbon as graphite; phosphorus as black phosphorus; and selenium as grey selenium. These elements are alternatively described as being 'near metalloidal', showing metalloidal character, or having metalloid-like or some metalloid(al) or metallic properties.

### **Carbon Group**

The **carbon group** is a periodic table group consisting of carbon (**C**), silicon (**Si**), germanium (**Ge**), tin (**Sn**), lead (**Pb**), and flerovium (**Fl**).

In modern IUPAC notation, it is called **Group 14**. In the old IUPAC and CAS systems, it was called **Group IVB** and **Group IVA**, respectively.

In the field of semiconductor physics, it is still universally called **Group IV**. The group was once also known as the **tetrels** (from Greek *tetra*, four), stemming from the Roman numeral IV in the group names, or (not coincidentally) from the fact that these elements have four valence electrons (see below). Elements in the group are sometimes also referred as **tetragens**.

## Characteristics

### Chemical

Like other groups, the members of this family show patterns in its electron configuration, especially the outermost shells resulting in trends in chemical behavior:

Z	Element	No. of electrons/shell
6	Carbon	2, 4
14	Silicon	2, 8, 4
32	Germanium	2, 8, 18, 4
50	Tin	2, 8, 18, 18, 4
82	Lead	2, 8, 18, 32, 18, 4
114	Flerovium	2, 8, 18, 32, 32, 18, 4 (predicted)

Each of the elements in this group has 4 electrons in its outer energy level. The last orbital of all these elements is the  $p^2$  orbital. In most cases, the elements share their electrons. The tendency to lose electrons increases as the size of the atom increases, as it does with increasing atomic number.

Carbon alone forms negative ions, in the form of carbide ( $C^{4-}$ ) ions. Silicon and germanium, both metalloids, each can form +4 ions. Tin and lead both are metals while flerovium is a synthetic, radioactive (its half-life is very short), element that may have a few noble gas-like properties, though it is still most likely a post-transition metal. Tin and lead are both capable of forming +2 ions.

### Physical

#### Occurrence

Except for germanium and flerovium, all of these elements are familiar in daily life either as the pure element or in the form of compounds. However, except for silicon and carbon, none of these elements are particularly plentiful in the Earth's crust. Carbon forms a very large variety of compounds, in both the plant and animal kingdoms. Silicon and silicate minerals are fundamental components of the Earth's crust; silica (silicon dioxide) is the most common constituent of sand.

Tin and lead, although with very low abundances in the crust, are nevertheless common in everyday life. They occur in highly concentrated mineral deposits, can be obtained easily in the metallic state from those minerals, and are useful as metals and as alloys in many applications.

Germanium, on the other hand, forms few characteristic minerals and is most commonly found only in small concentrations in association with the mineral zinc blende and in coals. Although germanium is indeed one of the rarer elements, it assumed importance upon recognition of its properties as a semiconductor.



## Iron

**Iron** is a chemical element with the symbol **Fe** (from Latin: *ferrum*) and atomic number 26. It is a metal in the first transition series. It is the most common element (by mass) forming the planet Earth as a whole, forming much of Earth's outer and inner core. It is the fourth most common element in the Earth's crust. Iron's very common presence in rocky planets like Earth is due to its abundant production as a result of fusion in high-mass stars, where the production of nickel-56 (which decays to the most common isotope of iron) is the last nuclear fusion reaction that is exothermic. This causes radioactive nickel to become the last element to be produced before collapse of a supernova leads to the explosive events that scatter this precursor radionuclide of iron abundantly into space.

Like other group 8 elements, iron exists in a wide range of oxidation states,  $-2$  to  $+6$ , although  $+2$  and  $+3$  are the most common. Elemental iron occurs in meteoroids and other low oxygen environments, but is reactive to oxygen and water.



Fresh iron surfaces appear lustrous silvery-gray, but oxidize in normal air to give iron oxides, also known as rust. Unlike many other metals which form passivating oxide layers, iron oxides occupy more volume than iron metal, and thus iron oxides flake off and expose fresh surfaces for corrosion.

Iron metal has been used since ancient times, though copper alloys, which have lower melting temperatures, were used first in history. Pure iron is soft (softer than aluminum), but is unobtainable by smelting. The material is significantly hardened and strengthened by impurities from the smelting process, such as carbon.

A certain proportion of carbon (between 0.2% and 2.1%) produces steel, which may be up to 1000 times harder than pure iron.

Crude iron metal is produced in blast furnaces, where ore is reduced by coke to pig iron, which has a high carbon content. Further refinement with oxygen reduces the carbon content to the correct proportion to make steel.

Steels and low carbon iron alloys with other metals (alloy steels) are by far the most common metals in industrial use, due to their great range of desirable properties and the abundance of iron.

Iron chemical compounds, which include ferrous and ferric compounds, have many uses. Iron oxide mixed with aluminum powder can be ignited to create a thermite reaction, used in welding and purifying ores. It forms binary compounds with the halogens and the chalcogens.

Among its organometallic compounds is ferrocene, the first sandwich compound discovered. Iron plays an important role in biology, forming complexes with molecular oxygen in hemoglobin and myoglobin; these two compounds are common oxygen transport proteins in vertebrates. Iron is also the metal used at the active site of many important redox enzymes dealing with cellular respiration and oxidation and reduction in plants and animals.

The mechanical properties of iron and its alloys can be evaluated using a variety of tests, including the Brinell test, Rockwell test and the Vickers hardness test. The data on iron is so consistent that it is often used to calibrate measurements or to compare tests. However, the mechanical properties of iron are significantly affected by the sample's purity: pure research-purpose single crystals of iron are actually softer than aluminum, and the purest industrially produced iron (99.99%) has a hardness of 20–30 Brinell.

An increase in the carbon content of the iron will initially cause a significant corresponding increase in the iron's hardness and tensile strength. Maximum hardness of 65 R<sub>c</sub> is achieved with a 0.6% carbon content, although this produces a metal with a low tensile strength.

### Mechanical Properties

Characteristic values of tensile strength (TS) and Brinell hardness (BH) of different forms of iron.

Material	TS (MPa)	BH (Brinell)
Iron whiskers	11000	
Ausformed steel	(hardened) 2930	850–1200
Martensitic steel	2070	600
Bainitic steel	1380	400
Pearlitic steel	1200	350
Cold-worked iron	690	200
Small-grain iron	340	100
Carbon-containing iron	140	40
Pure, single-crystal iron	10	3

### Phase Diagram and Allotropes

Iron represents an example of allotropy in a metal. There are at least four allotropic forms of iron, known as  $\alpha$ ,  $\gamma$ ,  $\delta$ , and  $\epsilon$ ; at very high pressures, some controversial experimental evidence exists for a phase  $\beta$  stable at very high pressures and temperatures.

As molten iron cools down it crystallizes at 1538 °C into its  $\delta$  allotrope, which has a body-centered cubic (bcc) crystal structure. As it cools further its crystal structure changes to face-centered cubic (fcc) at 1394 °C, when it is known as  $\gamma$ -iron, or austenite. At 912 °C the crystal structure again becomes bcc as  $\alpha$ -iron, or ferrite, is formed, and at 770 °C (the Curie point, T<sub>c</sub>) iron becomes magnetic.

As the iron passes through the Curie temperature there is no change in crystalline structure, but there is a change in "domain structure", where each domain contains iron atoms with a particular electronic spin. In unmagnetized iron, all the electronic spins of the atoms within one domain are in the same direction; the neighboring domains point in various directions and thus cancel out.

In magnetized iron, the electronic spins of all the domains are aligned, so that the magnetic effects of neighboring domains reinforce each other. Although each domain contains billions of atoms, they are very small, about 10 micrometers across.<sup>[9]</sup> At pressures above approximately 10 GPa and temperatures of a few hundred kelvin or less,  $\alpha$ -iron changes into a hexagonal close-packed (hcp) structure, which is also known as  $\epsilon$ -iron; the higher-temperature  $\gamma$ -phase also changes into  $\epsilon$ -iron, but does so at higher pressure. The  $\beta$ -phase, if it exists, would appear at pressures of at least 50 GPa and temperatures of at least 1500 K; it has been thought to have an orthorhombic or a double hcp structure.

Iron is of greatest importance when mixed with certain other metals and with carbon to form steels. There are many types of steels, all with different properties, and an understanding of the properties of the allotropes of iron is key to the manufacture of good quality steels.

$\alpha$ -iron, also known as ferrite, is the most stable form of iron at normal temperatures. It is a fairly soft metal that can dissolve only a small concentration of carbon (no more than 0.021% by mass at 910 °C).

Above 912 °C and up to 1400 °C  $\alpha$ -iron undergoes a phase transition from bcc to the fcc configuration of  $\gamma$ -iron, also called austenite. This is similarly soft and metallic but can dissolve considerably more carbon (as much as 2.04% by mass at 1146 °C). This form of iron is used in the type of stainless steel used for making cutlery, and hospital and food-service equipment.

The high-pressure phases of iron are important as endmember models for the solid parts of planetary cores. The inner core of the Earth is generally assumed to consist essentially of an iron-nickel alloy with  $\epsilon$  (or  $\beta$ ) structure.

The melting point of iron is experimentally well constrained for pressures up to approximately 50 GPa. For higher pressures, different studies placed the  $\gamma$ - $\epsilon$ -liquid triple point at pressures differing by tens of gigapascals and yielded differences of more than 1000 K for the melting point. Generally speaking, molecular dynamics computer simulations of iron melting and shock wave experiments suggest higher melting points and a much steeper slope of the melting curve than static experiments carried out in diamond anvil cells.

### **Iron Nucleosynthesis**

Iron is created by extremely large, extremely hot (over 2.5 billion kelvin) stars through the silicon burning process. It is the heaviest stable element to be produced in this manner. The process starts with the second largest stable nucleus created by silicon burning: calcium. One stable nucleus of calcium fuses with one helium nucleus, creating unstable titanium. Before the titanium decays, it can fuse with another helium nucleus, creating unstable chromium. Before the chromium decays, it can fuse with another helium nucleus, creating unstable iron. Before the iron decays, it can fuse with another helium nucleus, creating unstable nickel-56.

Any further fusion of nickel-56 consumes energy instead of producing energy, so after the production of nickel-56, the star does not produce the energy necessary to keep the core from collapsing. Eventually, the nickel-56 decays to unstable cobalt-56 which, in turn decays to stable iron-56.

## Occurrence

### Planetary Occurrence

Iron is the sixth most abundant element in the Universe, and the most common refractory element. It is formed as the final exothermic stage of stellar nucleosynthesis, by silicon fusion in massive stars.

Metallic or native iron is rarely found on the surface of the Earth because it tends to oxidize, but its oxides are pervasive and represent the primary ores. While it makes up about 5% of the Earth's crust, both the Earth's inner and outer core are believed to consist largely of an iron-nickel alloy constituting 35% of the mass of the Earth as a whole. Iron is consequently the most abundant element on Earth, but only the fourth most abundant element in the Earth's crust.

Most of the iron in the crust is found combined with oxygen as iron oxide minerals such as hematite and magnetite. Large deposits of iron are found in banded iron formations. These geological formations are a type of rock consisting of repeated thin layers of iron oxides, either magnetite ( $\text{Fe}_3\text{O}_4$ ) or hematite ( $\text{Fe}_2\text{O}_3$ ), alternating with bands of iron-poor shale and chert.

About 1 in 20 meteorites consist of the unique iron-nickel minerals taenite (35–80% iron) and kamacite (90–95% iron). Although rare, iron meteorites are the main form of natural metallic iron on the Earth's surface. It was proven by Mössbauer spectroscopy that the red color of the surface of Mars is derived from an iron oxide-rich regolith.

## Chemistry and Compounds

Oxidation state	Representative compound
-2	Disodium tetracarbonylferrate (Collman's reagent)
-1	
0	Iron pentacarbonyl
1	Cyclopentadienyliron dicarbonyl dimer ("Fp <sub>2</sub> ")
2	Ferrous sulfate, ferrocene
3	Ferric chloride, ferrocenium tetrafluoroborate
4	Barium ferrate(IV)
5	
6	Potassium ferrate

Iron forms compounds mainly in the +2 and +3 oxidation states. Traditionally, iron(II) compounds are called ferrous, and iron(III) compounds ferric. Iron also occurs in higher oxidation states, an example being the purple potassium ferrate ( $\text{K}_2\text{FeO}_4$ ) which contains iron in its +6 oxidation state. Iron(IV) is a common intermediate in many in biochemical oxidation reactions. Numerous organometallic compounds contain formal oxidation states of +1, 0, -1, or even -2.

The oxidation states and other bonding properties are often assessed using the technique of Mössbauer spectroscopy. There are also many mixed valence compounds that contain both iron(II) and iron(III) centers, such as magnetite and Prussian blue ( $\text{Fe}_4(\text{Fe}[\text{CN}]_6)_3$ ). The latter is used as the traditional "blue" in blueprints.

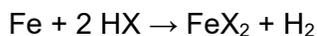
The iron compounds produced on the largest scale in industry are iron(II) sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and iron (III) chloride ( $\text{FeCl}_3$ ). The former is one of the most readily available sources of iron(II), but is less stable to aerial oxidation than Mohr's salt ( $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ). Iron(II) compounds tend to be oxidized to iron(III) compounds in the air.

Unlike many other metals, iron does not form amalgams with mercury. As a result, mercury is traded in standardized 76 pound flasks (34 kg) made of iron.

### Binary Compounds

Iron reacts with oxygen in the air to form various oxide and hydroxide compounds; the most common are iron (II,III) oxide ( $\text{Fe}_3\text{O}_4$ ), and iron (III) oxide ( $\text{Fe}_2\text{O}_3$ ). Iron (II) oxide also exists, though it is unstable at room temperature. These oxides are the principal ores for the production of iron (see bloomery and blast furnace). They are also used in the production of ferrites, useful magnetic storage media in computers, and pigments. The best known sulfide is iron pyrite ( $\text{FeS}_2$ ), also known as fool's gold owing to its golden luster.

The binary ferrous and ferric halides are well known, with the exception of ferric iodide. The ferrous halides typically arise from treating iron metal with the corresponding binary halogen acid to give the corresponding hydrated salts.



Iron reacts with fluorine, chlorine, and bromine to give the corresponding ferric halides, ferric chloride being the most common:



### Iron Coordination and Organometallic Compounds

Several cyanide complexes are known. The most famous example is Prussian blue, ( $\text{Fe}_4(\text{Fe}[\text{CN}]_6)_3$ ). Potassium ferricyanide and potassium ferrocyanide are also known; the formation of Prussian blue upon reaction with iron (II) and iron (III) respectively forms the basis of a "wet" chemical test. Prussian blue is also used as an antidote for thallium and radioactive caesium poisoning. Prussian blue can be used in laundry bluing to correct the yellowish tint left by ferrous salts in water.

Several carbonyl compounds of iron are known. The premier iron (0) compound is iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , which is used to produce carbonyl iron powder, a highly reactive form of metallic iron.

Thermolysis of iron pentacarbonyl gives the trinuclear cluster, triiron dodecacarbonyl. Collman's reagent, disodium tetracarbonylferrate, is a useful reagent for organic chemistry; it contains iron in the -2 oxidation state. Cyclopentadienyliron dicarbonyl dimer contains iron in the rare +1 oxidation state.

Ferrocene is an extremely stable complex. The first sandwich compound, it contains an iron (II) center with two cyclopentadienyl ligands bonded through all ten carbon atoms. This arrangement was a shocking novelty when it was first discovered, but the discovery of ferrocene has led to a new branch of organometallic chemistry.

Ferrocene itself can be used as the backbone of a ligand, e.g. dppf. Ferrocene can itself be oxidized to the ferrocenium cation ( $\text{Fc}^+$ ); the ferrocene/ferrocenium couple is often used as a reference in electrochemistry.

## Oxygen

**Oxygen** is a chemical element with symbol **O** and atomic number 8. Its name derives from the Greek roots ὀξύς (oxys) ("acid", literally "sharp", referring to the sour taste of acids) and -γόνοϛ (-gonos) ("producer", literally "begetter"), because at the time of naming, it was mistakenly thought that all acids required oxygen in their composition. At standard temperature and pressure, two atoms of the element bind to form dioxygen, colorless, odorless, tasteless diatomic gas with the formula  $O_2$ . This compound is an important part of the atmosphere, and is necessary to sustain terrestrial life.

Oxygen is a member of the chalcogen group on the periodic table and is a highly reactive nonmetallic element that readily forms compounds (notably oxides) with almost all other elements.

Oxygen is a strong oxidizing agent and has the second-highest electronegativity of all reactive elements, second only to fluorine. By mass, oxygen is the third-most abundant element in the universe, after hydrogen and helium and the most abundant element by mass in the Earth's crust, making up almost half of the crust's mass. Free oxygen is too chemically reactive to appear on Earth without the photosynthetic action of living organisms, which use the energy of sunlight to produce elemental oxygen from water. Elemental  $O_2$  only began to accumulate in the atmosphere after the evolutionary appearance of these organisms, roughly 2.5 billion years ago. Diatomic oxygen gas constitutes 20.8% of the volume of air.

Because it comprises most of the mass in water, oxygen comprises most of the mass of living organisms (for example, about two-thirds of the human body's mass). All major classes of structural molecules in living organisms, such as proteins, carbohydrates, and fats, contain oxygen, as do the major inorganic compounds that comprise animal shells, teeth, and bone. Elemental oxygen is produced by cyanobacteria, algae and plants, and is used in cellular respiration for all complex life.

Oxygen is toxic to obligately anaerobic organisms, which were the dominant form of early life on Earth until  $O_2$  began to accumulate in the atmosphere. Another form (allotrope) of oxygen, ozone ( $O_3$ ), helps protect the biosphere from ultraviolet radiation with the high-altitude ozone layer, but is a pollutant near the surface where it is a by-product of smog. At even higher low earth orbit altitudes atomic oxygen is a significant presence and a cause of erosion for spacecraft.

Oxygen was independently discovered by Carl Wilhelm Scheele, in Uppsala, in 1773 or earlier, and Joseph Priestley in Wiltshire, in 1774, but Priestley is often given priority because his work was published first. The name *oxygen* was coined in 1777 by Antoine Lavoisier, whose experiments with oxygen helped to discredit the then-popular phlogiston theory of combustion and corrosion.

Oxygen is produced industrially by fractional distillation of liquefied air, use of zeolites with pressure-cycling to concentrate oxygen from air, electrolysis of water and other means. Uses of oxygen include the production of steel, plastics and textiles; rocket propellant; oxygen therapy; and life support in aircraft, submarines, spaceflight and diving.

## Structure

At standard temperature and pressure, oxygen is a very pale blue, odorless gas with the molecular formula  $O_2$ , in which the two oxygen atoms are chemically bonded to each other with a spin triplet electron configuration. This bond has a bond order of two, and is often simplified in description as a double bond or as a combination of one two-electron bond and two three-electron bonds.

Triplet oxygen (not to be confused with ozone,  $O_3$ ) is the ground state of the  $O_2$  molecule. The electron configuration of the molecule has two unpaired electrons occupying two degenerate molecular orbitals. These orbitals are classified as antibonding (weakening the bond order from three to two), so the diatomic oxygen bond is weaker than the diatomic nitrogen triple bond in which all bonding molecular orbitals are filled, but some antibonding orbitals are not.

In normal triplet form,  $O_2$  molecules are paramagnetic. That is, they form a magnet in the presence of a magnetic field—because of the spin magnetic moments of the unpaired electrons in the molecule, and the negative exchange energy between neighboring  $O_2$  molecules. Liquid oxygen is attracted to a magnet to a sufficient extent that, in laboratory demonstrations, a bridge of liquid oxygen may be supported against its own weight between the poles of a powerful magnet.

Singlet oxygen is a name given to several higher-energy species of molecular  $O_2$  in which all the electron spins are paired. It is much more reactive towards common organic molecules than is molecular oxygen per se. In nature, singlet oxygen is commonly formed from water during photosynthesis, using the energy of sunlight. It is also produced in the troposphere by the photolysis of ozone by light of short wavelength, and by the immune system as a source of active oxygen. Carotenoids in photosynthetic organisms (and possibly also in animals) play a major role in absorbing energy from singlet oxygen and converting it to the unexcited ground state before it can cause harm to tissues.

## Allotropes

The common allotrope of elemental oxygen on Earth is called dioxygen,  $O_2$ . It has a bond length of 121 pm and a bond energy of  $498 \text{ kJ}\cdot\text{mol}^{-1}$ . This is the form that is used by complex forms of life, such as animals, in cellular respiration and is the form that is a major part of the Earth's atmosphere. Other aspects of  $O_2$  are covered in the remainder of this article.

Trioxxygen ( $O_3$ ) is usually known as ozone and is a very reactive allotrope of oxygen that is damaging to lung tissue. Ozone is produced in the upper atmosphere when  $O_2$  combines with atomic oxygen made by the splitting of  $O_2$  by ultraviolet (UV) radiation. Since ozone absorbs strongly in the UV region of the spectrum, the ozone layer of the upper atmosphere functions as a protective radiation shield for the planet. Near the Earth's surface, however, it is a pollutant formed as a by-product of automobile exhaust. The metastable molecule tetraoxygen ( $O_4$ ) was discovered in 2001, and was assumed to exist in one of the six phases of solid oxygen. It was proven in 2006 that this phase, created by pressurizing  $O_2$  to 20 GPa, is in fact a rhombohedral  $O_8$  cluster.

This cluster has the potential to be a much more powerful oxidizer than either  $O_2$  or  $O_3$  and may therefore be used in rocket fuel. A metallic phase was discovered in 1990 when solid oxygen is subjected to a pressure of above 96 GPa and it was shown in 1998 that at very low temperatures, this phase becomes superconducting.

### Physical Properties of Iron

Oxygen is more soluble in water than nitrogen is; water contains approximately 1 molecule of O<sub>2</sub> for every 2 molecules of N<sub>2</sub>, compared to an atmospheric ratio of approximately 1:4. The solubility of oxygen in water is temperature-dependent, and about twice as much (14.6 mg·L<sup>-1</sup>) dissolves at 0 °C than at 20 °C (7.6 mg·L<sup>-1</sup>). At 25 °C and 1 standard atmosphere (101.3 kPa) of air, freshwater contains about 6.04 milliliters (mL) of oxygen per liter, whereas seawater contains about 4.95 mL per liter. At 5 °C the solubility increases to 9.0 mL (50% more than at 25 °C) per liter for water and 7.2 mL (45% more) per liter for sea water.

Oxygen condenses at 90.20 K (−182.95 °C, −297.31 °F), and freezes at 54.36 K (−218.79 °C, −361.82 °F). Both liquid and solid O<sub>2</sub> are clear substances with a light sky-blue color caused by absorption in the red (in contrast with the blue color of the sky, which is due to Rayleigh scattering of blue light). High-purity liquid O<sub>2</sub> is usually obtained by the fractional distillation of liquefied air. Liquid oxygen may also be produced by condensation out of air, using liquid nitrogen as a coolant. It is a highly reactive substance and must be segregated from combustible materials.

### Occurrence

Ten most common elements in the Milky Way Galaxy estimated spectroscopically

Z	Element	Mass fraction in parts per million	
1	Hydrogen	739,000	71 × mass of oxygen (red bar)
2	Helium	240,000	23 × mass of oxygen (red bar)
8	Oxygen	10,400	
6	Carbon	4,600	
10	Neon	1,340	
26	Iron	1,090	
7	Nitrogen	960	
14	Silicon	650	
12	Magnesium	580	
16	Sulfur	440	

Oxygen is the most abundant chemical element, by mass, in the Earth's biosphere, air, sea and land. Oxygen is the third most abundant chemical element in the universe, after hydrogen and helium. About 0.9% of the Sun's mass is oxygen. Oxygen constitutes 49.2% of the Earth's crust by mass and is the major component of the world's oceans (88.8% by mass).

Oxygen gas is the second most common component of the Earth's atmosphere, taking up 20.8% of its volume and 23.1% of its mass (some 10<sup>15</sup> tons). Earth is unusual among the planets of the Solar System in having such a high concentration of oxygen gas in its atmosphere: Mars (with 0.1% O<sub>2</sub> by volume) and Venus have far lower concentrations. However, the O<sub>2</sub> surrounding these other planets is produced solely by ultraviolet radiation impacting oxygen-containing molecules such as carbon dioxide.

The unusually high concentration of oxygen gas on Earth is the result of the oxygen cycle. This biogeochemical cycle describes the movement of oxygen within and between its three main reservoirs on Earth: the atmosphere, the biosphere, and the lithosphere. The main driving factor of the oxygen cycle is photosynthesis, which is responsible for modern Earth's atmosphere. Photosynthesis releases oxygen into the atmosphere, while respiration and decay remove it from the atmosphere. In the present equilibrium, production and consumption occur at the same rate of roughly 1/2000th of the entire atmospheric oxygen per year.

Free oxygen also occurs in solution in the world's water bodies. The increased solubility of O<sub>2</sub> at lower temperatures has important implications for ocean life, as polar oceans support a much higher density of life due to their higher oxygen content. Polluted water may have reduced amounts of O<sub>2</sub> in it, depleted by decaying algae and other biomaterials through a process called eutrophication. Scientists assess this aspect of water quality by measuring the water's biochemical oxygen demand, or the amount of O<sub>2</sub> needed to restore it to a normal concentration

### **Compounds**

The oxidation state of oxygen is -2 in almost all known compounds of oxygen. The oxidation state -1 is found in a few compounds such as peroxides. Compounds containing oxygen in other oxidation states are very uncommon: -1/2 (superoxides), -1/3 (ozonides), 0 (elemental, hypofluorous acid), +1/2 (dioxygenyl), +1 (dioxygen difluoride), and +2 (oxygen difluoride).

### **Oxides and other Inorganic Compounds**

Water (H<sub>2</sub>O) is the oxide of hydrogen and the most familiar oxygen compound. Hydrogen atoms are covalently bonded to oxygen in a water molecule but also have an additional attraction (about 23.3 kJ·mol<sup>-1</sup> per hydrogen atom) to an adjacent oxygen atom in a separate molecule. These hydrogen bonds between water molecules hold them approximately 15% closer than what would be expected in a simple liquid with just van der Waals forces.

Due to its electronegativity, oxygen forms chemical bonds with almost all other elements at elevated temperatures to give corresponding oxides. However, some elements readily form oxides at standard conditions for temperature and pressure; the rusting of iron is an example. The surface of metals like aluminum and titanium are oxidized in the presence of air and become coated with a thin film of oxide that passivates the metal and slows further corrosion.

Some of the transition metal oxides are found in nature as non-stoichiometric compounds, with a slightly less metal than the chemical formula would show. For example, the natural occurring FeO (wüstite) is actually written as Fe<sub>1-x</sub>O, where x is usually around 0.05.

Oxygen as a compound is present in the atmosphere in trace quantities in the form of carbon dioxide (CO<sub>2</sub>). The Earth's crustal rock is composed in large part of oxides of silicon (silica SiO<sub>2</sub>, found in granite and sand), aluminum (aluminum Al<sub>2</sub>O<sub>3</sub>, in bauxite and corundum), iron (iron (III) oxide Fe<sub>2</sub>O<sub>3</sub>, in hematite and rust), and calcium carbonate (in limestone). The rest of the Earth's crust is also made of oxygen compounds, in particular various complex silicates (in silicate minerals). The Earth's mantle, of much larger mass than the crust, is largely composed of silicates of magnesium and iron.

Water-soluble silicates in the form of  $\text{Na}_4\text{SiO}_4$ ,  $\text{Na}_2\text{SiO}_3$ , and  $\text{Na}_2\text{Si}_2\text{O}_5$  are used as detergents and adhesives.

Oxygen also acts as a ligand for transition metals, forming metal– $\text{O}_2$  bonds with the iridium atom in Vaska's complex, with the platinum in  $\text{PtF}_6$ , and with the iron center of the heme group of hemoglobin.

### **Organic Compounds and Biomolecules**

Among the most important classes of organic compounds that contain oxygen are (where "R" is an organic group): alcohols ( $\text{R-OH}$ ); ethers ( $\text{R-O-R}$ ); ketones ( $\text{R-CO-R}$ ); aldehydes ( $\text{R-CO-H}$ ); carboxylic acids ( $\text{R-COOH}$ ); esters ( $\text{R-COO-R}$ ); acid anhydrides ( $\text{R-CO-O-CO-R}$ ); and amides ( $\text{R-C(O)-NR}_2$ ). There are many important organic solvents that contain oxygen, including: acetone, methanol, ethanol, isopropanol, furan, THF, diethyl ether, dioxane, ethyl acetate, DMF, DMSO, acetic acid, and formic acid.

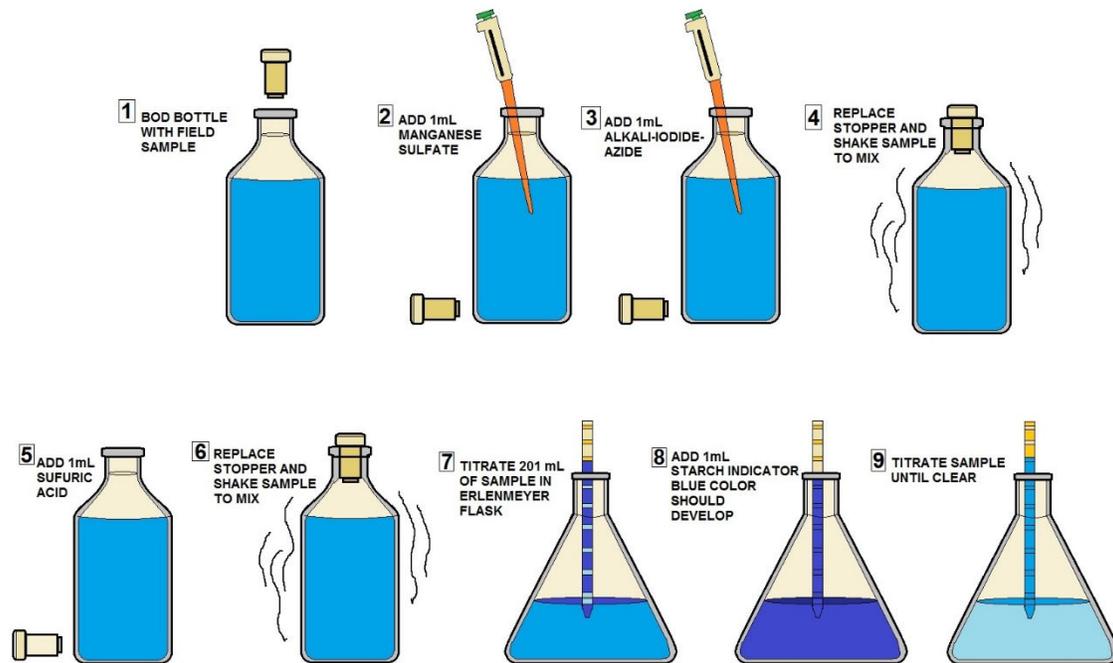
Acetone ( $(\text{CH}_3)_2\text{CO}$ ) and phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) are used as feeder materials in the synthesis of many different substances. Other important organic compounds that contain oxygen are: glycerol, formaldehyde, glutaraldehyde, citric acid, acetic anhydride, and acetamide. Epoxides are ethers in which the oxygen atom is part of a ring of three atoms.

Oxygen reacts spontaneously with many organic compounds at or below room temperature in a process called autoxidation. Most of the organic compounds that contain oxygen are not made by direct action of  $\text{O}_2$ . Organic compounds important in industry and commerce that are made by direct oxidation of a precursor include ethylene oxide and peracetic acid.

The element is found in almost all biomolecules that are important to (or generated by) life. Only a few common complex biomolecules, such as squalene and the carotenes, contain no oxygen.

Of the organic compounds with biological relevance, carbohydrates contain the largest proportion by mass of oxygen. All fats, fatty acids, amino acids, and proteins contain oxygen (due to the presence of carbonyl groups in these acids and their ester residues).

Oxygen also occurs in phosphate ( $\text{PO}_3\text{-4}$ ) groups in the biologically important energy-carrying molecules ATP and ADP, in the backbone and the purines (except adenine) and pyrimidines of RNA and DNA, and in bones as calcium phosphate and hydroxylapatite.



### HOW TO MEASURE DISSOLVED OXYGEN IN A WATER SAMPLE

## Phosphorus

**Phosphorus** is a chemical element with symbol **P** and atomic number 15. A multivalent nonmetal of the nitrogen group, phosphorus as a mineral is almost always present in its maximally oxidized state, as inorganic phosphate rocks.

Elemental phosphorus exists in two major forms—white phosphorus and red phosphorus—but due to its high reactivity, phosphorus is never found as a free element on Earth.

The first form of elemental phosphorus to be produced (white phosphorus, in 1669) emits a faint glow upon exposure to oxygen..

The term "phosphorescence", meaning glow after illumination, originally derives from this property of phosphorus, although this word has since been used for a different physical process that produces a glow.

The glow of phosphorus itself originates from oxidation of the white (but not red) phosphorus— a process now termed chemiluminescence.



The vast majority of phosphorus compounds are consumed as fertilizers. Other applications include the role of organophosphorus compounds in detergents, pesticides and nerve agents, and matches.

Phosphorus is essential for life. As phosphate, it is a component of DNA, RNA, ATP, and also the phospholipids that form all cell membranes. Demonstrating the link between phosphorus and life, elemental phosphorus was historically first isolated from human urine, and bone ash was an important early phosphate source.

Phosphate minerals are fossils. Low phosphate levels are an important limit to growth in some aquatic systems. The chief commercial use of phosphorus compounds for production of fertilizers is due to the need to replace the phosphorus that plants remove from the soil.

### Characteristics

#### Physical

Phosphorus exists as several forms (allotropes) that exhibit strikingly different properties.<sup>[6]</sup> The two most common allotropes are **white phosphorus** and **red phosphorus**. Another form, scarlet phosphorus, is obtained by allowing a solution of white phosphorus in carbon disulfide to evaporate in sunlight.

Black phosphorus is obtained by heating white phosphorus under high pressures (about 12,000 standard atmospheres or 1.2 gigapascals). In appearance, properties, and structure, it resembles graphite, being black and flaky, a conductor of electricity, and has puckered sheets of linked atoms. Another allotrope is diphosphorus; it contains a phosphorus dimer as a structural unit and is highly reactive.

### **White Phosphorus and Related Molecular Forms**

The most important form of elemental phosphorus from the perspective of applications and the chemical literature is white phosphorus. It consists of tetrahedral  $P_4$  molecules, in which each atom is bound to the other three atoms by a single bond. This  $P_4$  tetrahedron is also present in liquid and gaseous phosphorus up to the temperature of 800 °C when it starts decomposing to  $P_2$  molecules. Solid white exists in two forms. At low-temperatures, the  $\beta$  form is stable. At high-temperatures the  $\alpha$  form is predominant. These forms differ in terms of the relative orientations of the constituent  $P_4$  tetrahedra.

White phosphorus is the least stable, the most reactive, the most volatile, the least dense, and the most toxic of the allotropes. White phosphorus gradually changes to red phosphorus. This transformation is accelerated by light and heat, and samples of white phosphorus almost always contain some red phosphorus and accordingly appear yellow. For this reason, it is also called yellow phosphorus.

It glows in the dark (when exposed to oxygen) with a very faint tinge of green and blue, is highly flammable and pyrophoric (self-igniting) upon contact with air and is toxic (causing severe liver damage on ingestion).

Owing to its pyrophoricity, white phosphorus is used as an additive in napalm. The odor of combustion of this form has a characteristic garlic smell, and samples are commonly coated with white "(di)phosphorus pentoxide", which consists of  $P_4O_{10}$  tetrahedra with oxygen inserted between the phosphorus atoms and at their vertices. White phosphorus is insoluble in water but soluble in carbon disulfide.

Thermolysis (cracking) of  $P_4$  at 1100 kelvin) gives diphosphorus,  $P_2$ . This species is not stable as a solid or liquid. The dimeric unit contains a triple bond and is analogous to  $N_2$ . It can also be generated as a transient intermediate in solution by thermolysis of organophosphorus precursor reagents.<sup>[10]</sup> At still higher temperatures,  $P_2$  dissociates into atomic P.

Although the term phosphorescence is derived from phosphorus, the reaction that gives phosphorus its glow is properly called chemiluminescence (glowing due to a cold chemical reaction), not phosphorescence (re-emitting light that previously fell onto a substance and excited it).

### **Red Phosphorus**

Red phosphorus is polymeric in structure. It can be viewed as a derivative of  $P_4$  wherein one P-P bond is broken, and one additional bond is formed between the neighboring tetrahedron resulting in a chain-like structure. Red phosphorus may be formed by heating white phosphorus to 250 °C (482 °F) or by exposing white phosphorus to sunlight. Phosphorus after this treatment is amorphous. Upon further heating, this material crystallizes.

In this sense, red phosphorus is not an allotrope, but rather an intermediate phase between the white and violet phosphorus, and most of its properties have a range of values. For example, freshly prepared, bright red phosphorus is highly reactive and ignites at about 300 °C, though it is still more stable than white phosphorus, which ignites at about 30 °C. After prolonged heating or storage, the color darkens; the resulting product is more stable and does not spontaneously ignite in air.

### Violet Phosphorus

Violet phosphorus is a form of phosphorus that can be produced by day-long annealing of red phosphorus above 550 °C. In 1865, Hittorf discovered that when phosphorus was recrystallized from molten lead, a red/purple form is obtained. Therefore this form is sometimes known as "Hittorf's phosphorus" (or violet or  $\alpha$ -metallic phosphorus).

### Black Phosphorus

Black phosphorus is the least reactive allotrope and the thermodynamically stable form below 550 °C. It is also known as  $\beta$ -metallic phosphorus and has a structure somewhat resembling that of graphite. High pressures are usually required to produce black phosphorus, but it can also be produced at ambient conditions using metal salts as catalysts.

### Properties of some allotropes of phosphorus

Form	white( $\alpha$ )	white( $\beta$ )	violet	black
<b>Symmetry</b>	Body-centered cubic	Triclinic	Monoclinic	Orthorhombic
<b>Pearson symbol</b>		aP24	mP84	oS8
<b>Space group</b>	I43m	P1 No.2	P2/c No.13	Cmca No.64
<b>Density (g/cm<sup>3</sup>)</b>	1.828	1.88	2.36	2.69
<b>Bandgap (eV)</b>	2.1		1.5	0.34
<b>Refractive index</b>	1.8244		2.6	2.4

### Isotopes

Twenty-three isotopes of phosphorus are known, including all possibilities from <sup>24</sup>P up to <sup>46</sup>P. Only <sup>31</sup>P is stable and is therefore present at 100% abundance. The half-integer nuclear spin and high abundance of <sup>31</sup>P make phosphorus-31 NMR spectroscopy a very useful analytical tool in studies of phosphorus-containing samples.

Two radioactive isotopes of phosphorus have half-lives that make them useful for scientific experiments. <sup>32</sup>P has a half-life of 14.262 days and <sup>33</sup>P has a half-life of 25.34 days. Biomolecules can be "tagged" with a radioisotope to allow for the study of very dilute samples.

Radioactive isotopes of phosphorus include

- <sup>32</sup>P, a beta-emitter (1.71 MeV) with a half-life of 14.3 days, which is used routinely in life-science laboratories, primarily to produce radiolabeled DNA and RNA probes, e.g. for use in Northern blots or Southern blots. Because the high energy beta particles produced penetrate skin and corneas, and because any <sup>32</sup>P ingested, inhaled, or absorbed is readily incorporated into bone and nucleic acids, Occupational Safety and Health Administration in the United States, and similar institutions in other developed countries require that a lab coat, disposable gloves and safety glasses or goggles be worn when working with <sup>32</sup>P, and that working directly over an open container be avoided in order to protect the eyes. Monitoring

personal, clothing, and surface contamination is also required. In addition, due to the high energy of the beta particles, shielding this radiation with the normally used dense materials (e.g. lead), gives rise to secondary emission of X-rays via Bremsstrahlung (braking radiation). Therefore shielding must be accomplished with low density materials, e.g. Plexiglas (Lucite), other plastics, water, or (when transparency is not required), even wood.

- $^{33}\text{P}$ , a beta-emitter (0.25 MeV) with a half-life of 25.4 days. It is used in life-science laboratories in applications in which lower energy beta emissions are advantageous such as DNA sequencing.

### Occurrence

In terms of stellar nucleosynthesis, stable forms of phosphorus are produced in large (greater than 3 solar masses) stars by fusing two oxygen atoms together. This requires temperatures above 1,000 megakelvins.

Phosphorus is not found free in nature, but it is widely distributed in many minerals, mainly phosphates. Phosphate rock, which is partially made of apatite (an impure tri-calcium phosphate mineral), is an important commercial source of this element. About 50 percent of the global phosphorus reserves are in the Arab nations. Large deposits of apatite are located in China, Russia, Morocco, Florida, Idaho, Tennessee, Utah, and elsewhere. Albright and Wilson in the United Kingdom and their Niagara Falls plant, for instance, were using phosphate rock in the 1890s and 1900s from the Îles du Connétable, Tennessee and Florida; by 1950 they were using phosphate rock mainly from Tennessee and North Africa. In the early 1990s Albright and Wilson's purified wet phosphoric acid business was being adversely affected by phosphate rock sales by China and the entry of their long-standing Moroccan phosphate suppliers into the purified wet phosphoric acid business.

### Production

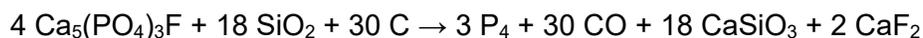
The majority of phosphorus-containing compounds are produced for use as fertilizers. For this purpose, phosphate-containing minerals are converted to phosphoric acid. Two distinct routes are employed, the main one being treatment of phosphate minerals with sulfuric acid. The other process utilizes white phosphorus, which may be produced by reaction and distillation from very low grade phosphate sources. The white phosphorus is then oxidized to phosphoric acid and subsequently neutralized with base to give phosphate salts. Phosphoric acid obtained via white phosphorus is relatively pure and is the main source of phosphates used in detergents and other non-fertilizer applications.

### Elemental Phosphorus

About 1,000,000 short tons (910,000 t) of elemental phosphorus is produced annually. Calcium phosphate (phosphate rock), mostly mined in Florida and North Africa, can be heated to 1,200–1,500 °C with sand, which is mostly  $\text{SiO}_2$ , and coke (impure carbon) to produce vaporized  $\text{P}_4$ .

The product is subsequently condensed into a white powder under water to prevent oxidation by air.

Even under water, white phosphorus is slowly converted to the more stable red phosphorus allotrope. The chemical equation for this process when starting with fluoroapatite, a common phosphate mineral, is:



Side products from this production include ferrophosphorus, a crude form of  $\text{Fe}_2\text{P}$ , resulting from iron impurities in the mineral precursors. The silicate slag is a useful construction material.

The fluoride is sometimes recovered for use in water fluoridation. More problematic is a "mud" containing significant amounts of white phosphorus. Production of white phosphorus is conducted in large facilities in part because it is energy intensive. The white phosphorus is transported in molten form.

Some major accidents have occurred during transportation, train derailments at Brownston, Nebraska and Miamisburg, Ohio led to large fires. The worst incident in recent times was an environmental one in 1968 when the sea became contaminated due to spillages and/or inadequately treated sewage from a white phosphorus plant at Placentia Bay, Newfoundland.

Another process by which elemental phosphorus is extracted includes applying at high temperatures (1500 °C):



Thermphos International is Europe's only producer of elemental phosphorus with the annual capacity of 80,000 t provided by a plant at Vlissingen, the Netherlands.

## Compounds

### Oxoacids of Phosphorus

Phosphorous oxoacids are extensive, often commercially important, and sometimes structurally complicated.

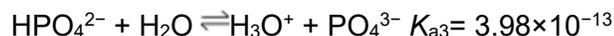
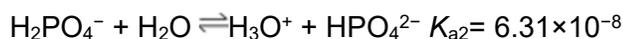
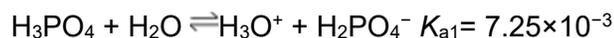
They all have acidic protons bound to oxygen atoms and some have nonacidic protons that are bonded directly to phosphorus. Although many oxoacids of phosphorus are formed, only nine are important, and three of them, hypophosphorous acid, phosphorous acid, and phosphoric acid, are particularly important ones.

Oxidation state	Formula	Name	Acidic protons	Compounds
+1	$\text{HH}_2\text{PO}_2$	Hypophosphorous acid	1	acid, salts
+3	$\text{H}_2\text{HPO}_3$	Phosphorous acid	2	acid, salts
+3	$\text{HPO}_2$	metaphosphorous acid	1	salts
+3	$\text{H}_3\text{PO}_3$	(ortho)phosphorous acid	3	acid, salts
+5	$(\text{HPO}_3)_n$	metaphosphoric acids	n	salts (n=3,4,6)
+5	$\text{H}(\text{HPO}_3)_n\text{OH}$	polyphosphoric acids	n+2	acids, salts (n=1-6)
+5	$\text{H}_5\text{P}_3\text{O}_{10}$	tripolyphosphoric acid	3	salts
+5	$\text{H}_4\text{P}_2\text{O}_7$	pyrophosphoric acid	4	acid, salts
+5	$\text{H}_3\text{PO}_4$	(ortho)phosphoric acid	3	acid, salts

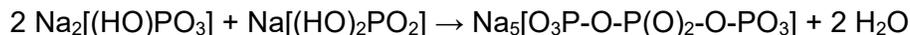
## Phosphorus (V) Compounds

### Oxides

The most prevalent compounds of phosphorus are derivatives of phosphate ( $\text{PO}_4^{3-}$ ), a tetrahedral anion. Phosphate is the conjugate base of phosphoric acid, which is produced on a massive scale for use in fertilizers. Being triprotic, phosphoric acid converts stepwise to three conjugate bases:



Phosphate exhibits the tendency to form chains and rings with P-O-P bonds. Many polyphosphates are known, including ATP. Polyphosphates arise by dehydration of hydrogen phosphates such as  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$ . For example, the industrially important trisodium triphosphate (also known as sodium tripolyphosphate, STPP) is produced industrially on a megaton scale via this condensation reaction:



Phosphorus pentoxide ( $\text{P}_4\text{O}_{10}$ ) is the acid anhydride of phosphoric acid, but several intermediates are known between the two. This waxy white solid reacts vigorously with water.

With metal cations, phosphate forms a variety of salts. These solids are polymeric, featuring P-O-M linkages. When the metal cation has a charge of 2+ or 3+, the salts are generally insoluble; hence they exist as common minerals. Many phosphate salts are derived from hydrogen phosphate ( $\text{HPO}_4^{2-}$ ).

$\text{PCl}_5$  and  $\text{PF}_5$  are common compounds. Both are volatile and pale or colorless. The other two halides,  $\text{PBr}_5$  and  $\text{PI}_5$  are unstable. The pentachloride and pentafluoride adopt trigonal bipyramidal molecular geometry and are Lewis acids.

With fluoride,  $\text{PF}_5$  forms  $\text{PF}_6^-$ , an anion that is isoelectronic with  $\text{SF}_6$ . The most important oxyhalide is phosphorus oxychloride ( $\text{POCl}_3$ ), which is tetrahedral.

Before extensive computer calculations were feasible, it was proposed that bonding in phosphorus(V) compounds involved *d* orbitals. It is now accepted that the bonding can be better explained by molecular orbital theory and involves only s- and p-orbitals on phosphorus.

### Nitrides

Compounds of the formula  $(\text{PNCl}_2)_n$  exist mainly as rings such as the trimer hexachlorophosphazene. The phosphazenes arise by treatment of phosphorus pentachloride with ammonium chloride:  $\text{PCl}_5 + \text{NH}_4\text{Cl} \rightarrow 1/n (\text{NPCl}_2)_n + 4 \text{HCl}$  The chloride groups can be replaced by alkoxide ( $\text{RO}^-$ ) to give rise to a family of polymers with potentially useful properties.

## Sulfides

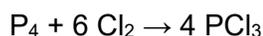
Phosphorus forms a wide range of sulfides, where phosphorus can be P(V), P(III) or other oxidation states. Most famous is the three-fold symmetric  $P_4S_3$  used in strike-anywhere matches.  $P_4S_{10}$  and  $P_4O_{10}$  have analogous structures.

## Phosphorus (III) Compounds

Phosphine ( $PH_3$ ) and its organic derivatives ( $PR_3$ ) are structural analogues with ammonia ( $NH_3$ ) but the bond angles at phosphorus are closer to  $90^\circ$  for phosphine and its organic derivatives. It is an ill-smelling, toxic compound. Phosphine is produced by hydrolysis of calcium phosphide,  $Ca_3P_2$ . Unlike ammonia, phosphine is oxidized by air. Phosphine is also far less basic than ammonia.

All four symmetrical trihalides are well known: gaseous  $PF_3$ , the yellowish liquids  $PCl_3$  and  $PBr_3$ , and the solid  $PI_3$ . These materials are moisture sensitive, hydrolyzing to give phosphorus acid.

The trichloride, a common reagent, is produced by chlorination of white phosphorus:



The trifluoride is produced by from the trichloride by halide exchange.  $PF_3$  is toxic because it binds to hemoglobin.

Phosphorus(III) oxide,  $P_4O_6$  (also called tetraphosphorus hexoxide) is the anhydride of  $P(OH)_3$ , the minor tautomer of phosphorous acid. The structure of  $P_4O_6$  is like that of  $P_4O_{10}$  less the terminal oxide groups.

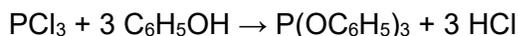
Mixed oxyhalides and oxyhydrides of phosphorus (III) are almost unknown.

## Organophosphorus Compounds

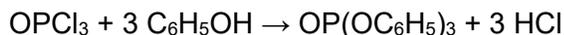
Compounds with P-C and P-O-C bonds are often classified as organophosphorus compounds. They are widely used commercially. The  $PCl_3$  serves as a source of  $P^{3+}$  in routes to organophosphorus (III) compounds. For example it is the precursor to triphenylphosphine:



Treatment of phosphorus trihalides with alcohols and phenols gives phosphites, e.g. triphenylphosphite:



Similar reactions occur for phosphorus oxychloride, affording triphenylphosphate:



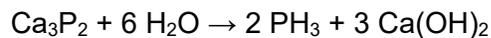
## Phosphorus (I) and phosphorus (II) compounds

These compounds generally feature P-P bonds. Examples include catenated derivatives of phosphine and organophosphines. The highly flammable gas diphosphine ( $P_2H_4$ ) is the first of a series of derivatives of this type.

Diphosphine is an analogue of hydrazine. Compounds containing P=P double bonds have also been observed, although they are rare.

### **Phosphides**

The phosphide ion is  $P^{3-}$ . Phosphides arise by reaction of metals with red phosphorus. Salts of  $P^{3-}$  do not exist in solution and these derivatives are refractory, reflecting their high lattice energy. Illustrated by the behavior calcium phosphide, many metal phosphides hydrolyze in water with release of phosphine:



Schreibersite is a naturally occurring phosphide found in meteorites. Many polyphosphides are known such as derivatives of  $OsP_2$ . These can be structurally complex ranging from  $Na_3P_7$  and derivatives of  $P_{26}^{4-}$ . Often these species adopt cage-like structures that resemble fragments of violet phosphorus.

## Selenium- Inorganic Contaminant 0.05 mg/L MCL

Selenium (Se) is an essential element for human nutrition, with the majority of our intake coming from foods such as nuts, cereals, meat, fish, and eggs. The concentration of Selenium in drinking water is usually low, and comes from natural minerals. In soils, selenium often occurs in soluble forms such as selenate, which are leached into rivers very easily by runoff increasing the amount of selenium in groundwater. Selenium in water is also a by-product of copper mining / smelting. Selenium is also used in photoelectric devices because its electrical conductivity varies with light.

Naturally occurring selenium compounds have not been shown to be carcinogenic in animals.

However, acute toxicity caused by high levels of selenium in water or other sources of intake has been observed in laboratory animals and in animals grazing in areas where high selenium levels exist in the soil. The US EPA has established the MCL for selenium in water at 0.05 mg/l.



### What are selenium's health effects?

Some people who drink water containing selenium well in excess of the maximum contaminant level (MCL) for many years could experience hair or fingernail losses, numbness in fingers or toes, or problems with their circulation.

This health effects language is not intended to catalog all possible health effects for selenium.

Rather, it is intended to inform consumers of some of the possible health effects associated with selenium in drinking water when the rule was finalized.

### What are EPA's drinking water regulations for selenium?

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for selenium is 0.05 mg/L or 50 ppb. EPA has set this level of protection based on the best available science to prevent potential health problems.

EPA has set an enforceable regulation for selenium, called a maximum contaminant level (MCL), at 0.05 mg/L or 50 ppb. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.

The Phase II Rule, the regulation for selenium, became effective in 1992. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed selenium as part of the Six Year Review and determined that the 0.05 mg/L or 50 ppb MCLG and 0.05 mg/L or 50 ppb MCL for selenium are still protective of human health.

### **Selenium Water Treatment**

Selenium contamination of water systems may result whenever new agricultural runoff courses through normally dry undeveloped lands. If you have high levels of selenium in your water the following are recommended selenium water treatment options. Anion exchange can reduce the amount of selenium in drinking water by 60 - 95%. Reverse Osmosis Systems are excellent at removing selenium in drinking water.

Selenium shows borderline metalloid or nonmetal behavior. Its most stable form, the grey trigonal allotrope, is sometimes called 'metallic' selenium. This is because its electrical conductivity is several orders of magnitude greater than that of the red monoclinic form.

### **The metallic character of selenium is further shown by the following properties:**

- Its luster.
- Its crystalline structure, which is thought to include weakly 'metallic' interchain bonding.
- Its capacity, when molten, to be drawn into thin threads.
- Its reluctance to acquire 'the high positive oxidation numbers characteristic of nonmetals'.
- Its capacity to form cyclic polycations (such as  $\text{Se}_2^{+8}$ ) when dissolved in oleums (an attribute it shares with sulfur and tellurium).
- The existence of a hydrolyzed cationic salt in the form of trihydroxoselenium (IV) perchlorate  $[\text{Se}(\text{OH})_3]^+ \cdot \text{ClO}_4^-$ .

### **The Non-metallic Character of Selenium is shown by:**

- Its brittleness.
- Its electronic band structure, which is that of a semiconductor.
- The low electrical conductivity ( $\sim 10^{-9}$  to  $10^{-12} \text{ S} \cdot \text{cm}^{-1}$ ) of its highly purified form. This is comparable to or less than that of bromine ( $7.95 \times 10^{-12} \text{ S} \cdot \text{cm}^{-1}$ ), a nonmetal.
- Its relatively high electronegativity (2.55 revised Pauling scale).
- The retention of its semiconducting properties in liquid form.
- Its reaction chemistry, which is mainly that of its nonmetallic anionic forms  $\text{Se}^{2-}$ ,  $\text{SeO}_2^{3-}$  and  $\text{SeO}_2^{4-}$ .

### **Selenium Explained**

**Selenium** is a chemical element with symbol **Se** and atomic number 34. It is a nonmetal with properties that are intermediate between those of its periodic table column-adjacent chalcogen elements sulfur and tellurium. It rarely occurs in its elemental state in nature, or as pure ore compounds.

Selenium (Greek *σελήνη* *selene* meaning "Moon") was discovered in 1817 by Jöns Jakob Berzelius, who noted the similarity of the new element to the previously-known tellurium (named for the Earth).

Selenium is found impurely in metal sulfide ores, where it partially replaces the sulfur. Commercially, selenium is produced as a byproduct in the refining of these ores, most often during copper production.

Minerals that are pure selenide or selenate compounds are known, but are rare. The chief commercial uses for selenium today are in glassmaking and in pigments. Selenium is a semiconductor and is used in photocells. Uses in electronics, once important, have been mostly supplanted by silicon semiconductor devices. Selenium continues to be used in a few types of DC power surge protectors and one type of fluorescent quantum dot.

Selenium salts are toxic in large amounts, but trace amounts are necessary for cellular function in many organisms, including all animals. Selenium is a component of the antioxidant enzymes glutathione peroxidase and thioredoxin reductase (which indirectly reduce certain oxidized molecules in animals and some plants). It is also found in three deiodinase enzymes, which convert one thyroid hormone to another. Selenium requirements in plants differ by species, with some plants requiring relatively large amounts, and others apparently requiring none.

### **Characteristics**

#### **Physical Properties**

Selenium exists in several allotropes that interconvert upon heating and cooling carried out at different temperatures and rates. As prepared in chemical reactions, selenium is usually amorphous, brick-red powder. When rapidly melted, it forms the black, vitreous form, which is usually sold industrially as beads. The structure of black selenium is irregular and complex and consists of polymeric rings with up to 1000 atoms per ring. Black Se is a brittle, lustrous solid that is slightly soluble in CS<sub>2</sub>. Upon heating, it softens at 50 °C and converts to gray selenium at 180 °C; the transformation temperature is reduced by presence of halogens and amines.

The red-colored  $\alpha$ ,  $\beta$  and  $\gamma$  forms are produced from solutions of black selenium by varying evaporation rates of the solvent (usually CS<sub>2</sub>). They all have relatively low, monoclinic crystal symmetries and contain nearly identical puckered Se<sub>8</sub> rings arranged in different fashions, as in sulfur. The packing is most dense in the  $\alpha$  form. In the Se<sub>8</sub> rings, the Se-Se distance is 233.5 pm and Se-Se-Se angle is 105.7 degrees. Other selenium allotropes may contain Se<sub>6</sub> or Se<sub>7</sub> rings.

The most stable and dense form of selenium has a gray color and hexagonal crystal lattice consisting of helical polymeric chains, wherein the Se-Se distance is 237.3 pm and Se-Se-Se angle is 130.1 degrees. The minimum distance between chains is 343.6 pm. Gray Se is formed by mild heating of other allotropes, by slow cooling of molten Se, or by condensing Se vapors just below the melting point. Whereas other Se forms are insulators, gray Se is a semiconductor showing appreciable photoconductivity.

Contrary to other allotropes, it is insoluble in CS<sub>2</sub>. It resists oxidation by air and is not attacked by non-oxidizing acids. With strong reducing agents, it forms polyselenides. Selenium does not exhibit the unusual changes in viscosity that sulfur undergoes when gradually heated.

## Isotopes

Selenium has six naturally occurring isotopes, five of which are stable:  $^{74}\text{Se}$ ,  $^{76}\text{Se}$ ,  $^{77}\text{Se}$ ,  $^{78}\text{Se}$ , and  $^{80}\text{Se}$ . The last three also occur as fission products, along with  $^{79}\text{Se}$ , which has a half-life of 327,000 years. The final naturally occurring isotope,  $^{82}\text{Se}$ , has a very long half-life ( $\sim 10^{20}$  yr, decaying via double beta decay to  $^{82}\text{Kr}$ ), which, for practical purposes, can be considered to be stable. Twenty-three other unstable isotopes have been characterized.

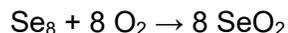
See also *Selenium-79* for more information on recent changes in the measured half-life of this long-lived fission product, important for the dose calculations performed in the frame of the geological disposal of long-lived radioactive waste.

## Chemical Compounds

Selenium compounds commonly exist in the oxidation states  $-2$ ,  $+2$ ,  $+4$ , and  $+6$ .

## Chalcogen Compounds

Selenium forms two oxides: selenium dioxide ( $\text{SeO}_2$ ) and selenium trioxide ( $\text{SeO}_3$ ). Selenium dioxide is formed by the reaction of elemental selenium with oxygen:



It is a polymeric solid that forms monomeric  $\text{SeO}_2$  molecules in the gas phase. It dissolves in water to form selenous acid,  $\text{H}_2\text{SeO}_3$ . Selenous acid can also be made directly by oxidizing elemental selenium with nitric acid:



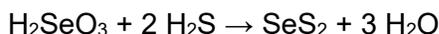
Unlike sulfur, which forms a stable trioxide, selenium trioxide is thermodynamically unstable and decomposes to the dioxide above  $185^\circ\text{C}$ :



Selenium trioxide is produced in the laboratory by the reaction of anhydrous potassium selenate ( $\text{K}_2\text{SeO}_4$ ) and sulfur trioxide ( $\text{SO}_3$ ).

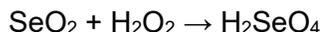
Salts of selenous acid are called *selenites*. These include silver selenite ( $\text{Ag}_2\text{SeO}_3$ ) and sodium selenite ( $\text{Na}_2\text{SeO}_3$ ).

Hydrogen sulfide reacts with aqueous selenous acid to produce selenium disulfide:



Selenium disulfide consists of 8-membered rings of a nearly statistical distribution of sulfur and selenium atoms. It has an approximate composition of  $\text{SeS}_2$ , with individual rings varying in composition, such as  $\text{Se}_4\text{S}_4$  and  $\text{Se}_2\text{S}_6$ . Selenium disulfide has been used in shampoo as an anti-dandruff agent, an inhibitor in polymer chemistry, a glass dye, and a reducing agent in fireworks.

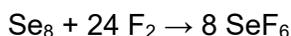
Selenium trioxide may be synthesized by dehydrating selenic acid,  $\text{H}_2\text{SeO}_4$ , which is itself produced by the oxidation of selenium dioxide with hydrogen peroxide:



Hot, concentrated selenic acid is capable of dissolving gold, forming gold(III) selenate.

### Halogen Compounds

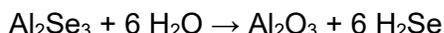
Iodides of selenium are not well known. The only stable chloride is selenium monochloride ( $\text{Se}_2\text{Cl}_2$ ), which might be better known as selenium(I) chloride; the corresponding bromide is also known. These species are structurally analogous to the corresponding disulfur dichloride. Selenium dichloride is an important reagent in the preparation of selenium compounds (e.g. the preparation of  $\text{Se}_7$ ). It is prepared by treating selenium with sulfur chloride ( $\text{SO}_2\text{Cl}_2$ ). Selenium reacts with fluorine to form selenium hexafluoride:



In comparison with its sulfur counterpart (sulfur hexafluoride), selenium hexafluoride ( $\text{SeF}_6$ ) is more reactive and is a toxic pulmonary irritant. Some of the selenium oxyhalides, such as selenium oxyfluoride ( $\text{SeOF}_2$ ) and selenium oxychloride ( $\text{SeOCl}_2$ ) have been used as specialty solvents.

### Selenides

Analogous to the behavior of other chalcogens, selenium forms a dihydride  $\text{H}_2\text{Se}$ . It is a strongly odiferous, toxic, and colorless gas. It is more acidic than  $\text{H}_2\text{S}$ . In solution it ionizes to  $\text{HSe}^-$ . The selenide dianion  $\text{Se}^{2-}$  forms a variety of compounds, including the minerals from which selenium is obtained commercially. Illustrative selenides include mercury selenide ( $\text{HgSe}$ ), lead selenide ( $\text{PbSe}$ ), zinc selenide ( $\text{ZnSe}$ ), and copper indium gallium diselenide ( $\text{Cu}(\text{Ga}, \text{In})\text{Se}_2$ ). These materials are semiconductors. With highly electropositive metals, such as aluminum, these selenides are prone to hydrolysis:

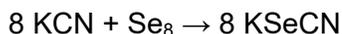


Alkali metal selenides react with selenium to form polyselenides,  $\text{Se}_{2-x}$ , which exist as chains.

### Other Compounds

Tetraselenium tetranitride,  $\text{Se}_4\text{N}_4$ , is an explosive orange compound analogous to tetrasulfur tetranitride ( $\text{S}_4\text{N}_4$ ). It can be synthesized by the reaction of selenium tetrachloride ( $\text{SeCl}_4$ ) with  $[(\text{CH}_3)_3\text{Si}]_2\text{N}_2\text{Se}$ .

Selenium reacts with cyanides to yield selenocyanates:



### Organoselenium Compounds

Selenium, especially in the II oxidation state, forms stable bonds to carbon, which are structurally analogous to the corresponding organosulfur compounds. Especially common are selenides ( $\text{R}_2\text{Se}$ , analogues of thioethers), diselenides ( $\text{R}_2\text{Se}_2$ , analogues of disulfides), and selenols ( $\text{RSeH}$ , analogues of thiols).

Representatives of selenides, diselenides, and selenols include respectively selenomethionine, diphenyldiselenide, and benzeneselenol. The sulfoxide in sulfur chemistry is represented in selenium chemistry by the selenoxides (formula  $RSe(O)R$ ), which are intermediates in organic synthesis, as illustrated by the selenoxide elimination reaction. Consistent with trends indicated by the double bond rule, selenoketones,  $R(C=Se)R$ , and selenaldehydes,  $R(C=Se)H$ , are rarely observed.

### History

Selenium (Greek *σελήνη* *selene* meaning "Moon") was discovered in 1817 by Jöns Jakob Berzelius and Johan Gottlieb Gahn. Both chemists owned a chemistry plant near Gripsholm, Sweden producing sulfuric acid by the lead chamber process. The pyrite from the Falun mine created a red precipitate in the lead chambers which was presumed to be an arsenic compound, and so the pyrite's use to make acid was discontinued. Berzelius and Gahn wanted to use the pyrite and they also observed that the red precipitate gave off a smell like horseradish when burned.

This smell was not typical of arsenic, but a similar odor was known from tellurium compounds. Hence, Berzelius's first letter to Alexander Marcet stated that this was a tellurium compound. However, the lack of tellurium compounds in the Falun mine minerals eventually led Berzelius to reanalyze the red precipitate, and in 1818 he wrote a second letter to Marcet describing a newly found element similar to sulfur and tellurium. Because of its similarity to tellurium, named for the Earth, Berzelius named the new element after the Moon.

In 1873, Willoughby Smith found that the electrical resistance of grey selenium was dependent on the ambient light. This led to its use as a cell for sensing light. The first of commercial products using selenium were developed by Werner Siemens in the mid-1870s. The selenium cell was used in the photophone developed by Alexander Graham Bell in 1879. Selenium transmits an electric current proportional to the amount of light falling on its surface.

This phenomenon was used in the design of light meters and similar devices. Selenium's semiconductor properties found numerous other applications in electronics. The development of selenium rectifiers began during the early 1930s, and these replaced copper oxide rectifiers because of their superior efficiencies. These lasted in commercial applications until the 1970s, following which they were replaced with less expensive and even more efficient silicon rectifiers. Selenium came to medical notice later because of its toxicity to human beings working in industries.

Selenium was also recognized as an important veterinary toxin, which is seen in animals that have eaten high-selenium plants. In 1954, the first hints of specific biological functions of selenium were discovered in microorganisms. Its essentiality for mammalian life was discovered in 1957. In the 1970s, it was shown to be present in two independent sets of enzymes. This was followed by the discovery of selenocysteine in proteins.

### Occurrence

Native (i.e., elemental) selenium is a rare mineral, which does not usually form good crystals, but, when it does, they are steep rhombohedra or tiny acicular (hair-like) crystals. Isolation of selenium is often complicated by the presence of other compounds and elements.

Selenium occurs naturally in a number of inorganic forms, including selenide-, selenate-, and selenite-containing minerals, but these minerals are rare. The common mineral selenite is *not* a selenium mineral, and contains no selenite ion, but is rather a type of gypsum (calcium sulfate hydrate) named like selenium for the moon well before the discovery of selenium. Selenium is most commonly found quite impurely, replacing a small part of the sulfur in sulfide ores of many metals.

In living systems, selenium is found in the amino acids selenomethionine, selenocysteine, and methylselenocysteine. In these compounds, selenium plays a role analogous to that of sulfur. Another naturally occurring organoselenium compound is dimethyl selenide.

Certain solids are selenium-rich, and selenium can be bioconcentrated by certain plants. In soils, selenium most often occurs in soluble forms such as selenate (analogous to sulfate), which are leached into rivers very easily by runoff. Ocean water contains significant amounts of selenium. Anthropogenic sources of selenium include coal burning and the mining and smelting of sulfide ores.

### **Production**

Selenium is most commonly produced from selenide in many sulfide ores, such as those of copper, silver, or lead. Electrolytic metal refining is particularly conducive to producing selenium as a byproduct, and it is obtained from the anode mud of copper refineries. Another source was the mud from the lead chambers of sulfuric acid plants but this method to produce sulfuric acid is no longer used.

These muds can be processed by a number of means to obtain selenium. However, most elemental selenium comes as a byproduct of refining copper or producing sulfuric acid.

Since the invention of solvent extraction and electrowinning (SX/EW) for the production of copper this method takes an increasing share of the world wide copper production. This changes the availability of selenium because only a comparably small part of the selenium in the ore is leached together with the copper.

Industrial production of selenium usually involves the extraction of selenium dioxide from residues obtained during the purification of copper. Common production from the residue then begins by oxidation with sodium carbonate to produce selenium dioxide.



## Sulfur

**Sulfur** or **sulphur** (British English; is a chemical element with symbol **S** and atomic number 16. It is an abundant, multivalent non-metal. Under normal conditions, sulfur atoms form cyclic octatomic molecules with chemical formula  $S_8$ . Elemental sulfur is a bright yellow crystalline solid when at room temperature. Chemically, sulfur can react as either an oxidant or reducing agent. It oxidizes most metals and several nonmetals, including carbon, which leads to its negative charge in most organosulfur compounds, but it reduces several strong oxidants, such as oxygen and fluorine.

Sulfur occurs naturally as the pure element (native sulfur) and as sulfide and sulfate minerals. Elemental sulfur crystals are commonly sought after by mineral collectors for their brightly colored polyhedron shapes. Being abundant in native form, sulfur was known in ancient times, mentioned for its uses in ancient Greece, China and Egypt. Fumes from burning sulfur were used as fumigants, and sulfur-containing medicinal mixtures were used as balms and antiparasitics.



Sulfur is referenced in the Bible as *brimstone* (burn stone) in English, with this name still used in several nonscientific tomes. It was needed to make the best quality of black gunpowder. In 1777, Antoine Lavoisier helped convince the scientific community that sulfur was a basic element, rather than a compound.

Elemental sulfur was once extracted from salt domes where it sometimes occurs in nearly pure form, but this method has been obsolete since the late 20th century. Today, almost all elemental sulfur is produced as a byproduct of removing sulfur-containing contaminants from natural gas and petroleum. The element's commercial uses are primarily in fertilizers, because of the relatively high requirement of plants for it, and in the manufacture of sulfuric acid, a primary industrial chemical.

Other well-known uses for the element are in matches, insecticides and fungicides. Many sulfur compounds are odiferous, and the smell of odorized natural gas, skunk scent, grapefruit, and garlic is due to sulfur compounds. Hydrogen sulfide produced by living organisms imparts the characteristic odor to rotting eggs and other biological processes.

Sulfur is an essential element for all life, and is widely used in biochemical processes. In metabolic reactions, sulfur compounds serve as both fuels and respiratory (oxygen-alternative) materials for simple organisms.

Sulfur in organic form is present in the vitamins biotin and thiamine, the latter being named for the Greek word for sulfur. Sulfur is an important part of many enzymes and in antioxidant molecules like glutathione and thioredoxin. Organically bonded sulfur is a component of all proteins, as the amino acids cysteine and methionine.

Disulfide bonds are largely responsible for the mechanical strength and insolubility of the protein keratin, found in outer skin, hair, and feathers, and the element contributes to their pungent odor when burned.

## Characteristics

### Physical Properties

Sulfur forms polyatomic molecules with different chemical formulas, with the best-known allotrope being octasulfur, cyclo-S<sub>8</sub>. Octasulfur is a soft, bright-yellow solid with only a faint odor, similar to that of matches. It melts at 115.21 °C, boils at 444.6 °C and sublimates easily. At 95.2 °C, below its melting temperature, cyclo-octasulfur changes from α-octasulfur to the β-polymorph. The structure of the S<sub>8</sub> ring is virtually unchanged by this phase change, which affects the intermolecular interactions. Between its melting and boiling temperatures, octasulfur changes its allotrope again, turning from β-octasulfur to γ-sulfur, again accompanied by a lower density but increased viscosity due to the formation of polymers. At even higher temperatures, however, the viscosity decreases as depolymerization occurs. Molten sulfur assumes a dark red color above 200 °C. The density of sulfur is about 2 g·cm<sup>-3</sup>, depending on the allotrope; all of its stable allotropes are excellent electrical insulators.

### Chemical Properties

Sulfur burns with a blue flame concomitant with formation of sulfur dioxide, notable for its peculiar suffocating odor. Sulfur is insoluble in water but soluble in carbon disulfide and, to a lesser extent, in other nonpolar organic solvents, such as benzene and toluene. The first and the second ionization energies of sulfur are 999.6 and 2252 kJ·mol<sup>-1</sup>, respectively. Despite such figures, S<sup>2+</sup> is rare, S<sup>4,6+</sup> being more common. The fourth and sixth ionization energies are 4556 and 8495.8 kJ·mol<sup>-1</sup>, the magnitude of the figures caused by electron transfer between orbitals; these states are only stable with strong oxidants as fluorine, oxygen, and chlorine.

### Allotropes

Sulfur forms over 30 solid allotropes, more than any other element. Besides S<sub>8</sub>, several other rings are known. Removing one atom from the crown gives S<sub>7</sub>, which is more deeply yellow than S<sub>8</sub>. HPLC analysis of "elemental sulfur" reveals an equilibrium mixture of mainly S<sub>8</sub>, but with S<sub>7</sub> and small amounts of S<sub>6</sub>. Larger rings have been prepared, including S<sub>12</sub> and S<sub>18</sub>.

Amorphous or "plastic" sulfur is produced by rapid cooling of molten sulfur—for example, by pouring it into cold water. X-ray crystallography studies show that the amorphous form may have a helical structure with eight atoms per turn. The long coiled polymeric molecules make the brownish substance elastic, and in bulk this form has the feel of crude rubber. This form is metastable at room temperature and gradually reverts to crystalline molecular allotrope, which is no longer elastic. This process happens within a matter of hours to days, but can be rapidly catalyzed.

### Isotopes

Sulfur has 25 known isotopes, four of which are stable: <sup>32</sup>S (95.02%), <sup>33</sup>S (0.75%), <sup>34</sup>S (4.21%), and <sup>36</sup>S (0.02%). Other than <sup>35</sup>S, with a half-life of 87 days and formed in cosmic ray spallation of <sup>40</sup>Ar, the radioactive isotopes of sulfur have half-lives less than 170 minutes.

When sulfide minerals are precipitated, isotopic equilibration among solids and liquid may cause small differences in the δS-34 values of co-genetic minerals. The differences between minerals can be used to estimate the temperature of equilibration.

The δC-13 and δS-34 of coexisting carbonate minerals and sulfides can be used to determine the pH and oxygen fugacity of the ore-bearing fluid during ore formation.

In most forest ecosystems, sulfate is derived mostly from the atmosphere; weathering of ore minerals and evaporites contribute some sulfur. Sulfur with a distinctive isotopic composition has been used to identify pollution sources, and enriched sulfur has been added as a tracer in hydrologic studies. Differences in the natural abundances can be used in systems where there is sufficient variation in the  $^{34}\text{S}$  of ecosystem components. Rocky Mountain lakes thought to be dominated by atmospheric sources of sulfate have been found to have different  $\delta^{34}\text{S}$  values from lakes believed to be dominated by watershed sources of sulfate.

### **Natural occurrence**

Sulfur, usually as sulfide, is present in many types of meteorites. Ordinary chondrites contain on average 2.1% sulfur, and carbonaceous chondrites may contain as much as 6.6%. It is normally present as troilite ( $\text{FeS}$ ), but there are exceptions, with carbonaceous chondrites containing free sulfur, sulfates and other sulfur compounds. The distinctive colors of Jupiter's volcanic moon Io are attributed to various forms of molten, solid and gaseous sulfur.

On Earth, elemental sulfur can be found near hot springs and volcanic regions in many parts of the world, especially along the Pacific Ring of Fire; such volcanic deposits are currently mined in Indonesia, Chile, and Japan. Such deposits are polycrystalline, with the largest documented single crystal measuring  $22 \times 16 \times 11$  cm. Historically; Sicily was a large source of sulfur in the Industrial Revolution.

Common naturally occurring sulfur compounds include the sulfide minerals, such as pyrite (iron sulfide), cinnabar (mercury sulfide), galena (lead sulfide), sphalerite (zinc sulfide) and stibnite (antimony sulfide); and the sulfates, such as gypsum (calcium sulfate), alunite (potassium aluminum sulfate), and barite (barium sulfate). On Earth, just as upon Jupiter's moon Io, elemental sulfur occurs naturally in volcanic emissions, including emissions from hydrothermal vents.

### **Production**

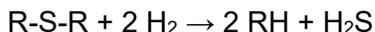
Sulfur may be found by itself and historically was usually obtained in this way, while pyrite has been a source of sulfur via sulfuric acid. In volcanic regions in Sicily, in ancient times, it was found on the surface of the Earth, and the "*Sicilian process*" was used: sulfur deposits were piled and stacked in brick kilns built on sloping hillsides, with airspaces between them. Then, some sulfur was pulverized, spread over the stacked ore and ignited, causing the free sulfur to melt down the hills.

Today's sulfur production is as a side product of other industrial processes such as oil refining; in these processes, sulfur often occurs as undesired or detrimental compounds that are extracted and converted to elemental sulfur.

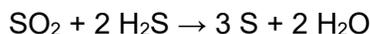
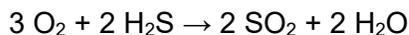
As a mineral, native sulfur under salt domes is thought to be a fossil mineral resource, produced by the action of ancient bacteria on sulfate deposits. It was removed from such salt-dome mines mainly by the Frasch process. In this method, superheated water was pumped into a native sulfur deposit to melt the sulfur, and then compressed air returned the 99.5% pure melted product to the surface. Throughout the 20th century this procedure produced elemental sulfur that required no further purification.

Today, sulfur is produced from petroleum, natural gas, and related fossil resources, from which it is obtained mainly as hydrogen sulfide.

Organosulfur compounds, undesirable impurities in petroleum, may be upgraded by subjecting them to hydrodesulfurization, which cleaves the C–S bonds:



The resulting hydrogen sulfide from this process, and also as it occurs in natural gas, is converted into elemental sulfur by the Claus process. This process entails oxidation of some hydrogen sulfide to sulfur dioxide and then the comproportionation of the two:



### Compounds

Common oxidation states of sulfur range from –2 to +6. Sulfur forms stable compounds with all elements except the noble gases.

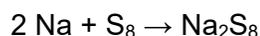
### Sulfides

Treatment of sulfur with hydrogen gives hydrogen sulfide. When dissolved in water, hydrogen sulfide is mildly acidic:



Hydrogen sulfide gas and the hydrosulfide anion are extremely toxic to mammals, due to their inhibition of the oxygen-carrying capacity of hemoglobin and certain cytochromes in a manner analogous to cyanide and azide.

Reduction of elemental sulfur gives polysulfides, which consist of chains of sulfur atoms terminated with S<sup>–</sup> centers:



This reaction highlights arguably the single most distinctive property of sulfur: its ability to catenate (bind to itself by formation of chains). Protonation of these polysulfide anions gives the polysulfanes, H<sub>2</sub>S<sub>x</sub> where x = 2, 3, and 4. Ultimately reduction of sulfur gives sulfide salts:

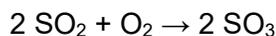
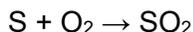


The interconversion of these species is exploited in the sodium-sulfur battery. The radical anion S<sub>3</sub><sup>–</sup> gives the blue color of the mineral lapis lazuli.

With very strong oxidants, S<sub>8</sub> can be oxidized, for example, to give bicyclic S<sub>8</sub><sup>2+</sup>.

## Oxides and Oxyanions

The principal sulfur oxides are obtained by burning sulfur:



Other oxides are known, e.g. sulfur monoxide and disulfur mono- and dioxides, but they are unstable.

The sulfur oxides form numerous oxyanions with the formula  $\text{SO}_n^{2-}$ . Sulfur dioxide and sulfites ( $\text{SO}_2^{2-}$ ) are related to the unstable sulfurous acid ( $\text{H}_2\text{SO}_3$ ). Sulfur trioxide and sulfates ( $\text{SO}_4^{2-}$ ) are related to sulfuric acid. Sulfuric acid and  $\text{SO}_3$  combine to give oleum, a solution of pyrosulfuric acid ( $\text{H}_2\text{S}_2\text{O}_7$ ) in sulfuric acid.

Peroxides convert sulfur into unstable such as  $\text{S}_8\text{O}$ , a sulfoxide. Peroxymonosulfuric acid ( $\text{H}_2\text{SO}_5$ ) and peroxydisulfuric acids ( $\text{H}_2\text{S}_2\text{O}_8$ ), made from the action of  $\text{SO}_3$  on concentrated  $\text{H}_2\text{O}_2$ , and  $\text{H}_2\text{SO}_4$  on concentrated  $\text{H}_2\text{O}_2$  respectively.

Thiosulfate salts ( $\text{S}_2\text{O}_3^{2-}$ ), sometimes referred as "hyposulfites", used in photographic fixing (HYPO) and as reducing agents, feature sulfur in two oxidation states. Sodium dithionite, ( $\text{S}_2\text{O}_4^{2-}$ ), contains the more highly reducing dithionite anion. Sodium dithionate ( $\text{Na}_2\text{S}_2\text{O}_6$ ) is the first member of the polythionic acids ( $\text{H}_2\text{S}_n\text{O}_6$ ), where  $n$  can range from 3 to many.

## Halides and Oxyhalides

The two main sulfur fluorides are sulfur hexafluoride, a dense gas used as nonreactive and nontoxic propellant, and sulfur tetrafluoride, a rarely used organic reagent that is highly toxic. Their chlorinated analogs are sulfur dichloride and sulfur monochloride. Sulfuryl chloride and chlorosulfuric acid are derivatives of sulfuric acid; thionyl chloride ( $\text{SOCl}_2$ ) is a common reagent in organic synthesis.

## Pnictides

An important S–N compound is the cage tetrasulfur tetranitride ( $\text{S}_4\text{N}_4$ ). Heating this compound gives polymeric sulfur nitride ( $(\text{SN})_x$ ), which has metallic properties even though it does not contain any metal atoms. Thiocyanates contain the  $\text{SCN}^-$  group. Oxidation of thiocyanate gives thiocyanogen,  $(\text{SCN})_2$  with the connectivity  $\text{NCS-SCN}$ . Phosphorus sulfides are numerous, the most important commercially being the cages  $\text{P}_4\text{S}_{10}$  and  $\text{P}_4\text{S}_3$ .

## Metal Sulfides

The principal ores of copper, zinc, nickel, cobalt, molybdenum, and other metals are sulfides. These materials tend to be dark-colored semiconductors that are not readily attacked by water or even many acids. They are formed, both geochemically and in the laboratory, by the reaction of hydrogen sulfide with metal salts.

The mineral galena ( $\text{PbS}$ ) was the first demonstrated semiconductor and found a use as a signal rectifier in the cat's whiskers of early crystal radios.

The iron sulfide called pyrite, the so-called "fool's gold," has the formula  $\text{FeS}_2$ . The upgrading of these ores, usually by roasting, is costly and environmentally hazardous. Sulfur corrodes many metals via the process called tarnishing.

## Tin

Tin is a chemical element with symbol **Sn** (for Latin: *stannum*) and atomic number 50. It is a main group metal in group 14 of the periodic table. Tin shows chemical similarity to neighboring group 14 elements, germanium and lead and has two possible oxidation states, +2 and the slightly more stable +4. Tin is the 49th most abundant element and has, with 10 stable isotopes, the largest number of stable isotopes in the periodic table. Tin is obtained chiefly from the mineral cassiterite, where it occurs as tin dioxide,  $\text{SnO}_2$ .

This silvery, malleable post-transition metal is not easily oxidized in air and is used to coat other metals to prevent corrosion. The first alloy, used in large scale since 3000 BC, was bronze, an alloy of tin and copper. After 600 BC pure metallic tin was produced.

Pewter, which is an alloy of 85–90% tin with the remainder commonly consisting of copper, antimony and lead, was used for flatware from the Bronze Age until the 20th century. In modern times tin is used in many alloys, most notably tin/lead soft solders, typically containing 60% or more of tin.

Another large application for tin is corrosion-resistant tin plating of steel. Because of its low toxicity, tin-plated metal is also used for food packaging, giving the name to tin cans, which are made mostly of steel.



### Characteristics

#### Physical Properties

Tin is a malleable, ductile and highly crystalline silvery-white metal. When a bar of tin is bent, a crackling sound known as the tin cry can be heard due to the twinning of the crystals. Tin melts at a low temperature of about 232 °C (449.6 °F);, which is further reduced to 177.3 °C (351 °F) for 11-nm particles.

$\beta$ -tin (the metallic form, or white tin), which is stable at and above room temperature, is malleable. In contrast,  $\alpha$ -tin (nonmetallic form, or gray tin), which is stable below 13.2 °C (56 °F), is brittle.  $\alpha$ -tin has a diamond cubic crystal structure, similar to diamond, silicon or germanium.  $\alpha$ -tin has no metallic properties at all because its atoms form a covalent structure where electrons cannot move freely.

It is a dull-gray powdery material with no common uses, other than a few specialized semiconductor applications. These two allotropes,  $\alpha$ -tin and  $\beta$ -tin, are more commonly known as *gray tin* and *white tin*, respectively.

Two more allotropes,  $\gamma$  and  $\sigma$ , exist at temperatures above 161 °C (322 °F) and pressures above several GPa. Although the  $\alpha$ - $\beta$  transformation temperature is nominally 13.2 °C, impurities (e.g. Al, Zn, etc.) lower the transition temperature well below 0 °C (32 °F), and upon addition of Sb or Bi the transformation may not occur at all, increasing the durability of the tin.

Commercial grades of tin (99.8%) resist transformation because of the inhibiting effect of the small amounts of bismuth, antimony, lead and silver present as impurities. Alloying elements such as copper, antimony, bismuth, cadmium and silver increase its hardness. Tin tends rather easily to form hard, brittle intermetallic phases, which are often undesirable. It does not form wide solid solution ranges in other metals in general, and there are few elements that have appreciable solid solubility in tin. Simple eutectic systems, however, occur with bismuth, gallium, lead, thallium and zinc.

Tin becomes a superconductor below 3.72 K. In fact, tin was one of the first superconductors to be studied; the Meissner effect, one of the characteristic features of superconductors, was first discovered in superconducting tin crystals.

### **Chemical properties**

Tin resists corrosion from water but can be attacked by acids and alkalis. Tin can be highly polished and is used as a protective coat for other metals. In this case the formation of a protective oxide layer is used to prevent further oxidation. This oxide layer forms on pewter and other tin alloys. Tin acts as a catalyst when oxygen is in solution and helps accelerate chemical attack.

### **Isotopes**

Tin is the element with the greatest number of stable isotopes, ten; these include all those with atomic masses between 112 and 124, with the exception of 113, 121 and 123. Of these, the most abundant ones are  $^{120}\text{Sn}$  (at almost a third of all tin),  $^{118}\text{Sn}$ , and  $^{116}\text{Sn}$ , while the least abundant one is  $^{115}\text{Sn}$ . The isotopes possessing even mass numbers have no nuclear spin while the odd ones have a spin of  $+1/2$ . Tin, with its three common isotopes  $^{115}\text{Sn}$ ,  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$ , is among the easiest elements to detect and analyze by NMR spectroscopy, and its chemical shifts are referenced against  $\text{SnMe}_4$ .

This large number of stable isotopes is thought to be a direct result of tin possessing an atomic number of 50, which is a "magic number" in nuclear physics. There are 28 additional unstable isotopes that are known, encompassing all the remaining ones with atomic masses between 99 and 137.

Aside from  $^{126}\text{Sn}$ , which has a half-life of 230,000 years, all the radioactive isotopes have a half-life of less than a year. The radioactive  $^{100}\text{Sn}$  is one of the few nuclides possessing a "doubly magic" nucleus and was discovered relatively recently, in 1994. Another 30 metastable isomers have been characterized for isotopes between 111 and 131, the most stable of which being  $^{121\text{m}}\text{Sn}$ , with a half-life of 43.9 years.

### **Etymology**

The Latin name *stannum* originally meant an alloy of silver and lead, and came to mean 'tin' in the 4th century BC—the earlier Latin word for it was *plumbum candidum* 'white lead'.

### **History**

**Tin** extraction and use can be dated to the beginnings of the Bronze Age around 3000 BC, when it was observed that copper objects formed of polymetallic ores with different metal contents had different physical properties.

The earliest bronze objects had tin or arsenic content of less than 2% and are therefore believed to be the result of unintentional alloying due to trace metal content in the copper ore. The addition of a second metal to copper increases its hardness, lowers the melting temperature, and improves the casting process by producing a more fluid melt that cools to a denser, less spongy metal.

This was an important innovation that allowed for the much more complex shapes cast in closed molds of the Bronze Age. Arsenical bronze objects appear first in the Near East where arsenic is commonly found in association with copper ore, but the health risks were quickly realized and the quest for sources of the much less hazardous tin ores began early in the Bronze Age. This created the demand for rare tin metal and formed a trade network that linked the distant sources of tin to the markets of Bronze Age cultures.

Cassiterite ( $\text{SnO}_2$ ), the tin oxide form of tin, was most likely the original source of tin in ancient times. Other forms of tin ores are less abundant sulfides such as stannite that require a more involved smelting process. Cassiterite often accumulates in alluvial channels as placer deposits due to the fact that it is harder, heavier, and more chemically resistant than the granite in which it typically forms.

These deposits can be easily seen in river banks as cassiterite is usually black, purple or otherwise dark in color, a feature exploited by early Bronze Age prospectors. It is likely that the earliest deposits were alluvial in nature, and perhaps exploited by the same methods used for panning gold in placer deposits.

### **Compounds and Chemistry**

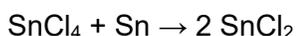
In the great majority of its compounds, tin has the oxidation state II or IV.

#### **Inorganic Compounds**

Halide compounds are known for both oxidation states. For Sn(IV), all four halides are well known:  $\text{SnF}_4$ ,  $\text{SnCl}_4$ ,  $\text{SnBr}_4$ , and  $\text{SnI}_4$ . The three heavier members are volatile molecular compounds, whereas the tetrafluoride is polymeric. All four halides are known for Sn(II) also:  $\text{SnF}_2$ ,  $\text{SnCl}_2$ ,  $\text{SnBr}_2$ , and  $\text{SnI}_2$ . All are polymeric solids. Of these eight compounds, only the iodides are colored.

Tin (II) chloride (also known as stannous chloride) is the most important tin halide in a commercial sense. Illustrating the routes to such compounds, chlorine reacts with tin metal to give  $\text{SnCl}_4$  whereas the reaction of hydrochloric acid and tin gives  $\text{SnCl}_2$  and hydrogen gas.

Alternatively  $\text{SnCl}_4$  and Sn combine to stannous chloride via a process called comproportionation:



Tin can form many oxides, sulfides, and other chalcogenide derivatives. The dioxide  $\text{SnO}_2$  (cassiterite) forms when tin is heated in the presence of air.  $\text{SnO}_2$  is amphoteric, which means that it dissolves in both acidic and basic solutions.

There are also stannates with the structure  $[\text{Sn}(\text{OH})_6]^{2-}$ , like  $\text{K}_2[\text{Sn}(\text{OH})_6]$ , although the free stannic acid  $\text{H}_2[\text{Sn}(\text{OH})_6]$  is unknown. The sulfides of tin exist in both the +2 and +4 oxidation states: tin (II) sulfide and tin (IV) sulfide (mosaic gold).

### Hydrides

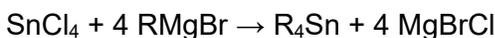
Stannane ( $\text{SnH}_4$ ), where tin is in the +4 oxidation state, is unstable. Organotin hydrides are however well known, e.g. tributyltin hydride ( $\text{Sn}(\text{C}_4\text{H}_9)_3\text{H}$ ). These compound release transient tributyl tin radicals, rare examples of compounds of tin (III).

### Organotin Compounds

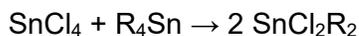
Organotin compounds, sometimes called stannanes, are chemical compounds with tin-carbon bonds. Of the compounds of tin, the organic derivatives are the most useful commercially. Some organotin compounds are highly toxic and have been used as biocides. The first organotin compound to be reported was diethyltin diiodide ( $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ ), reported by Edward Frankland in 1849.

Most organotin compounds are colorless liquids or solids that are stable to air and water. They adopt tetrahedral geometry. Tetraalkyl- and tetraaryltin compounds can be prepared using

### Grignard reagents:



The mixed halide-alkyls, which are more common and more important commercially than the tetraorgano derivatives, are prepared by redistribution reactions:

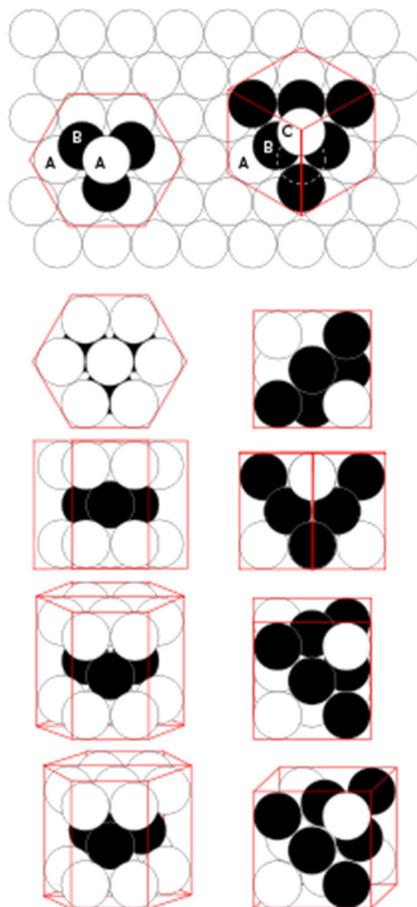


Divalent organotin compounds are uncommon, although more common than related divalent organogermanium and organosilicon compounds. The greater stabilization enjoyed by  $\text{Sn}(\text{II})$  is attributed to the "inert pair effect". Organotin(II) compounds include both stannylenes (formula:  $\text{R}_2\text{Sn}$ , as seen for singlet carbenes) and distannylenes ( $\text{R}_4\text{Sn}_2$ ), which are roughly equivalent to alkenes. Both classes exhibit unusual reactions.

## Metals Section

A **metal** (from Greek "μέταλλον" – *métallon*, "mine, quarry, metal") is an element, compound, or alloy that is a good conductor of both electricity and heat. Metals are usually malleable, ductile and shiny. The meaning of the term "metal" differs for various communities. Many elements and compounds that are not normally classified as metals become metallic under high pressures.

### Structure and Bonding



hcp and fcc close-packing of spheres

Metals typically consist of close-packed atoms, meaning that the atoms are arranged like closely packed spheres. Two packing motifs are common, one being body-centered cubic wherein each metal atom is surrounded by eight equivalent atoms. The other main motif is face-centered cubic where the metal atoms are surrounded by six neighboring atoms. Several metals adopt both structures, depending on the temperature.

In a metal, atoms readily lose electrons to form positive ions (cations). Those ions are surrounded by de-localized electrons, which are responsible for the conductivity. The solid thus produced is held together by electrostatic interactions between the ions and the electron cloud, which are called metallic bonds.

## Properties

### Chemical

Metals are usually inclined to form cations through electron loss, reacting with oxygen in the air to form oxides over various timescales (iron rusts over years, while potassium burns in seconds).

Examples:



The transition metals (such as iron, copper, zinc, and nickel) are slower to oxidize because they form passivating layer of oxide that protects the interior. Others, like palladium, platinum and gold, do not react with the atmosphere at all. Some metals form a barrier layer of oxide on their surface which cannot be penetrated by further oxygen molecules and thus retain their shiny appearance and good conductivity for many decades (like aluminum, magnesium, some steels, and titanium). The oxides of metals are generally basic, as opposed to those of nonmetals, which are acidic.

Painting, anodizing or plating metals are good ways to prevent their corrosion. However, a more reactive metal in the electrochemical series must be chosen for coating, especially when chipping of the coating is expected. Water and the two metals form an electrochemical cell, and if the coating is less reactive than the coatee, the coating actually *promotes* corrosion.

### Physical

Metals in general have high electrical conductivity, high thermal conductivity, and high density. Typically they are malleable and ductile, deforming under stress without cleaving. In terms of optical properties, metals are shiny and lustrous. Sheets of metal beyond a few micrometers in thickness appear opaque, but gold leaf transmits green light.

Although most metals have higher densities than most nonmetals, there is wide variation in their densities, Lithium being the least dense solid element and osmium the densest. The alkali and alkaline earth metals in groups I A and II A are referred to as the light metals because they have low density, low hardness, and low melting points. The high density of most metals is due to the tightly packed crystal lattice of the metallic structure.

The strength of metallic bonds for different metals reaches a maximum around the center of the transition metal series, as those elements have large amounts of delocalized electrons in tight binding type metallic bonds. However, other factors (such as atomic radius, nuclear charge, number of bonds orbitals, overlap of orbital energies, and crystal form) are involved as well.

### Electrical

The electrical and thermal conductivities of metals originate from the fact that their outer electrons are delocalized. Metals can be viewed as a collection of atoms embedded in a sea of electrons, which are highly mobile.

The electrical conductivity, as well as the electrons' contribution to the heat capacity and heat conductivity of metals can be calculated from the free electron model, which does not take into account the detailed structure of the ion lattice.

When considering the band structure and binding energy of a metal, it is necessary to take into account the positive potential caused by the specific arrangement of the ion cores – which is periodic in crystals. The most important consequence of the periodic potential is the formation of a small band gap at the boundary of the Brillouin zone. Mathematically, the potential of the ion cores can be treated by various models, the simplest being the nearly free electron model.

### **Mechanical**

Mechanical properties of metals include ductility, i.e. their capacity for plastic deformation. Reversible elastic deformation in metals can be described by Hooke's Law for restoring forces, where the stress is linearly proportional to the strain. Forces larger than the elastic limit, or heat, may cause a permanent (irreversible) deformation of the object, known as plastic deformation or plasticity.

This irreversible change in atomic arrangement may occur as a result of:

- The action of an applied force (or work). An applied force may be tensile (pulling) force, compressive (pushing) force, shear, bending or torsion (twisting) forces.
- A change in temperature (heat). A temperature change may affect the mobility of the structural defects such as grain boundaries, point vacancies, line and screw dislocations, stacking faults and twins in both crystalline and non-crystalline solids. The movement or displacement of such mobile defects is thermally activated, and thus limited by the rate of atomic diffusion.

Viscous flow near grain boundaries, for example, can give rise to internal slip, creep and fatigue in metals. It can also contribute to significant changes in the microstructure like grain growth and localized densification due to the elimination of intergranular porosity. Screw dislocations may slip in the direction of any lattice plane containing the dislocation, while the principal driving force for "dislocation climb" is the movement or diffusion of vacancies through a crystal lattice.

In addition, the non-directional nature of metallic bonding is also thought to contribute significantly to the ductility of most metallic solids.

When the planes of an ionic bond slide past one another, the resultant change in location shifts ions of the same charge into close proximity, resulting in the cleavage of the crystal; such shift is not observed in covalently bonded crystals where fracture and crystal fragmentation occurs.

### **Alloys**

An alloy is a mixture of two or more elements in solid solution in which the major component is a metal. Most pure metals are either too soft, brittle or chemically reactive for practical use. Combining different ratios of metals as alloys modifies the properties of pure metals to produce desirable characteristics. The aim of making alloys is generally to make them less brittle, harder, resistant to corrosion, or have a more desirable color and luster.

Of all the metallic alloys in use today, the alloys of iron (steel, stainless steel, cast iron, tool steel, alloy steel) make up the largest proportion both by quantity and commercial value. Iron alloyed with various proportions of carbon gives low, mid and high carbon steels, with increasing carbon levels reducing ductility and toughness. The addition of silicon will produce cast irons, while the addition of chromium, nickel and molybdenum to carbon steels (more than 10%) results in stainless steels.

Other significant metallic alloys are those of aluminum, titanium, copper and magnesium. Copper alloys have been known since prehistory—bronze gave the Bronze Age its name—and have many applications today, most importantly in electrical wiring. The alloys of the other three metals have been developed relatively recently; due to their chemical reactivity they require electrolytic extraction processes. The alloys of aluminum, titanium and magnesium are valued for their high strength-to-weight ratios; magnesium can also provide electromagnetic shielding.

These materials are ideal for situations where high strength-to-weight ratio is more important than material cost, such as in aerospace and some automotive applications. Alloys specially designed for highly demanding applications, such as jet engines, may contain more than ten elements.

## **Categories**

### **Base Metal**

In chemistry, the term *base metal* is used informally to refer to a metal that oxidizes or corrodes relatively easily, and reacts variably with dilute hydrochloric acid (HCl) to form hydrogen. Examples include iron, nickel, lead and zinc. Copper is considered a base metal as it oxidizes relatively easily, although it does not react with HCl. It is commonly used in opposition to noble metal.

In alchemy, a *base metal* was a common and inexpensive metal, as opposed to precious metals, mainly gold and silver. A longtime goal of the alchemists was the transmutation of base metals into precious metals.

### **Ferrous metal**

The term "ferrous" is derived from the Latin word meaning "containing iron". This can include pure iron, such as wrought iron, or an alloy such as steel. Ferrous metals are often magnetic, but not exclusively.

### **Noble Metal**

*Noble metals* are metals that are resistant to corrosion or oxidation, unlike most base metals. They tend to be precious metals, often due to perceived rarity. Examples include gold, platinum, silver and rhodium.

### **Precious Metal**

Chemically, the precious metals are less reactive than most elements, have high luster and high electrical conductivity. Historically, precious metals were important as currency, but are now regarded mainly as investment and industrial commodities. Gold, silver, platinum and palladium each have an ISO 4217 currency code. The best-known precious metals are gold and silver. While both have industrial uses, they are better known for their uses in art, jewelry, and coinage. Other precious metals include the platinum group metals: ruthenium, rhodium, palladium, osmium, iridium, and platinum, of which platinum is the most widely traded.

The demand for precious metals is driven not only by their practical use, but also by their role as investments and a store of value. Silver is substantially less expensive than these metals, but is often traditionally considered a precious metal for its role in coinage and jewelry.

### **Extraction**

Metals are often extracted from the Earth by means of mining, resulting in ores that are relatively rich sources of the requisite elements. Ore is located by prospecting techniques, followed by the exploration and examination of deposits.

Mineral sources are generally divided into surface mines, which are mined by excavation using heavy equipment, and subsurface mines. Once the ore is mined, the metals must be extracted, usually by chemical or electrolytic reduction.

Pyrometallurgy uses high temperatures to convert ore into raw metals, while hydrometallurgy employs aqueous chemistry for the same purpose. The methods used depend on the metal and their contaminants.

When a metal ore is an ionic compound of that metal and a non-metal, the ore must usually be smelted — heated with a reducing agent — to extract the pure metal. Many common metals, such as iron, are smelted using carbon as a reducing agent. Some metals, such as aluminum and sodium, have no commercially practical reducing agent, and are extracted using electrolysis instead.

Sulfide ores are not reduced directly to the metal but are roasted in air to convert them to oxides.



## Summaries of EPA Arsenic Publications - Arsenic

### Regulations on the Disposal of Arsenic Residuals from Drinking Water Treatment Plants EPA 600-R-00-025

As with other production processes, water treatment systems produce a product and a residual of that product. With the passage of the various federal statutes, restrictions have been placed on the discharge of residuals to water bodies and onto land. This report summarizes federal regulations and selected state regulations that govern the management of residuals produced by small drinking water treatment systems removing arsenic from drinking water. Arsenic is a naturally occurring contaminant in ground water and many small water treatment facilities use ground water as their primary source of water. Under the Safe Drinking Water Act (SDWA), a maximum contaminant level (MCL) of 0.05 mg/L has been established for arsenic in drinking water. Under the 1996 SDWA Amendments, the EPA is required to develop a revised arsenic regulation by January 2001. Concerns have been raised as to the technical feasibility and regulatory implication of a more stringent arsenic MCL on the disposal of the residuals from arsenic removal processes. This document reports on five water treatment processes known to be effective for arsenic removal from small ground water systems. The five processes are anion exchange, activated alumina adsorption, iron/manganese removal, media adsorption, and membrane processes. For each technology, a brief description is provided of the treatment process along with a discussion of the residual production characteristics.

An overview is provided of the federal regulations that apply to the management of residuals, with a focus on arsenic removal residuals. The purpose of this overview is to provide guidance to water suppliers on the federal regulatory requirements of residuals management to better evaluate compliance of existing practices and to plan for needed changes in treatment plant operations.

Specific disposal methods are summarized by the form of the residuals including liquid residuals (direct discharges, indirect discharges, underground injection, and land disposal) and solid/sludge residuals (solid waste landfill, hazardous waste landfill, lagoons, reuse of hazardous waste, reuse of solid waste, and off-site disposal) and the method in which the residuals are managed. Federal regulations summarized include the Clean Water Act (NPDES, Pretreatment), SDWA (Underground Injection Control and lagoons), and Resource Conservation and Recovery Act (Subtitles C/D). In addition to the federal regulations that impact the management of arsenic drinking water treatment residuals, regulations imposed by seven states were also reviewed.

The seven states (Arizona, California, Maine, Nebraska, New Mexico, Nevada, and Pennsylvania) were chosen based on arsenic occurrence and regional representation. The review of the state regulations also focused on characterizing the requirements that apply to different management options available for liquid and solid residuals generated by treatment systems that remove arsenic from drinking water. It was found that many components of the state regulatory programs were generally consistent with the federal minimum requirements.

## **Arsenic Removal from Drinking Water by Coagulation/filtration and Lime Softening Plants** EPA 600-R-00-063

This report documents treatment plant information as well as results of sampling and analysis at two coagulation/filtration plants (referred to in this document as Plants A and B) and one lime softening plant (referred to as Plant C). The objective of sampling and analysis was to evaluate the effectiveness of the water treatment plants to consistently remove arsenic (As) from source water. Additionally, data were collected in this study to evaluate the characteristics of the residuals produced by the treatment processes.

The study was divided into three phases: source water sampling, preliminary sampling, and long-term evaluation. The first phase, source water sampling, was conducted to evaluate source water characteristics at each plant. The second phase, preliminary sampling, consisted of a four-week sampling period to refine procedures prior to implementing the long-term evaluation phase. The third phase, long-term evaluation, consisted of weekly sample collection and analysis for approximately 1 year. Sludge samples also were collected at each facility during a single sampling event from settling lagoons/ponds during a two-month period.

Samples of recycle supernatant water (Plant A) and supernatant discharge water (Plants B and C) were collected monthly beginning in November 1998 and continuing until June 1999. Long-term evaluation of Plants A and B demonstrated that conventional coagulation/filtration can consistently achieve low levels of arsenic in the treated water (i.e., less than 5 µg/L). The total arsenic concentrations at Plant A were reduced by an average of 52%, which represents a decrease of average arsenic concentrations from 7.5 µg/L in the source water to 3.5 µg/L in the finished water. Average total arsenic removal efficiency at Plant B was 79%, with an average source water concentration of 19.1 µg/L and an average finished water concentration of 4.0 µg/L. Adsorption and coprecipitation of As(V) with iron and aluminum flocs are believed to have been the primary arsenic removal mechanisms at these plants.

The lime softening facility, Plant C, was not able to consistently reduce arsenic to low levels in treated water. The average total arsenic concentration in Plant C source water was 32.0 µg/L, and the lime softening plant reduced the average total arsenic concentration to 16.6 µg/L in the finished water, which equals a 45% removal efficiency. As(III) was the primary species of soluble arsenic in the raw water and was almost completely oxidized to As(V) as a result of two chlorination steps that occurred prior to softening and prior to filtration.

The primary mechanism of arsenic removal was likely adsorption and coprecipitation of As(V) with iron that was present in the source water. Plant C operated at a pH of 9.6, a level at which arsenic removal by coprecipitation with calcium carbonate is reported to be less than 10% (Sorg and Logsdon, 1978; McNeill and Edwards, 1997b).

None of the sludge samples collected at Plants A, B, and C qualified as a hazardous waste based on Toxicity Characteristic Leaching Procedure (TCLP) testing for metals. Therefore, nonhazardous waste landfills should be able to accept the sludge generated by these treatment processes.

## Arsenic Removal from Drinking Water by Iron Removal Plants

EPA 600-R-00-086

The study was divided into three phases: source water sampling, preliminary sampling, and longterm evaluation. The first phase, source water sampling, was conducted to evaluate source water characteristics at each plant. The second phase, preliminary sampling, was initiated at Plant A in April 1998 and at Plant B in May 1998. This phase consisted of a four-week sampling period to refine procedures for subsequent events during the third phase.

The third phase, long-term evaluation, consisted of weekly sample collection and analysis beginning in June 1998 and continuing through June 1999 at Plant A and through December 1998 at Plant B. Plant personnel conducted all sampling during the long-term evaluation phase and Battelle coordinated sampling logistics. Sludge samples also were collected at Plant A during a single sampling event from an outdoor settling pond in November 1998. Samples of supernatant discharge (Plant A) and recycle supernatant (Plant B) were collected monthly beginning in November 1998 and continuing until June 1999 at Plant A and until January 1999 at Plant B.

Results from the long-term evaluation phase were varied regarding the ability of the iron removal process to consistently achieve low-level arsenic concentrations (e.g.,  $<5 \mu\text{g/L}$  in the finished water). The total arsenic concentrations at Plant A were reduced by an average of 87%, which represents a decrease in average arsenic concentration from  $20.3 \mu\text{g/L}$  to  $3.0 \mu\text{g/L}$ .

Adsorption and coprecipitation with iron hydroxide precipitates are believed to be the primary arsenic removal mechanisms. The total arsenic concentrations at Plant B were reduced by an average of 74%, which represents a decrease in average arsenic concentration from  $48.5 \mu\text{g/L}$  to  $11.9 \mu\text{g/L}$ . At Plant B, it appeared that only the particulate arsenic in the source water was removed. This particulate arsenic was most likely associated with the oxidized iron particles present in the source water (i.e., arsenic sorbed onto iron particles).

The primary difference in arsenic removal efficiency at Plants A and B is believed to be the amount of iron in the source water. Source water at Plant A averaged  $2,284 \mu\text{g/L}$  of iron, while Plant B averaged  $1,137 \mu\text{g/L}$ . Increasing the iron in the source water at Plant B using a coagulant, such as ferric chloride, would likely enable Plant B to consistently achieve lower levels of arsenic.

None of the sludge samples collected at Plant A qualified as a hazardous waste based on the Toxicity Characteristic Leaching Procedure (TCLP) test for metals. Therefore, nonhazardous waste landfills should be able to accept the sludge generated by this treatment facility. Stricter hazardous waste classification regulations in some states, such as California, on total arsenic concentrations in solid waste also were met at Plant A. Sludge samples were not collected at Plant B; however, analytical results were provided from a 1994 sludge sampling event.

## **Arsenic Removal from Drinking Water by Ion Exchange and Activated Alumina Plants**

EPA 600-R-00-088

This report documents treatment plant information as well as results of year-long sampling and analysis at two ion exchange (IX) plants (referred to as Plants A and B) and two activated alumina (AA) plants (referred to as Plants C and D), with capacities varying from 800 to 3,000 gallons per day (gpd). The objective of sampling and analysis was to evaluate the performance of the full-scale water treatment plants to consistently remove arsenic from source water. Additionally, data were collected to evaluate the chemical characteristics of residuals produced by these treatment processes.

The study was divided into three phases: source water sampling, preliminary sampling, and long-term evaluation.

Source water sampling was conducted to evaluate source water characteristics at each plant. Preliminary sampling was initiated in August 1998 and consisted of four sampling events conducted at each facility on either a weekly or biweekly basis to refine procedures for subsequent events during the third phase.

Samples from resin regeneration were collected at Plant A from March to June 1999. Spent AA samples were collected at Plants C and D during the media change-out events in December 1998 and May 1999, respectively. Results from the long-term evaluation demonstrated that both the IX and AA systems are capable of achieving arsenic levels of less than 5 µg/L in the treated water, provided that the IX resin was regenerated or the AA medium was changed out before arsenic breakthrough occurred. The two IX systems had inlet arsenic concentrations between 45 and 65 µg/L [primarily As(V)].

When Plant A was operated beyond 3,000 to 3,200 bed volumes (BV) of water, arsenic chromatographic peaking occurred. Arsenic breakthrough was not observed at Plant B where an average 97% of removal efficiency was achieved, leaving only 0.8 to 4.5 µg/L arsenic in the finished water. Both AA systems consisted of two parallel treatment trains with a roughing AA column followed by a polishing column in each train.

The systems operated on a media throwaway basis. The average arsenic removal efficiencies achieved at Plants C and D were 87% and 98%, respectively. The raw water at Plant C (34 to 76 µg/L total arsenic) contained approximately 0.3 to 28.8 µg/L As(III), which was nearly completely removed, even though no oxidation treatment was provided. The water at Plant D contained slightly higher total arsenic concentrations (53.3 to 87 µg/L) but no As(III), which was consistently removed to less than 5 µg/L in the finished water.

The AA media in the roughing tanks were exhausted and disposed of about every 1 to 1.5 years after treating approximately 9,600 BV at Plant C and 5,260 BV at Plant D. The regeneration process at Plant A recovered from 67 to 86% of arsenic from the spent brine. The spent AA at Plants C and D passed the Toxicity Characteristic Leaching Procedure (TCLP) test for metals including arsenic, and therefore was disposed of as nonhazardous waste.

## Laboratory Study on the Oxidation of Arsenic III to Arsenic V

EPA 600-R-01-021

A one-year laboratory study was performed to determine the ability of seven oxidants to oxidize As(III) to As(V).

These included chlorine, permanganate, ozone, chlorine dioxide, monochloramine, a solid-phase oxidizing media, and 254 nm ultraviolet light. Chlorine and permanganate rapidly oxidized As(III) to As(V) in the pH range of 6.3 to 8.3. Dissolved manganese, dissolved iron, sulfide and TOC slowed the rate of oxidation slightly, but essentially complete oxidation was obtained in less than one minute with chlorine and permanganate under all conditions studied.

In the absence of interfering reductants, ozone rapidly oxidized As(III). Although, dissolved manganese and dissolved iron had no significant effect on As(III) oxidation, the presence of sulfide considerably slowed the oxidation reaction. The presence of TOC had a quenching effect on As(III) oxidation by ozone, producing incomplete oxidation at the higher TOC concentration studied.

Only limited As(III) oxidation was obtained using chlorine dioxide, which was probably due to the presence of chlorine (as a by-product) in the chlorine dioxide stock solutions. The reason for the ineffectiveness of chlorine dioxide was not studied.

Preformed monochloramine was ineffective for As(III) oxidation, whereas limited oxidation was obtained when monochloramine was formed in-situ. This showed that the injected chlorine probably reacted with As(III) before being quenched by ammonia to form monochloramine. Filox, a manganese dioxide-based media, was effective for As(III) oxidation. When dissolved oxygen (DO) was not limiting, complete oxidation was observed under all conditions studied.

However, when DO was reduced, incomplete oxidation was obtained in the presence of interfering reductants. The adverse effect of interfering reductants was completely eliminated by either (a) supplying enough DO or (b) increasing the contact time. In addition to oxidizing As(III), the Filox media also removed some arsenic by adsorption, which diminished greatly as the media came into equilibrium with the As(III)-spiked synthetic water.

UV light alone (254 nm) was not very effective for As(III) oxidation. Significant oxidation was observed only at very low flow rates representing 0.6 - 2.5% of the rated capacities of the two UV sterilizer units tested. However, as reported in a patented process, complete oxidation by UV light was observed when the challenge water was spiked with 1.0 mg/L sulfite.

## Treatment of Arsenic Residuals from Drinking Water Removal Processes

EPA 600-R-01-033

The drinking water MCL was recently lowered from 0.05 mg/L to 0.01 mg/L. One concern was that a reduction in the TCLP arsenic limit in response to the drinking water MCL could be problematic with regard to disposal of solid residuals generated at arsenic removal facilities. This project focused on developing a short-list of arsenic removal options for residuals produced by ion exchange (Ion Ex), reverse osmosis (RO), nanofiltration (NF), activated alumina (AA), and iron removal processes. Both precipitation and adsorption processes were evaluated to assess their arsenic removal effectiveness.

In precipitation tests, ferric chloride outperformed alum for removal of arsenic from residuals by sedimentation, generally resulting in arsenic removals of 88 to 99 percent. Arsenic removal from the high alkalinity ion exchange samples was poorer. The required iron-to-arsenic molar ratio for best removal of arsenic in these screening tests varied widely from 4:1 to 191:1, depending on residuals type, and best arsenic removal using ferric chloride typically occurred between pH 5.0 and 6.2.

Polymer addition typically did not significantly improve arsenic removal using either coagulant. Supernatant total arsenic levels of 0.08 mg/L or lower were attained with ferric chloride precipitation for membrane concentrates and residuals from iron removal facilities compared to an in-stream arsenic limit of 0.05 mg/L in place in some states. Settling alone with no coagulant also effectively removed arsenic from iron removal facility residuals.

Even with ferric chloride dosages of 50 to 200 mg/L applied to ion exchange regenerants, supernatant arsenic levels after treatment were 1 to 18 mg/L. Required iron-to-arsenic molar ratios developed in precipitation work could be used by utilities as guidelines for establishing coagulant dose needs to meet in-stream standards, and to develop preliminary treatment costs. Adsorption tests demonstrated the potential for different types of media and resins to remove arsenic from liquid residuals, but did not assess ultimate capacity.

Overall, the iron-based granular ferric hydroxide media evaluated in testing outperformed the aluminum-based media and ion exchange resin for removal of arsenic. However, activated alumina and the iron-based media provided comparable arsenic removals of close to 100 percent with an empty bed contact time (EBCT) of 3-min for most of the membrane concentrates and the settled iron removal facility residuals. Removal of suspended solids was key to the success of adsorption for spent filter backwash water and clarifier flush residuals.

Arsenic breakthrough occurred very rapidly for the ion exchange samples and for one RO concentrate, all of which had an alkalinity of more than 1,000 mg/L (as CaCO<sub>3</sub>). This again suggests that alkalinity significantly interferes with adsorption of arsenic. Based on this work, use of adsorption media for treatment of arsenic-laden water plant residuals merits further exploration.

## Oxidation of As(III) by Aeration and Storage

EPA 600-R-01-102

A study of the effects of aeration and storage on the oxidation of arsenic(III) was undertaken at three utilities in the U.S. to establish the engineering significance of aeration as a potential pre-treatment method for arsenic removal.

Aeration has been referred to in the literature as a possible useful pre-treatment method to ensure that arsenic is in the arsenic(V) state before subsequent removal by any of several treatment processes. Since aeration is a common process for treating groundwater for iron oxidation, radon, volatile organics, carbon dioxide, and hydrogen sulfide, it is reasonable to investigate its effectiveness for arsenic(III) oxidation.

The results of this study clearly establish that aeration and aerobic storage do not oxidize arsenic(III). The major conclusion is that aeration is not effective for this purpose and should not be relied upon or expected to contribute to the oxidation of arsenic(III). One of the test sites in this study clearly showed that arsenic(III) is significantly removed by the oxidation and precipitation of iron, but this should not be attributed to an oxidation of arsenic(III) to arsenic(V) by dissolved oxygen.

Past research has established that iron precipitation can be partially effective for the adsorptive removal of arsenic(III), and this is the likely explanation for the apparent drop in arsenic(III) at the site that had high iron.

The effect of iron precipitation on the removal of arsenic was also present in the long term storage of aerated water in this study. When all of the iron (initial iron at 2.7 mg/L) precipitated from the quiescent storage water, the remaining aqueous total arsenic was entirely dissolved and in the arsenic(V) state. The aqueous arsenic(III) was below detection and apparently completely removed or converted by the insoluble iron.

Even in this case it is doubtful if DO was responsible for any oxidation of arsenic(III), because the loss directly correlated to the loss of iron precipitate and no other instance of arsenic(III) oxidation occurred at the other sites. In summary, the data supported the fact that iron is extremely important in the removal of arsenic(III), but did not support the idea that arsenic(III) is oxidized by aeration. This is true at least for the conditions used in this study.

While the subtleties of the results are interesting, especially for the site with high iron, it is important to emphasize the original objective of this study, which was to establish if typical aeration and storage methods could oxidize arsenic(III).

Based upon the results of this study, it is concluded that aeration does not oxidize arsenic(III) and that subsequent storage for up to five days does not result in arsenic(III) oxidation. Dissolved oxygen should not be considered as a candidate for arsenic(III) oxidation; however, aeration will continue to be considered a very effective process for the oxidation of iron. In that way, aeration can be said to be effective in bringing about the removal of As via the oxidative precipitation of iron.

## **Design Manual: Removal of Arsenic from Drinking Water by Adsorptive Media**

EPA 600-R-03-019

This design manual is an in-depth presentation of the steps required to design and operate a water treatment plant for removal of excess arsenic from drinking water using the adsorptive media process.

This treatment process is very reliable, simple and cost-effective. Several adsorptive media products are available in the market-place that have successfully demonstrated their capability to remove arsenic from drinking water to levels well below the revised MCL, 0.010 mg/L.

Other new products continue to be developed. The adsorptive media products are preferential for the removal of arsenic over other competing ions. Therefore, unless a water system requires treatment capability for removal of other suspended or dissolved contaminants, the adsorptive media treatment method merits evaluation.

The adsorptive media process is implemented with operational options which vary with the product selected. For water systems that are primarily concerned with financial feasibility, capital and operating costs, each operational option along with each available adsorptive media product should be evaluated. This design manual provides the methods for competently performing each evaluation.

The arsenic removal capacity of some adsorptive media products, such as activated alumina, are very sensitive to the pH of the water passing thru treatment. Others, such as iron-based products, are not. Treatment processes incorporating pH adjustment capability require careful handling and storage of corrosive chemicals (acid and caustic).

Some adsorptive media products, such as activated alumina, are capable of being chemically regenerated for repetition of treatment cycles using the same corrosive chemicals as those used for pH adjustment in the treatment process. Regeneration is not recommended for other adsorptive media products.

Whether or not pH of water being treated is adjusted, the adsorptive media can be replaced in place of regeneration upon exhaustion of arsenic capacity. This design manual presents the information necessary to design and operate treatment systems for any combination of operational options and for any adsorptive media. It also discusses the capital and operating costs including the many variables which can raise or lower costs for identical treatment systems.

## **Design Manual: Removal of Arsenic from Drinking Water by Ion Exchange**

EPA 600-R-03-080

This design manual is an in-depth presentation of the steps required to design and operate a water treatment plant for removing arsenic in the As(V) form from drinking water using the anion exchange process. Because As(III) occurs as an uncharged anion in ground water in the pH range of 6.5 to 8, the process will not remove As(III) unless it is first oxidized to As(V). The manual also discusses the capital and operating costs, including many of the variables that can raise or lower costs for identical treatment systems.

The anion exchange treatment process is very reliable, simple, and cost-effective. The treatment process removes arsenic using a strong base anion exchange resin in either the chloride or hydroxide form, with chloride the preferred form because salt can be used as the regenerant.

The process preferentially removes sulfate over arsenic; and, therefore, as the sulfate increases in the raw water, the process becomes less efficient and more costly.

Furthermore, because sulfate occurs in significantly higher concentrations than arsenic, treatment run lengths are dependent almost entirely on the sulfate concentration of the raw water. The ion exchange process is a proven efficient and cost-effective treatment method for removing As(V) from water supplies with low sulfate levels.

The configuration of an anion exchange system for As(V) removal can take several forms. The method presented in this design manual uses three vertical cylindrical pressure vessels operating in a downflow mode. Two of the three treatment vessels are piped in parallel to form the primary arsenic removal stage.

The third treatment vessel is piped in series in the lag position. In the primary stage, raw water flows through one of the two treatment vessels while the second vessel is held in the standby position. When the treatment capacity of the first vessel approaches exhaustion, it is removed from service and replaced by the second primary stage vessel.

While out of service, the first vessel is regenerated and placed in the standby position. The role of the third treatment vessel in the lag position is to ensure that any arsenic that breaks (peaking) through one of the lead vessels does not enter the distribution system. Although this design concept results in higher capital costs, it prevents high arsenic concentrations in the treated water, if operated properly.

# Capital Costs of Arsenic Removal Technologies Demonstration Program Round 1

EPA 600-R-04-201

As part of this Arsenic Rule Implementation Research Program, EPA's Office of Research and Development (ORD) proposed a project to conduct a series of full-scale, long-term, on-site demonstrations of arsenic removal technologies, process modifications, and engineering approaches applicable to small systems in order to evaluate the efficiency and effectiveness of arsenic removal systems at meeting the new arsenic MCL. For the Round 1 demonstration study, the selected arsenic treatment technologies include nine adsorptive media systems, one ion exchange system, one coagulation/filtration system, and one process modification.

The adsorptive media systems use four different adsorptive media, including three iron-based media, i.e., ADI's G2, Severn Trent and AdEdge's E33, and USFilter's GFH, and one iron-modified activated alumina media, i.e., Kinetico's AAFS50 (a product of Alcan). Since the inception of the project, 10 of 12 systems have been installed, with flowrates at all systems ranging from 37 to 640 gpm.

A key objective of the long-term demonstration project is to determine the cost-effectiveness of the technologies. This report provides a brief description of each of the 12 Round 1 demonstration sites and the respective technologies being evaluated.

Capital costs were organized into three categories— equipment, engineering, and installation—and then summed to arrive at a total capital investment cost for each system. Operations and maintenance (O&M) costs associated with the treatment systems are not yet available; however, vendor-supplied estimates on media replacement costs also are provided in this report.

Excluding the cost for one system modification site, the total capital investment costs range from \$90,757 to \$305,000, and vary by flowrate, system design, material of construction, monitoring equipment, and specific site conditions. Based on a 3% interest rate and a 20-year return period, the unit costs of the total capital investment range from \$0.03 to \$0.79 per 1,000 gallons of water treated. In general, the unit cost decreases as the size of a treatment system increases.

The equipment costs for the treatment systems range from \$66,235 to \$218,000, representing 54 to 80% of the total capital investment cost. Engineering costs for the treatment systems range from \$4,907 to \$50,659, accounting for 5 to 22% of the total capital investment with an average of 12%. Installation costs for the treatment systems range from \$13,150 to \$77,574, which accounts for 12 to 34% of the total capital investment with an average of 22%.

Finally, building cost information obtained from the host facilities also is provided in the report. Building costs range from \$3,700 to \$186,000, varying according to differences in location, size, design, material of construction, and choice of construction contractor.

## **Technology Selection and System Design, USEPA Arsenic Demonstration Program Round 1**

EPA 600-R-05-001

On January 18, 2001, the U.S. Environmental Protection Agency (EPA) finalized the maximum contaminant level (MCL) for arsenic at 0.01 mg/L. EPA subsequently revised the rule text to express the MCL as 0.010 mg/L (10 µg/L). The final rule requires all community and non-transient, non-community water systems to comply with the new standard by February 2006. In October 2001, EPA announced an initiative for additional research and development of cost-effective technologies to help small community water systems (<10,000 customers) meet the new arsenic standard, and to provide technical assistance to operators of small systems in order to reduce compliance costs.

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The adsorptive media systems use four different adsorptive media, including three iron-based media (i.e., ADI's G2, Severn Trent and AdEdge's E33, and USFilter's GFH), and one iron-modified activated alumina media (i.e., Kinetico's AAFS50, a product of Alcan). The flowrate of these systems ranges from 37 to 640 gallons per minute (gpm).

This report provides the source water quality characteristics at each of the 12 demonstration sites and the general rationale used to select the technologies for demonstration at each site. Information on the design and operation of each treatment system also is presented.

The selection of the technologies for demonstration at each location was a cooperative decision made by the water system, state, and EPA. Many factors were considered in the selection process, including water quality, residual production and disposal, complexity of system operation, and costs.

The selection of the adsorptive media and pretreatment methods depended on a number of factors that affect the system performance, including arsenic concentration and speciation, pH, and the presence of competing anions, as well as media-specific characteristics such as costs, media life, and empty-bed contact time (EBCT) requirements.

## **Using DWSRF Funds to Comply with the New Arsenic Rule**

EPA 816-F-02-004

The Drinking Water State Revolving Fund (DWSRF) program was established by the 1996 Safe Drinking Water Act (SDWA) Amendments and authorizes grants to states to capitalize revolving loan funds. The states provide low-interest loans to eligible systems for infrastructure improvements needed to ensure compliance with the SDWA and protect public health. The DWSRF program can play a significant role in helping systems, especially small systems, to meet the challenges of complying with new drinking water standards.

The Environmental Protection Agency (EPA) published revisions to the Arsenic Rule in 2001 which further reduce exposure to arsenic in drinking water by adopting a new arsenic maximum contaminant level (MCL) of 10 ppb. The new MCL will impose a financial burden on some water systems. The DWSRF can provide assistance to systems to help ease this burden, increase compliance, and protect public health.

## **Rural Development-Rural Utilities Service, Loan, and Grant Program: Fact Sheet**

EPA 816-F-03-009

USDA/Rural Development/Rural Utilities Service (RUS) administers water and wastewater loan and grant programs to improve the quality of life and promote economic development in Rural America. These programs were previously administered by the Farmers Home Administration (FmHA)

## **Implementation Guidance for the Arsenic Rule - Drinking Water Regulations for Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring**

EPA 816-K-02-018

The final Implementation Guidance for the Arsenic Rule is based on the final rule published in the Federal Register on January 22, 2001. It incorporates comments received on the previous draft implementation guidances, and from the training sessions on the arsenic rule held throughout the country.

The guidance summarizes key sections of the Proposed Rule and provides a "how to approach" for EPA Regions and States to implement the regulation. It contains an explanation of the rule's requirements and guidance for preparing State primacy revision applications. The document incorporates comments received from Regions, States, technical assistance providers, water systems, and others.

## **Regulations on the Disposal of Arsenic Residuals from Drinking Water Treatment Plants**

EPA 600-R-00-025

As with other production processes, water treatment systems produce a product and a residual of that product. With the passage of the various federal statutes, restrictions have been placed on the discharge of residuals to water bodies and onto land. This report summarizes federal regulations and selected state regulations that govern the management of residuals produced by small drinking water treatment systems removing arsenic from drinking water.

Arsenic is a naturally occurring contaminant in ground water and many small water treatment facilities use ground water as their primary source of water. Under the Safe Drinking Water Act (SDWA), a maximum contaminant level (MCL) of 0.05 mg/L has been established for arsenic in drinking water.

Under the 1996 SDWA Amendments, the EPA is required to develop a revised arsenic regulation by January 2001. Concerns have been raised as to the technical feasibility and regulatory implication of a more stringent arsenic MCL on the disposal of the residuals from arsenic removal processes.

This document reports on five water treatment processes known to be effective for arsenic removal from small ground water systems. The five processes are anion exchange, activated alumina adsorption, iron/manganese removal, media adsorption, and membrane processes. For each technology, a brief description is provided of the treatment process along with a discussion of the residual production characteristics.

An overview is provided of the federal regulations that apply to the management of residuals, with a focus on arsenic removal residuals.

The purpose of this overview is to provide guidance to water suppliers on the federal regulatory requirements of residuals management to better evaluate compliance of existing practices and to plan for needed changes in treatment plant operations.

Specific disposal methods are summarized by the form of the residuals including liquid residuals (direct discharges, indirect discharges, underground injection, and land disposal) and solid/sludge residuals (solid waste landfill, hazardous waste landfill, lagoons, reuse of hazardous waste, reuse of solid waste, and off-site disposal) and the method in which the residuals are managed.

## **Complying With the Revised Drinking Water Standard for Arsenic: Small Entity Compliance Guide**

EPA 816-R-02-008A

This guide is designed for owners and operators of community water systems (CWSs) and non-transient non-community water systems (NTNCWSs) serving 10,000 or fewer persons. CWSs include all systems (regardless of ownership) serving at least 25 year-round residents or 15 year-round service connections.

NTNCWSs include all systems (regardless of ownership) that are not CWSs and that regularly serve at least 25 of the same people for more than 6 months a year. Systems that will typically find this guide useful include:

- Small towns
- Rural water districts
- Tribal systems
- Mobile home parks

Federal regulations summarized include the Clean Water Act (NPDES, Pretreatment), SDWA (Underground Injection Control and lagoons), and Resource Conservation and Recovery Act (Subtitles C/D). In addition to the federal regulations that impact the management of arsenic drinking water treatment residuals, regulations imposed by seven states were also reviewed.

The seven states (Arizona, California, Maine, Nebraska, New Mexico, Nevada, and Pennsylvania) were chosen based on arsenic occurrence and regional representation.

The review of the state regulations also focused on characterizing the requirements that apply to different management options available for liquid and solid residuals generated by treatment systems that remove arsenic from drinking water. It was found that many components of the state regulatory programs were generally consistent with the federal minimum requirements.

However, the state programs differed from federal program requirements and each other in several aspects including surface water quality standards applicable to control the amount of arsenic in direct discharges of liquid effluent, the local limits that specify how much arsenic may be discharged to a sanitary sewer system, the regulation of solid waste landfills, the protection of ground water resources, and the regulation of land application activities.

## **Arsenic Removal from Drinking Water by Coagulation/filtration and Lime Softening Plants**

EPA 600-R-00-063

This report documents treatment plant information as well as results of sampling and analysis at two coagulation/filtration plants (referred to in this document as Plants A and B) and one lime softening plant (referred to as Plant C). The objective of sampling and analysis was to evaluate the effectiveness of the water treatment plants to consistently remove arsenic (As) from source water. Additionally, data were collected in this study to evaluate the characteristics of the residuals produced by the treatment processes.

The study was divided into three phases: source water sampling, preliminary sampling, and long-term evaluation. The first phase, source water sampling, was conducted to evaluate source water characteristics at each plant.

The second phase, preliminary sampling, consisted of a four-week sampling period to refine procedures prior to implementing the long-term evaluation phase. The third phase, long-term evaluation, consisted of weekly sample collection and analysis for approximately 1 year. Sludge samples also were collected at each facility during a single sampling event from settling lagoons/ponds during a two-month period.

Samples of recycle supernatant water (Plant A) and supernatant discharge water (Plants B and C) were collected monthly beginning in November 1998 and continuing until June 1999. Long-term evaluation of Plants A and B demonstrated that conventional coagulation/filtration can consistently achieve low levels of arsenic in the treated water (i.e., less than 5  $\mu\text{g/L}$ ).

The total arsenic concentrations at Plant A were reduced by an average of 52%, which represents a decrease of average arsenic concentrations from 7.5  $\mu\text{g/L}$  in the source water to 3.5  $\mu\text{g/L}$  in the finished water. Average total arsenic removal efficiency at Plant B was 79%, with an average source water concentration of 19.1  $\mu\text{g/L}$  and an average finished water concentration of 4.0  $\mu\text{g/L}$ . Adsorption and coprecipitation of As(V) with iron and aluminum flocs are believed to have been the primary arsenic removal mechanisms at these plants.

The lime softening facility, Plant C, was not able to consistently reduce arsenic to low levels in treated water. The average total arsenic concentration in Plant C source water was 32.0  $\mu\text{g/L}$ , and the lime softening plant reduced the average total arsenic concentration to 16.6  $\mu\text{g/L}$  in the finished water, which equals a 45% removal efficiency. As(III) was the primary species of soluble arsenic in the raw water and was almost completely oxidized to As(V) as a result of two chlorination steps that occurred prior to softening and prior to filtration.

The primary mechanism of arsenic removal was likely adsorption and coprecipitation of As(V) with iron that was present in the source water. Plant C operated at a pH of 9.6, a level at which arsenic removal by coprecipitation with calcium carbonate is reported to be less than 10% (Sorg and Logsdon, 1978; McNeill and Edwards, 1997b).

## Arsenic Removal from Drinking Water by Iron Removal Plants

EPA 600-R-00-086

The objective of sampling and analysis was to evaluate the effectiveness of the water treatment plants to consistently remove arsenic (As) from source water. Additionally, data were collected in this study to evaluate the chemical characteristics of residuals produced by the treatment processes.

The study was divided into three phases: source water sampling, preliminary sampling, and long-term evaluation. The first phase, source water sampling, was conducted to evaluate source water characteristics at each plant. The second phase, preliminary sampling, was initiated at Plant A in April 1998 and at Plant B in May 1998. This phase consisted of a four-week sampling period to refine procedures for subsequent events during the third phase. The third phase, long-term evaluation, consisted of weekly sample collection and analysis beginning in June 1998 and continuing through June 1999 at Plant A and through December 1998 at Plant B. Plant personnel conducted all sampling during the long-term evaluation phase and Battelle coordinated sampling logistics. Sludge samples also were collected at Plant A during a single sampling event from an outdoor settling pond in November 1998. Samples of supernatant discharge (Plant A) and recycle supernatant (Plant B) were collected monthly beginning in November 1998 and continuing until June 1999 at Plant A and until January 1999 at Plant B.

Results from the long-term evaluation phase were varied regarding the ability of the iron removal process to consistently achieve low-level arsenic concentrations (e.g.,  $<5 \mu\text{g/L}$  in the finished water). The total arsenic concentrations at Plant A were reduced by an average of 87%, which represents a decrease in average arsenic concentration from  $20.3 \mu\text{g/L}$  to  $3.0 \mu\text{g/L}$ .

Adsorption and coprecipitation with iron hydroxide precipitates are believed to be the primary arsenic removal mechanisms. The total arsenic concentrations at Plant B were reduced by an average of 74%, which represents a decrease in average arsenic concentration from  $48.5 \mu\text{g/L}$  to  $11.9 \mu\text{g/L}$ . At Plant B, it appeared that only the particulate arsenic in the source water was removed. This particulate arsenic was most likely associated with the oxidized iron particles present in the source water (i.e., arsenic sorbed onto iron particles).

The primary difference in arsenic removal efficiency at Plants A and B is believed to be the amount of iron in the source water. Source water at Plant A averaged  $2,284 \mu\text{g/L}$  of iron, while Plant B averaged  $1,137 \mu\text{g/L}$ . Increasing the iron in the source water at Plant B using a coagulant, such as ferric chloride, would likely enable Plant B to consistently achieve lower levels of arsenic. None of the sludge samples collected at Plant A qualified as a hazardous waste based on the Toxicity Characteristic Leaching Procedure (TCLP) test for metals.

Therefore, nonhazardous waste landfills should be able to accept the sludge generated by this treatment facility. Stricter hazardous waste classification regulations in some states, such as California, on total arsenic concentrations in solid waste also were met at Plant A. Sludge samples were not collected at Plant B; however, analytical results were provided from a 1994 sludge sampling event.

# **Arsenic Removal from Drinking Water by Ion Exchange and Activated Alumina Plants**

EPA 600-R-00-088

This report documents treatment plant information as well as results of year-long sampling and analysis at two ion exchange (IX) plants (referred to as Plants A and B) and two activated alumina (AA) plants (referred to as Plants C and D), with capacities varying from 800 to 3,000 gallons per day (gpd). The objective of sampling and analysis was to evaluate the performance of the full-scale water treatment plants to consistently remove arsenic from source water. Additionally, data were collected to evaluate the chemical characteristics of residuals produced by these treatment processes.

The study was divided into three phases: source water sampling, preliminary sampling, and long-term evaluation. Source water sampling was conducted to evaluate source water characteristics at each plant. Preliminary sampling was initiated in August 1998 and consisted of four sampling events conducted at each facility on either a weekly or biweekly basis to refine procedures for subsequent events during the third phase. Long-term evaluation consisted of weekly or biweekly sampling at each facility from September 1998 to September 1999.

Samples from resin regeneration were collected at Plant A from March to June 1999. Spent AA samples were collected at Plants C and D during the media change-out events in December 1998 and May 1999, respectively. Results from the long-term evaluation demonstrated that both the IX and AA systems are capable of achieving arsenic levels of less than 5 µg/L in the treated water, provided that the IX resin was regenerated or the AA medium was changed out before arsenic breakthrough occurred. The two IX systems had inlet arsenic concentrations between 45 and 65 µg/L [primarily As(V)]. When Plant A was operated beyond 3,000 to 3,200 bed volumes (BV) of water, arsenic chromatographic peaking occurred. Arsenic breakthrough was not observed at Plant B where an average 97% of removal efficiency was achieved, leaving only 0.8 to 4.5 µg/L arsenic in the finished water.

Both AA systems consisted of two parallel treatment trains with a roughing AA column followed by a polishing column in each train. The systems operated on a media throwaway basis. The average arsenic removal efficiencies achieved at Plants C and D were 87% and 98%, respectively.

The raw water at Plant C (34 to 76 µg/L total arsenic) contained approximately 0.3 to 28.8 µg/L As(III), which was nearly completely removed, even though no oxidation treatment was provided. The water at Plant D contained slightly higher total arsenic concentrations (53.3 to 87 µg/L) but no As(III), which was consistently removed to less than 5 µg/L in the finished water.

The AA media in the roughing tanks were exhausted and disposed of about every 1 to 1.5 years after treating approximately 9,600 BV at Plant C and 5,260 BV at Plant D. The regeneration process at Plant A recovered from 67 to 86% of arsenic from the spent brine. The spent AA at Plants C and D passed the Toxicity Characteristic Leaching Procedure (TCLP) test for metals including arsenic, and therefore was disposed of as nonhazardous waste.

## Laboratory Study on the Oxidation of Arsenic III to Arsenic V

EPA 600-R-01-021

A one-year laboratory study was performed to determine the ability of seven oxidants to oxidize As(III) to As(V). These included chlorine, permanganate, ozone, chlorine dioxide, monochloramine, a solid-phase oxidizing media, and 254 nm ultraviolet light. Chlorine and permanganate rapidly oxidized As(III) to As(V) in the pH range of 6.3 to 8.3. Dissolved manganese, dissolved iron, sulfide and TOC slowed the rate of oxidation slightly, but essentially complete oxidation was obtained in less than one minute with chlorine and permanganate under all conditions studied.

In the absence of interfering reductants, ozone rapidly oxidized As(III). Although, dissolved manganese and dissolved iron had no significant effect on As(III) oxidation, the presence of sulfide considerably slowed the oxidation reaction.

The presence of TOC had a quenching effect on As(III) oxidation by ozone, producing incomplete oxidation at the higher TOC concentration studied. Only limited As(III) oxidation was obtained using chlorine dioxide, which was probably due to the presence of chlorine (as a by-product) in the chlorine dioxide stock solutions. The reason for the ineffectiveness of chlorine dioxide was not studied.

Preformed monochloramine was ineffective for As(III) oxidation, whereas limited oxidation was obtained when monochloramine was formed in-situ. This showed that the injected chlorine probably reacted with As(III) before being quenched by ammonia to form monochloramine. Filox, a manganese dioxide-based media, was effective for As(III) oxidation.

When dissolved oxygen (DO) was not limiting, complete oxidation was observed under all conditions studied. However, when DO was reduced, incomplete oxidation was obtained in the presence of interfering reductants. The adverse effect of interfering reductants was completely eliminated by either (a) supplying enough DO or (b) increasing the contact time.

In addition to oxidizing As(III), the Filox media also removed some arsenic by adsorption, which diminished greatly as the media came into equilibrium with the As(III)-spiked synthetic water.

UV light alone (254 nm) was not very effective for As(III) oxidation. Significant oxidation was observed only at very low flow rates representing 0.6 - 2.5% of the rated capacities of the two UV sterilizer units tested. However, as reported in a patented process, complete oxidation by UV light was observed when the challenge water was spiked with 1.0 mg/L sulfite.

## Treatment of Arsenic Residuals from Drinking Water Removal Processes

EPA 600-R-01-033

The drinking water MCL was recently lowered from 0.05 mg/L to 0.01 mg/L. One concern was that a reduction in the TCLP arsenic limit in response to the drinking water MCL could be problematic with regard to disposal of solid residuals generated at arsenic removal facilities. This project focused on developing a short-list of arsenic removal options for residuals produced by ion exchange (Ion Ex), reverse osmosis (RO), nanofiltration (NF), activated alumina (AA), and iron removal processes. Both precipitation and adsorption processes were evaluated to assess their arsenic removal effectiveness.

In precipitation tests, ferric chloride outperformed alum for removal of arsenic from residuals by sedimentation, generally resulting in arsenic removals of 88 to 99 percent. Arsenic removal from the high alkalinity ion exchange samples was poorer. The required iron-to-arsenic molar ratio for best removal of arsenic in these screening tests varied widely from 4:1 to 191:1, depending on residuals type, and best arsenic removal using ferric chloride typically occurred between pH 5.0 and 6.2.

Polymer addition typically did not significantly improve arsenic removal using either coagulant. Supernatant total arsenic levels of 0.08 mg/L or lower were attained with ferric chloride precipitation for membrane concentrates and residuals from iron removal facilities compared to an in-stream arsenic limit of 0.05 mg/L in place in some states.

Adsorption tests demonstrated the potential for different types of media and resins to remove arsenic from liquid residuals, but did not assess ultimate capacity. Overall, the iron-based granular ferric hydroxide media evaluated in testing outperformed the aluminum-based media and ion exchange resin for removal of arsenic.

However, activated alumina and the iron-based media provided comparable arsenic removals of close to 100 percent with an empty bed contact time (EBCT) of 3-min for most of the membrane concentrates and the settled iron removal facility residuals.

Removal of suspended solids was key to the success of adsorption for spent filter backwash water and clarifier flush residuals. Arsenic breakthrough occurred very rapidly for the ion exchange samples and for one RO concentrate, all of which had an alkalinity of more than 1,000 mg/L (as CaCO<sub>3</sub>). This again suggests that alkalinity significantly interferes with adsorption of arsenic. Based on this work, use of adsorption media for treatment of arsenic-laden water plant residuals merits further exploration.

Of all of the residuals streams tested, Ion Ex regenerants were the most difficult to treat using precipitation or adsorption. Disposal of supernatant streams resulting from treatment of arsenic-laden residuals from ion exchange plants could pose a major challenge. TCLP arsenic levels in all residuals generated in this work and in full-scale solid media samples were far below the regulatory limit of 5 mg/L, and in fact were below 0.5 mg/L.

## Oxidation of As(III) by Aeration and Storage

EPA 600-R-01-102

A study of the effects of aeration and storage on the oxidation of arsenic(III) was undertaken at three utilities in the U.S. to establish the engineering significance of aeration as a potential pre-treatment method for arsenic removal. Aeration has been referred to in the literature as a possible useful pre-treatment method to ensure that arsenic is in the arsenic(V) state before subsequent removal by any of several treatment processes. Since aeration a common process for treating groundwater for iron oxidation, radon, volatile organics, carbon dioxide, and hydrogen sulfide, it is reasonable to investigate its effectiveness for arsenic(III) oxidation.

The results of this study clearly establish that aeration and aerobic storage do not oxidize arsenic (III). The major conclusion is that aeration is not effective for this purpose and should not be relied upon or expected to contribute to the oxidation of arsenic(III).

One of the test sites in this study clearly showed that arsenic(III) is significantly removed by the oxidation and precipitation of iron, but this should not be attributed to an oxidation of arsenic(III) to arsenic(V) by dissolved oxygen.

Past research has established that iron precipitation can be partially effective for the adsorptive removal of arsenic(III), and this is the likely explanation for the apparent drop in arsenic(III) at the site that had high iron.

The effect of iron precipitation on the removal of arsenic was also present in the long term storage of aerated water in this study. When all of the iron (initial iron at 2.7 mg/L) precipitated from the quiescent storage water, the remaining aqueous total arsenic was entirely dissolved and in the arsenic (V) state.

The aqueous arsenic (III) was below detection and apparently completely removed or converted by the insoluble iron. Even in this case it is doubtful if DO was responsible for any oxidation of arsenic(III), because the loss directly correlated to the loss of iron precipitate and no other instance of arsenic(III) oxidation occurred at the other sites. In summary, the data supported the fact that iron is extremely important in the removal of arsenic(III), but did not support the idea that arsenic(III) is oxidized by aeration. This is true at least for the conditions used in this study.

While the subtleties of the results are interesting, especially for the site with high iron, it is important to emphasize the original objective of this study, which was to establish if typical aeration and storage methods could oxidize arsenic(III).

Based upon the results of this study, it is concluded that aeration does not oxidize arsenic(III) and that subsequent storage for up to five days does not result in arsenic(III) oxidation. Dissolved oxygen should not be considered as a candidate for arsenic(III) oxidation; however, aeration will continue to be considered a very effective process for the oxidation of iron. In that way, aeration can be said to be effective in bringing about the removal of As via the oxidative precipitation of iron.

## **Design Manual: Removal of Arsenic from Drinking Water by Adsorptive Media**

EPA 600-R-03-019

This design manual is an in-depth presentation of the steps required to design and operate a water treatment plant for removal of excess arsenic from drinking water using the adsorptive media process.

This treatment process is very reliable, simple and cost-effective. Several adsorptive media products are available in the market-place that have successfully demonstrated their capability to remove arsenic from drinking water to levels well below the revised MCL, 0.010 mg/L. Other new products continue to be developed.

The adsorptive media products are preferential for the removal of arsenic over other competing ions. Therefore, unless a water system requires treatment capability for removal of other suspended or dissolved contaminants, the adsorptive media treatment method merits evaluation.

The adsorptive media process is implemented with operational options which vary with the product selected. For water systems that are primarily concerned with financial feasibility, capital and operating costs, each operational option along with each available adsorptive media product should be evaluated.

This design manual provides the methods for competently performing each evaluation. The arsenic removal capacity of some adsorptive media products, such as activated alumina, are very sensitive to the pH of the water passing thru treatment.

Others, such as iron-based products, are not. Treatment processes incorporating pH adjustment capability require careful handling and storage of corrosive chemicals (acid and caustic). Some adsorptive media products, such as activated alumina, are capable of being chemically regenerated for repetition of treatment cycles using the same corrosive chemicals as those used for pH adjustment in the treatment process.

Regeneration is not recommended for other adsorptive media products. Whether or not pH of water being treated is adjusted, the adsorptive media can be replaced in place of regeneration upon exhaustion of arsenic capacity.

This design manual presents the information necessary to design and operate treatment systems for any combination of operational options and for any adsorptive media. It also discusses the capital and operating costs including the many variables which can raise or lower costs for identical treatment systems.

## **Design Manual: Removal of Arsenic from Drinking Water by Ion Exchange**

EPA 600-R-03-080

This design manual is an in-depth presentation of the steps required to design and operate a water treatment plant for removing arsenic in the As(V) form from drinking water using the anion exchange process. Because As(III) occurs as an uncharged anion in ground water in the pH range of 6.5 to 8, the process will not remove As(III) unless it is first oxidized to As(V). The manual also discusses the capital and operating costs, including many of the variables that can raise or lower costs for identical treatment systems.

The anion exchange treatment process is very reliable, simple, and cost-effective. The treatment process removes arsenic using a strong base anion exchange resin in either the chloride or hydroxide form, with chloride the preferred form because salt can be used as the regenerant. The process preferentially removes sulfate over arsenic; and, therefore, as the sulfate increases in the raw water, the process becomes less efficient and more costly.

Furthermore, because sulfate occurs in significantly higher concentrations than arsenic, treatment run lengths are dependent almost entirely on the sulfate concentration of the raw water. The ion exchange process is a proven efficient and cost-effective treatment method for removing As(V) from water supplies with low sulfate levels.

The configuration of an anion exchange system for As(V) removal can take several forms. The method presented in this design manual uses three vertical cylindrical pressure vessels operating in a downflow mode. Two of the three treatment vessels are piped in parallel to form the primary arsenic removal stage.

The third treatment vessel is piped in series in the lag position. In the primary stage, raw water flows through one of the two treatment vessels while the second vessel is held in the standby position. When the treatment capacity of the first vessel approaches exhaustion, it is removed from service and replaced by the second primary stage vessel.

While out of service, the first vessel is regenerated and placed in the standby position. The role of the third treatment vessel in the lag position is to ensure that any arsenic that breaks (peaking) through one of the lead vessels does not enter the distribution system. Although this design concept results in higher capital costs, it prevents high arsenic concentrations in the treated water, if operated properly.

# Capital Costs of Arsenic Removal Technologies Demonstration Program Round 1

EPA 600-R-04-201

On January 18, 2001, the U.S. Environmental Protection Agency (EPA) finalized the maximum contaminant level (MCL) for arsenic at 0.01 mg/L. EPA subsequently revised the rule text to express the MCL as 0.010 mg/L (10 µg/L). The final rule requires all community and non-transient, non-community water systems to comply with the new standard by February 2006. In October 2001, the EPA announced an initiative for additional research and development of cost-effective technologies to help small community water systems (<10,000 customers) meet the new arsenic standard, and to provide technical assistance to operators of small systems in order to reduce compliance costs.

For the Round 1 demonstration study, the selected arsenic treatment technologies include nine adsorptive media systems, one ion exchange system, one coagulation/filtration system, and one process modification. The adsorptive media systems use four different adsorptive media, including three iron-based media, i.e., ADI's G2, Severn Trent and AdEdge's E33, and USFilter's GFH, and one iron-modified activated alumina media, i.e., Kinetico's AAFS50 (a product of Alcan). Since the inception of the project, 10 of 12 systems have been installed, with flowrates at all systems ranging from 37 to 640 gpm.

A key objective of the long-term demonstration project is to determine the cost-effectiveness of the technologies. This report provides a brief description of each of the 12 Round 1 demonstration sites and the respective technologies being evaluated.

Capital costs were organized into three categories— equipment, engineering, and installation—and then summed to arrive at a total capital investment cost for each system. Operations and maintenance (O&M) costs associated with the treatment systems are not yet available; however, vendor-supplied estimates on media replacement costs also are provided in this report.

Excluding the cost for one system modification site, the total capital investment costs range from \$90,757 to \$305,000, and vary by flowrate, system design, material of construction, monitoring equipment, and specific site conditions. Based on a 3% interest rate and a 20-year return period, the unit costs of the total capital investment range from \$0.03 to \$0.79 per 1,000 gallons of water treated. In general, the unit cost decreases as the size of a treatment system increases.

The equipment costs for the treatment systems range from \$66,235 to \$218,000, representing 54 to 80% of the total capital investment cost. Engineering costs for the treatment systems range from \$4,907 to \$50,659, accounting for 5 to 22% of the total capital investment with an average of 12%. Installation costs for the treatment systems range from \$13,150 to \$77,574, which accounts for 12 to 34% of the total capital investment with an average of 22%. Finally, building cost information obtained from the host facilities also is provided in the report. Building costs range from \$3,700 to \$186,000, varying according to differences in location, size, design, material of construction, and choice of construction contractor.

## **Technology Selection and System Design, USEPA Arsenic Demonstration Program Round 1**

EPA 600-R-05-001

On January 18, 2001, the U.S. Environmental Protection Agency (EPA) finalized the maximum contaminant level (MCL) for arsenic at 0.01 mg/L. EPA subsequently revised the rule text to express the MCL as 0.010 mg/L (10 µg/L). The final rule requires all community and non-transient, non-community water systems to comply with the new standard by February 2006. In October 2001, EPA announced an initiative for additional research and development of cost-effective technologies to help small community water systems (<10,000 customers) meet the new arsenic standard, and to provide technical assistance to operators of small systems in order to reduce compliance costs.

As part of this Arsenic Rule Implementation Research Program, EPA's Office of Research and Development (ORD) proposed a project to conduct a series of full-scale, long-term, on-site demonstrations of arsenic removal technologies, process modifications, and engineering approaches applicable to small systems in order to evaluate the efficiency and effectiveness of arsenic removal systems at meeting the new arsenic MCL. For the Round 1 demonstration study, the selected arsenic treatment technologies include nine adsorptive media systems, one ion exchange system, one coagulation /filtration system, and one process modification.

The adsorptive media systems use four different adsorptive media, including three iron-based media (i.e., ADI's G2, Severn Trent and AdEdge's E33, and USFilter's GFH), and one iron-modified activated alumina media (i.e., Kinetico's AAFS50, a product of Alcan). The flowrate of these systems ranges from 37 to 640 gallons per minute (gpm).

This report provides the source water quality characteristics at each of the 12 demonstration sites and the general rationale used to select the technologies for demonstration at each site. Information on the design and operation of each treatment system also is presented.

The selection of the technologies for demonstration at each location was a cooperative decision made by the water system, state, and EPA. Many factors were considered in the selection process, including water quality, residual production and disposal, complexity of system operation, and costs.

The selection of the adsorptive media and pretreatment methods depended on a number of factors that affect the system performance, including arsenic concentration and speciation, pH, and the presence of competing anions, as well as media-specific characteristics such as costs, media life, and empty-bed contact time (EBCT) requirements.

## **Using DWSRF Funds to Comply with the New Arsenic Rule**

EPA 816-F-02-004

The Drinking Water State Revolving Fund (DWSRF) program was established by the 1996 Safe Drinking Water Act (SDWA) Amendments and authorizes grants to states to capitalize revolving loan funds. The states provide low-interest loans to eligible systems for infrastructure improvements needed to ensure compliance with the SDWA and protect public health. The DWSRF program can play a significant role in helping systems, especially small systems, to meet the challenges of complying with new drinking water standards.

The Environmental Protection Agency (EPA) published revisions to the Arsenic Rule in 2001 which further reduce exposure to arsenic in drinking water by adopting a new arsenic maximum contaminant level (MCL) of 10 ppb. The new MCL will impose a financial burden on some water systems. The DWSRF can provide assistance to systems to help ease this burden, increase compliance, and protect public health.

## **Rural Development-Rural Utilities Service, Loan, and Grant Program: Fact Sheet**

EPA 816-F-03-009

USDA/Rural Development/Rural Utilities Service (RUS) administers water and wastewater loan and grant programs to improve the quality of life and promote economic development in Rural America. These programs were previously administered by the Farmers Home Administration (FmHA)

## **Implementation Guidance for the Arsenic Rule - Drinking Water Regulations for Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring**

EPA 816-K-02-018

The final Implementation Guidance for the Arsenic Rule is based on the final rule published in the Federal Register on January 22, 2001. It incorporates comments received on the previous draft implementation guidances, and from the training sessions on the arsenic rule held throughout the country.

The guidance summarizes key sections of the Proposed Rule and provides a "how to approach" for EPA Regions and States to implement the regulation. It contains an explanation of the rule's requirements and guidance for preparing State primacy revision applications. The document incorporates comments received from Regions, States, technical assistance providers, water systems, and others.

## **Complying With the Revised Drinking Water Standard for Arsenic: Small Entity Compliance Guide**

EPA 816-R-02-008A

This guide is designed for owners and operators of community water systems (CWSs) and non-transient non-community water systems (NTNCWSs) serving 10,000 or fewer persons. CWSs include all systems (regardless of ownership) serving at least 25 year-round residents or 15 year-round service connections. NTNCWSs include all systems (regardless of ownership) that are not CWSs and that regularly serve at least 25 of the same people for more than 6 months a year. Systems that will typically find this guide useful include:

- Small towns
- Rural water districts
- Tribal systems
- Mobile home parks
- Home owners associations

## Laboratory Safety Introduction

**OSHA's Occupational Exposure to Hazardous Chemicals in Laboratories standard (29 CFR 1910.1450) addresses the unique features of laboratory work**

- Laboratories use a greater variety of hazardous substances than the typical industrial workplace, but in smaller quantities. OSHA defines "laboratory scale" operations as those that use containers designed to be easily and safely manipulated by one person.
- Substances and procedures used tend to change frequently and unpredictably.
- Workers and supervisors are usually highly trained and educated about the substances.

All laboratory personnel should be informed of the contents of "Occupational Exposure to Hazardous Chemicals in Laboratories," OSHA Standard 29 CFR 1910.1450, and the location and contents of your employer's Chemical Hygiene Plan.

All laboratory personnel will be informed of the OSHA Permissible Exposure Limits (**PELs**) and ACGIH Threshold Limit Values (**TLVs**). A listing of OSHA PELs is located in Appendix B.

### Training

Your training will consist of methods and observations that may be used to detect the presence or release of a hazardous chemical, the physical and health hazards of chemicals in the work area, the measures employees can take to protect themselves from exposure, including engineering controls, personal protective equipment, work practices, and emergency procedures.

Your training should also cover your employer's Chemical Hygiene Plan and Hazardous Waste Management Procedures.



A normal day for a Lab Tech will include the washing of lab glassware. Sometimes the Tech will use acid to wash certain glass bottles. Notice the broken glass or Sharps container.



Clearly marked and different types of hazardous waste disposal containers need to be present in your lab.

**Common terms used in this course.**

**Hazardous chemical** is a chemical for which there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur in exposed employees.

**Health Hazard** The term "**health hazard**" includes chemicals which are carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, neurotoxins, agents which act on the hematopoietic systems, and agents which damage the lungs, skin, eyes, or mucous membranes.

**Employee** is an individual employed in a laboratory workplace who may be exposed to hazardous chemicals in the course of his or her assignments.

## Employees' Right to Know

### Employers must train workers about:

- Hazards in the lab, including criteria for too much chemical exposure.
- Protective clothing and equipment and how to use them.
- Emergency procedures.
- Detailed safety information about chemicals in safety data sheets (SDS) Formerly (MSDS).
- Free medical consultation/treatment in case of overexposure to hazardous chemicals.

### Permissible Exposure Limits and Exposure Determination

Employees of laboratories using OSHA-regulated substances cannot be exposed to these substances beyond the OSHA permissible exposure limits. Employers are required to measure employees' exposure to any regulated substances if that substance is required by a standard for monitoring. Employers must also inform employees of the monitoring results.

### Safety Precautions

Caution and common sense prevent safety problems:

- Assume that any unfamiliar chemical is hazardous.
- Read the label and SDS for important safety information before working with any chemical.
- Consider a mixture to be at least as hazardous as its most hazardous component.
- Never use anything that is not labeled.
- Never combine substances unless instructed to do so. They might react with one another, causing an explosion or release of harmful vapors. Don't add a chemical to a container that isn't clean and empty.
- Follow all safety procedures to the letter.
- In case of chemical overexposure, get medical attention, inform the supervisor, and check the SDS for first-aid information.
- Report any spill. Don't attempt to contain or clean up the spill **UNLESS** trained and equipped to do so.



Fish tanks are common where water or wastewater treatment is being used. Fish are a great detector/ indicator to chemical contention.

**Employees shall be informed of:**

- (i) The contents of this standard and its appendices which shall be made available to employees;
- (ii) The location and availability of the employer's Chemical Hygiene Plan;
- (iii) The permissible exposure limits for OSHA regulated substances or recommended exposure limits for other hazardous chemicals where there is no applicable OSHA standard;
- (iv) Signs and symptoms associated with exposures to hazardous chemicals used in the laboratory; and
- (v) The location and availability of known reference material on the hazards, safe handling, storage and disposal of hazardous chemicals found in the laboratory including, but not limited to, Material Safety Data Sheets received from the chemical supplier.



Notice the anti-slip mat and the several different types of gloves necessary to handle the different chemicals that could be present. Notice how each bottle and drawer is clearly marked.

## The Chemical Hygiene Plan (CHP)

Like the written hazard communication plan, the CHP covers procedures for protecting employees from hazards and keeping exposures below permissible limits. But it's more flexible so as to allow labs to adopt procedures for their individual needs. **Any CHP must include:**

- Standard operating procedures for lab work using hazardous substances.
- How the company will determine and reduce employee exposure to hazardous substances, examples, engineering controls, personal protective equipment, and hygiene practices.
- Measures to ensure that fume hoods and other protective equipment function properly.
- How the company will inform employees about potential health hazards and train them to protect themselves.
- Circumstances in which a particular operation, procedure, or activity will have to be pre-approved by the company.
- Provisions for medical consultation and medical examinations.
- Designation of personnel responsible for implementation of the CHP.
- Provisions for additional employee protection for work with particularly hazardous substances.

### Personal Protective Equipment

Always use assigned PPE and make sure it's in good condition. Types of PPE include goggles or side shield safety glasses; gloves; long sleeves; lab coats, aprons, coveralls; sturdy shoes; and respirators. Contact lenses could trap vapors-check with a safety director before wearing them.

### Lab Equipment

- Glassware can break, causing chemical contact or cuts:
- Use the right type of glass for the task.
- Discard chipped or cracked glassware.
- Don't use force on glassware.

### Autoclaves and other heating equipment:

- Use tongs or heat-resistant gloves.

### Electrical equipment creates electric shock hazard:

- Don't touch with wet hands or while standing on a wet floor.
- Report any incidents of shock.
- Don't attempt repairs unless you've been trained.

### Centrifuges and other equipment with moving parts can catch or open suddenly:

- Keep clothing and long hair away from equipment.
- Make sure the load is balanced, top is locked, and movement has stopped before opening. Compressed gas cylinders can explode or cause a fire; keep clean and chained in place.

## Fire and Burn Hazards

### **Guidelines for safe work practices:**

- Be cautious and follow rules for open flames, reactive substances, and flammables.
- Wear gloves when handling hot glass or tools.
- Keep water and wet hands away from electrical equipment.
- Don't use electrical equipment with worn cords, damaged plugs, etc.

## Emergency Preparedness

- Don't work alone in the lab.
- Post emergency phone numbers.
- Keep SDSs on hand-and read them.
- Know what to do in an emergency.
- Know the location of showers, eyewash stations, fire extinguishers.

Know which type of fire extinguisher to use for the chemicals with which you are working. Consult organization procedures, SDSs, and your supervisor.



Work closely with your emergency services and practice annual drills with these agencies. It may be required by OSHA or EPA depending upon your chemical or biological storage at your facility. Don't risk a tragedy or a violation. It is bad press and a lot of red tape.

## Summary

- Remember that safety is the first priority in the lab!
- Read and understand the Chemical Hygiene Plan (CHP).
- Learn about the hazards of the chemicals you use.
- Take your time and concentrate on your work.
- Avoid contact with hazardous chemicals.
- Assume that unknown chemicals are hazardous.
- Follow all warning signs and instructions.
- Use the correct PPE.
- Follow all instructions for proper equipment operation.



## SAFETY INFORMATION



**CARL WILHELM SCHEELE (1742-1786)**

By the time he was a teenager, Scheele had learned the dominant theory of gases in the 1770s, the phlogiston theory. Phlogiston, classified as "matter of fire", was supposed to be released from any burning material, and when it was exhausted, combustion would stop. When Scheele discovered oxygen he called it "fire air" because it supported combustion, but he explained oxygen using phlogistical terms because he did not believe that his discovery disproved the phlogiston theory.

Before Scheele made his discovery of oxygen, he studied air. Air was thought to be an element that made up the environment in which chemical reactions took place but did not interfere with the reactions. Scheele's investigation of air enabled him to conclude that air was a mixture of "fire air" and "foul air;" in other words, a mixture of two gases.

He performed numerous experiments in which he burned substances such as saltpeter (potassium nitrate), manganese dioxide, heavy metal nitrates, silver carbonate and mercuric oxide. In all of these experiments, he isolated gas with the same properties: his "fire air," which he believed combined with phlogiston to be released during heat-releasing reactions. However, his first publication, *A Chemical Treatise on Air and Fire*, was not released until 1777, at which time both Joseph Priestley and Lavoisier had already published their experimental data and conclusions concerning oxygen and the phlogiston theory.

## Chemical Hygiene Plan Introduction

The purpose of this Chemical Hygiene Plan is to define work practices and procedures to help ensure that faculty, staff, students, workers, and the environment are protected from hazards associated with the handling, storage, and use of chemicals in laboratories.

Occupational Safety and Health Administration (OSHA) Regulations (29 CFR 1900.1450) require all employers engaged in the laboratory use of hazardous chemicals to develop and carry out the provisions of a Chemical Hygiene Plan that is capable of protecting employees from health hazards associated with hazardous chemicals and capable of keeping exposures below Permissible Exposure Limits (PELs).

See Appendix A in the rear of this manual for the full text of "**Occupational Exposure to Hazardous Chemicals in Laboratories**". OSHA defines a laboratory as "**a workplace where relatively small quantities of hazardous chemicals are used on a non-production basis.**" Laboratories involve a greater variety of possible hazards than most work places, and some hazards call for precautions not ordinarily encountered. None of the labs at your place of employment are without hazards of some kind and degree.

This Chemical Hygiene Plan applies to all laboratory workers. An example of a laboratory worker would be a university teaching assistant or a faculty member instructing an academic lab. Your employer also has the special responsibility of administering instructional labs with relatively inexperienced students who must be introduced to the safety procedures necessary to conduct various laboratory operations.



A perfect example of an unsafe laboratory, cluttered and without a Chemical Hygiene Plan. An accident is just waiting to happen.



**Select Carcinogen** means any substance which meets one of the following criteria:

- (i) It is regulated by OSHA as a carcinogen; or
- (ii) It is listed under the category, "*known to be carcinogens*," in the Annual Report on Carcinogens published by the National Toxicology Program (NTP) (latest edition); or
- (iii) It is listed under Group 1 ("carcinogenic to humans") by the International Agency for Research on Cancer Monographs (IARC) (latest editions); or
- (iv) It is listed in either Group 2A or 2B by IARC or under the category, "*reasonably anticipated to be carcinogens*" by NTP, and causes statistically significant tumor incidence in experimental animals in accordance with any of the following criteria:
  - (A) After inhalation exposure of 6-7 hours per day, 5 days per week, for a significant portion of a lifetime to dosages of less than 10 ug 3 ;
  - (B) After repeated skin application of less than 300 (ug/kg of body weight) per week; or
  - (C) After oral dosages of less than 50 ug/kg of body weight per day.

## Example of Chemical Hygiene Responsibilities Policy

If you do not have a policy, you need to implement one. Here is an example you can utilize:

### Program Coordinator

The Environmental Health and Safety Coordinator or equivalent will serve as the program's coordinator. The Environmental Health and Safety Coordinator will do the following:

- Provide technical assistance to laboratory supervisors and workers concerning appropriate storage, handling, and disposal of hazardous chemicals.
- Remain current on rules and regulations concerning chemicals used in laboratories on campus.
- Conduct Laboratory Safety Surveys (**LSSs**) to assess level of compliance with the CHP.
- Inform new faculty and staff of the information contained in the CHP. Train or coordinate for retraining of Department Chemical Hygiene Officers and Laboratory Supervisors.
- Maintain a library of Safety Data Sheets (**SDSs**) and other laboratory health and safety literature.
- Interact with regulators and agencies, maintain records, and file required reports.
- Oversee and maintain the Chemical Inventory Management System (**ChIM**).

### Department Chairperson

Each department chairperson of a science department that uses chemicals will:

- Support the CHP and assist their Department Chemical Hygiene Officer (**DCHO**) or equivalent in maintaining awareness and compliance with the plan.
- Prepare budget requests for health and safety improvements.

List your current department chairpersons here:

### Department Chemical Hygiene Officer (DCHO)

Essential to our Chemical Hygiene Plan are Departmental Chemical Hygiene Officers. The following individuals have experience and knowledge of their department's operations and will act as DCHO's for their respective departments. List your current DCHOs here:

#### The duties and responsibilities of the DCHO are to :

- Coordinate with the departmental faculty and staff in developing and carrying out appropriate laboratory safety, hygiene, and disposal programs specific to their individual departments.
- Maintain and distribute current legal documents for regulated substances used within their department.
- Conduct periodic safety inspections at least once a semester; coordinate for the correction of deficiencies.

## Laboratory Supervisors

A laboratory supervisor is anyone overseeing any type of laboratory work. This could include faculty and staff mentors, principal investigators, instructors, and/or other researchers. No one is exempt from the appropriate safety precautions.

Lab supervisors must serve as good role models for their technical staff and students by observing all rules and recommendations, wearing protective equipment, and being enthusiastic about safety.

Laboratory supervisors are responsible for administration of the Chemical Hygiene Plan. Untrained workers (or students) cannot be permitted to work with chemicals. Every laboratory supervisor will ensure that:

- All personnel working in their laboratory(s) are aware of and practice appropriate precautions.
- Rules and Standard Operating Procedures (**SOPs**) are enforced and discipline is maintained.
- Emergency equipment is available and in proper working order and everyone has been trained on its use.
- Information and training on special or unusual hazards or equipment is provided and documented.
- Appropriate safety plans and emergency procedures have been developed and are followed.
- Safety Data Sheets (**SDSs**) are readily accessible and are reviewed before unfamiliar work or work with new chemicals commences.
- Personal protective equipment is available and used.
- All Hazardous Waste Regulations, including waste minimization, are complied with.
- Periodic inspections and surveys of the laboratory work area are conducted.
- Notify the DCHO prior to commencement of any new process or activities covered by this program.

## Employees

- Follow all health and safety procedures and rules.
- Report all hazardous conditions to your supervisor immediately.
- Report any job related injury or illnesses to your supervisor and seek treatment as soon as possible.
- Refrain from the operation of any equipment or instruments without proper instruction and authorization.
- Wear or use prescribed personal protective equipment.
- Remain aware of the hazards of **ALL** chemicals in the laboratory and how to handle hazardous chemicals safely.
- Request information and training when unsure about how to handle an unfamiliar or hazardous chemical or procedure.

## Chemical Inventory Management Example Policy

### Scope

The management and control of chemicals is the responsibility of everyone involved in the acquisition, use, and disposition of them. Your employer has a responsibility to comply with a myriad of federal, state, and local regulations covering chemical purchase, use, transportation, storage, emergency planning, and disposal.

To satisfy this obligation, your employer has implemented a comprehensive Chemical Management System that includes up to date inventories of laboratory chemicals.

The following policies and procedures for chemical inventory control are designed to help users understand and meet the above responsibilities and requirements. The procedures cannot be designed to cover every situation.

The system allows for flexibility provided that there is **PRIOR** coordination with the Environmental Health and Safety (**EHS**) Office. All chemical users must comply, and are urged to provide suggestions to assist in continuously improving these procedures.

### Objectives

The goals of our system are to:

- Ensure that chemicals are properly identified in the records of your employer and that pertinent health, safety, and other information regarding each item in the inventory is readily available and accessible.
- Facilitate the physical inventory of chemicals through maintenance of a standard numbering system (bar coded tag) and an automated chemical inventory system.
- Minimize waste generation and control waste disposal costs.
- Facilitate budget preparation and planning by maintaining information on usage patterns, age, shelf-life, and cost.
- Minimize the number and amount of chemicals stored throughout the facility.
- Develop accountability procedures to comply with federal, state, and local laws governing purchases, storage, transportation, use, emergency planning, and disposal of the chemicals used at your place of employment.

The benefits of meeting our Chemical Management goals are reduced purchasing and disposal costs, regulatory compliance, and a safe and healthy environment for students, faculty, and staff.

### Overview

Your employer has implemented a computerized Chemical Inventory System to provide a perpetual inventory record of all chemicals located in the Division. The components of the system are shown in figure 1. All chemical purchases are made through the EHS Office. Users place chemical orders on a special three-part Chemical Requisition Form.

The form can be mailed or hand carried to the EHS Office. The EHS Coordinator evaluates and approves the chemical order after checking available stock. Next, the requisition form goes to the Purchasing Department and an order is placed with the specified vendor.

The vendor ships the order to Central Receiving, where it is processed and then delivered. The order is unpacked and checked and a barcode tag is placed on each container greater than 25 g or 25 ml.

Bar code tagging of chemical containers is central to an automated system because all information about a specific chemical container and its contents is keyed to a unique bar code tag number.

The bar code tag number is like a license plate; the number is not coded to contain intelligent data. Rather it is the key pointer in a relational database to other information that relates specifically to that number. The tag number is printed in bar code 39 symbology and human readable format.

Tags are also being applied to rooms, cabinets, and shelves to speed re-inventory. The quantity, user name, location, PO #, vendor, date, and price are some of the information recorded for each chemical container in a database called ChIM (Chemical Inventory Management). Health, safety, and storage information is recorded under the Chemical Abstracts Service (**CAS**) Registry Number.

For more information see your Chemical Management Guide.

The acceptance of gifts is or should ALWAYS be prohibited without the consent of the EHS Coordinator and Department Chemical Hygiene Officer (**DCHO**). Approved gifts must be tagged and entered into the Chemical Inventory System.

Once the initial physical inventory is completed the labs will be reinventoried on a regular basis using a handheld data collector and laser reader. The re-inventory data is downloaded into a PC so that location changes and disposal information can be updated.

A blue recycling bin is located in most of the laboratories for collecting empty containers. This is so that the inventory can be maintained as up to date as possible. It is essential that all users comply with this collection system. Please get in the habit of saving all containers for collection.

Once a chemical is consumed, it must be removed from the system to provide maximum benefits from the inventory. The recycling bins will be emptied by the EHS Office periodically. If chemical containers are saved and washed for reuse, please provide the EHS Office with the tag number(s) from the empty container(s).

### **Chemical Requisition Forms**

The Chemical Requisition Forms are for ordering chemicals, only. Please place orders for equipment and other non-chemical items separately on the Requisition for Supplies Form.

Requisition forms are available in department offices and should be filled out and filed as follows:

### **Complete DEPT, DATE, CHARGE TO, and USER NAME.**

The ROOM # is the room or lab where the chemical(s) will be used and/or stored. This MUST be completed for proper inventory tracking. Complete the VENDOR section; for withdrawals indicate Chemical Stores or Stockroom.

Complete the QUANTITY/SIZE, DESCRIPTION, and CATALOG/PRODUCT #. Often it is best to leave the price box blank if unknown, because the current market or discounted price is usually different from the stated catalogue price. Circle YES in the CONFIRMING box if the order has already been placed to prevent duplication. The PO number should be recorded as well. If the shipping or delivery METHOD is known, complete this block, otherwise leave it blank.

The AUTHORIZED SIGNATURE block is for the signature of the person authorized for the account code in the CHARGE TO box.

### **Filing the Chemical Requisition Form Examples**

#### **Pink Copy**

For new orders, keep the pink copy for department records. For withdrawals, leave the pink copy attached. It will be mailed to the department secretary by the EHS Office after the transaction has been completed (usually at the end of the month).

#### **Yellow and White Copy**

The user always sends the white AND yellow copies to the EHS Office. This is true of orders placed by the user. The EHS Coordinator must initial the form in the approved box before it goes to purchasing. Forms can be dropped off at the EHS Office during window hours for faster service.

#### **White Copy**

The EHS Office sends the white copy to purchasing. As stated above, Purchasing does not accept white copies that have not been initialed by the EHS Coordinator. Therefore, sending white copies directly to purchasing will delay the receipt of your order.



## Glossary

### A

**ABSENCE OF OXYGEN:** The complete absence of oxygen in water described as Anaerobic.

**ABSOLUTE ZERO:** A theoretical condition concerning a system at zero Kelvin where a system does not emit or absorb energy (all atoms are at rest).

**ACCURACY:** How close a value is to the actual or true value; also see precision. How closely an instrument measures the true or actual value.

**ACID AND BASE ARE MIXED:** When an acid and a base are mixed, an explosive reaction occurs and decomposition products are created under certain conditions.

**ACID ANHYDRIDE:** A compound with two acyl groups bound to a single oxygen atom.

**ACID DISSOCIATION CONSTANT:** An equilibrium constant for the dissociation of a weak acid.

**ACID RAIN:** A result of airborne pollutants.

**ACID:** Slowly add the acid to water while stirring. An operator should not mix acid and water or acid to a strong base.

**ACTINIDES:** The fifteen chemical elements that are between actinium (89) and lawrencium (103).

**ACTIVATED CARBON FILTRATION:** Can remove organic chemicals that produce off-taste and odor. These compounds are not dangerous to health but can make the water unpleasant to drink. Carbon filtration comes in several forms, from small filters that attach to sink faucets to large tanks that contain removable cartridges. Activated carbon filters require regular maintenance or they can become a health hazard.

**ACTIVATED CHARCOAL (GAC or PAC):** Granular Activated Charcoal or Powered Activated Charcoal. Used for taste and odor removal. A treatment technique that is not included in the grading of a water facility.

**ACTIVATED COMPLEX:** A structure that forms because of a collision between molecules while new bonds are formed.

**ACTIVATION ENERGY:** The minimum energy that must be input to a chemical system.

**ADDITION REACTION:** Within organic chemistry, when two or more molecules combine to make a larger one.

**ADSORPTION CLARIFIERS:** The concept of the adsorption clarifier package plant was developed in the early 1980s. This technology uses an up-flow clarifier with low-density plastic bead media, usually held in place by a screen. This adsorption media is designed to enhance the sedimentation/clarification process by combining flocculation and sedimentation into one step. In this step, turbidity is reduced by adsorption of the coagulated and flocculated solids onto the adsorption media and onto the solids already adsorbed onto the media. Air scouring cleans adsorption clarifiers followed by water flushing. Cleaning of this type of clarifier is initiated more often than filter backwashing because the clarifier removes more solids. As with the tube-settler type of package plant, the sedimentation/clarification process is followed by mixed-media filtration and disinfection to complete the water treatment.

**ADSORPTION:** Not to be confused with absorption. Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins, and water purification.

**AERATION:** The mixing of air into a liquid or solid.

**AGGLOMERATION:** A jumbled cluster or mass of varied parts. The act or process of agglomerating.

**AIR ENTRAINMENT:** The dissolution or inclusion of air bubbles into water.

**AIR GAP SEPARATION:** A physical separation space that is present between the discharge vessel and the receiving vessel; for an example, a kitchen faucet.

**AIR HOOD:** The most suitable protection when working with a chemical that produces dangerous fumes.

**ALGAE:** Microscopic plants that are free-living and usually live in water. They occur as single cells floating in water, or as multicellular plants like seaweed or strands of algae that attach to rocks.

**ALKALI METALS:** The metals of Group 1 on the periodic table.

**ALKALINITY:** Alkalinity or AT is a measure of the ability of a solution to neutralize acids to the equivalence point of carbonate or bicarbonate. Alkalinity is closely related to the acid neutralizing capacity (ANC) of a solution and ANC is often incorrectly used to refer to alkalinity. However, the acid neutralizing capacity refers to the combination of the solution and solids present (e.g., suspended matter, or aquifer solids), and the contribution of solids can dominate the ANC (see carbonate minerals below).

**ALKALINE EARTH METALS:** The metals of Group 2 on the periodic table.

**ALLOMER:** A substance that has different composition than another, but has the same crystalline structure.

**ALLOTROPY:** Elements that can have different structures (and therefore different forms), such as Carbon (diamonds, graphite, and fullerene).

**ALPHA AND BETA RADIOACTIVITY:** Represent two common forms of radioactive decay. Radioactive elements have atomic nuclei so heavy that the nucleus will break apart, or disintegrate spontaneously. When decay occurs, high-energy particles are released. These high-energy particles are called radioactivity. Although radioactivity from refined radioactive elements can be dangerous, it is rare to find dangerous levels of radioactivity in natural waters. An alpha particle is a doubly-charged helium nucleus comprised of two protons, two neutrons, and no electrons. A beta particle is a high-speed electron. Alpha particles do not penetrate matter easily, and are stopped by a piece of paper. Beta particles are much more penetrating and can pass through a millimeter of lead.

**ALTERNATIVE DISINFECTANTS:** Disinfectants - other than chlorination (halogens) - used to treat water, e.g. ozone, ultraviolet radiation, chlorine dioxide, and chloramine. There is limited experience and scientific knowledge about the by-products and risks associated with the use of alternatives.

**ALUMINUM SULFATE:** The chemical name for Alum. The molecular formula of Alum is  $Al_2(SO_4)_3 \cdot 14H_2O$ . It is a cationic polymer.

**AMMONIA:**  $NH_3$  A chemical made with Nitrogen and Hydrogen and used with chlorine to disinfect water. Most ammonia in water is present as the ammonium ion rather than as ammonia.

**AMMONIATOR:** AA control device which meters gaseous ammonia directly into water under positive pressure.

**AMMONIATOR:**

**AMOEBIA:** Amoeba (sometimes amoeba or ameba, plural amoebae) is a genus of protozoa that moves by means of pseudopods, and is well-known as a representative unicellular organism. The word amoeba or ameba is variously used to refer to it and its close relatives, now grouped as the Amoebozoa, or to all protozoa that move using pseudopods, otherwise termed amoeboids.

**ANAEROBIC CONDITIONS:** When anaerobic conditions exist in either the metalimnion or hypolimnion of a stratified lake or reservoir, water quality problems may make the water unappealing for domestic use without costly water treatment procedures. Most of these problems are associated with Reduction in the stratified waters.

**ANAEROBIC:** An abnormal condition in which color and odor problems are most likely to occur.

**ANEROID:** Using no fluid, as in aneroid barometer.

**ANION:** Negatively charge ions.

**ANODE:** The positive side of a dry cell battery or a cell.

**AQUIFER PARAMETERS:** Referring to such attributes as specific capacity, aquifer storage, transmissivity, hydraulic conductivity, gradient, and water levels. Refers to all of the components of Darcy's Law and related parameters.

**AROMATICITY:** Chemical property of conjugated rings that results in unusual stability. See also benzene.

**AS NITROGEN:** An expression that tells how the concentration of a chemical is expressed mathematically. The chemical formula for the nitrate ion is  $NO_3$ , with a mass of 62. The concentration of nitrate can be expressed either in terms of the nitrate ion or in terms of the principal element, nitrogen. The mass of the nitrogen atom is 14. The ratio of the nitrate ion mass

to the nitrogen atom mass is 4.43. Thus a concentration of 10 mg/L nitrate expressed as nitrogen would be equivalent to a concentration of 44.3 mg/L nitrate expressed as nitrate ion. When dealing with nitrate numbers it is very important to know how numeric values are expressed.

As: The chemical symbol of Arsenic.

ASEPTIC: Free from the living germs of disease, fermentation, or putrefaction.

ASYNCHRONOUS: Not occurring at the same time.

ATOM: The general definition of an ion is an atom with a positive or negative charge. Electron is the name of a negatively charged atomic particle.

ATOMIC NUMBER: The number representing an element which corresponds with the number of protons within the nucleus.

ATOMIC ORBITAL: The region where the electron of the atom may be found.

AVOGADRO'S NUMBER: Is the number of particles in a mole of a substance ( $6.02 \times 10^{23}$ ).

## B

BACKFLOW PREVENTION: To stop or prevent the occurrence of, the unnatural act of reversing the normal direction of the flow of liquid, gases, or solid substances back in to the public potable (drinking) water supply. See Cross-connection control.

BACKFLOW: To reverse the natural and normal directional flow of a liquid, gases, or solid substances back in to the public potable (drinking) water supply. This is normally an undesirable effect.

BACKSIPHONAGE: A liquid substance that is carried over a higher point. It is the method by which the liquid substance may be forced by excess pressure over or into a higher point.

BACTERIA: Small, one-celled animals too small to be seen by the naked eye. Bacteria are found everywhere, including on and in the human body. Humans would be unable to live without the bacteria that inhabit the intestines and assist in digesting food. Only a small percentage of bacteria cause disease in normal, healthy humans. Other bacteria can cause infections if they get into a cut or wound. Bacteria are the principal concern in evaluating the microbiological quality of drinking water, because some of the bacteria-caused diseases that can be transmitted by drinking water are potentially life-threatening.

BACTERIOPHAGE: Any of a group of viruses that infect specific bacteria, usually causing their disintegration or dissolution. A bacteriophage (from 'bacteria' and Greek phagein, 'to eat') is any one of a number of viruses that infect bacteria. The term is commonly used in its shortened form, phage. Typically, bacteriophages consist of an outer protein hull enclosing genetic material. The genetic material can be ssRNA (single stranded RNA), dsRNA, ssDNA, or dsDNA between 5 and 500 kilo base pairs long with either circular or linear arrangement. Bacteriophages are much smaller than the bacteria they destroy - usually between 20 and 200 nm in size.

BARITE: Processed barium sulfate often used to increase drilling fluid densities in mud rotary.

BAROMETER: A device used to measure the pressure in the atmosphere.

BASE: A substance that accepts a proton and has a high pH; a common example is sodium hydroxide (NaOH).

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE (BAT): A level of technology based on the best existing control and treatment measures that are economically achievable within the given industrial category or subcategory.

BEST MANAGEMENT PRACTICES (BMPs): Schedules of activities, prohibitions of practices, maintenance procedures, and other management practices to prevent or reduce the pollution of waters of the U.S. BMPs also include treatment requirements, operating procedures and practices to control plant site runoff, spillage or leaks, sludge or waste disposal, or drainage from raw material storage.

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE (BPT): A level of technology represented by the average of the best existing wastewater treatment performance levels within an industrial category or subcategory.

BEST PROFESSIONAL JUDGMENT (BPJ): The method used by a permit writer to develop technology-based limitations on a case-by-case basis using all reasonably available and relevant data.

**BEST PROFESSIONAL JUDGMENT (BPJ):** The method used by a permit writer to develop technology-based limitations on a case-by-case basis using all reasonably available and relevant data.

**BIOCHEMISTRY:** The chemistry of organisms.

**BOILING POINT:** The temperature in which the substance starts to boil.

**BOILING POINT ELEVATION:** The process where the boiling point is elevated by adding a substance.

**BOILING:** The phase transition of liquid vaporizing.

**BOND:** The attraction and repulsion between atoms and molecules that is a cornerstone of chemistry.

**BREAK POINT CHLORINATION:** The process of chlorinating the water with significant quantities of chlorine to oxidize all contaminants and organic wastes and leave all remaining chlorine as free chlorine.

**BRIDGING:** The tendency of sediment, filter, or seal media to create an obstruction if installed in too small an annulus or too rapidly. Also can occur within filter packs requiring development.

**BROMINE:** Chemical disinfectant (HALOGEN) that kills bacteria and algae. This chemical disinfectant has been used only on a very limited scale for water treatment because of its handling difficulties. This chemical causes skin burns on contact, and a residual is difficult to obtain.

**BRONSTED-LOWREY ACID:** A chemical species that donates a proton.

**BRONSTED-LOWREY BASE:** A chemical species that accepts a proton.

**BUFFER:** Chemical that resists pH change, e.g. sodium bicarbonate

**BUFFERED SOLUTION:** An aqueous solution consisting of a weak acid and its conjugate base or a weak base and its conjugate acid that resists changes in pH when strong acids or bases are added.

**BURETTE (also BURET):** Glassware used to dispense specific amounts of liquid when precision is necessary (e.g. titration and resource dependent reactions).

## C

**Ca:** The chemical symbol for calcium.

**CADMIUM:** A contaminant that is usually not found naturally in water or in very small amounts.

**CALCIUM HARDNESS:** A measure of the calcium salts dissolved in water.

**CALCIUM ION:** Is divalent because it has a valence of +2.

**CALCIUM, MAGNESIUM AND IRON:** The three elements that cause hardness in water.

**CaOCl<sub>2</sub>·4H<sub>2</sub>O:** The molecular formula of Calcium hypochlorite.

**CARBON DIOXIDE GAS:** The pH will decrease and alkalinity will change as measured by the Langelier index after pumping carbon dioxide gas into water.

**CARBONATE HARDNESS:** Carbonate hardness is the measure of Calcium and Magnesium and other hard ions associated with carbonate (CO<sub>3</sub><sup>2-</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>) ions contained in a solution, usually water. It is usually expressed either as parts per million (ppm or mg/L), or in degrees (KH - from the German "Karbonathärte"). One German degree of carbonate hardness is equivalent to about 17.8575 mg/L. Both measurements (mg/L or KH) are usually expressed "as CaCO<sub>3</sub>" – meaning the amount of hardness expressed as if calcium carbonate was the sole source of hardness. Every bicarbonate ion only counts for half as much carbonate hardness as a carbonate ion does. If a solution contained 1 liter of water and 50 mg NaHCO<sub>3</sub> (baking soda), it would have a carbonate hardness of about 18 mg/L as CaCO<sub>3</sub>. If you had a liter of water containing 50 mg of Na<sub>2</sub>CO<sub>3</sub>, it would have a carbonate hardness of about 29 mg/L as CaCO<sub>3</sub>.

**CARBONATE, BICARBONATE AND HYDROXIDE:** Chemicals that are responsible for the alkalinity of water.

**CATALYST:** A chemical compound used to change the rate (either to speed up or slow down) of a reaction, but is regenerated at the end of the reaction.

**CATHODIC PROTECTION:** An operator should protect against corrosion of the anode and/or the cathode by painting the copper cathode. Cathodic protection interrupts corrosion by supplying an electrical current to overcome the corrosion-producing mechanism. Guards against stray current corrosion.

**CATION:** Positively charged ion.

**CAUSTIC SODA:** Also known as sodium hydroxide and is used to raise pH.

**CAUSTIC:** NaOH (also called Sodium Hydroxide) is a strong chemical used in the treatment process to neutralize acidity, increase alkalinity or raise the pH value.

**CEILING AREA:** The specific gravity of ammonia gas is 0.60. If released, this gas will accumulate first at the ceiling area. Cl<sub>2</sub> gas will settle on the floor.

**CELL POTENTIAL:** The force in a galvanic cell that pulls electron through reducing agent to oxidizing agent.

**CENTRIFUGE:** Equipment used to separate substances based on density by rotating the tubes around a centered axis

**CESIUM (also Caesium):** Symbol Cs- A soft, silvery-white ductile metal, liquid at room temperature, the most electropositive and alkaline of the elements, used in photoelectric cells and to catalyze hydrogenation of some organic compounds.

**CHAIN OF CUSTODY (COC):** A record of each person involved in the possession of a sample from the person who collects the sample to the person who analyzes the sample in the laboratory.

**CHECK VALVE:** Allows water to flow in only one direction.

**CHELATION:** A chemical process used to control scale formation in which a chelating agent "captures" scale-causing ions and holds them in solution.

**CHEMICAL FEED RATE:** Chemicals are added to the water in order to improve the subsequent treatment processes. These may include pH adjusters and coagulants. Coagulants are chemicals, such as alum, that neutralize positive or negative charges on small particles, allowing them to stick together and form larger particles that are more easily removed by sedimentation (settling) or filtration. A variety of devices, such as baffles, static mixers, impellers and in-line sprays, can be used to mix the water and distribute the chemicals evenly.

**CHEMICAL LAW:** Certain rules that pertain to the laws of nature and chemistry.

**CHEMICAL OXIDIZER:** KMnO<sub>4</sub> or Potassium Permanganate is used for taste and odor control

**CHEMICAL REACTION RATE:** In general, when the temperature decreases, the chemical reaction rate also decreases. The opposite is true for when the temperature increases.

**CHEMICAL REACTION:** The change of one or more substances into another or multiple substances.

**CHEMISORPTION: (or chemical adsorption)** Is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds.

**CHLORAMINATION:** Treating drinking water by applying chlorine before or after ammonia. This creates persistent disinfectant residual called chloramines.

**CHLORAMINES:** A group of chlorine ammonia compounds formed when chlorine combines with organic wastes in the water. Chloramines are not effective as disinfectants and are responsible for eye and skin irritation as well as strong chlorine odors.

**CHLORINATION:** The process in water treatment of adding chlorine (gas or solid hypochlorite) for purposes of disinfection.

**CHLORINE DEMAND:** Amount of chlorine required to react on various water impurities before a residual is obtained. Also, means the amount of chlorine required to produce a free chlorine residual of 0.1 mg/l after a contact time of fifteen minutes as measured by iodometric method of a sample at a temperature of twenty degrees in conformance with Standard methods.

**CHLORINE FEED:** Chlorine may be delivered by vacuum-controlled solution feed chlorinators. The chlorine gas is controlled, metered, introduced into a stream of injector water and then conducted as a solution to the point of application.

**CHLORINE, FREE:** Chlorine available to kill bacteria or algae. The amount of chlorine available for sanitization after the chlorine demand has been met. Also known as chlorine residual.

**CHLORINE:** A chemical used to disinfect water. Chlorine is extremely reactive, and when it comes in contact with microorganisms in water it kills them. Chlorine is added to swimming pools to keep the water safe for swimming. Chlorine is available as solid tablets for swimming pools. Some public water system's drinking water treatment plants use chlorine in a gas form because of the large volumes required. Chlorine is very effective against algae, bacteria and viruses. Protozoa are resistant to chlorine because they have thick coats; protozoa are removed from drinking water by filtration.

**CHRONIC:** A stimulus that lingers or continues for a relatively long period of time, often one-tenth of the life span or more. Chronic should be considered a relative term depending on the life span of an organism. The measurement of chronic effect can be reduced growth, reduced reproduction, etc., in addition to lethality.

**Circulation:** The continual flow of drilling fluid from injection to recovery and recirculation at the surface.

**CLEAR WELL:** A large underground storage facility sometimes made of concrete. A clear well or a plant storage reservoir is usually filled when demand is low. The final step in the conventional filtration process, the clearwell provides temporary storage for the treated water. The two main purposes for this storage are to have filtered water available for backwashing the filter and to provide detention time (or contact time) for the chlorine (or other disinfectant) to kill any microorganisms that may remain in the water.

**CIO<sub>2</sub>:** The molecular formula of Chlorine dioxide.

**COAGULATION:** The best pH range for coagulation is between 5 and 7. Mixing is an important part of the coagulation process you want to complete the coagulation process as quickly as possible.

**COLIFORM TESTING:** The effectiveness of disinfection is usually determined by Coliform bacteria testing. A positive sample is a bad thing and indicates that you have bacteria contamination.

**COLIFORM:** Bacteria normally found in the intestines of warm-blooded animals. Coliform bacteria are present in high numbers in animal feces. They are an indicator of potential contamination of water. Adequate and appropriate disinfection effectively destroys coliform bacteria. Public water systems are required to deliver safe and reliable drinking water to their customers 24 hours a day, 365 days a year. If the water supply becomes contaminated, consumers can become seriously ill. Fortunately, public water systems take many steps to ensure that the public has safe, reliable drinking water. One of the most important steps is to regularly test the water for coliform bacteria. Coliform bacteria are organisms that are present in the environment and in the feces of all warm-blooded animals and humans. Coliform bacteria will not likely cause illness. However, their presence in drinking water indicates that disease-causing organisms (pathogens) could be in the water system. Most pathogens that can contaminate water supplies come from the feces of humans or animals. Testing drinking water for all possible pathogens is complex, time-consuming, and expensive. It is relatively easy and inexpensive to test for coliform bacteria. If coliform bacteria are found in a water sample, water system operators work to find the source of contamination and restore safe drinking water. There are three different groups of coliform bacteria; each has a different level of risk.

**COLLOID:** Mixture of evenly dispersed substances, such as many milks.

**COLLOIDAL SUSPENSIONS:** Because both iron and manganese react with dissolved oxygen to form insoluble compounds, they are not found in high concentrations in waters containing dissolved oxygen except as colloidal suspensions of the oxide.

**COLORIMETRIC MEASUREMENT:** A means of measuring an unknown chemical concentration in water by measuring a sample's color intensity.

**COMBINED CHLORINE:** The reaction product of chlorine with ammonia or other pollutants, also known as chloramines.

**COMBUSTION:** An exothermic reaction between an oxidant and fuel with heat and often light

**COMMUNITY WATER SYSTEM:** A water system which supplies drinking water to 25 or more of the same people year-round in their residences.

**COMPLIANCE CYCLE:** A 9-calendar year time-frame during which a public water system is required to monitor. Each compliance cycle consists of 3 compliance periods.

**COMPLIANCE PERIOD:** A 3-calendar year time-frame within a compliance cycle.

**COMPOSITE SAMPLE:** A water sample that is a combination of a group of samples collected at various intervals during the day.

**COMPOUND:** A substance that is made up of two or more chemically bonded elements.

**CONDENSATION:** The phase change from gas to liquid. The process that changes water vapor to tiny droplets or ice crystals.

**CONDENSATION:** The process that changes water vapor to tiny droplets or ice crystals.

**CONDUCTOR:** Material that allows electric flow more freely.

**CONTACT TIME, pH and LOW TURBIDITY:** Factors which are important in providing good disinfection using chlorine. If the water temperature decreases from 70°F (21°C) to 40°F (4°C). The operator needs to increase the detention time to maintain good disinfection of the water.

**CONTAINS THE ELEMENT CARBON:** A simple definition of an organic compound.

**CONTAMINANT:** Any natural or man-made physical, chemical, biological, or radiological substance or matter in water, which is at a level that may have an adverse effect on public health, and which is known or anticipated to occur in public water systems.

**CONTAMINATE:** 1. To make impure or unclean by contact or mixture. 2. To expose to or permeate with radioactivity.

**CONTAMINATION:** A degradation in the quality of groundwater in result of the it's becoming polluted with unnatural or previously non-existent constituents.

**CONTROL TASTE AND ODOR PROBLEMS:** KMnO<sub>4</sub> Potassium permanganate is a strong oxidizer commonly used to control taste and odor problems.

**Conventional:** A standard or common procedure to a group of more complex methods. (ex – Direct Rotary conventional vs. Reverse non-conventional)

**COPPER:** The chemical name for the symbol Cu.

**CORROSION:** The removal of metal from copper, other metal surfaces and concrete surfaces in a destructive manner. Corrosion is caused by improperly balanced water or excessive water velocity through piping or heat exchangers.

**CORROSIVITY:** The Langelier Index measures corrosivity.

**COUPON:** A coupon placed to measure corrosion damage in the water mains.

**COVALENT BOND:** Chemical bond that involves sharing electrons.

**CROSS-CONNECTION:** A physical connection between a public water system and any source of water or other substance that may lead to contamination of the water provided by the public water system through backflow. Might be the source of an organic substance causing taste and odor problems in a water distribution system.

**CROSS-CONTAMINATION:** The mixing of two unlike qualities of water. For example, the mixing of good water with a polluting substance like a chemical.

**CRYPTOSPORIDIUM:** A disease-causing parasite, resistant to chlorine disinfection. It may be found in fecal matter or contaminated drinking water. Cryptosporidium is a protozoan pathogen of the Phylum Apicomplexa and causes a diarrheal illness called cryptosporidiosis. Other apicomplexan pathogens include the malaria parasite Plasmodium, and Toxoplasma, the causative agent of toxoplasmosis. Unlike Plasmodium, which transmits via a mosquito vector, Cryptosporidium does not utilize an insect vector and is capable of completing its life cycle within a single host, resulting in cyst stages which are excreted in feces and are capable of transmission to a new host.

**CRYSTAL:** A solid that is packed with ions, molecules or atoms in an orderly fashion.

**CUVETTE:** Glassware used in spectroscopic experiments. It is usually made of plastic, glass or quartz and should be as clean and clear as possible.

**CYANOBACTERIA:** Cyanobacteria, also known as blue-green algae, blue-green bacteria or Cyanophyta, is a phylum of bacteria that obtain their energy through photosynthesis. The name "cyanobacteria" comes from the color of the bacteria (Greek: kyanós = blue). They are a significant component of the marine nitrogen cycle and an important primary producer in many areas of the ocean, but are also found on land.

**CYANURIC ACID:** White, crystalline, water-soluble solid, C<sub>3</sub>H<sub>3</sub>O<sub>3</sub>N<sub>3</sub>·2H<sub>2</sub>O, used chiefly in organic synthesis. Chemical used to prevent the decomposition of chlorine by ultraviolet (UV) light.

## D

**DAILY MAXIMUM LIMITATIONS:** The maximum allowable discharge of pollutants during a 24 hour period. Where daily maximum limitations are expressed in units of mass, the daily discharge is the total mass discharged over the course of the day. Where daily maximum limitations are expressed in terms of a concentration, the daily discharge is the arithmetic average measurement of the pollutant concentration derived from all measurements taken that day.

**DANGEROUS CHEMICALS:** The most suitable protection when working with a chemical that produces dangerous fumes is to work under an air hood or fume hood.

**DARCY'S LAW:** ( $Q=KIA$ ) A fundamental equation used in the groundwater sciences to determine aquifer characteristics, where  $Q$ =Flux,  $K$ =Hydraulic Conductivity (Permeability),  $I$  = Hydraulic Gradient (change in head), and  $A$  = Cross Sectional Area of flow.

**DECOMPOSE:** To decay or rot.

**DECOMPOSITION OF ORGANIC MATERIAL:** The decomposition of organic material in water produces taste and odors.

**DEIONIZATION:** The removal of ions, and in water's case mineral ions such as sodium, iron and calcium.

**DELIQUESCE:** Substances that absorb water from the atmosphere to form liquid solutions.

**DEMINERALIZATION PROCESS:** Mineral concentration of the feed water is the most important consideration in the selection of a demineralization process. Acid feed is the most common method of scale control in a membrane demineralization treatment system.

**DENTAL CARIES PREVENTION IN CHILDREN:** The main reason that fluoride is added to a water supply.

**DEPOLARIZATION:** The removal of hydrogen from a cathode.

**DEPOSITION:** Settling of particles within a solution or mixture.

**DESICCANT:** When shutting down equipment which may be damaged by moisture, the unit may be protected by sealing it in a tight container. This container should contain a desiccant.

**DESORPTION:** Desorption is a phenomenon whereby a substance is released from or through a surface. The process is the opposite of sorption (that is, adsorption and absorption). This occurs in a system being in the state of sorption equilibrium between bulk phase (fluid, i.e. gas or liquid solution) and an adsorbing surface (solid or boundary separating two fluids). When the concentration (or pressure) of substance in the bulk phase is lowered, some of the sorbed substance changes to the bulk state. In chemistry, especially chromatography, desorption is the ability for a chemical to move with the mobile phase. The more a chemical desorbs, the less likely it will adsorb, thus instead of sticking to the stationary phase, the chemical moves up with the solvent front. In chemical separation processes, stripping is also referred to as desorption as one component of a liquid stream moves by mass transfer into a vapor phase through the liquid-vapor interface.

**DETENTION LAG:** Is the period of time between the moment of change in a chlorinator control system and the moment when the change is sensed by the chlorine residual indicator.

**DEVELOPMENT:** The cleaning of the well and bore once construction is complete.

**DIATOMACEOUS EARTH:** A fine silica material containing the skeletal remains of algae.

**DIPOLE:** Electric or magnetic separation of charge.

**DIPOLE MOMENT:** The polarity of a polar covalent bond.

**DIRECT CURRENT:** A source of direct current (DC) may be used for standby lighting in a water treatment facility. The electrical current used in a DC system may come from a battery.

**DISINFECT:** The application of a chemical to kill most, but not all, microorganisms that may be present. Chlorine is added to public water drinking systems drinking water for disinfection.

Depending on your state rule, drinking water must contain a minimum of 0.2 mg/L free chlorine.

Disinfection makes drinking water safe to consume from the standpoint of killing pathogenic microorganisms including bacteria and viruses. Disinfection does not remove all bacteria from drinking water, but the bacteria that can survive disinfection with chlorine are not pathogenic bacteria that can cause disease in normal healthy humans.

**DISINFECTION BY-PRODUCTS (DBPs):** The products created due to the reaction of chlorine with organic materials (e.g. leaves, soil) present in raw water during the water treatment process. The EPA has determined that these DBPs can cause cancer. Chlorine is added to drinking water to kill or inactivate harmful organisms that cause various diseases. This process is called disinfection. However, chlorine is a very active substance and it reacts with naturally occurring substances to form compounds known as disinfection byproducts (DBPs). The most common DBPs formed when chlorine is used are trihalomethanes (THMs), and haloacetic acids (HAAs).

**DISINFECTION:** The treatment of water to inactivate, destroy, and/or remove pathogenic bacteria, viruses, protozoa, and other parasites.

**Dissolution:** The chemical and physical process of dissolving rock. Typically, limestone or carbonate rocks can be dissolved via the percolation or movement of groundwater that, in its infancy, is slightly acidic. As time goes on, the rock may also be physically worn away by the

rapid movement of groundwater through the interconnected open spaces created by the initial chemical dissolving process.

DISSOLUTION or SOLVATION: The spread of ions in a monosaccharide.

DISSOLVED OXYGEN: Can be added to zones within a lake or reservoir that would normally become anaerobic during periods of thermal stratification.

DISTILLATION, REVERSE OSMOSIS AND FREEZING: Processes that can be used to remove minerals from the water.

DOUBLE BOND: Sharing of two pairs of electradsodes.

DRY ACID: A granular chemical used to lower pH and or total alkalinity.

## E

E. COLI, Escherichia coli: A bacterium commonly found in the human intestine. For water quality analyses purposes, it is considered an indicator organism. These are considered evidence of water contamination. Indicator organisms may be accompanied by pathogens, but do not necessarily cause disease themselves.

EARTH METAL: See alkaline earth metal.

EFFECTIVENESS OF CHLORINE: The factors which influence the effectiveness of chlorination the most are pH, turbidity and temperature. Effectiveness of Chlorine decreases occurs during disinfection in source water with excessive turbidity.

ELECTRIC CHARGE: A measured property (coulombs) that determine electromagnetic interaction

ELECTROCHEMICAL CELL: Using a chemical reaction's current, electromotive force is made

ELECTROLYTE: A solution that conducts a certain amount of current and can be split categorically as weak and strong electrolytes.

ELECTROMAGNETIC RADIATION: A type of wave that can go through vacuums as well as material and classified as a self-propagating wave.

ELECTROMAGNETISM: Fields that have electric charge and electric properties that change the way that particles move and interact.

ELECTROMOTIVE FORCE: A device that gains energy as electric charges pass through it.

ELECTRON: A subatomic particle with a net charge that is negative.

ELECTRON SHELLS: An orbital around the atom's nucleus that has a fixed number electrons (usually two or eight).

ELECTRON: The name of a negatively charged atomic particle.

ELEMENT: An atom that is defined by its atomic number.

ELEMENTARY BUSINESS PLAN: Technical Capacity, Managerial Capacity, and Financial Capacity make up the elementary business plan. To become a new public water system, an owner shall file an elementary business plan for review and approval by state environmental agency.

EMERGENCY RESPONSE TEAM: A local team that is thoroughly trained and equipped to deal with emergencies, e.g. chlorine gas leak. In case of a chlorine gas leak, get out of the area and notify your local emergency response team in case of a large uncontrolled chlorine leak.

EMPOROCAL FORMULA: Also called the simplest formula, gives the simplest whole :number ratio of atoms of each element present in a compound.

ENERGY: A system's ability to do work.

ENHANCED COAGULATION: The process of joining together particles in water to help remove organic matter.

ENTAMOEBA HISTOLYTICA: Entamoeba histolytica, another water-borne pathogen, can cause diarrhea or a more serious invasive liver abscess. When in contact with human cells, these amoebae are cytotoxic. There is a rapid influx of calcium into the contacted cell, it quickly stops all membrane movement save for some surface blebbing. Internal organization is disrupted, organelles lyse, and the cell dies. The ameba may eat the dead cell or just absorb nutrients released from the cell.

ENTEROVIRUS: A virus whose presence may indicate contaminated water; a virus that may infect the gastrointestinal tract of humans.

ENTHALPY: Measure of the total energy of a thermodynamic system (usually symbolized as H).

**ENTROPY:** The amount of energy not available for work in a closed thermodynamic system (usually symbolized as S).

**ENZYME:** A protein that speeds up (catalyzes) a reaction.

**EPPENDORF TUBE:** Generalized and trademarked term used for a type of tube; see microcentrifuge.

**EUGLENA:** Euglena are common protists, of the class Euglenoidea of the phylum Euglenophyta. Currently, over 1000 species of Euglena have been described. Marin et al. (2003) revised the genus so and including several species without chloroplasts, formerly classified as *Astasia* and *Khawkinea*. Euglena sometimes can be considered to have both plant and animal features. *Euglena gracilis* has a long hair-like thing that stretches from its body. You need a very powerful microscope to see it. This is called a flagellum, and the euglena uses it to swim. It also has a red eyespot. *Euglena gracilis* uses its eyespot to locate light. Without light, it cannot use its chloroplasts to make itself food.

**EVOLUTION:** Any process of formation or growth; development: the evolution of a language; the evolution of the airplane. A product of such development; something evolved: The exploration of space is the evolution of decades of research.

## F

**F:** The chemical symbol of Fluorine.

**FARADAY CONSTANT:** A unit of electrical charge widely used in electrochemistry and equal to ~ 96,500 coulombs. It represents 1 mol of electrons, or the Avogadro number of electrons:  $6.022 \times 10^{23}$  electrons.  $F = 96\,485.339\,9(24) \text{ C/mol}$ .

**FARADAY'S LAW OF ELECTROLYSIS:** A two part law that Michael Faraday published about electrolysis. The mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode. The mass of an elemental material altered at an electrode is directly proportional to the element's equivalent weight.

**FAUCET WITH AN AERATOR:** When collecting a water sample from a distribution system, a faucet with an aerator should not be used as a sample location.

**FECAL COLIFORM:** A group of bacteria that may indicate the presence of human or animal fecal matter in water. Total coliform, fecal coliform, and *E. coli* are all indicators of drinking water quality. The total coliform group is a large collection of different kinds of bacteria. Fecal coliforms are types of total coliform that mostly exist in feces. *E. coli* is a sub-group of fecal coliform. When a water sample is sent to a lab, it is tested for total coliform. If total coliform is present, the sample will also be tested for either fecal coliform or *E. coli*, depending on the lab testing method.

**FILTER CLOGGING:** An inability to meet demand may occur when filters are clogging.

**FILTRATION METHODS:** The conventional type of water treatment filtration method includes coagulation, flocculation, sedimentation, and filtration. Direct filtration method is similar to conventional except that the sedimentation step is omitted. Slow sand filtration process does not require pretreatment, has a flow of 0.1 gallons per minute per square foot of filter surface area, and is simple to operate and maintain. The Diatomaceous earth method uses a thin layer of fine siliceous material on a porous plate. This type of filtration medium is only used for water with low turbidity. Sedimentation, adsorption, and biological action treatment methods are filtration processes that involve a number of interrelated removal mechanisms. Demineralization is primarily used to remove total dissolved solids from industrial wastewater, municipal water, and seawater.

**FILTRATION:** The process of passing water through materials with very small holes to strain out particles. Most conventional water treatment plants used filters composed of gravel, sand, and anthracite. These materials settle into a compact mass that forms very small holes. Particles are filtered out as treated water passes through these holes. These holes are small enough to remove microorganisms including algae, bacteria, and protozoans, but not viruses. Viruses are eliminated from drinking water through the process of disinfection using chlorine. A series of processes that physically removes particles from water. A water treatment step used to remove turbidity, dissolved organics, odor, taste and color.

**FINISHED WATER:** Treated drinking water that meets minimum state and federal drinking water regulations.

**FLOC SHEARING:** Likely to happen to large floc particles when they reach the flocculation process.

**FLOC SHEARING:** Likely to happen to large floc particles when they reach the flocculation process.

**FLOCCULANTS:** Flocculants, or flocculating agents, are chemicals that promote flocculation by causing colloids and other suspended particles in liquids to aggregate, forming a floc. Flocculants are used in water treatment processes to improve the sedimentation or filterability of small particles. For example, a flocculant may be used in swimming pool or drinking water filtration to aid removal of microscopic particles which would otherwise cause the water to be cloudy and which would be difficult or impossible to remove by filtration alone. Many flocculants are multivalent cations such as aluminum, iron, calcium or magnesium. These positively charged molecules interact with negatively charged particles and molecules to reduce the barriers to aggregation. In addition, many of these chemicals, under appropriate pH and other conditions such as temperature and salinity, react with water to form insoluble hydroxides which, upon precipitating, link together to form long chains or meshes, physically trapping small particles into the larger floc.

**FLOCCULATION BASIN:** A compartmentalized basin with a reduction of speed in each compartment. This set-up or basin will give the best overall results.

**FLOCCULATION:** The process of bringing together destabilized or coagulated particles to form larger masses that can be settled and/or filtered out of the water being treated. Conventional coagulation–flocculation–sedimentation practices are essential pretreatments for many water purification systems—especially filtration treatments. These processes agglomerate suspended solids together into larger bodies so that physical filtration processes can more easily remove them. Particulate removal by these methods makes later filtering processes far more effective. The process is often followed by gravity separation (sedimentation or flotation) and is always followed by filtration. A chemical coagulant, such as iron salts, aluminum salts, or polymers, is added to source water to facilitate bonding among particulates. Coagulants work by creating a chemical reaction and eliminating the negative charges that cause particles to repel each other. The coagulant-source water mixture is then slowly stirred in a process known as flocculation. This water churning induces particles to collide and clump together into larger and more easily removable clots, or “flocs.” The process requires chemical knowledge of source water characteristics to ensure that an effective coagulant mix is employed. Improper coagulants make these treatment methods ineffective. The ultimate effectiveness of coagulation/flocculation is also determined by the efficiency of the filtering process with which it is paired.

**FLOOD RIM:** The point of an object where the water would run over the edge of something and begin to cause a flood.

**FLOW MUST BE MEASURED:** A recorder that measures flow is most likely to be located in a central location.

**FLUORIDE FEEDING:** Always review fluoride feeding system designs and specifications to determine whether locations for monitoring readouts and dosage controls are convenient to the operation center and easy to read and correct.

**FLUORIDE:** High levels of fluoride may stain the teeth of humans. This is called Mottling. This chemical must not be overfed due to a possible exposure to a high concentration of the chemical. The most important safety considerations to know about fluoride chemicals are that all fluoride chemicals are extremely corrosive. These are the substances most commonly used to furnish fluoride ions to water: Sodium fluoride, Sodium silicofluoride and Hydrofluosilicic acid.

**FLUX:** The term flux describes the rate of water flow through a semipermeable membrane. When the water flux decreases through a semipermeable membrane, it means that the mineral concentration of the water is increasing.

**FORMATION OF TUBERCLES:** This condition is of the most concern regarding corrosive water effects on a water system. It is the creation of mounds of rust inside the water lines.

**Formation:** A series of layers, deposits, or bodies of rock, which are geologically similar and related in depositional environment or origin. A formation can be clearly distinguished relative to bounding deposits or formations due to its particular characteristics and composition.

**Fracture:** A discrete break in a rock or formation.

**FREE CHLORINE RESIDUAL:** Regardless of whether pre-chlorination is practiced or not, a free chlorine residual of at least 10 mg/L should be maintained in the clear well or distribution reservoir immediately downstream from the point of post-chlorination. The reason for chlorinating past the breakpoint is to provide protection in case of backflow.

**FREE CHLORINE:** In disinfection, chlorine is used in the form of free chlorine or as hypochlorite ion.

**FREEZING:** Phase transition from liquid to solid.

**FREQUENCY:** Number of cycles per unit of time. Unit: 1 hertz = 1 cycle per 1 second.

## G

**GALVANIC CELL:** Battery made up of electrochemical with two different metals connected by salt bridge.

**GAS:** Particles that fill their container though have no definite shape or volume.

**GEOCHEMISTRY:** The chemistry of and chemical composition of the Earth.

**GIARDIA LAMBLIA:** Giardia lamblia (synonymous with Lamblia intestinalis and Giardia duodenalis) is a flagellated protozoan parasite that colonizes and reproduces in the small intestine, causing giardiasis. The giardia parasite attaches to the epithelium by a ventral adhesive disc, and reproduces via binary fission. Giardiasis does not spread via the bloodstream, nor does it spread to other parts of the gastro-intestinal tract, but remains confined to the lumen of the small intestine. Giardia trophozoites absorb their nutrients from the lumen of the small intestine, and are anaerobes.

**GIARDIASIS, HEPATITIS OR TYPHOID:** Diseases that may be transmitted through the contamination of a water supply but not AIDS.

**GIBBS ENERGY:** Value that indicates the spontaneity of a reaction (usually symbolized as G).

**GOOD CONTACT TIME, pH and LOW TURBIDITY:** These are factors that are important in providing good disinfection when using chlorine.

**GPM:** Gallons per minute.

**GRAB SAMPLE:** A sample which is taken from a water or wastestream on a one-time basis with no regard to the flow of the water or wastestream and without consideration of time. A single grab sample should be taken over a period of time not to exceed 15 minutes.

**GT:** Represents (Detention time) x (mixing intensity) in flocculation.

## H

**H<sub>2</sub>SO<sub>4</sub>:** The molecular formula of Sulfuric acid.

**HALIDES:** A halide is a binary compound, of which one part is a halogen atom and the other part is an element or radical that is less electronegative than the halogen, to make a fluoride, chloride, bromide, iodide, or astatide compound. Many salts are halides. All Group 1 metals form halides with the halogens and they are white solids. A halide ion is a halogen atom bearing a negative charge. The halide anions are fluoride (F), chloride (Cl), bromide (Br), iodide (I) and astatide (At). Such ions are present in all ionic halide salts.

**HALL EFFECT:** Refers to the potential difference (Hall voltage) on the opposite sides of an electrical conductor through which an electric current is flowing, created by a magnetic field applied perpendicular to the current. Edwin Hall discovered this effect in 1879.

**HALOACETIC ACIDS:** Haloacetic acids are carboxylic acids in which a halogen atom takes the place of a hydrogen atom in acetic acid. Thus, in a monohaloacetic acid, a single halogen would replace a hydrogen atom. For example, chloroacetic acid would have the structural formula CH<sub>2</sub>ClCO<sub>2</sub>H. In the same manner, in dichloroacetic acid two chlorine atoms would take the place of two hydrogen atoms (CHCl<sub>2</sub>CO<sub>2</sub>H).

**HALOGENS:** Group 7 on the Periodic Table and are all non-metals.

**HARD WATER:** Hard water causes a buildup of scale in household hot water heaters. Hard water is a type of water that has high mineral content (in contrast with soft water). Hard water primarily consists of calcium (Ca<sup>2+</sup>), and magnesium (Mg<sup>2+</sup>) metal cations, and sometimes other dissolved compounds such as bicarbonates and sulfates. Calcium usually enters the water as either calcium carbonate (CaCO<sub>3</sub>), in the form of limestone and chalk, or calcium sulfate (CaSO<sub>4</sub>), in the form of other mineral deposits. The predominant source of magnesium is dolomite (CaMg (CO<sub>3</sub>)<sub>2</sub>). Hard water is generally not harmful. The simplest way to determine the

hardness of water is the lather/froth test: soap or toothpaste, when agitated, lathers easily in soft water but not in hard water. More exact measurements of hardness can be obtained through a wet titration. The total water 'hardness' (including both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions) is read as parts per million or weight/volume (mg/L) of calcium carbonate ( $\text{CaCO}_3$ ) in the water. Although water hardness usually only measures the total concentrations of calcium and magnesium (the two most prevalent, divalent metal ions), iron, aluminum, and manganese may also be present at elevated levels in some geographical locations.

**HARDNESS:** A measure of the amount of calcium and magnesium salts in water. More calcium and magnesium lead to greater hardness. The term "hardness" comes from the fact that it is hard to get soap suds from soap or detergents in hard water. This happens because calcium and magnesium react strongly with negatively-charged chemicals like soap to form insoluble compounds.

**HARTSHORN:** The antler of a hart, formerly used as a source of ammonia. Ammonium carbonate.

**HAZARDS OF POLYMERS:** Slippery and difficult to clean-up are the most common hazards associated with the use of polymers in a water treatment plant.

**HEAD:** The measure of the pressure of water expressed in feet of height of water. 1 PSI = 2.31 feet of water or 1 foot of head equals about a half a pound of pressure or .433 PSI. There are various types of heads of water depending upon what is being measured. Static (water at rest) and Residual (water at flow conditions).

**HEADWORKS:** The facility at the "head" of the water source where water is first treated and routed into the distribution system.

**HEALTH ADVISORY:** An EPA document that provides guidance and information on contaminants that can affect human health and that may occur in drinking water, but which the EPA does not currently regulate in drinking water.

**HEAT:** Energy transferred from one system to another by thermal interaction.

**HERTZ:** The term used to describe the frequency of cycles in an alternating current (AC) circuit.

**HETEROTROPHIC PLATE COUNT:** A test performed on drinking water to determine the total number of all types of bacteria in the water.

**HF:** The molecular formula of Hydrofluoric acid.

**HIGH TURBIDITY CAUSING INCREASED CHLORINE DEMAND:** May occur or be caused by the inadequate disinfection of water.

**hydraulic conductivity:** A primary factor in Darcy's Law, the measure of a soil or formations ability to transmit water, measured in gallons per day (gpd) See also Permeability and Darcy's Law.

**HYDRIDES:** Hydride is the name given to the negative ion of hydrogen, H. Although this ion does not exist except in extraordinary conditions, the term hydride is widely applied to describe compounds of hydrogen with other elements, particularly those of groups 1–16. The variety of compounds formed by hydrogen is vast, arguably greater than that of any other element. Various metal hydrides are currently being studied for use as a means of hydrogen storage in fuel cell-powered electric cars and batteries. They also have important uses in organic chemistry as powerful reducing agents, and many promising uses in hydrogen economy.

**HYDROCHLORIC AND HYPOCHLOROUS ACIDS:** HCL and HOCL The compounds that are formed in water when chlorine gas is introduced.

**HYDROFLUOSILICIC ACID:** ( $\text{H}_2\text{SiF}_6$ ) a clear, fuming corrosive liquid with a pH ranging from 1 to 1.5. Used in water treatment to fluoridate drinking water.

**HYDROGEN SULFIDE OR CHLORINE GAS:** These chemicals can cause olfactory fatigue.

**Hydrologic Cycle:** (Water Cycle) The continual process of precipitation (rain and snowfall), evaporation (primarily from the oceans), percolation (recharge to groundwater), runoff (surface water), and transpiration (plants) constituting the renew ability and recycling of each component.

**HYDROPHOBIC:** Does not mix readily with water.

**HYGROSCOPIC:** Absorbing or attracting moisture from the air.

**HYPOCHLORITE ( $\text{OCL}^-$ ) AND ORGANIC MATERIALS:** Heat and possibly fire may occur when hypochlorite is brought into contact with an organic material.

**HYPOLIMNION:** The layer of water in a thermally stratified lake that lies below the thermocline, is noncirculating, and remains perpetually cold.

I

**IMPELLERS:** The semi-open or closed props or blades of a turbine pump that when rotated generate the pumping force.

**IMPERVIOUS:** Not allowing, or allowing only with great difficulty, the movement of water.

**In Series:** Several components being connected one to the other without a bypass, requiring each component to work dependent on the one before it.

**INDICATOR:** A special compound added to solution that changes color depending on the acidity of the solution; different indicators have different colors and effective pH ranges.

**INFECTIOUS PATHOGENS/MICROBES/GERMS:** Are considered disease-producing bacteria, viruses and other microorganisms.

**Infiltration:** The percolation of fluid into soil or formation. See also percolation.

**INFORMATION COLLECTION RULE:** ICR EPA collected data required by the Information Collection Rule (May 14, 1996) to support future regulation of microbial contaminants, disinfectants, and disinfection byproducts. The rule was intended to provide EPA with information on chemical byproducts that form when disinfectants used for microbial control react with chemicals already present in source water (disinfection byproducts (DBPs)); disease-causing microorganisms (pathogens), including Cryptosporidium; and engineering data to control these contaminants.

**INITIAL MONITORING YEAR:** An initial monitoring year is the calendar year designated by the Department within a compliance period in which a public water system conducts initial monitoring at a point of entry.

**INORGANIC CHEMISTRY:** A part of chemistry concerned with inorganic compounds.

**INORGANIC COMPOUND:** Compounds that do not contain carbon, though there are exceptions.

**INORGANIC CONTAMINANTS:** Mineral-based compounds such as metals, nitrates, and asbestos. These contaminants are naturally-occurring in some water, but can also get into water through farming, chemical manufacturing, and other human activities. EPA has set legal limits on 15 inorganic contaminants.

**INORGANIC IONS:** Present in all waters. Inorganic ions are essential for human health in small quantities, but in larger quantities they can cause unpleasant taste and odor or even illness. Most community water systems will commonly test for the concentrations of seven inorganic ions: nitrate, nitrite, fluoride, phosphate, sulfate, chloride, and bromide. Nitrate and nitrite can cause an illness in infants called methemoglobinemia. Fluoride is actually added to the drinking water in some public water systems to promote dental health. Phosphate, sulfate, chloride, and bromide have little direct effect on health, but high concentrations of inorganic ions can give water a salty or briny taste.

**INSOLUBLE COMPOUNDS:** Are types of compounds cannot be dissolved. When iron or manganese reacts with dissolved oxygen (DO) insoluble compound are formed.

**INSULATOR:** Material that resists the flow of electric current.

**INTAKE FACILITIES:** One of the more important considerations in the construction of intake facilities is the ease of operation and maintenance over the expected lifetime of the facility. Every intake structure must be constructed with consideration for operator safety and for cathodic protection.

**ION:** A molecule that has gained or lost one or more electrons.

**ION EXCHANGE:** An effective treatment process used to remove iron and manganese in a water supply. The hardness of the source water affects the amount of water an ion exchange softener may treat before the bed requires regeneration.

**IONIC BOND:** Electrostatic attraction between oppositely charged ions.

**IONIZATION:** The breaking up of a compound into separate ions.

**IRON AND MANGANESE:** Fe and Mn In water they can usually be detected by observing the color of the inside walls of filters and the filter media. If the raw water is pre-chlorinated, there will be black stains on the walls below the water level and a black coating over the top portion of the sand filter bed. When significant levels of dissolved oxygen are present, iron and manganese exist in an oxidized state and normally precipitate into the reservoir bottom sediments. The presence of iron and manganese in water promote the growth of Iron bacteria. Only when a water sample has been acidified then you can perform the analysis beyond the 48 hour holding time. Iron and Manganese in water may be detected by observing the color of the of the filter media.

Maintaining a free chlorine residual and regular flushing of water mains may control the growth of iron bacteria in a water distribution system.

IRON BACTERIA: Perhaps the most troublesome consequence of iron and manganese in the water is they promote the growth of a group of microorganism known as Iron Bacteria.

IRON FOULING: You should look for an orange color on the resin and backwash water when checking an ion exchange unit for iron fouling

IRON: Fe The elements iron and manganese are undesirable in water because they cause stains and promote the growth of iron bacteria.

IUPAC: International Union of Pure and Applied Chemistry

## J

JODIUM: Latin name of the halogen element iodine.

JOULE: The SI unit of energy, defined as a newton-meter.

## K

KILL = C X T: Where other factors are constant, the disinfecting action may be represented by: Kill=C x T. C= Chlorine T= Contact time.

KINETIC ENERGY: The energy of an object due to its motion. The ability of an object to do work by virtue of its motion. The energy terms that are used to describe the operation of a pump are pressure and head.

KINETICS: A sub-field of chemistry specializing in reaction rates.

## L

L.O.T.O.: Lock Out, Tag Out. If a piece of equipment is locked out, the key to the lock-out device the key should be held by the person who is working on the equipment. The tag is an identification device and the lock is a physical restraint.

LACRIMATION: The secretion of tears, esp. in abnormal abundance Also, lachrymation, lachrimation.

LANGELIER INDEX: A measurement of Corrosivity. The water is becoming corrosive in the distribution system causing rusty water if the Langelier index indicates that the pH has decreased from the equilibrium point. Mathematically derived factor obtained from the values of calcium hardness, total alkalinity, and pH at a given temperature. A Langelier index of zero indicates perfect water balance (i.e., neither corroding nor scaling). The Langelier Saturation Index (sometimes Langelier Stability Index) is a calculated number used to predict the calcium carbonate stability of water. It indicates whether the water will precipitate, dissolve, or be in equilibrium with calcium carbonate. Langelier developed a method for predicting the pH at which water is saturated in calcium carbonate (called pHs). The LSI is expressed as the difference between the actual system pH and the saturation pH.

LANTHANIDES: Elements 57 through 71.

LATTICE: Unique arrangement of atoms or molecules in a crystalline liquid or solid.

LAW OF MOTION: An object in motion stay in motion an object in rest stays in rest unless an unbalanced force acts on it.

LEACHING: A chemical reaction between water and metals that allows for removal of soluble materials.

LEAD AND COPPER: Initial tap water monitoring for lead and copper must be conducted during 2 consecutive 6-month periods.

LIGHT: Portion of the electromagnetic spectrum which is visible to the naked eye. Also called "visible light."

LIME SODA SOFTENING: In a lime soda softening process, to the pH of the water is raised to 11.0. In a lime softening process, excess lime is frequently added to remove Calcium and Magnesium Bicarbonate. The minimum hardness which can be achieved by the lime-soda ash process is 30 to 40 mg/L as calcium carbonate. The hardness due to noncarbonate hardness is most likely to determine the choice between lime softening and ion exchange to remove hardness.

LIME SOFTENING: Lime softening is primarily used to "soften" water—that is to remove calcium and magnesium mineral salts. But it also removes harmful toxins like radon and arsenic. Though

there is no consensus, some studies have even suggested that lime softening is effective at removal of Giardia. Hard water is a common condition responsible for numerous problems. Users often recognize hard water because it prevents their soap from lathering properly. However, it can also cause buildup (“scale”) in hot water heaters, boilers, and hot water pipes. Because of these inconveniences, many treatment facilities use lime softening to soften hard water for consumer use. Before lime softening can be used, managers must determine the softening chemistry required. This is a relatively easy task for groundwater sources, which remain more constant in their composition. Surface waters, however, fluctuate widely in quality and may require frequent changes to the softening chemical mix. In lime softening, lime and sometimes sodium carbonate are added to the water as it enters a combination solids contact clarifier. This raises the pH (i.e., increases alkalinity) and leads to the precipitation of calcium carbonate. Later, the pH of the effluent from the clarifier is reduced again, and the water is then filtered through a granular media filter. The water chemistry requirements of these systems require knowledgeable operators, which may make lime softening an economic challenge for some very small systems.

LIME: Is a chemical that may be added to water to reduce the corrosivity. When an operator adds lime to water, Calcium and magnesium become less soluble.

LIQUID: A state of matter which takes the shape of its container.

LONDON DISERSION FORCES: A weak intermolecular force.

LSI = pH - pHs

## M

M.S.D.S.: Material Safety Data Sheet, now S.D.S. (Safety Data Sheet). A safety document must an employer provide to an operator upon request.

MAGNESIUM HARDNESS: Measure of the magnesium salts dissolved in water – it is not a factor in water balance.

MARBLE AND LANGELIER TESTS: Are used to measure or determine the corrosiveness of a water source.

MAXIMUM CONTAMINANT LEVEL (MCLs): The maximum allowable level of a contaminant that federal or state regulations allow in a public water system. If the MCL is exceeded, the water system must treat the water so that it meets the MCL.

MAXIMUM CONTAMINANT LEVEL GOAL (MCLG): The level of a contaminant at which there would be no risk to human health. This goal is not always economically or technologically feasible, and the goal is not legally enforceable.

MCL for TURBIDITY: Turbidity is undesirable because it causes health hazards. An MCL for turbidity was established by the EPA because turbidity does not allow for proper disinfection.

MEASURE CORROSION DAMAGE: A coupon such as a strip of metal and is placed to measure corrosion damage in the distribution system in a water main.

MEDIUM WATER SYSTEM: More than 3,300 persons and 50,000 or fewer persons.

MELTING: The phase change from a solid to a liquid.

M-ENDO BROTH: The coliform group is used as indicators of fecal pollution in water, for assessing the effectiveness of water treatment and disinfection, and for monitoring water quality. m-Endo Broth is used for selectively isolating coliform bacteria from water and other specimens using the membrane filtration technique. m-Endo Broth is prepared according to the formula of Fifield and Schaufus.<sup>1</sup> It is recommended by the American Public Health Association in standard total coliform membrane filtration procedure for testing water, wastewater, and foods.<sup>2,3</sup> The US EPA specifies using m-Endo Broth in the total coliform methods for testing water using single-step, two-step, and delayed incubation membrane filtration methods.: The media shall be brought to the boiling point when preparing M-Endo broth to be used in the membrane filter test for total coliform.

METAL: Chemical element that is a good conductor of both electricity and heat and forms cations and ionic bonds with non-metals.

METALIMNION: Thermocline, middle layer of a thermally stratified lake which is characterized by a rapid decrease in temperature in proportion to depth.

METALLOID: Metalloid is a term used in chemistry when classifying the chemical elements. On the basis of their general physical and chemical properties, nearly every element in the periodic

table can be termed either a metal or a nonmetal. A few elements with intermediate properties are, however, referred to as metalloids. (In Greek metallon = metal and eidos = sort)  
METHANE: Methane is a chemical compound with the molecular formula CH<sub>4</sub>. It is the simplest alkane, and the principal component of natural gas. Methane's bond angles are 109.5 degrees. Burning methane in the presence of oxygen produces carbon dioxide and water. The relative abundance of methane and its clean burning process makes it a very attractive fuel. However, because it is a gas at normal temperature and pressure, methane is difficult to transport from its source. In its natural gas form, it is generally transported in bulk by pipeline or LNG carriers; few countries still transport it by truck.

METHYLENE BLUE: A heterocyclic aromatic chemical compound with the molecular formula C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl.

Mg/L: Stands for "milligrams per liter." A common unit of chemical concentration. It expresses the mass of a chemical that is present in a given volume of water. A milligram (one one-thousandth of a gram) is equivalent to about 18 grains of table salt. A liter is equivalent to about one quart.

MICROBE OR MICROBIAL: Any minute, simple, single-celled form of life, especially one that causes disease.

MICROBIAL CONTAMINANTS: Microscopic organisms present in untreated water that can cause waterborne diseases.

MICROBIOLOGICAL: Is a type of analysis in which a composite sample unacceptable.

MICROCENTRIFUGE: A small plastic container that is used to store small amounts of liquid.

MICROORGANISMS: Very small animals and plants that are too small to be seen by the naked eye and must be observed using a microscope. Microorganisms in water include algae, bacteria, viruses, and protozoa. Algae growing in surface waters can cause off-taste and odor by producing the chemicals MIB and geosmin. Certain types of bacteria, viruses, and protozoa can cause disease in humans. Bacteria are the most common microorganisms found in treated drinking water. The great majority of bacteria are not harmful. In fact, humans would not be able to live without the bacteria that inhabit the intestines. However, certain types of bacteria called coliform bacteria can signal the presence of possible drinking water contamination.

MILLILITER: One one-thousandth of a liter. A liter is a little more than a quart. A milliliter is about two drops from an eye dropper.

MOISTURE AND POTASSIUM PERMANGANATE: The combination of moisture and potassium permanganate produces heat.

MOISTURE: If a material is hygroscopic, it must be protected from water.

MOLE: Abbreviated mol : a measurement of an amount of substance; a single mole contains approximately  $6.022 \times 10^{23}$  units or entities .A mole of water contains  $6.022 \times 10^{23}$  H<sub>2</sub>O molecules.

MOLECULAR ORBITAL: Region where an electron can be found in a molecule (as opposed to an atom).

MOLECULAR WEIGHT: The molecular mass (abbreviated Mr) of a substance, formerly also called molecular weight and abbreviated as MW, is the mass of one molecule of that substance, relative to the unified atomic mass unit u (equal to 1/12 the mass of one atom of carbon-12). This is distinct from the relative molecular mass of a molecule, which is the ratio of the mass of that molecule to 1/12 of the mass of carbon 12 and is a dimensionless number. Relative molecular mass is abbreviated to Mr.

MOLECULE: A chemically bonded number of atoms that are electrically neutral.

MOTTLING: High levels of fluoride may stain the teeth of humans.

MUD BALLS IN FILTER MEDIA: Is a possible result of an ineffective or inadequate filter backwash.

Mud Cake: A film of mud drilling fluid that builds up on borehole walls adding to borehole stability and limits the groundwater's ability to enter the borehole while drilling.

Mud Caking: The process of building up the mud cake.

Mud Engineer: A specially trained individual who's responsible for maintaining proper drilling fluid densities and viscosity.

Mud Pit: Single or multiple subsurface or surface containment system used for settling cuttings out of drilling fluid and for recirculation of drilling fluid.

MURIATIC ACID: An acid used to reduce pH and alkalinity. Also used to remove stain and scale.

MYCOTOXIN: A toxin produced by a fungus.

## N

NaOCl: Is the molecular formula of Sodium hypochlorite.

NaOH: Is the molecular formula of Sodium hydroxide.

NASCENT: Coming into existence; emerging.

NASCENT: Coming into existence; emerging.

NATURAL GRAVEL PACK (Naturally packed): Refers to a well that has no gravel pack installed but is simply allowed to develop a filter pack composed of the aquifer particles itself. Usually coarse grained and hard rock aquifers are naturally packed.

NEAT: Conditions with a liquid reagent or gas performed with no added solvent or co-solvent.

NEUTRINO: A particle that can travel at speeds close to the speed of light and are created as a result of radioactive decay.

NEUTRON: A neutral unit or subatomic particle that has no net charge.

NH<sub>3</sub>: The molecular formula of Ammonia.

NH<sub>4</sub><sup>+</sup>: The molecular formula of the Ammonium ion.

NITRATES: A dissolved form of nitrogen found in fertilizers and sewage by-products that may leach into groundwater and other water sources. Nitrates may also occur naturally in some waters. Over time, nitrates can accumulate in aquifers and contaminate groundwater.

NITROGEN AND PHOSPHORUS: Pairs of elements and major plant nutrients that cause algae to grow.

NITROGEN: Nitrogen is a nonmetal, with an electronegativity of 3.0. It has five electrons in its outer shell and is therefore trivalent in most compounds. The triple bond in molecular nitrogen (N<sub>2</sub>) is one of the strongest in nature. The resulting difficulty of converting (N<sub>2</sub>) into other compounds, and the ease (and associated high energy release) of converting nitrogen compounds into elemental N<sub>2</sub>, have dominated the role of nitrogen in both nature and human economic activities.

NO<sub>3</sub><sup>-</sup>: The molecular formula of the Nitrate ion.

NO<sub>3</sub><sup>-</sup>: The molecular formula of the Nitrate ion.

NOBLE GASES: Group 18 elements, those whose outer electron shell is filled.

NON-CARBONATE HARDNESS: The portion of the total hardness in excess of the alkalinity.

NON-CARBONATE IONS: Water contains non-carbonate ions if it cannot be softened to a desired level through the use of lime only.

NON-METAL: An element which is not metallic.

NON-POINT SOURCE POLLUTION: Air pollution may leave contaminants on highway surfaces. This non-point source pollution adversely impacts reservoir water and groundwater quality.

NON-TRANSIENT, NON-COMMUNITY WATER SYSTEM: A water system which supplies water to 25 or more of the same people at least six months per year in places other than their residences. Some examples are schools, factories, office buildings, and hospitals which have their own water systems.

NORMALITY: It is the number of equivalent weights of solute per liter of solution. Normality highlights the chemical nature of salts: in solution, salts dissociate into distinct reactive species (ions such as H<sup>+</sup>, Fe<sup>3+</sup>, or Cl<sup>-</sup>). Normality accounts for any discrepancy between the concentrations of the various ionic species in a solution. For example, in a salt such as MgCl<sub>2</sub>, there are two moles of Cl<sup>-</sup> for every mole of Mg<sup>2+</sup>, so the concentration of Cl<sup>-</sup> as well as of Mg<sup>2+</sup> is said to be 2 N (read: "two normal"). Further examples are given below. A normal is one gram equivalent of a solute per liter of solution. The definition of a gram equivalent varies depending on the type of chemical reaction that is discussed - it can refer to acids, bases, redox species, and ions that will precipitate. It is critical to note that normality measures a single ion which takes part in an overall solute. For example, one could determine the normality of hydroxide or sodium in an aqueous solution of sodium hydroxide, but the normality of sodium hydroxide itself has no meaning. Nevertheless it is often used to describe solutions of acids or bases, in those cases it is implied that the normality refers to the H<sup>+</sup> or OH<sup>-</sup> ion. For example, 2 Normal sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), means that the normality of H<sup>+</sup> ions is 2, or that the molarity of the sulfuric acid is 1. Similarly for 1 Molar H<sub>3</sub>PO<sub>4</sub> the normality is 3 as it contains three H<sup>+</sup> ions.

NTNCWS: Non-transient non-community water system.

NTU (Nephelometric turbidity unit): A measure of the clarity or cloudiness of water.  
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY: Technique that exploits the magnetic properties of certain nuclei, useful for identifying unknown compounds.  
NUCLEAR: Of or pertaining to the atomic nucleus.  
NUCLEUS: The center of an atom made up of neutrons and protons, with a net positive charge.  
NUMBER DENSITY: A measure of concentration of countable objects (atoms, molecules, etc.) in space; number per volume.

## O

O<sub>3</sub>: The molecular formula of ozone.  
OLIGOTROPHIC: A reservoir that is nutrient-poor and contains little plant or animal life. An oligotrophic ecosystem or environment is one that offers little to sustain life. The term is commonly utilized to describe bodies of water or soils with very low nutrient levels. It derives etymologically from the Greek oligo (small, little, few) and trophe (nutrients, food). Oligotrophic environments are of special interest for the alternative energy sources and survival strategies upon which life could rely.  
ORBITAL: May refer to either an atomic orbital or a molecular orbital.  
ORGANIC CHEMISTRY: A part of chemistry concerned with organic compounds.  
ORGANIC COMPOUND: Compounds that contain carbon.  
ORGANIC PRECURSORS: Natural or man-made compounds with chemical structures based upon carbon that, upon combination with chlorine, leading to trihalomethane formation.  
OSMOSIS: Osmosis is the process by which water moves across a semi permeable membrane from a low concentration solute to a high concentration solute to satisfy the pressure differences caused by the solute.  
OXIDE: An oxide is a chemical compound containing at least one oxygen atom as well as at least one other element. Most of the Earth's crust consists of oxides. Oxides result when elements are oxidized by oxygen in air. Combustion of hydrocarbons affords the two principal oxides of carbon, carbon monoxide and carbon dioxide. Even materials that are considered to be pure elements often contain a coating of oxides. For example, aluminum foil has a thin skin of Al<sub>2</sub>O<sub>3</sub> that protects the foil from further corrosion.  
OXIDIZING: The process of breaking down organic wastes into simpler elemental forms or by products. Also used to separate combined chlorine and convert it into free chlorine.  
OXYGEN DEFICIENT ENVIRONMENT: One of the most dangerous threats to an operator upon entering a manhole.  
OZONE DOES NOT PROVIDE A RESIDUAL: One of the major drawbacks to using ozone as a disinfectant.  
OZONE, CHLORINE DIOXIDE, UV, CHLORAMINES: These chemicals may be used as alternative disinfectants.  
OZONE: Ozone or trioxygen (O<sub>3</sub>) is a triatomic molecule, consisting of three oxygen atoms. It is an allotrope of oxygen that is much less stable than the diatomic O<sub>2</sub>. Ground-level ozone is an air pollutant with harmful effects on the respiratory systems of animals. Ozone in the upper atmosphere filters potentially damaging ultraviolet light from reaching the Earth's surface. It is present in low concentrations throughout the Earth's atmosphere. It has many industrial and consumer applications. Ozone, the first allotrope of a chemical element to be recognized by science, was proposed as a distinct chemical compound by Christian Friedrich Schönbein in 1840, who named it after the Greek word for smell (ozein), from the peculiar odor in lightning storms. The formula for ozone, O<sub>3</sub>, was not determined until 1865 by Jacques-Louis Soret and confirmed by Schönbein in 1867. Ozone is a powerful oxidizing agent, far better than dioxygen. It is also unstable at high concentrations, decaying to ordinary diatomic oxygen (in about half an hour in atmospheric conditions):  
$$2 \text{O}_3 = 3 \text{O}_2$$

## P

PAC: A disadvantage of using PAC is it is very abrasive and requires careful maintenance of equipment. One precaution that should be taken in storing PAC is that bags of carbon should not be stored near bags of HTH. Removes tastes and odors by adsorption only. Powered activated carbon frequently used for taste and odor control because PAC is non-specific and removes a

broad range of compounds. Jar tests and threshold odor number testing determines the application rate for powdered activated carbon. Powdered activated carbon, or PAC, commonly used for in a water treatment plant for taste and odor control. Powdered activated carbon may be used with some success in removing the precursors of THMs.

**PACKING:** Material, usually of woven fiber, placed in rings around the shaft of a pump and used to control the leakage from the stuffing box.

**PARAMECIUM:** Paramecia are a group of unicellular ciliate protozoa formerly known as slipper animalcules from their slipper shape. They are commonly studied as a representative of the ciliate group. Simple cilia cover the body which allows the cell to move with a synchronous motion (like a caterpillar). There is also a deep oral groove containing inconspicuous compound oral cilia (as found in other peniculids) that is used to draw food inside. They generally feed upon bacteria and other small cells. Osmoregulation is carried out by a pair of contractile vacuoles, which actively expel water absorbed by osmosis from their surroundings. Paramecia are widespread in freshwater environments, and are especially common in scums. Paramecia are attracted by acidic conditions. Certain single-celled eukaryotes, such as Paramecium, are examples for exceptions to the universality of the genetic code (translation systems where a few codons differ from the standard ones).

**PATHOGENS:** Disease-causing pathogens; waterborne pathogens A pathogen may contaminate water and cause waterborne disease.

**Pb:** The chemical symbol of Lead.

**PCE:** Perchloroethylene. Known also as perc or tetrachloroethylene, perchloroethylene is a clear, colorless liquid with a distinctive, somewhat ether-like odor. It is non-flammable, having no measurable flashpoint or flammable limits in air. Effective over a wide range of applications, perchloroethylene is supported by closed loop transfer systems, stabilizers and employee exposure monitoring.

**pCi/L:** Picocuries per liter A curie is the amount of radiation released by a set amount of a certain compound. A picocurie is one quadrillionth of a curie.

**PERKINESIS:** The aggregation resulting from random thermal motion of fluid molecules.

**PEAK DEMAND:** The maximum momentary load placed on a water treatment plant, pumping station or distribution system.

**PEPTIDOGLYCAN:** A polymer found in the cell walls of prokaryotes that consists of polysaccharide and peptide chains in a strong molecular network. Also called mucopeptide, murein.

**PERMEATE:** The term for water which has passed through the membrane of a reverse osmosis unit.

**pH OF SATURATION:** The ideal pH for perfect water balance in relation to a particular total alkalinity level and a particular calcium hardness level, at a particular temperature. The pH where the Langelier Index equals zero.

**pH:** A unit of measure which describes the degree of acidity or alkalinity of a solution. The pH scale runs from 0 to 14 with 7 being the mid-point or neutral. A pH of less than 7 is on the acid side of the scale with 0 as the point of greatest acid activity. A pH of more than 7 is on the basic (alkaline) side of the scale with 14 as the point of greatest basic activity. The term pH is derived from "p", the mathematical symbol of the negative logarithm, and "H", the chemical symbol of Hydrogen. The definition of pH is the negative logarithm of the Hydrogen ion activity.  $pH = -\log[H^+]$ .

**PHENOL RED:** Chemical reagent used for testing pH in the range of 6.8 - 8.4.

**PHENOLPHTHALEIN/TOTAL ALKALINITY:** The relationship between the alkalinity constituent's bicarbonate, carbonate, and hydroxide can be based on the P and T alkalinity measurement.

**PHOSPHATE, NITRATE AND ORGANIC NITROGEN:** Nutrients in a domestic water supply reservoir may cause water quality problems if they occur in moderate or large quantities.

**PHOTON:** A carrier of electromagnetic radiation of all wavelength (such as gamma rays and radio waves).

**PHYSISORPTION:** (Or physical adsorption) Is adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapors, and which do not involve a significant

change in the electronic orbital patterns of the species involved. The term van der Waals adsorption is synonymous with physical adsorption, but its use is not recommended.

PICOCURIE: A unit of radioactivity. "Pico" is a metric prefix that means one one-millionth of one one-millionth. A picocurie is one one-millionth of one one-millionth of a Curie. A Curie is that quantity of any radioactive substance that undergoes 37 billion nuclear disintegrations per second. Thus a picocurie is that quantity of any radioactive substance that undergoes 0.037 nuclear disintegrations per second.

PLANKTON: The aggregate of passively floating, drifting, or somewhat motile organisms occurring in a body of water, primarily comprising microscopic algae and protozoa.

PLASMA: State of matter similar to gas in which a certain portion of the particles are ionized.

PLATFORM: The portion of the drilling rig where a driller and crew operate the drill rig.

Plug: A removable cap installed behind the pilot and cutter bits on hollow stem auger flighting.

PLUNGER: See Surge-block.

POINT OF ENTRY: POE.

POLLUTION: To make something unclean or impure. See Contaminated.

POLYMER: A type of chemical when combined with other types of coagulants aid in binding small suspended particles to larger particles to help in the settling and filtering processes.

POLYPHOSPHATES: Chemicals that may be added to remove low levels of iron and manganese.

POLYPHOSPHATES: Chemicals that may be added to remove low levels of iron and manganese.

POST-CHLORINE: Where the water is chlorinated to make sure it holds a residual in the distribution system.

POTABLE: Good water which is safe for drinking or cooking purposes. Non-Potable: A liquid or water that is not approved for drinking.

POTENTIAL ENERGY: Energy stored in a body or in a system due to its position in a force field or due to its configuration.

PPM: Abbreviation for parts per million.

PRE-CHLORINATION: The addition of chlorine before the filtration process will help:

PRE-CHLORINE: Where the raw water is dosed with a large concentration of chlorine.

PRESIPITATE: Formation of a solid in a solution or inside another solid during a chemical reaction or by diffusion in a solid.

PRESSURE MEASUREMENT: Bourdon tube, Bellows gauge and Diaphragm are commonly used to measure pressure in waterworks systems. A Bellows-type sensor reacts to a change in pressure.

PRESSURE: Pressure is defined as force per unit area. It is usually more convenient to use pressure rather than force to describe the influences upon fluid behavior. The standard unit for pressure is the Pascal, which is a Newton per square meter. For an object sitting on a surface, the force pressing on the surface is the weight of the object, but in different orientations it might have a different area in contact with the surface and therefore exert a different pressure.

PREVENTION: To take action; stop something before it happens.

PROTIST: Any of a group of eukaryotic organisms belonging to the kingdom Protista according to some widely used modern taxonomic systems. The protists include a variety of unicellular, coenocytic, colonial, and multicellular organisms, such as the protozoans, slime molds, brown algae, and red algae. A unicellular protist in taxonomic systems in which the protists are considered to form a kingdom.

PROTOCTIST: Any of various unicellular eukaryotic organisms and their multicellular, coenocytic, or colonial descendants that belong to the kingdom Protoctista according to some taxonomic systems. The protoctists include the protozoans, slime molds, various algae, and other groups. In many new classification systems, all protoctists are considered to be protists.

PROTON: A positive unit or subatomic particle that has a positive charge.

PROTON, NEUTRON AND ELECTRON: Are the 3 fundamental particles of an atom.

PROTONATION: The addition of a proton (H<sup>+</sup>) to an atom, molecule, or ion.

PROTOZOA: Microscopic animals that occur as single cells. Some protozoa can cause disease in humans. Protozoa form cysts, which are specialized cells like eggs that are very resistant to chlorine. Cysts can survive the disinfection process, then "hatch" into normal cells that can cause

disease. Protozoa must be removed from drinking water by filtration, because they cannot be effectively killed by chlorine.

**PUBLIC NOTIFICATION:** An advisory that EPA requires a water system to distribute to affected consumers when the system has violated MCLs or other regulations. The notice advises consumers what precautions, if any, they should take to protect their health.

**PUBLIC WATER SYSTEM (PWS):** Any water system which provides water to at least 25 people for at least 60 days annually. There are more than 170,000 PWSs providing water from wells, rivers and other sources to about 250 million Americans. The others drink water from private wells. There are differing standards for PWSs of different sizes and types.

**PWS:** 3 types of public water systems. Community water system, non-transient non-community water system, transient non-community water system.

## Q

**QUANTA:** It is the minimum amount of bundle of energy.

**QUANTUM MECHANICS:** The study of how atoms, molecules, subatomic particles, etc. behave and are structured.

**QUARKS:** Elementary particle and a fundamental constituent of matter.

## R

**RADIATION:** Energy in the form of waves or subatomic particles when there is a change from high energy to low energy states.

**RADIOACTIVE DECAY:** The process of an unstable atomic nucleus losing energy by emitting radiation.

**RADIOCHEMICALS:** (Or radioactive chemicals) Occur in natural waters. Naturally radioactive ores are particularly common in the Southwestern United States, and some streams and wells can have dangerously high levels of radioactivity. Total alpha and beta radioactivity and isotopes of radium and strontium are the major tests performed for radiochemicals. The federal drinking water standard for gross alpha radioactivity is set at 5 picocuries per liter.

**RAW TURBIDITY:** The turbidity of the water coming to the treatment plant from the raw water source.

**RAW WATER:** Water that has not been treated in any way; it is generally considered to be unsafe to drink.

**REAGENT:** A substance used in a chemical reaction to measure, detect, examine, or produce other substances.

**RECHARGE:** The infiltration component of the hydrologic cycle. Often used in the context of referring to: The infiltration of water back into an aquifer, resulting in the restoration of lost storage and water levels which had been decreased due to pumping and/or natural discharges from the aquifer.

**RECORDER, FLOW:** A flow recorder that measures flow is most likely to be located anywhere in the plant where a flow must be measured and in a central location.

**RED WATER AND SLIME:** Iron bacteria are undesirable in a water distribution system because of red water and slime complaints.

**REDOX POTENTIAL:** Reduction potential (also known as redox potential, oxidation / reduction potential or ORP) is the tendency of a chemical species to acquire electrons and thereby be reduced. Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced. In aqueous solutions, the reduction potential is the tendency of the solution to either gain or lose electrons when it is subject to change by introduction of a new species. A solution with a higher (more positive) reduction potential than the new species will have a tendency to gain electrons from the new species (i.e. to be reduced by oxidizing the new species) and a solution with a lower (more negative) reduction potential will have a tendency to lose electrons to the new species (i.e. to be oxidized by reducing the new species).

**RELAY LOGIC:** The name of a popular method of automatically controlling a pump, valve, chemical feeder, and other devices.

**RESERVOIR:** An impoundment used to store water.

**RESIDUAL DISINFECTION PROTECTION:** A required level of disinfectant that remains in treated water to ensure disinfection protection and prevent recontamination throughout the distribution system (i.e., pipes).

**REVERSE OSMOSIS:** Forces water through membranes that contain holes so small that even salts cannot pass through. Reverse osmosis removes microorganisms, organic chemicals, and inorganic chemicals, producing very pure water. For some people, drinking highly purified water exclusively can upset the natural balance of salts in the body. Reverse osmosis units require regular maintenance or they can become a health hazard.

**ROTAMETER:** The name of transparent tube with a tapered bore containing a ball is often used to measure the rate of flow of a gas or liquid.

**ROTIFER:** Rotifers get their name (derived from Greek and meaning "wheel-bearer"; they have also been called wheel animalcules) from the corona, which is composed of several ciliated tufts around the mouth that in motion resemble a wheel. These create a current that sweeps food into the mouth, where it is chewed up by a characteristic pharynx (called the mastax) containing a tiny, calcified, jaw-like structure called the trophi. The cilia also pull the animal, when unattached, through the water. Most free-living forms have pairs of posterior toes to anchor themselves while feeding. Rotifers have bilateral symmetry and a variety of different shapes. There is a well-developed cuticle which may be thick and rigid, giving the animal a box-like shape, or flexible, giving the animal a worm-like shape; such rotifers are respectively called loricate and illoricate.

## S

**S- BLOCK ELEMENTS:** Group 1 and 2 elements (alkali and alkaline metals), which includes Hydrogen and Helium.

**S.T.P.:** Standard temperature and pressure standard temperature and pressure the temperature of 0°C and pressure of 1 atmosphere, usually taken as the conditions when stating properties of gases.

**SAFE YIELD:** A possible consequence when the "safe yield" of a well is exceeded and water continues to be pumped from a well, is land subsidence around the well will occur. Safe yield refers to a long-term balance between the water that is naturally and artificially recharged to an aquifer and the groundwater that is pumped out. When more water is removed than is recharged, the aquifer is described as being out of safe yield. When the water level in the aquifer then drops, we are said to be mining groundwater.

**SALINE SOLUTION:** General term for NaCl in water.

**SALT BRIDGE:** Devices used to connection reduction with oxidation half-cells in an electrochemical cell.

**SALTS:** Ionic compounds composed of anions and cations.

**SALTS ARE ABSENT:** Is a strange characteristic that is unique to water vapor in the atmosphere.

**SAMPLE:** The water that is analyzed for the presence of EPA-regulated drinking water contaminants. Depending on the regulation, EPA requires water systems and states to take samples from source water, from water leaving the treatment facility, or from the taps of selected consumers. **Sampling Location:** A location where soil or cuttings samples may be readily and accurately collected.

**SANITARY SURVEY:** Persons trained in public health engineering and the epidemiology of waterborne diseases should conduct the sanitary survey. The importance of a detailed sanitary survey of a new water source cannot be overemphasized. An on-site review of the water sources, facilities, equipment, operation, and maintenance of a public water systems for the purpose of evaluating the adequacy of the facilities for producing and distributing safe drinking water. The purpose of a non-regulatory sanitary survey is to identify possible biological and chemical pollutants which might affect a water supply.

**SANITIZER:** A disinfectant or chemical which disinfects (kills bacteria), kills algae and oxidizes organic matter.

**SATURATION INDEX:** See Langelier's Index.

**SATURATOR:** A device which produces a fluoride solution for the fluoride process. Crystal-grade types of sodium fluoride should be fed with a saturator. Overfeeding must be prevented to protect public health when using a fluoridation system.

**SCADA:** A remote method of monitoring pumps and equipment. 130 degrees F is the maximum temperature that transmitting equipment is able to with stand. If the level controller may be set with too close a tolerance 45 could be the cause of a control system that is frequently turning a pump on and off.

**SCALE:** Crust of calcium carbonate, the result of unbalanced water. Hard insoluble minerals deposited (usually calcium bicarbonate) which forms on pool and spa surfaces and clog filters, heaters and pumps. Scale is caused by high calcium hardness and/or high pH. The regular use of stain prevention chemicals can prevent scale.

**SCHMUTZDECKE:** German, "grime or filth cover", sometimes spelt schmutzedecke) is a complex biological layer formed on the surface of a slow sand filter. The schmutzdecke is the layer that provides the effective purification in potable water treatment, the underlying sand providing the support medium for this biological treatment layer. The composition of any particular schmutzdecke varies, but will typically consist of a gelatinous biofilm matrix of bacteria, fungi, protozoa, rotifera and a range of aquatic insect larvae. As a schmutzdecke ages, more algae tend to develop, and larger aquatic organisms may be present including some bryozoan, snails and annelid worms.

**SCHRODINGER EQUATION:** Quantum state equation which represents the behavior of an electron around an atom.

**SCROLL AND BASKET:** The two basic types of centrifuges used in water treatment.

**SEAL:** For wells: to abandon a well by filling up the well with approved seal material including cementing with grout from a required depth to the land surface.

**SECONDARY DRINKING WATER STANDARDS:** Non-enforceable federal guidelines regarding cosmetic effects (such as tooth or skin discoloration) or aesthetic effects (such as taste, odor, or color) of drinking water.

**SECTIONAL MAP:** The name of a map that provides detailed drawings of the distribution system's zones. Sometimes we call these quarter-sections.

**Sediment:** Grains of soil, sand, gravel, or rock deposited by and generated by water movement.

**SEDIMENTATION BASIN:** Where the thickest and greatest concentration of sludge will be found. Twice a year sedimentation tanks should be drained and cleaned if the sludge buildup interferes with the treatment process.

**SEDIMENTATION:** The process of suspended solid particles settling out (going to the bottom of the vessel) in water.

**SEMICONDUCTOR:** An electrically conductive solid that is between a conductor and an insulator.

**SENSOR:** A float and cable system are commonly found instruments that may be used as a sensor to control the level of liquid in a tank or basin.

**SESSILE:** Botany. attached by the base, or without any distinct projecting support, as a leaf issuing directly from the stem. Zoology. permanently attached; not freely moving.

**SETTLED SOLIDS:** Solids that have been removed from the raw water by the coagulation and settling processes.

**SHOCK:** Also known as superchlorination or break point chlorination. Ridding a water of organic waste through oxidization by the addition of significant quantities of a halogen.

**SHORT-CIRCUITING:** Short Circuiting is a condition that occurs in tanks or basins when some of the water travels faster than the rest of the flowing water. This is usually undesirable since it may result in shorter contact, reaction or settling times in comparison with the presumed detention times.

**SINGLE BOND:** Sharing of one pair of electrons.

**SINGLE PHASE POWER:** The type of power used for lighting systems, small motors, appliances, portable power tools and in homes.

**SINUSOID:** A curve described by the equation  $y = a \sin x$ , the ordinate being proportional to the sine of the abscissa.

**SINUSOIDAL:** Mathematics. Of or pertaining to a sinusoid. Having a magnitude that varies as the sine of an independent variable: a sinusoidal current.

**SLUDGE BASINS:** After cleaning sludge basins and before returning the tanks into service the tanks should be inspected, repaired if necessary, and disinfected.

**SLUDGE REDUCTION:** Organic polymers are used to reduce the quantity of sludge. If a plant produces a large volume of sludge, the sludge could be dewatered, thickened, or conditioned to decrease the volume of sludge. Turbidity of source water, dosage, and type of coagulant used are the most important factors which determine the amount of sludge produced in a treatment of water.

**SMALL WATER SYSTEM:** 3,300 or fewer persons.

**SOC:** Synthetic organic chemical. A common way for a synthetic organic chemical such as dioxin to be introduced to a surface water supply is from an industrial discharge, agricultural drainage, or a spill.

**SODA ASH:** Chemical used to raise pH and total alkalinity (sodium carbonate).

**SODIUM BICARBONATE:** Commonly used to increase alkalinity of water and stabilize pH.

**SODIUM BISULFATE:** Chemical used to lower pH and total alkalinity (dry acid).

**SODIUM HYDROXIDE:** Also known as caustic soda, a by-product chlorine generation and often used to raise pH.

**SOFTENING WATER:** When the water has a low alkalinity it is advantageous to use soda ash instead of caustic soda for softening water.

**SOFTENING:** The process that removes the ions which cause hardness in water.

**SOL:** A suspension of solid particles in liquid. Artificial examples include sol-gels.

**SOLAR DRYING BEDS OR LAGOONS:** Are shallow, small-volume storage pond where sludge is concentrated and stored for an extended periods.

**SOLAR DRYING BEDS, CENTRIFUGES AND FILTER PRESSES:** Are procedures used in the dewatering of sludge.

**SOLDER:** A fusible alloy used to join metallic parts.

**SOLID:** One of the states of matter, where the molecules are packed close together, there is a resistance of movement/deformation and volume change; see Young's modulus.

**SOLID, LIQUID AND VAPOR:** 3 forms of matter.

**SOLUTE:** The part of the solution that is mixed into the solvent (NaCl in saline water).

**SOLUTION:** Homogeneous mixture made up of multiple substances. It is made up of solutes and solvents.

**SOLVENT:** The part of the solution that dissolves the solute (H<sub>2</sub>O in saline water).

**SPADNS:** The lab reagent called SPADNS solution is used in performing the Fluoride test.

**SPECTROSCOPY:** Study of radiation and matter, such as X-ray absorption and emission spectroscopy.

**SPEED OF LIGHT:** The speed of anything that has zero rest mass ( $E_{\text{rest}} = mc^2$  where m is the mass and c is the speed of light).

**SPIRIT OF HARTSHORN:** A colorless, pungent, suffocating, aqueous solution of about 28.5 percent ammonia gas: used chiefly as a detergent, for removing stains and extracting certain vegetable coloring agents, and in the manufacture of ammonium salts.

**SPLIT FLOW CONTROL SYSTEM:** This type of control system is to control the flow to each filter influent which is divided by a weir.

**SPRAY BOTTLE OF AMMONIA:** An operator should use ammonia to test for a chlorine leak around a valve or pipe. You will see white smoke if there is a leak.

**STANDARD CONDITIONS FOR TEMPERATURE AND PRESSURE or SATP :** A standardization used in order compare experimental results (25 °C and 100.000 kPa).

**STANDPIPE:** A water tank that is taller than it is wide. Should not be found in low point.

**STATE OF MATTER:** Matter having a homogeneous, macroscopic phase; gas, plasma, liquid, and solid are the most well-known (in increasing concentration).

**STERILIZED GLASSWARE:** The only type of glassware that should be used in testing for coliform bacteria.

**STORAGE TANKS:** Three types of water usage that determine the volume of a storage tank are fire suppression storage, equalization storage, and emergency storage. Equalization storage is the volume of water needed to supply the system for periods when demand exceeds supply.

Generally, a water storage tank's interior coating (paint) protects the interior about 3-5 years.

**SUBATOMIC PARTICLES:** Particles that are smaller than an atom; examples are protons, neutrons and electrons.

**SUBLIMATION:** A phase transition from solid to limewater fuel or gas.

**SUBSTANCE:** Material with definite chemical composition.

**SULFATE:** Will readily dissolve in water to form an anion. Sulfate is a substance that occurs naturally in drinking water. Health concerns regarding sulfate in drinking water have been raised because of reports that diarrhea may be associated with the ingestion of water containing high levels of sulfate. Of particular concern are groups within the general population that may be at greater risk from the laxative effects of sulfate when they experience an abrupt change from drinking water with low sulfate concentrations to drinking water with high sulfate concentrations.

**SULFIDE:** The term sulfide refers to several types of chemical compounds containing sulfur in its lowest oxidation number of -2. Formally, "sulfide" is the dianion,  $S^{2-}$ , which exists in strongly alkaline aqueous solutions formed from  $H_2S$  or alkali metal salts such as  $Li_2S$ ,  $Na_2S$ , and  $K_2S$ . Sulfide is exceptionally basic and, with a  $pK_a > 14$ , it does not exist in appreciable concentrations even in highly alkaline water, being undetectable at  $pH < \sim 15$  (8 M NaOH). Instead, sulfide combines with electrons in hydrogen to form  $HS^-$ , which is variously called hydrogen sulfide ion, hydrosulfide ion, sulfhydryl ion, or bisulfide ion. At still lower pH's (<7),  $HS^-$  converts to  $H_2S$ , hydrogen sulfide. Thus, the exact sulfur species obtained upon dissolving sulfide salts depends on the pH of the final solution. Aqueous solutions of transition metals cations react with sulfide sources ( $H_2S$ ,  $NaSH$ ,  $Na_2S$ ) to precipitate solid sulfides. Such inorganic sulfides typically have very low solubility in water and many are related to minerals. One famous example is the bright yellow species  $CdS$  or "cadmium yellow". The black tarnish formed on sterling silver is  $Ag_2S$ . Such species are sometimes referred to as salts. In fact, the bonding in transition metal sulfides is highly covalent, which gives rise to their semiconductor properties, which in turn is related to the practical applications of many sulfide materials.

**SUPERNATANT:** The liquid layer which forms above the sludge in a settling basin.

**SURFACE WATER SOURCES:** Surface water sources such as a river or lake are primarily the result of Runoff.

**SURFACE WATER:** Water that is open to the atmosphere and subject to surface runoff; generally, lakes, streams, rivers.

**SURFACTANT:** Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil. Surfactants are also often classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (dual charge).

**SUSCEPTIBILITY WAIVER:** A waiver that is granted based upon the results of a vulnerability assessment.

**SYNCHRONY:** Simultaneous occurrence; synchronism.

## T

**TALC:** A mineral representing the one on the Mohs Scale and composed of hydrated magnesium silicate with the chemical formula  $H_2Mg_3(SiO_3)_4$  or  $Mg_3Si_4O_{10}(OH)_2$ .

**TASTE AND ODORS:** The primary purpose to use potassium permanganate in water treatment is to control taste and odors. Anaerobic water undesirable for drinking water purposes because of color and odor problems are more likely to occur under these conditions. Taste and odor problems in the water may happen if sludge and other debris are allowed to accumulate in a water treatment plant.

**TCE, trichloroethylene:** A solvent and degreaser used for many purposes; for example dry cleaning, it is a common groundwater contaminant. Trichloroethylene is a colorless liquid which is used as a solvent for cleaning metal parts. Drinking or breathing high levels of trichloroethylene may cause nervous system effects, liver and lung damage, abnormal heartbeat, coma, and possibly death. Trichloroethylene has been found in at least 852 of the 1,430 National Priorities List sites identified by the Environmental Protection Agency (EPA).

**TDS-TOTAL DISSOLVED SOLIDS:** An expression for the combined content of all inorganic and organic substances contained in a liquid which are present in a molecular, ionized or micro-granular (colloidal sol) suspended form. Generally, the operational definition is that the solids (often abbreviated TDS) must be small enough to survive filtration through a sieve size of two micrometers. Total dissolved solids are normally only discussed for freshwater systems, since salinity comprises some of the ions constituting the definition of TDS. The principal application of TDS is in the study of water quality for streams, rivers and lakes, although TDS is generally considered not as a primary pollutant (e.g. it is not deemed to be associated with health effects), but it is rather used as an indication of aesthetic characteristics of drinking water and as an aggregate indicator of presence of a broad array of chemical contaminants. Ion exchange is an effective treatment process used to remove iron and manganese in a water supply. This process is ideal as long as the water does not contain a large amount of TDS. When determining the total dissolved solids, a sample should be filtered before being poured into an evaporating dish and dried. Demineralization may be necessary in a treatment process if the water has a very high value Total Dissolved Solids.

**TEMPERATURE:** The average energy of microscopic motions of particles.

**TEMPERATURE SAMPLE:** This test should be performed immediately in the field, this is a grab sample.

**THE RATE DECREASES:** In general, when the temperature decreases, the chemical reaction rate decreases also.

**THEORY:** A model describing the nature of a phenomenon.

**THERMAL CONDUCTIVITY:** A property of a material to conduct heat (often noted as  $k$ ).

**THERMOCHEMISTRY:** The study of absorption/release of heat within a chemical reaction.

**THERMODYNAMIC STABILITY:** When a system is in its lowest energy state with its environment (equilibrium).

**THERMODYNAMICS:** The study of the effects of changing temperature, volume or pressure (or work, heat, and energy) on a macroscopic scale.

**THERMOMETER:** Device that measures the average energy of a system.

**THICKENING, CONDITIONING AND DEWATERING:** Common processes that are utilized to reduce the volume of sludge.

**TIME FOR TURBIDITY BREAKTHROUGH AND MAXIMUM HEADLOSS:** Are the two factors which determine whether or not a change in filter media size should be made.

**TITRATION:** The process of titrating one solution with another, also called volumetric analysis. A method of testing by adding a reagent of known strength to a water sample until a specific color change indicates the completion of the reaction.

**TITRIMETRIC:** Chemistry. Using or obtained by titration. Titrimetrically, adverb.

**TOROID:** A surface generated by the revolution of any closed plane curve or contour about an axis lying in its plane. The solid enclosed by such a surface.

**TORR:** A unit to measure pressure (1 Torr is equivalent to 133.322 Pa or  $1.3158 \times 10^{-3}$  atm).

**TOTAL ALKALINITY:** A measure of the acid-neutralizing capacity of water which indicates its buffering ability, i.e. measure of its resistance to a change in pH. Generally, the higher the total alkalinity, the greater the resistance to pH change.

**TOTAL COLIFORM:** Total coliform, fecal coliform, and E. coli are all indicators of drinking water quality. The total coliform group is a large collection of different kinds of bacteria. Fecal coliforms are types of total coliform that mostly exist in feces. E. coli is a sub-group of fecal coliform. When a water sample is sent to a lab, it is tested for total coliform. If total coliform is present, the sample will also be tested for either fecal coliform or E. coli, depending on the lab testing method.

**TOTAL DISSOLVED SOLIDS (TDS):** The accumulated total of all solids that might be dissolved in water.

**TRANSIENT, NON-COMMUNITY WATER SYSTEM: TNCWS** A water system which provides water in a place such as a gas station or campground where people do not remain for long periods of time. These systems do not have to test or treat their water for contaminants which pose long-term health risks because fewer than 25 people drink the water over a long period. They still must test their water for microbes and several chemicals. A Transient Non-community Water System: Is not required to sample for VOC's.

**TRANSITION METAL:** Elements that have incomplete d sub-shells, but also may be referred to as the d-block elements.

**TRANSURANIC ELEMENT:** Element with atomic number greater than 92; none of the transuranic elements are stable.

**TREATED WATER:** Disinfected and/or filtered water served to water system customers. It must meet or surpass all drinking water standards to be considered safe to drink.

**TRIHALOMETHANES (THM):** Four separate compounds including chloroform, dichlorobromomethane, dibromochloromethane, and bromoform. The most common class of disinfection by-products created when chemical disinfectants react with organic matter in water during the disinfection process. See Disinfectant Byproducts.

**TRIPLE BOND:** The sharing of three pairs of electrons within a covalent bond (example N<sub>2</sub>).

**TRIPLE POINT:** The place where temperature and pressure of three phases are the same (Water has a special phase diagram).

**TUBE SETTLERS:** This modification of the conventional process contains many metal tubes that are placed in the sedimentation basin, or clarifier. These tubes are approximately 1 inch deep and 36 inches long, split-hexagonal shape and installed at an angle of 60 degrees or less. These tubes provide for a very large surface area upon which particles may settle as the water flows upward. The slope of the tubes facilitates gravity settling of the solids to the bottom of the basin, where they can be collected and removed. The large surface settling area also means that adequate clarification can be obtained with detention times of 15 minutes or less. As with conventional treatment, this sedimentation step is followed by filtration through mixed media.

**TUBERCLES:** The creation of this condition is of the most concern regarding corrosive water effects on a water system. Tubercles are formed due to joining dissimilar metals, causing electro-chemical reactions. Like iron to copper pipe. We have all seen these little rust mounds inside cast iron pipe.

**TUNDALL EFFECT:** The effect of light scattering by colloidal (mixture where one substance is dispersed evenly through another) or suspended particles.

**TURBIDIMETER:** Monitoring the filter effluent turbidity on a continuous basis with an in-line instrument is a recommended practice. Turbidimeter is best suited to perform this measurement.

**TURBIDITY:** A measure of the cloudiness of water caused by suspended particles.

## U

**U.S. ENVIRONMENTAL PROTECTION AGENCY:** In the United States, this agency responsible for setting drinking water standards and for ensuring their enforcement. This agency sets federal regulations which all state and local agencies must enforce.

**UN NUMBER:** A four digit code used to note hazardous and flammable substances.

**UNCERTAINTY:** A characteristic that any measurement that involves estimation of any amount cannot be exactly reproducible.

**UNCERTAINTY PRINCIPLE:** Knowing the location of a particle makes the momentum uncertain, while knowing the momentum of a particle makes the location uncertain.

**UNDER PRESSURE IN STEEL CONTAINERS:** After chlorine gas is manufactured, it is primarily transported in steel containers.

**UNIT CELL:** The smallest repeating unit of a lattice.

**UNIT FACTOR:** Statements used in converting between units.

**UNIT FILTER RUN VOLUME (UFRV):** One of the most popular ways to compare filter runs. This technique is the best way to compare water treatment filter runs.

**UNIVERSAL OR IDEAL GAS CONSTANT:** Proportionality constant in the ideal gas law (0.08206 L·atm/(K·mol)).

## V

**VALENCE BOND THEORY:** A theory explaining the chemical bonding within molecules by discussing valencies, the number of chemical bonds formed by an atom.

**VALENCE ELECTRON:** The outermost electrons of an atom, which are located in electron shells.

**VAN DER WAALS FORCE:** One of the forces (attraction/repulsion) between molecules.

**VAN'T HOFF FACTOR:** Ratio of moles of particles in solution to moles of solute dissolved.

**VANE:** That portion of an impeller that throws the water toward the volute.

VAPOR PRESSURE: Pressure of vapor over a liquid at equilibrium.

VAPOR: When a substance is below the critical temperature while in the gas phase.

VAPORIZATION: Phase change from liquid to gas.

VARIABLE DISPLACEMENT PUMP: A pump that will produce different volumes of water dependent on the pressure head against it.

VELOCITY HEAD: The vertical distance a liquid must fall to acquire the velocity with which it flows through the piping system. For a given quantity of flow, the velocity head will vary indirectly as the pipe diameter varies.

VENTURI: If water flows through a pipeline at a high velocity, the pressure in the pipeline is reduced. Velocities can be increased to a point that a partial vacuum is created.

VIRION: A complete viral particle, consisting of RNA or DNA surrounded by a protein shell and constituting the infective form of a virus.

VIRUSES: Are very small disease-causing microorganisms that are too small to be seen even with microscopes. Viruses cannot multiply or produce disease outside of a living cell.

VISCOSITY: The resistance of a liquid to flow (oil).

VITRIFICATION: Vitrification is a process of converting a material into a glass-like amorphous solid that is free from any crystalline structure, either by the quick removal or addition of heat, or by mixing with an additive. Solidification of a vitreous solid occurs at the glass transition temperature (which is lower than melting temperature,  $T_m$ , due to supercooling). When the starting material is solid, vitrification usually involves heating the substances to very high temperatures. Many ceramics are produced in such a manner. Vitrification may also occur naturally when lightning strikes sand, where the extreme and immediate heat can create hollow, branching rootlike structures of glass, called fulgurite. When applied to whiteware ceramics, vitreous means the material has an extremely low permeability to liquids, often but not always water, when determined by a specified test regime. The microstructure of whiteware ceramics frequently contain both amorphous and crystalline phases.

VOC WAIVER: The longest term VOC waiver that a public water system using groundwater could receive is 9 years.

Void: An opening, gap, or space within rock or sedimentary formations formed at the time of origin or deposition.

VOLATILE ORGANIC COMPOUNDS: (VOCs) Solvents used as degreasers or cleaning agents. Improper disposal of VOCs can lead to contamination of natural waters. VOCs tend to evaporate very easily. This characteristic gives VOCs very distinct chemical odors like gasoline, kerosene, lighter fluid, or dry cleaning fluid. Some VOCs are suspected cancer-causing agents. Volatile organic compounds (VOCs) are organic chemical compounds that have high enough vapor pressures under normal conditions to significantly vaporize and enter the atmosphere. A wide range of carbon-based molecules, such as aldehydes, ketones, and other light hydrocarbons are VOCs. The term often is used in a legal or regulatory context and in such cases the precise definition is a matter of law. These definitions can be contradictory and may contain "loopholes"; e.g. exceptions, exemptions, and exclusions. The United States Environmental Protection Agency defines a VOC as any organic compound that participates in a photoreaction; others believe this definition is very broad and vague as organics that are not volatile in the sense that they vaporize under normal conditions can be considered volatile by this EPA definition. The term may refer both to well characterized organic compounds and to mixtures of variable composition.

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VOLT: One joule of work per coulomb - the unit of electrical potential transferred.

VOLTAGE: Voltage (sometimes also called electric or electrical tension) is the difference of electrical potential between two points of an electrical or electronic circuit, expressed in volts. It measures the potential energy of an electric field to cause an electric current in an electrical conductor. Depending on the difference of electrical potential it is called extra low voltage, low voltage, high voltage or extra high voltage. Specifically Voltage is equal to energy per unit charge.

VOLTIMETER: Instrument that measures the cell potential.

VOLUMETRIC ANALYSIS: See titration.

VULNERABILITY ASSESSMENT: An evaluation of drinking water source quality and its vulnerability to contamination by pathogens and toxic chemicals.

VULNERABILITY ASSESSMENT: An evaluation of drinking water source quality and its vulnerability to contamination by pathogens and toxic chemicals.

## W

WAIVERS: Monitoring waivers for nitrate and nitrite are prohibited.

WATER H<sub>2</sub>O: A chemical substance, a major part of cells and Earth, and covalently bonded.

WATER PURVEYOR: The individuals or organization responsible to help provide, supply, and furnish quality water to a community.

WATER QUALITY CRITERIA: Comprised of both numeric and narrative criteria. Numeric criteria are scientifically derived ambient concentrations developed by EPA or States for various pollutants of concern to protect human health and aquatic life. Narrative criteria are statements that describe the desired water quality goal.

WATER QUALITY STANDARD: A statute or regulation that consists of the beneficial designated use or uses of a waterbody, the numeric and narrative water quality criteria that are necessary to protect the use or uses of that particular waterbody, and an antidegradation statement.

WATER QUALITY: The 4 broad categories of water quality are: Physical, chemical, biological, radiological. Pathogens are disease causing organisms such as bacteria and viruses. A positive bacteriological sample indicates the presence of bacteriological contamination. Source water monitoring for lead and copper be performed when a public water system exceeds an action level for lead or copper.

WATER VAPOR: A characteristic that is unique to water vapor in the atmosphere is that water does not contain any salts.

WATERBORNE DISEASE: A disease, caused by a virus, bacterium, protozoan, or other microorganism, capable of being transmitted by water (e.g., typhoid fever, cholera, amoebic dysentery, gastroenteritis).

WATERSHED: An area that drains all of its water to a particular water course or body of water. The land area from which water drains into a stream, river, or reservoir.

WAVE FUNCTION: A function describing the electron's position in a three-dimensional space.

Weathered: The existence of rock or formation in a chemically or physically broken down or decomposed state. Weathered material is in an unstable state.

WHOLE EFFLUENT TOXICITY: The total toxic effect of an effluent measured directly with a toxicity test.

WORK: The amount of force over distance and is in terms of joules (energy).

## X

X-RAY: Form of ionizing, electromagnetic radiation, between gamma and UV rays.

X-RAY DIFFRACTION: A method for establishing structures of crystalline solids using single wavelength X-rays and looking at diffraction pattern.

X-RAY PHOTOELECTRON SPECTROSCOPY: A spectroscopic technique to measure composition of a material.

## Y

YIELD: The amount of product produced during a chemical reaction.

Z

**ZONE MELTING:** A way to remove impurities from an element by melting it and slowly travel down an ingot (cast).

**ZWITTERION:** Is a chemical compound whose net charge is zero and hence is electrically neutral. But there are some positive and negative charges in it, due to the formal charge, owing to the partial charges of its constituent atoms.



## Common Water Quality and Sampling Statements

***All of these suggestions are not official law, please double check with your state drinking water or health agency before implementation***

### **1. What are the correct procedures to follow in collecting bacteriological samples?**

Use a sterile plastic or glass bottle. Sodium thiosulfate should be added to neutralize the chlorine residual. Refrigerate the sample to 4° C. The regulations call for a minimum of five samples for the month from any system that has positive sample results. Small systems that take only one sample per month have to take four (4) repeats when they get a total coliform positive test result. If any system has to take repeat samples, it must also take a minimum of five (5) routine samples the following month. Small systems that normally take less than 5 samples/month will have to increase the number to 5 samples. They can return to normal sampling schedules the following month if no repeats are required.

### **2. What are the proper sampling techniques for microbiological sampling?**

Proper sampling techniques are extremely important in obtaining accurate water quality information. An improperly taken coliform sample may indicate bacteriological contamination of your water when the water is actually safe. You can avoid the cost of additional testing by using good sampling procedures. Carefully follow these steps in taking a sample for bacteriological testing:

1. Select the sampling point. The sampling point must be a faucet from which water is commonly taken for public use.

- ✓ The sampling point should be a non-swivel faucet.
- ✓ Remove any aerator or screen and flush.
- ✓ It should not be a faucet that leaks, permitting water to run over the outside of the faucet. Leaking faucets can promote bacterial growth.
- ✓ If an outside faucet must be used, disconnect any hoses or other attachments and be sure to flush the line thoroughly.
- ✓ Do not use fire hydrants as sampling points. Do not dip the bottle in reservoirs, spring boxes or storage tanks in order to collect the sample.

### **3. What do the following abbreviations stand for and what do they mean: gpm, MGD, TTHM, psi, HAA, NTU, and mg/L.**

Gallons per minute- Million Gallons a Day - Total Trihalomethanes – Pounds Per Square Inch –Haloacetic acids - Nephelometric turbidity unit -Milligrams Per Liter

### **4. What is the relationship between mg/L and ppm; ug/L and ppb?**

**Milligram per liter:** Milligram per liter of substance and part per million are equal amounts in water. While you can easily convert between micrograms/liter and milligrams/liter, and between PPM and PPB, it's not so easy to convert between the different types of units such as milligrams/liter to PPM.

To convert micrograms per liter to milligrams per liter, divide by 1000.

To convert to PPM, you would first need to know the density of the substance, and the density of what the substance is in.

**5. Ug/L:** Represents the concentration of something in water or soil. One ppb represents one microgram of something per liter of water (ug/l), or one microgram of something per kilogram of soil (ug/kg).

*Parts per million (ppm) or Milligrams per liter (mg/l) - one part per million corresponds to one minute in two years or a single penny in \$10,000.*

*Parts per billion (ppb) or Micrograms per liter - one part per billion corresponds to one minute in 2,000 years, or a single penny in \$10,000,000.*

*Parts per trillion (ppt) or Nanograms per liter (nanograms/l) - one part per trillion corresponds to one minute in 2,000,000 years, or a single penny in \$10,000,000,000.*

**6. What do the following terms represent in reference to water quality.**

**Total coliform:** The coliform family has been divided into two groups. Results may come back as either total coliform positive (TC positive) or fecal coliform positive, or (FC positive or *E. coli* positive.) Total coliform positive means that no human coliform are present.

**7. Fecal Coliform:** Fecal coliform positive indicates the presence of *E. coli*, which means there is a greater chance of pathogens being present. The laboratory tests for coliform include the MPN method, the Membrane Filter test, the Colilert test, and the presence-absence test.

**8. Presence-absence Test:** Presence-Absence Broth is used for the detection of coliform bacteria in water treatment plants or distribution systems using the presence-absence coliform test.

**9. Physical Characteristics of Water:** A characteristic of water defined by the temperature, turbidity, color, taste, and odor of the water.

**10. Point-of-entry sample (POE):** A type of water sample taken after treatment and before reaching the first consumer.

**11. Acute Health Effect:** An immediate (i.e. within hours or days) effect that may result from exposure to certain drinking water contaminants (e.g., pathogens).

**12. Non-acute violation:** If the MCL is exceeded and none of the positive results indicated a presence of Fecal Coliform, a Tier 2 violation has occurred. This level of violation used to be called a non-acute violation.

**13. Routine Sample:** Samples collected on a routine basis to monitor for contamination. Collection should be in accordance with an approved sampling plan.

**14. Repeat Sample:** Short answer... Samples collected following a '*coliform present*' routine sample. The number of repeat samples to be collected is based on the number of routine samples you normally collect. Long Answer. Anytime a microbiological sample result comes back positive, indicating the presence of total or fecal coliform/ E.coli, repeat samples must be taken. Three repeats are usually required. One must be taken at the site of the positive sample. The two samples must be taken upstream and downstream of the original site (within five service connections). These repeat samples must be taken within 24 hours of notification of positive results. They must be identified as a Repeat Sample on the sample form. Repeat samples may be required to be sealed with a red evidentiary seal tape. The tape must cover the cap and extend down the sides of the bottle. The sample forms must also include the reference number for the positive sample.

There is an important exception to the three repeat samples rule. The regulations also state that when repeats are taken the minimum number of samples is raised to five for the month. A system that collects just one sample a month must collect four repeat samples, when the sample is positive, in order to have five samples as required.

Whenever a system has to take repeat samples, a minimum of five routine samples must also be submitted the following month. This is only an issue for systems that normally turn in four or fewer samples each month. If the five samples are negative the system can return to its normal sampling schedule the next month.

Small systems that have fewer than four sampling sites have a problem complying with the "upstream and downstream" aspects of the repeat sampling requirements. In this case, samples should be taken at as many separate sites as possible and then wait a minimum of 2 hours before resampling enough sites to get the required number of samples. Repeat sample with red seal tape.

**15. Treatment technique:** An enforceable procedure or level of technical performance which public water systems must follow to ensure control of a contaminant.

**16. Action level:** The level of lead or copper which, if exceeded, triggers treatment or other requirements that a water system must follow.

**17. What does the membrane filter test analyze with regards to bacteriological sampling?**

**Membrane Filter Technique:** A standard test used for measuring coliform numbers (quantity) in water is the membrane filter technique. This technique involves filtering a known volume of water through a special sterile filter. These filters are made of nitrocellulose acetate and polycarbonate, are 150  $\mu\text{m}$  thick, and have 0.45  $\mu\text{m}$  diameter pores. A grid pattern is printed on these filter disks in order to facilitate colony counting. When the water sample is filtered, bacteria (larger than 0.45  $\mu\text{m}$ ) in the sample are trapped on the surface of the filter. The filter is then carefully removed, placed in a sterile petri plate on a pad saturated with a liquid medium, and incubated for 20-24 hours at 37°C.

One assumes that each bacterium trapped on the filter will then grow into a separate colony. By counting the colonies one can directly determine the number of bacteria in the water sample that was filtered. The broth medium usually employed in detecting total coliforms is M-Endo Broth MF. Total coliform colonies will be pink to dark red in color and will appear to have a golden green color.

**18. What do the following terms mean in relation to drinking water quality: disinfection, pathogenic, toxic, pH, aesthetic, culinary and potable.**

**Disinfection:** The chemical process of killing or inactivating most microorganisms in water. See also Sterilization.

**19. Pathogenic:** Organisms or bugs that cause disease. These include bacteria, viruses, cysts and anything capable of causing disease in humans, like cryptosporidiosis, typhoid, cholera and so on. There are other organisms that do not create disease, these are called non-pathogenic organisms.

**20. Toxic:** Stuff that will kill you. A substance which is poisonous to living organisms.

**21. pH:** A measure of the acidity of water. The pH scale runs from 0 to 14 with 7 being the mid point or neutral. A pH of less than 7 is on the acid side of the scale with 0 as the point of greatest acid activity. A pH of more than 7 is on the basic (alkaline) side of the scale with 14 as the point of greatest basic activity. For example, the acidity of a sample with a pH of **5** is ten times greater than that of a sample with a pH of **6**. A difference of 2 units, from **6** to **4**, would mean that the acidity is one hundred times greater, and so on. Normal rain has a pH of **5.6** – slightly acidic because of the carbon dioxide picked up in the earth's atmosphere by the rain.

**22. Aesthetic:** Attractive or appealing water or things in water that will not make you sick but may appear to change the water's color or taste.

**23. Culinary:** Having to do with cooking food. Potable water is often called culinary water.

**24. Potable:** Water that is free of objectionable pollution, contamination, or infective agents. Generally speaking, we serve only potable water and not palatable water. Palatable is pleasant tasting water.

**25. What is hardness in water and what chemicals cause it?**

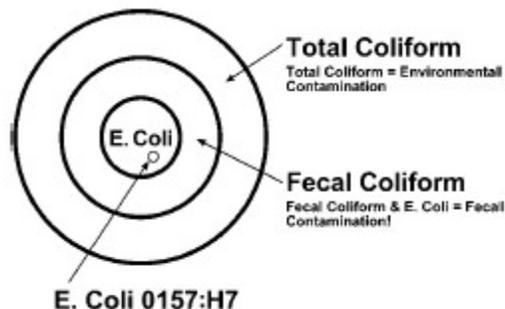
**Hardness:** Water that contains high amounts of dissolved minerals, specifically calcium and magnesium. **Ion Exchange:** A method of water softening where hardness causing ions are exchanged with sodium ions; also effective in removing many inorganic contaminants such as nitrates, copper, and lead; and treating aesthetic water problems.

**26. What is Escherichia Coliform and what does it indicate in relation to drinking water?**

**E. coli** is a sub-group of the fecal coliform group. Most *E. coli* bacteria are harmless and are found in great quantities in the intestines of people and warm-blooded animals. Some strains, however, can cause illness. The presence of *E. coli* in a drinking water sample almost always indicates recent fecal contamination meaning there is a greater risk that pathogens are present.

## TOTAL COLIFORM, FECAL COLIFORM AND E. COLI

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Total coliform, fecal coliform, and *E. coli* are all indicators of drinking water quality. The total coliform group is a large collection of different kinds of bacteria. Fecal coliforms are types of total coliform that mostly exist in feces. *E. coli* is a sub-group of fecal coliform. When a water sample is sent to a lab, it is tested for total coliform. If total coliform is present, the sample will also be tested for either fecal coliform or *E. coli*, depending on the lab testing method.

### **27. What problems are associated with Hydrogen Sulfide in the water?**

Hydrogen sulfide is a gas which, when dissolved in water, gives it a “rotten egg” odor. Chlorination will remove this gas from the water but the effectiveness of the chlorine for disinfection is lessened.

**28. When Hydrogen sulfide reacts with chlorine, it produces Sulfuric acid and elemental Sulfur:** It is therefore recommended that aeration be applied prior to the addition of chlorine for the most effective disinfection.

### **29. Why is it important to know what the turbidity of the water is when using chlorine?**

To be careful not to overdose with chlorine or properly dose with chlorine.

### **30. What is the log removal for Cryptosporidium?**

The LT1ESWTR extends further this necessary protection from Cryptosporidium to communities of fewer than 10,000 persons. Today's rule for the first time establishes Cryptosporidium control requirements for systems serving less than 10,000 persons by requiring a minimum 2-log removal for Cryptosporidium. The rule also strengthens filter performance requirements to ensure 2-log Cryptosporidium removal, establishes individual filter monitoring to minimize poor performance in individual units, includes Cryptosporidium in the definition of GWUDI, and explicitly considers unfiltered system watershed control provisions. The rule also reflects a commitment to the importance of maintaining existing levels of microbial protection in public water systems as plants take steps to comply with newly applicable DBP standards.

### **31. What is the log removal?**

This log-reduction terminology was developed by engineers as a way to express levels of decreased biological contamination in water by factors of 10 that could be easily converted to percent reduction. The most commonly used logarithmic base is 10 because it is compatible with our base-10 decimal system.

The log of 10 in the base 10 logarithmic system is 1 and the log of 100 is 2, with the log of 1000 being 3, etc. A 1-log reduction is nine out of 10 and would be equivalent to a 90 percent reduction. A 2-log reduction would be 99 out of 100 or 99 percent reduction and a 3-log reduction would be 999 out of 1000 or 99.9 percent reduction. A 99.99 percent reduction would be called a 4-log reduction.

### **32. What are the turbidity requirements for Direct and Conventional filtration plants?**

For conventional and direct filtration systems (including those systems utilizing in-line filtration), the turbidity level of representative samples of a system's filtered water (measured every four hours) must be less than or equal to **0.3 NTU** in at least 95 percent of the measurements taken each month. The turbidity level of representative samples of a system's filtered water must not exceed **1 NTU** at any time. Conventional filtration is defined as a series of processes including coagulation, flocculation, sedimentation, and filtration resulting in substantial particulate removal. Direct filtration is defined as a series of processes including coagulation and filtration but excluding sedimentation resulting in substantial particle removal.

### **33. What are chloramines, how are they formed, and do they have any beneficial use?**

**Chloramines:** Ammonia and Chlorine are combined.  $\text{Cl}_2\text{NH}_3$  Yes, limited use and this chemical will create less THMS than chlorine alone. Chloramine is a disinfectant used to treat drinking water. It is formed by mixing chlorine with ammonia.

Although it is a weaker disinfectant than chlorine, it is more stable and extends disinfectant benefits throughout a water utility's distribution system (a system of pipes water is delivered to homes through). Some water systems use chloramine as a secondary disinfectant to maintain a disinfectant residual throughout the distribution system so that drinking water remains safe as it travels from the treatment facility to the customer.

Chloramine has been used by water systems for almost 90 years, and its use is closely regulated. Since chloramine is not as reactive as chlorine, it forms fewer disinfection byproducts.

Some disinfection byproducts, such as the trihalomethanes (THMs) and haloacetic acids (HAAs), may have adverse health effects and are closely regulated. Because a chloramine residual is more stable and longer lasting than free chlorine, it provides better protection against bacterial regrowth in systems with large storage tanks and dead-end water mains. Chloramine, like chlorine, is effective in controlling biofilm, which is a coating in the pipe caused by bacteria. Controlling biofilm also tends to reduce coliform bacteria concentrations and biofilm-induced corrosion of pipes.

# Simple Math Conversion Factors

1 PSI = 2.31 Feet of Water  
 1 Foot of Water = .433 PSI  
 1.13 Feet of Water = 1 Inch of Mercury  
 454 Grams = 1 Pound  
 1 Gallon of Water = 8.34 Pounds  
 1 mg/L = 1 PPM  
 17.1 mg/L = 1 Grain/Gallon  
 1% = 10,000 mg/L  
 694 Gallons per Minute = MGD  
 1.55 Cubic Feet per Second = 1 MGD  
 60 Seconds = 1 Minute  
 1440 Minutes = 1 Day  
 .746 kW = 1 Horsepower

## LENGTH

12 Inches = 1 Foot  
 3 Feet = 1 Yard  
 5,280 Feet = 1 Mile

## AREA

144 Square Inches = 1 Square Foot  
 43,560 Square Feet = 1 Acre

## VOLUME

1000 Milliliters = 1 Liter  
 3.785 Liters = 1 Gallon  
 231 Cubic Inches = 1 Gallon  
 7.48 Gallons = 1 Cubic Foot  
 62.38 Pounds = 1 Cubic Foot of Water

## Dimensions

**SQUARE:** Area (sq.ft) = Length X Width  
 Volume (cu.ft) = Length (ft) X Width (ft) X Height (ft)

**CIRCLE:** Area (sq.ft) = 3.14 X Radius (ft) X Radius (ft)

**CYLINDER:** Volume (Cu. ft) = 3.14 X Radius (ft) X Radius (ft) X Depth (ft)

**PIPE VOLUME:** .785 X Diameter <sup>2</sup> X Length = Area X 7.48 for Gallons

**SPHERE:**  $\frac{(3.14) (\text{Diameter})^3}{(6)}$       Circumference = 3.14 X Diameter

## Flow Rate

Multiply	→	to get
to get	←	Divide
cc/min	1	mL/min
cfm (ft <sup>3</sup> /min)	28.31	L/min
cfm (ft <sup>3</sup> /min)	1.699	m <sup>3</sup> /hr
cfh (ft <sup>3</sup> /hr)	472	mL/min
cfh (ft <sup>3</sup> /hr)	0.125	GPM
GPH	63.1	mL/min
GPH	0.134	cfh
GPM	0.227	m <sup>3</sup> /hr
GPM	3.785	L/min
oz/min	29.57	mL/min

## General Conversions

**POUNDS PER DAY** = Concentration (mg/L) X Flow (MG) X 8.34

$$\text{PERCENT EFFICIENCY} = \frac{\text{In} - \text{Out}}{\text{In}} \times 100$$

$$\begin{aligned} \text{TEMPERATURE: } \quad {}^{\circ}\text{F} &= ({}^{\circ}\text{C} \times 9/5) + 32 & 9/5 &= 1.8 \\ {}^{\circ}\text{C} &= ({}^{\circ}\text{F} - 32) \times 5/9 & 5/9 &= .555 \end{aligned}$$

$$\text{CONCENTRATION: } \text{Conc. (A)} \times \text{Volume (A)} = \text{Conc. (B)} \times \text{Volume (B)}$$

$$\text{FLOW RATE (Q): } Q = A \times V \text{ (Quantity = Area} \times \text{Velocity)}$$

$$\text{FLOW RATE (gpm): } \text{Flow Rate (gpm)} = \frac{2.83 (\text{Diameter, in})^2 (\text{Distance, in})}{\text{Height, in}}$$

$$\% \text{ SLOPE} = \frac{\text{Rise (feet)}}{\text{Run (feet)}} \times 100$$

$$\text{ACTUAL LEAKAGE} = \frac{\text{Leak Rate (GPD)}}{\text{Length (mi.)} \times \text{Diameter (in)}}$$

$$\text{VELOCITY} = \frac{\text{Distance (ft)}}{\text{Time (Sec)}}$$

**N** = Manning's Coefficient of Roughness

**R** = Hydraulic Radius (ft.)

**S** = Slope of Sewer (ft/ft.)

$$\text{HYDRAULIC RADIUS (ft)} = \frac{\text{Cross Sectional Area of Flow (ft)}}{\text{Wetted pipe Perimeter (ft)}}$$

$$\text{WATER HORSEPOWER} = \frac{\text{Flow (gpm)} \times \text{Head (ft)}}{3960}$$

$$\text{BRAKE HORSEPOWER} = \frac{\text{Flow (gpm)} \times \text{Head (ft)}}{3960 \times \text{Pump Efficiency}}$$

$$\text{MOTOR HORSEPOWER} = \frac{\text{Flow (gpm)} \times \text{Head (ft)}}{3960 \times \text{Pump Eff.} \times \text{Motor Eff.}}$$

$$\text{MEAN OR AVERAGE} = \frac{\text{Sum of the Values}}{\text{Number of Values}}$$

$$\text{TOTAL HEAD (ft)} = \text{Suction Lift (ft)} \times \text{Discharge Head (ft)}$$

$$\text{SURFACE LOADING RATE} = \frac{\text{Flow Rate (gpm)}}{\text{Surface Area (sq. ft)}} \text{ (gal/min/sq.ft)}$$

$$\text{MIXTURE STRENGTH (\%)} = \frac{(\text{Volume 1, gal}) (\text{Strength 1, \%}) + (\text{Volume 2, gal}) (\text{Strength 2, \%})}{(\text{Volume 1, gal}) + (\text{Volume 2, gal})}$$

$$\text{INJURY FREQUENCY RATE} = \frac{(\text{Number of Injuries}) \times 1,000,000}{\text{Number of hours worked per year}}$$

$$\text{DETENTION TIME (hrs)} = \frac{\text{Volume of Basin (gals)} \times 24 \text{ hrs}}{\text{Flow (GPD)}}$$

$$\text{FLUORIDE ION PURITY (\%)} = \frac{(\text{Molecular weight of Fluoride}) (100\%)}{\text{Molecular weight of Chemical}}$$

$$\text{INJURY FREQUENCY RATE} = \frac{(\text{Number of Injuries}) \cdot 1,000,000}{\text{Number of hours worked per year}}$$

$$\text{DETENTION TIME (hrs)} = \frac{\text{Volume of Basin (gals)} \times 24 \text{ hrs}}{\text{Flow (GPD)}}$$

$$\text{BY-PASS WATER (gpd)} = \frac{\text{Total Flow (GPD)} \times \text{Plant Effluent Hardness (gpg)}}{\text{Filtered Hardness (gpg)}}$$

#### HARDNESS

$$\text{HARDNESS (mg/L as CaCO}_3) = \frac{A \text{ (mls of titrant)} \times 1000}{\text{Mls of Sample}}$$

$$\text{Ca HARDNESS as mg/L CaCO}_3 = 2.5 \times (\text{Ca, mg/L})$$

$$\text{Mg HARDNESS as mg/L CaCO}_3 = 4.12 (\text{Mg, mg/L})$$

$$\text{ALKALINITY TOTAL (mg/L)} = \frac{\text{Mls of Titrant} \times \text{Normality} \times 50,000}{\text{Mls of Sample}}$$

$$\text{EXCHANGE CAPACITY (grains)} = \text{Resin Volume (cu. ft)} \times \text{Removal Capacity}$$

$$\text{HARDNESS TO GRAIN/GALLON} = \frac{\text{Hardness (mg/L)} \times \text{gr./gal}}{17.1 \text{ mg/L}}$$

$$\text{LANGELIER INDEX} = \text{pH} - \text{pH}_s$$

#### CHEMICAL ADDITION

$$\text{CHEMICAL FEED RATE (gpm)} = \frac{\text{Chemical Feed (ml/min)}}{3785 \text{ ml/gal}}$$

$$\text{CHLORINE DOSE (mg/L)} = \text{Chlorine Demand (mg/L)} + \text{Chlorine Residual (mg/L)}$$

$$\text{POLYMER \%} = \frac{\text{Dry Polymer (lbs.)}}{\text{Dry Polymer (lbs.)} + \text{Water (lbs.)}}$$

$$\text{DESIRED PAC (lbs./MG)} = \frac{\text{Volume (MG)} \times \text{Dose (mg/L)} \times 8.34}{1 \text{ MG}}$$

$$\text{PAC (lbs./gal)} = \frac{\text{PAC (mg/L)} \times 3.785 \text{ (1/gallon)}}{1000 \text{ (mg/g)} \times 454 \text{ (g/lb.)}}$$

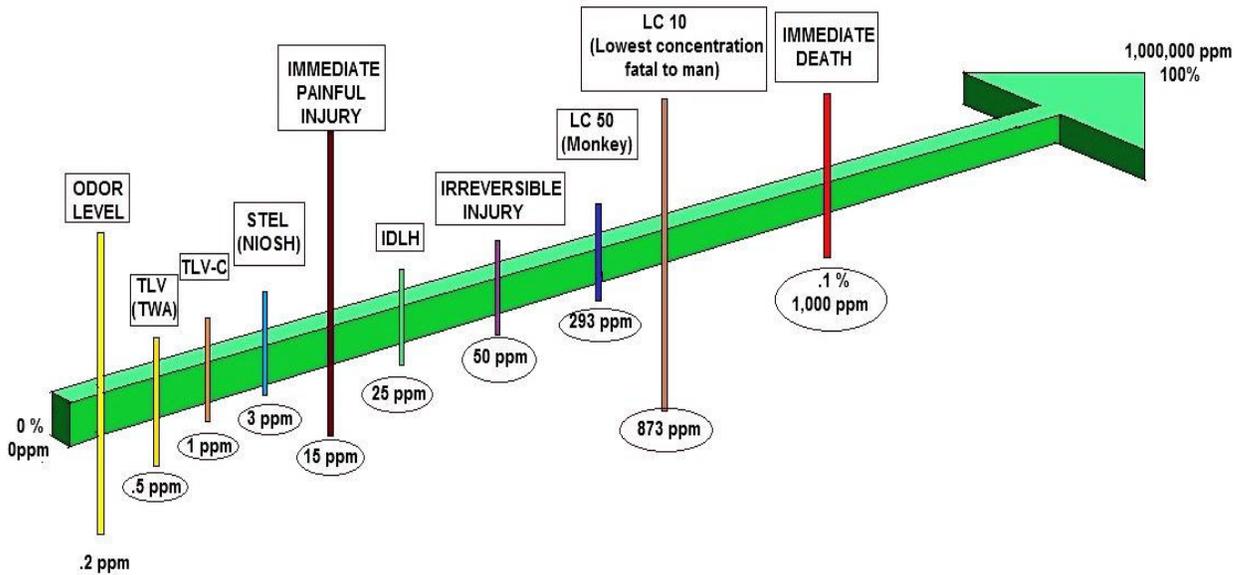
**FILTRATION**

$$\text{FILTRATION RATE} = \frac{\text{Flow Rate (gpm)}}{\text{Surface Area (sq. ft)}} \text{ (gpm/sq. ft)}$$

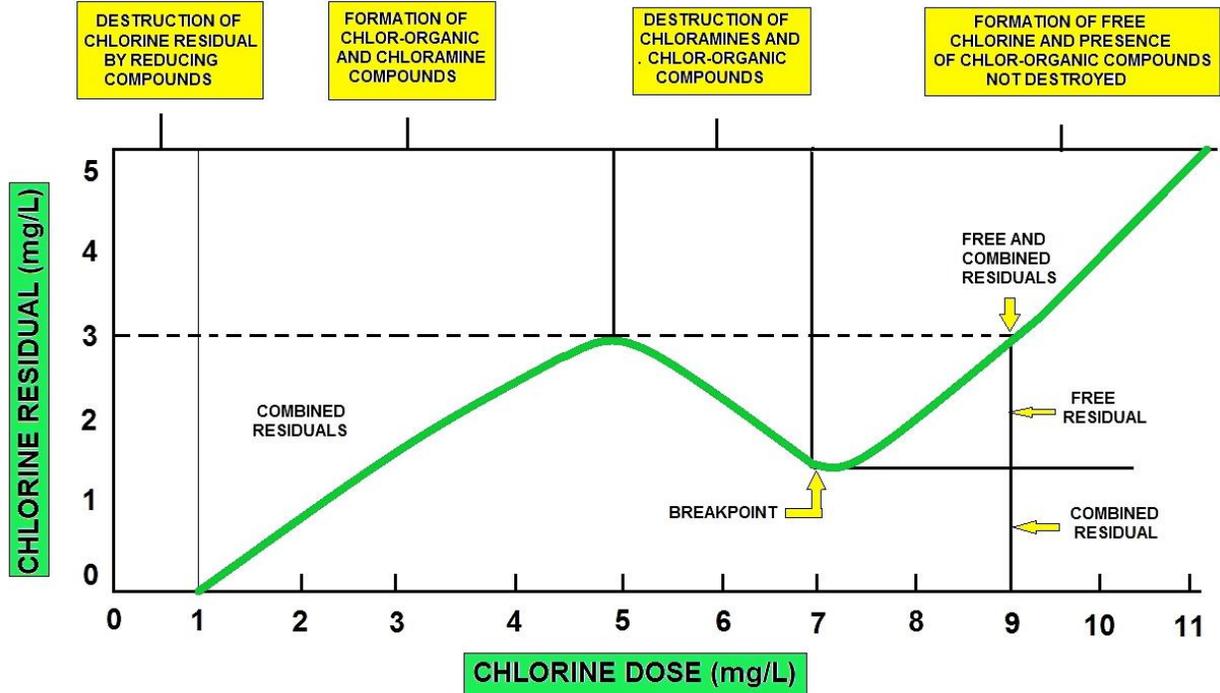
$$\text{BACKWASH PUMPING RATE} = \text{Filter Area (sq. ft)} \times \text{Backwash Rate (gpm/sq. ft)} \text{ (gpm)}$$

$$\text{FILTRATION RATE} = \frac{\text{Flow Rate (gpm)}}{\text{Filter Area (sq. ft)}} \text{ (gpm/sq. ft)}$$

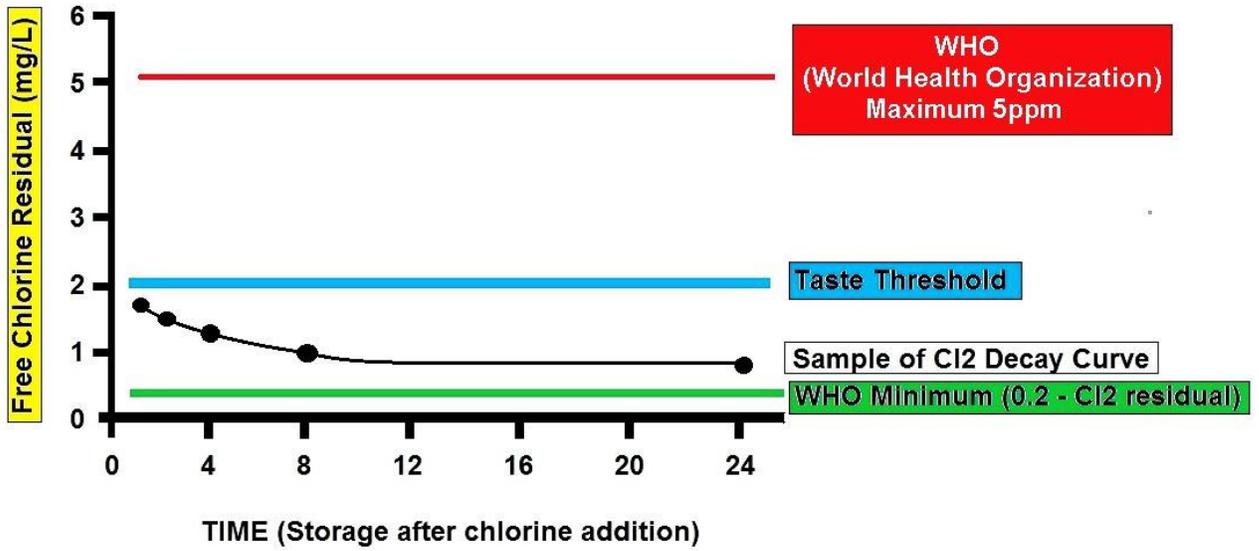
# Chlorine Charts



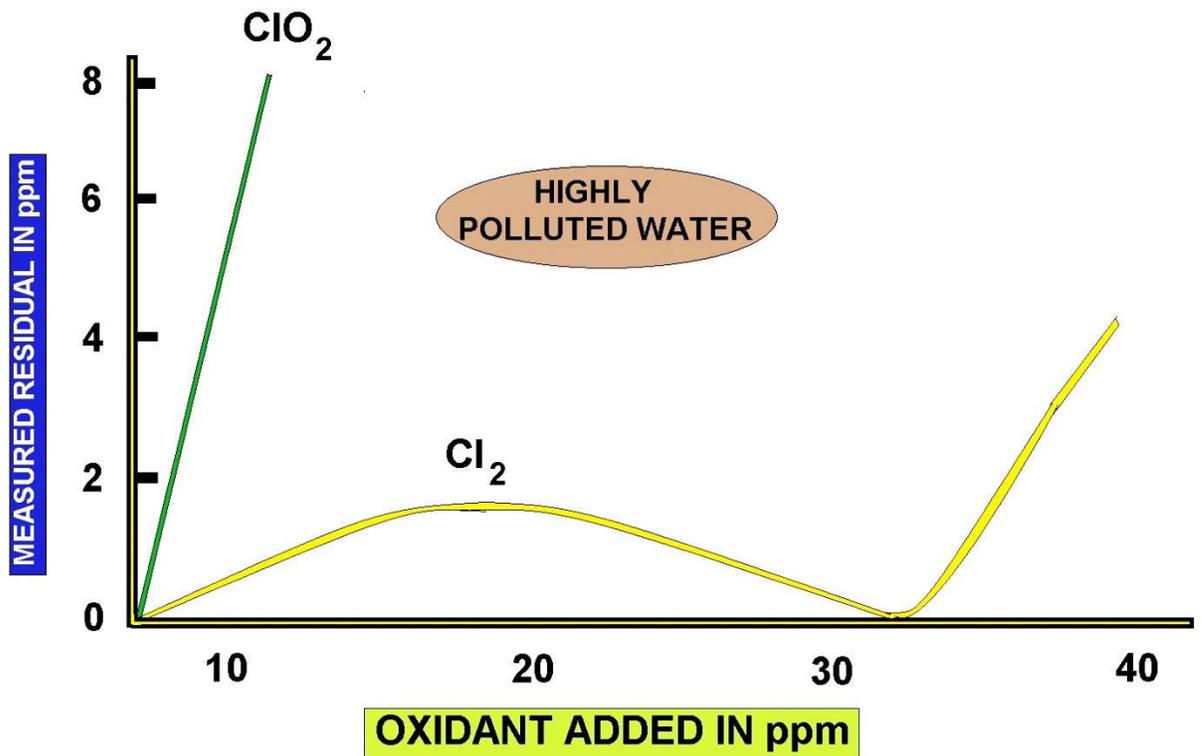
## CHLORINE POISON LINES



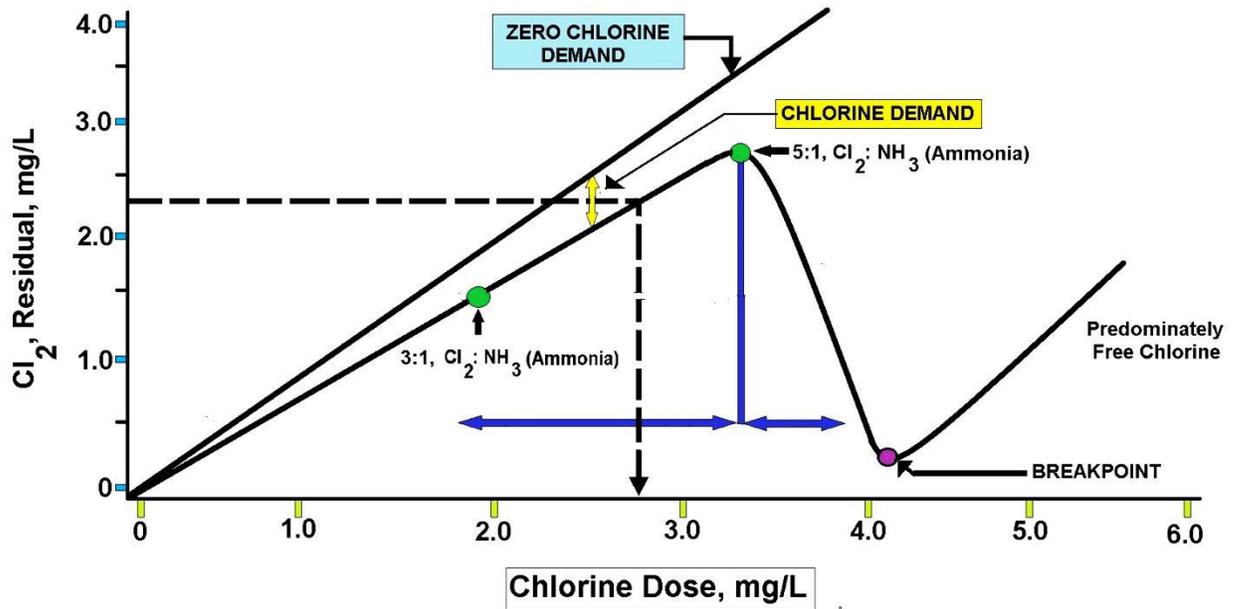
## CHLORINE BREAKPOINT



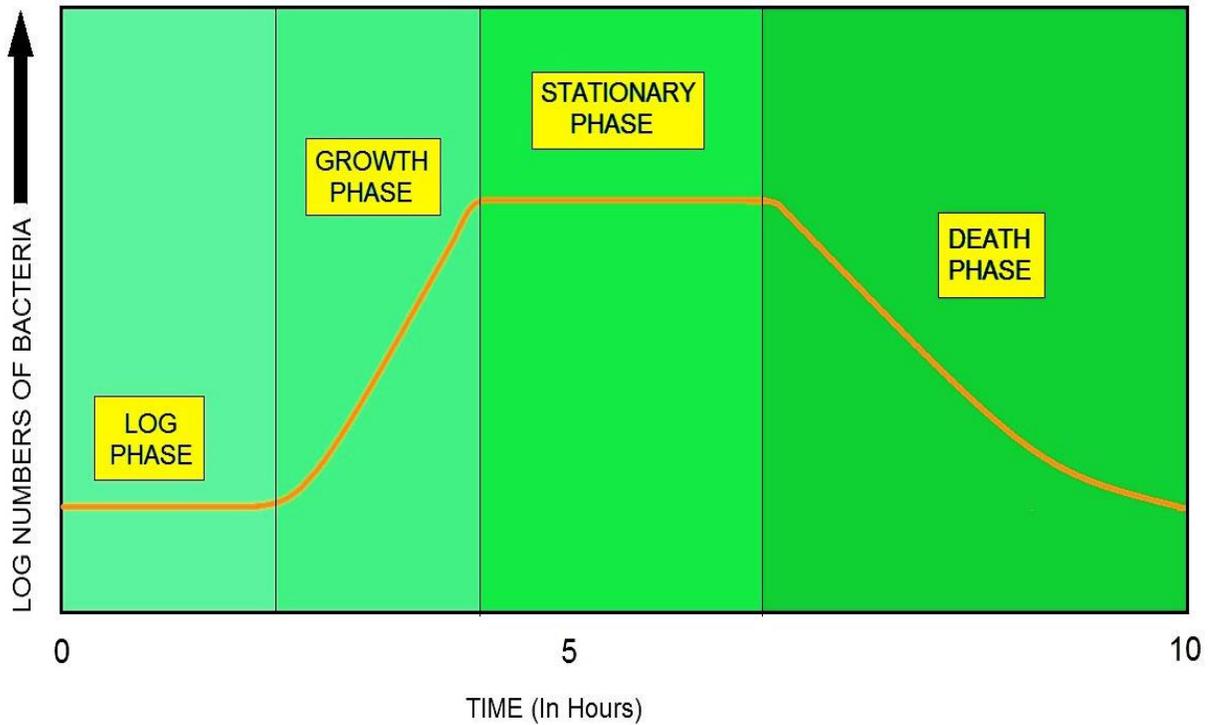
### CHLORINE DECAY CURVE

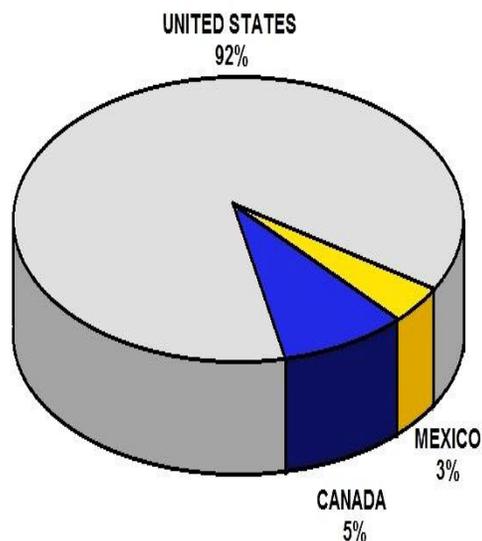
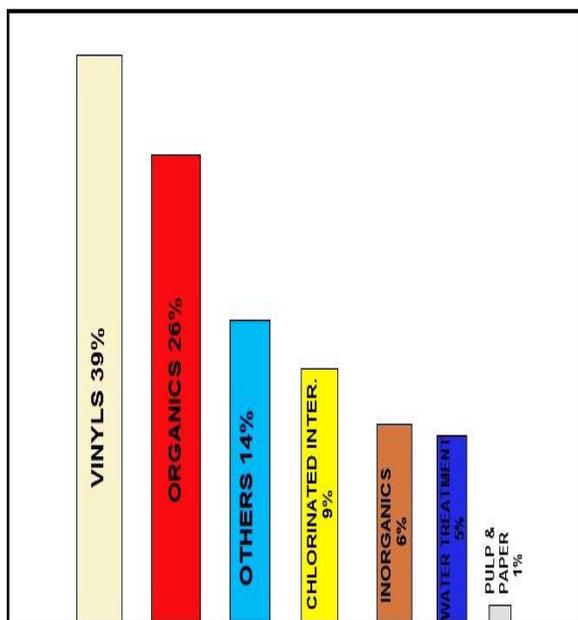
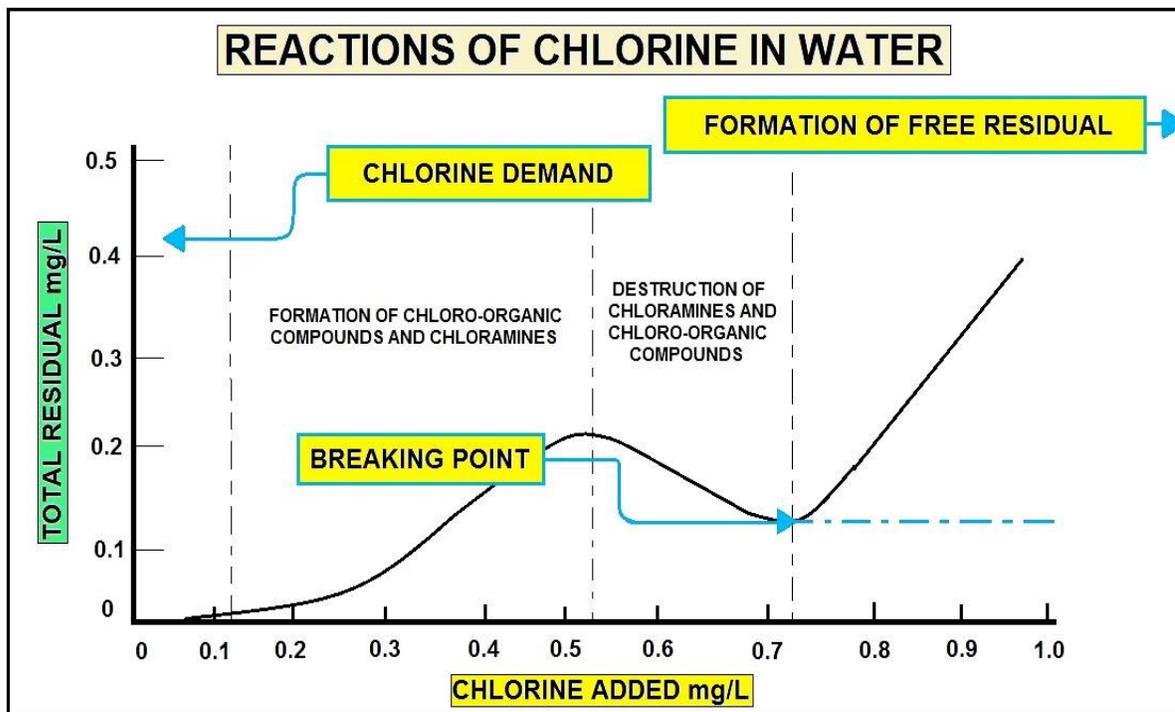


### USING CHLORINE DIOXIDE vs CHLORINE



## CHLORAMINATION

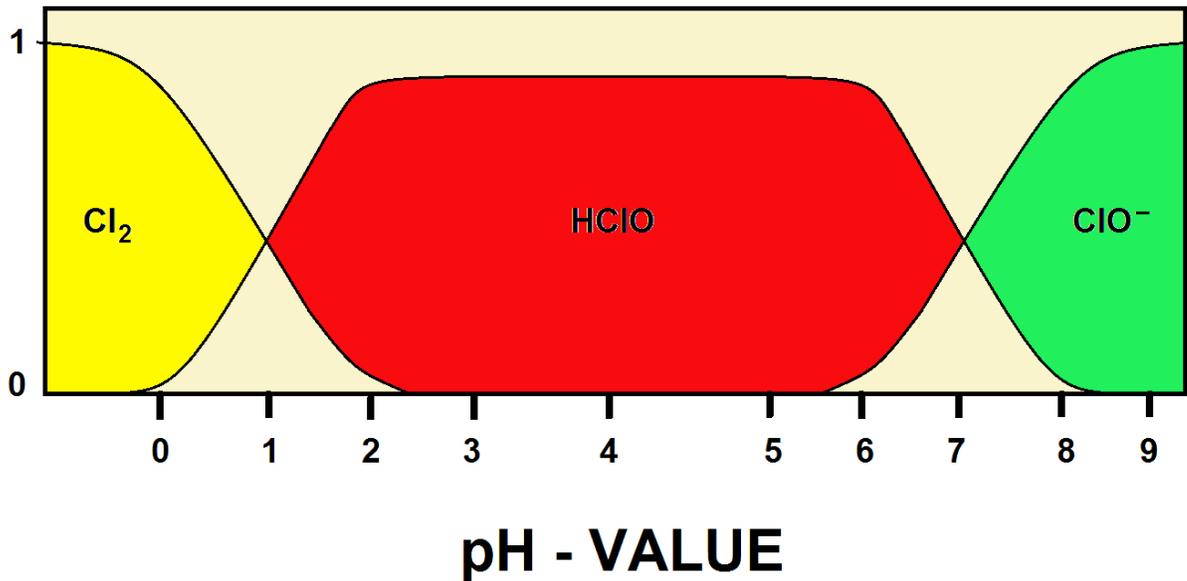


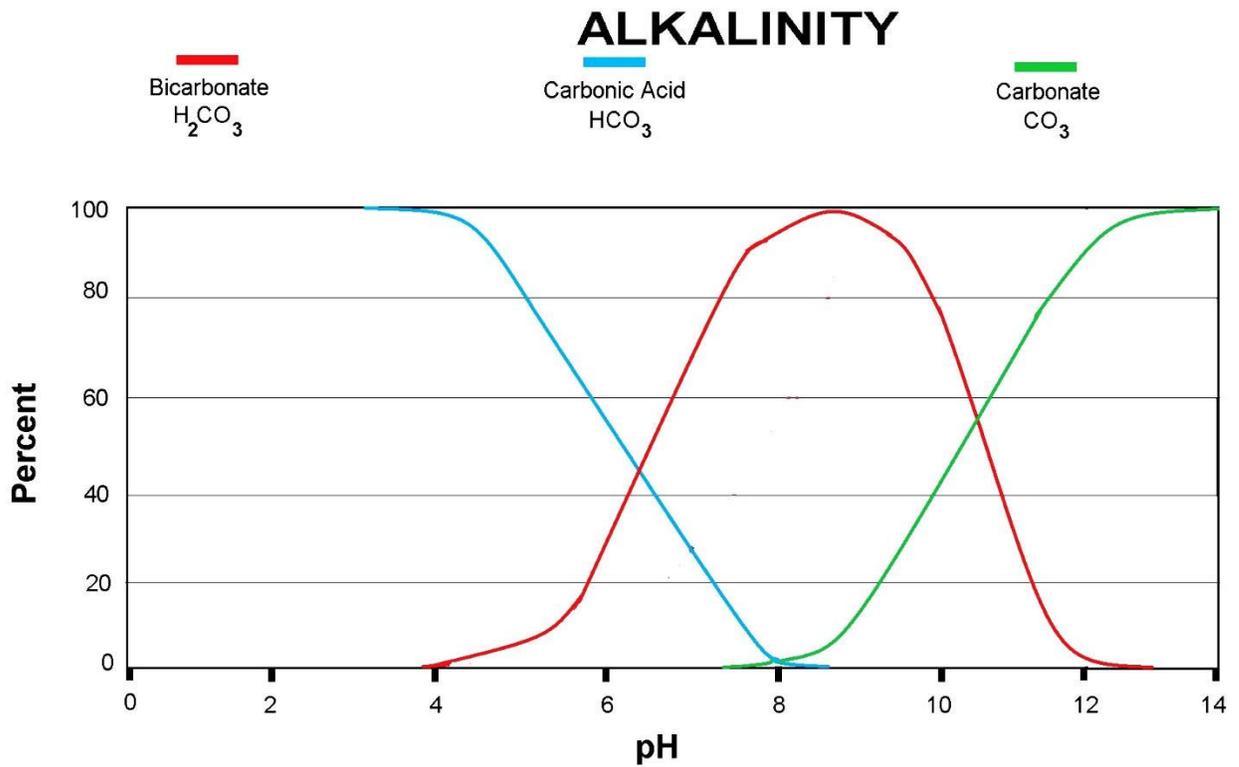
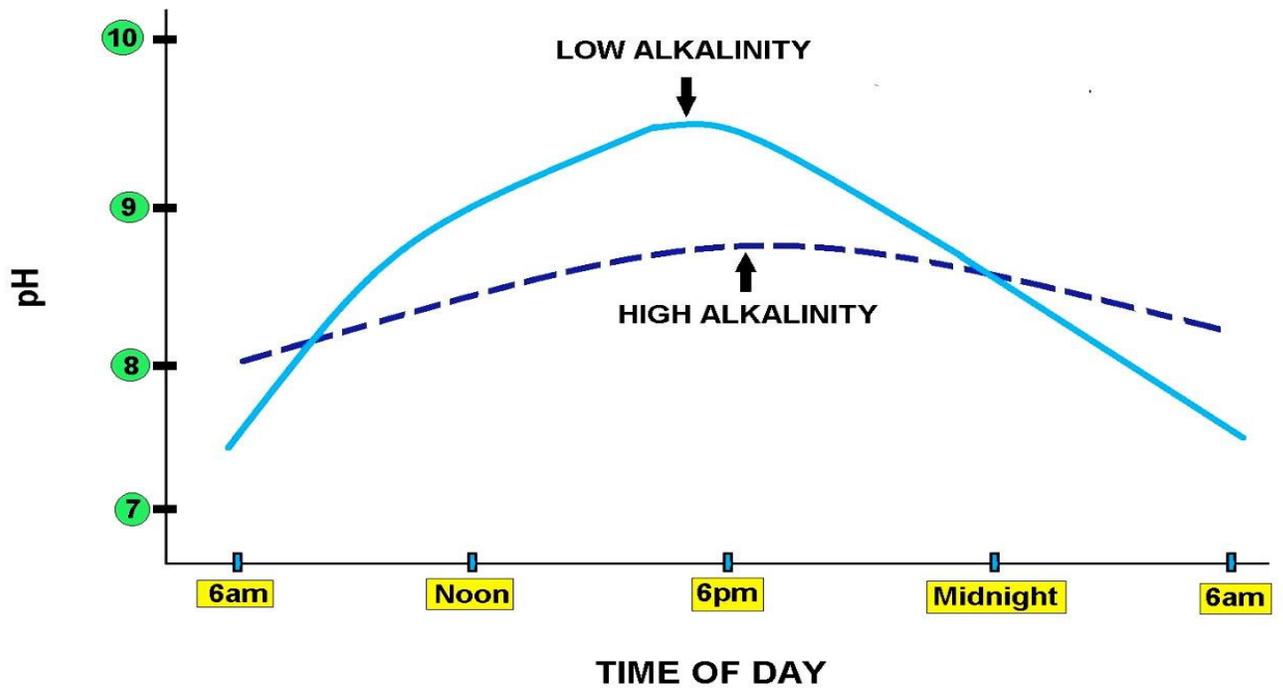


## NORTH AMERICA CHLORINE DEMAND COMPARISON

CHEMICAL NAME	CHEMICAL FORMULA	FORM	% CHLORINE	STORAGE	QUALITY	ADVANTAGE	DISADVANTAGE
CHLORINE GAS	$\text{Cl}_2$	GAS	100%	MAY STORE FOR LONG PERIODS	CONSISTENTLY HIGH QUALITY	COST EFFECTIVE	BY-PRODUCT FORMATIONS (THM'S, HAA)
SODIUM HYPOCHLORITE	$\text{NaOCl}$	LIQUID	~ 12%	LIMITED DUE TO DECOMPOSITION	POOR QUALITY DUE TO LIMITED CONTROL	LESS TRAINING REQUIRED TO HANDLE DUE TO FEWER REGULATIONS	LIMITED SHELF LIFE AND HIGHER COST

### CHLORINE GAS VS. SODIUM HYPOCHLORITE (BLEACH)





## EFFECTS OF ALKALINITY FROM pH

		MICROBIOLOGICAL SAFETY	CHEMICAL SAFETY	CUSTOMER AESTHETICS	EASE OF MONITORING	ABILITY TO TREAT DIFFICULT WATER	COST OF OPERATING	CAPITAL COSTS	STATE OF COMMERCIAL DEVELOPMENT	SCALE-UP	WASTE PRODUCTION AND ENERGY USE	RELIABILITY
GROUNDWATER	CHLORINE	-	-	-	+	+	+	+	+	+	+	-
	UF ONLY	-	+	+	-	+	●	●	-	-	●	-
	UV ONLY	+	+	+	●	+	+	●	+	+	●	●
	Alternate + Residual (1)	+	●	●	+	+	●	-	+	+	+	+
SURFACE WATER	CHLORINE ONLY	-	-	-	+	-	+	+	+	+	+	+
	Conventional pre-treat + CHLORINE	+	-	-	+	-	●	●	+	+	●	-
	UF ONLY	-	-	●	-	-	●	●	-	-	●	-
	Conventional pre-treat + UF	●	+	+	-	+	-	-	-	-	-	-
	Conventional pre-treat + OZONE + UF	-	●	-	-	+	-	-	-	-	-	-
	MF + UV	●	+	-	●	-	+	●	-	-	●	+
	Conventional pre-treat + UV	●	+	+	●	-	+	●	+	+	●	●
	Conventional pre-treat + OZONE + UV	+	●	+	+	+	-	-	+	+	●	+
	Alternative + Residual (2)	+	●	●	+	+	-	-	+	+	+	+

Conventional pre-treat = Coagulation / Sedimentation  
 UF - Ultrafiltration MF - Microfiltration  
 + = Better than average  
 - = Worse than average  
 ● = Average

(1) UF + Chlorine residual or Conv + UV + Chlorine residual  
 (2) Conv pre-treat + UF + Chlorine residual or MF + UV + Chlorine residual or Conv pre-treat + UV + Residual

## ASSESSMENT TO DETERMINE EFFECTIVE DISINFECTION METHODS

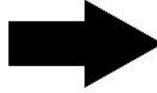
WATER	BLEACHING POWDER (25 - 35 %) (g)	HIGH STRENGTH CALCIUM HYPOCHLORITE (70 %) (g)	LIQUID BLEACH (5 % SODIUM HYPOCHLORITE ) (ml)
1	2.3	1.0	14
1.2	3.0	1.2	17
1.5	3.5	1.5	21
2	5.0	2.0	28
2.5	6.0	2.5	35
3	7.0	3.0	42
4	9.0	4.0	56
5	12	5.0	70
6	14	6.0	84
7	16	7.0	98
8	19	8.0	110
10	23	10	140
12	28	12	170
15	35	15	210
20	50	20	280
30	70	30	420
40	90	40	560
50	120	50	700
60	140	60	840
70	160	70	980
80	190	80	1 100
100	230	100	1 400
120	280	120	1 700
150	350	150	2 100
200	470	200	2 800
250	580	250	3 500
300	700	300	4 200
400	940	400	5 600
500	1 170	500	7 000

(\* Approximate dose = 0.7 mg of applied Chlorine per litre of water )

## CHLORINE DOSES WITH DIFFERENT TYPES OF CHLORINE

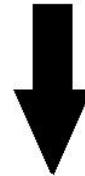
## 1. Do The Basics

- TEST WATER CHEMISTRY
- CHECK WATER FLOW RATE
- ESTIMATE CHLORINE DEMAND
- DETERMINE CONTACT TANK SIZE
- NOTE THE LINE PRESSURE WHERE CHLORINE WILL BE INJECTED INTO



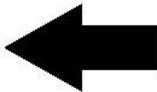
## 2. Choose A Chlorinator

- LIQUID CHLORINATOR OR DRY FEED
- WHERE TO INSTALL CHLORINATOR BEFORE / AFTER PRESSURE TANK
- PERISTALTIC METERING PUMP OR DIAPHRAGM PUMP



## 3. Installation

- BUY DIRECTLY AND INSTALL  
OR
- BUY DIRECTLY AND HIRE PLUMBER  
OR
- BUY FROM WATER TREATMENT DEALER



## 4. Quality Control

- SET-UP MAINTENANCE SCHEDULE
- CLIPBOARD WITH CHECKLIST
- TEST THE WATER ANNUALLY

# HOW TO DETERMINE A CHLORINATION SYSTEM



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