# CHEMICAL CONTAMINANTS 201 CONTINUING EDUCATION PROFESSIONAL DEVELOPMENT COURSE





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Benenson, Abram S., editor. 1990. Control of Communicable Diseases in Man. 15th ed. Baltimore: Victor Graphics, Inc.

Foster, Laurence, M.D. 1985. "Waterborne Disease - It's Our Job to Prevent It". PIPELINE newsletter, Oregon Health Division, Drinking Water Program, Portland, Oregon 1(4): 1-3.

Foster, Laurence, M.D. 1990. "Waterborne Disease," Methods for the Investigation and Prevention of Waterborne Disease Outbreaks. Ed. Gunther F. Craun. Cincinnati: U.S. Environmental Protection Agency

All other unacknowledged references are in the Water/ Wastewater Sampling and Water Chemistry Courses.



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Do not solely depend on TLC's Approval list for it may be outdated.

# A second certificate of completion for a second State Agency \$50 processing fee.

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.

### Important Information about this Manual

This manual has been prepared to assist employees in the general awareness of water and wastewater regulatory sampling and in dealing with often-complex procedures and requirements for safely handling hazardous and toxic materials. The scope of the material is quite large, requiring a major effort to bring it under control. Employee health and safety, as well as that of the public, depend upon careful application of federal and state regulations and safe working procedures.

This manual will cover general laws, regulations, required procedures and work rules relating to water and wastewater sampling. It should be noted, however, that the federal and state regulations are an ongoing process and subject to change over time. For this reason, a list of resources and hyperlinks is provided to assist in obtaining the most up-to-date information on various subjects.

This manual is a guidance document for employees who are involved with water quality and pollution control. It is not designed to meet the full requirements of the United States Environmental Protection Agency (EPA) or the Department of Labor-Occupational Safety and Health Administration (OSHA) rules and regulations.

This course manual will provide general guidance and should not be used as a preliminary basis for developing general water/wastewater sampling plans. This document is not a detailed water/wastewater textbook or a comprehensive source book on water/wastewater rules and regulations.

Technical Learning College makes 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 guidance and is not considered a legal document.

Individuals who are responsible for water/wastewater sampling and the health and safety of workers at hazardous waste sites 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.



# **CEU Course Description**

#### CHEMICAL CONTAMINANTS 201 CEU TRAINING COURSE

This CEU course is a review of commonly found chemical and elemental contaminants in water and wastewater. The majority of the course information will come from Environmental Protection Agency's Rules and Regulation related to water quality, water sampling and treated effluent standards.

This course will also cover water sampling techniques, contaminant identification, general water quality/sampling operations and MCLs. This course will apply to all categories of water and wastewater treatment, but is applicable to pretreatment and distribution/groundwater production as well. As water / wastewater treatment professionals, it is our responsibility to identify, and control all recognized chemical contaminants to EPA's minimum standards, and provide drinking water/ effluent that meets minimum drinking water or CWA standards.

Industrial, agricultural, and domestic wastes can contribute to the pollution of water, and water pollutants can damage human and animal health. One of the most important categories of water pollutants is inorganic chemical. These inorganic chemicals are usually substances of mineral origin. Metals, salt, and minerals are examples of inorganic chemicals.

#### Audience

Attention Pretreatment Operators, Laboratory Technicians, Water Distribution, Well Drillers, Pump Installers, and Water and Wastewater Treatment Operators. The target audience for this course is the person interested in working in a water treatment or distribution facility and wishing to maintain CEUs for certification license, meet education needs for promotion, or to learn how to do the job more safely and effectively.

#### Prerequisites: None

#### Final Examination for Credit

Opportunity to pass the final comprehensive examination is limited to three attempts per course enrollment.

#### **Course Procedures for Registration and Support**

All of Technical Learning College's (TLC) correspondence courses have complete registration and support services offered. Delivery of services will include, e-mail, web site, telephone, fax and mail support. TLC will attempt immediate and prompt service. When students register for a distance or correspondence course, they'll be assigned a start date and an ending date.

It is the student's responsibility to note dates for assignments and keep up with the course work. If a student falls behind, he/she must contact TLC and request an ending date extension in order to complete the course. It is the prerogative of TLC to decide whether to grant the request. All students will be tracked by a unique number assigned to the student.

#### **Disclaimer and Security Notice**

The student shall understand that it their responsibility to ensure that this CEU course is either approved or accepted in my State for CEU credit. The student shall understand and follow State laws and rules concerning distance learning courses and understand these rules change on a frequent basis and will not hold Technical Learning College responsible for any changes. The student shall understand that this type of study program deals with dangerous conditions and will not hold Technical Learning College, Technical Learning Consultants, Inc. (TLC) liable for any errors or omissions or advice contained in this CEU education training course material. The student shall contact TLC if they need help or assistance and double-check to ensure my registration page and assignment has been received and graded.

#### 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.

#### Student Information Personal Data Security Procedures

All information regarding the student is strict and privileged only. This information is held in secure databases and is not sold or provided to any one unless the student requests a copy or a State agency does an audit. Even during audits, we restrict confidential information unless the Agency can provide a legitimate excuse. Some of this security information and data is priority and details are not provided. Students are not provided with any passwords at this time.

#### Grading Criteria / Certificate of Completion

TLC will offer the student either pass/fail or a standard letter grading assignment. If TLC is not notified, the student 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.

#### Student Assistance

The student shall contact TLC if they need help or assistance and double-check to ensure my registration page and assignment has been received and graded.

#### Instructions for Written Assignments

The Chemical Contaminants 201 training CEU course uses multiple choice and true/false questions. Answers may be written in this manual or typed out on a separate answer sheet. TLC prefers that students type out and e-mail their answer sheets to info@tlch2o.com, but they may be faxed to (928) 468-0675.

#### Final Examination for Credit

Opportunity to pass the final comprehensive examination is limited to three attempts per course enrollment.

#### **Required Texts**

This course comes complete and does not require any other materials.

#### Feedback Mechanism (Examination Procedures)

A feedback form is included in the front of the assignment.

#### 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.

#### 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 these particular students.

#### 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 students opportunities to apply and understand the theory and skills needed for operator certification and environmental education,

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.



# ALKALINITY

#### When the Student finishes this course...

At the finish of this course, you (the student) should be able to explain and describe the various chemical contaminates commonly found in water and wastewater, including, elements, SOC, VOCs, IOCs and metalloids. Upon completion of this course, the student will obtain 16-24 hours (depending upon your State Agency) of continuing education relating to water/wastewater sampling procedures, proper chemical contaminate identification and EPA MCL recognition.

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.

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Ultraviolet Radiation.....

# 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	Nenhelometric Turbidity   Inits
PN	Public Notification
PN PWS	Public Notification Public Water Supply
PN PWS SDWA	Public Notification Public Water Supply Safe Drinking Water Act
PN PWS SDWA SMCL	Public Notification Public Water Supply Safe Drinking Water Act .Secondary Maximum Contaminant Level
PN PWS SDWA SMCL SOC	Public Notification Public Water Supply Safe Drinking Water Act .Secondary Maximum Contaminant Level Synthetic Organic Chemical
PN PWS SDWA SMCL SOC SWTR	Public Notification Public Water Supply Safe Drinking Water Act .Secondary Maximum Contaminant Level Synthetic Organic Chemical .Surface Water Treatment Rule
PN PWS SDWA SMCL SOC SWTR TCR	Public Notification Public Water Supply Safe Drinking Water Act .Secondary Maximum Contaminant Level Synthetic Organic Chemical .Surface Water Treatment Rule .Total Coliform Rule
PN PWS SDWA SMCL SOC SWTR TCR TT	Public Notification Public Water Supply Safe Drinking Water Act .Secondary Maximum Contaminant Level Synthetic Organic Chemical .Surface Water Treatment Rule .Total Coliform Rule .Treatment Technique
PN PWS SDWA SMCL SOC SWTR TCR TT USEPA	Public Notification Public Water Supply Safe Drinking Water Act .Secondary Maximum Contaminant Level Synthetic Organic Chemical .Surface Water Treatment Rule .Total Coliform Rule .Treatment Technique United States Environmental Protection Agency

VOC..... Volatile Organic Chemical

### Timeline of Existing Federal Water and State Drinking Water Quality Regulations



**National Interim Primary Drinking Water Regulations** (NIPDWR) Promulgated 1975-1981 Contained 7 contaminants Targeted: Trihalomethanes, Arsenic, and Radionuclides Established 22 drinking water standards.

Phase 1 Standards Promulgated 1987 Contained 8 contaminants Targeted: VOCs.

**Phase 2 Standards** Promulgated 1991 Contained 36 contaminants Targeted: VOCs, SOCs, and IOCs.

**Phase 5 Standards** Promulgated 1992 Contained 23 contaminants Targeted: VOCs, SOCs, and IOCs.

**Surface Water Treatment Rule** (SWTR) Promulgated 1989 Contained 5 contaminants Targeted: Microbiological and Turbidity.

**Stage 1 Disinfectant/Disinfection By-product** (D/DBP) Rule Promulgated 1998 Contained 14 contaminants Targeted: DBPs and precursors.

**Interim Enhanced Surface Water Treatment Rule** (IESWTR) Promulgated 1998 Contained 2 contaminants Targeted: Microbiological and Turbidity.

**Radionuclide Rule** Promulgated 2000 Contained 4 contaminants Targeted: Radionuclides.

Arsenic Rule Promulgated 2001 Contained 1 contaminant Targeted: Arsenic.

**Filter Backwash Recycling Rule** Promulgated 2001 Contained - Targeted: Microbiological and Turbidity.

### **Regulated Chemical Contaminants**

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, SOCs, and VOCs.

Phased RulesVOCSOCIOCPhase I, July 7, benzene1987carbon tetrachloride100(52 FR 25690)p-dichlorobenzeneFifective: 1989 trichloroethylene100
Phase I, July 7, benzene 1987 carbon tetrachloride (52 FR 25690) p-dichlorobenzene Effective: 1989 trichloroethylene
1987 carbon tetrachloride (52 FR 25690) p-dichlorobenzene Effective: 1989 trichloroethylene
(52 FR 25690) p-dichlorobenzene Effective: 1989 trichloroethylene
Effective: 1989 trichloroethylene
vinyl chloride
1,1,1-trichloroethane
1,1-dichloroethylene
1,2-dichloroethane
Phase II, cis-1,2-dichloroethylene alachlor asbestos
January 1991' ethylbenzene atrazine cadmium
(56 FR 3526) monochlorobenzene carboturan chromium
Effective: 1992 (chlorobenzene) chlordane filuoride
o-dichioroberizerie EDB (etrigierie dibromide) mercury
totrachloroothylono chloropropano) nitrito
teluano boptachiar colonium
trans_1.2-dichloroethylene_hentachlor_enovide
1.2-dichloropropane methoxychlor
toxaphene
PCBs
2.4-D

2.4.5-TP

Phased Rules VOC Phase IIB, July 1991 (56 FR 30266) Effective: 1993 SOC pentachlorophenol

IOC barium

Phase V, Julydichloromethane19921,1,2-trichloroethane(57 FR 31776)1,2,4-trichlorobenzeneEffective:1994

benzo(a)pyrene antimony beryllium dalapon di(ethylhexyl)-adipate cyanide di(ethylhexyl)-phthalate nickel dinoseb (remanded diquat 1995) endothall thallium endrin glyphosate hexachlorobenzene hexachlorocyclopentadiene oxymal picloram simazine 2,3,7,8-TCDD (dioxin)

<sup>1</sup>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 Goal (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 legal limits 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.

#### The Standardized Monitoring Framework

The Standardized Monitoring Framework (SMF), promulgated in the Phase II rule on January 30, 1991 and revised under Phases IIB and V, includes contaminants regulated under Phases I, II, IIB, V, the revised Arsenic Rule and the Radionuclides Rule Monitoring under the SMF began in 1993. The goal of the Standardized Monitoring Framework is to standardize, simplify, and consolidate drinking water monitoring requirements across contaminant groups. In order to do this, EPA has established nine-year compliance cycles. Each nine-year compliance cycle is divided into 3 three-year compliance periods, which may be further subdivided into annual and quarterly periods. Compliance periods run on a calendar year basis, from January 1 through December 31. Compliance cycle 1 began January 1, 1993 and ended December 31, 2001; the second compliance cycle began

January 1, 2002 and ends December 31, 2010; the third compliance cycle begins January 1, 2011 and ends December 31, 2019. Monitoring schedules and sample requirements are standardized for each compliance cycle for each contaminant group.

	U				
2nd Compliance Cycle		3rd Compliance Cycle			
1st Period	2nd Period	3rd Period	1st Period	2nd Period	3rd Period
2002	2005	2008	2011	2014	2017
2003	2006	2009	2012	2015	2018
2004	2007	2010	2013	2016	2019

Standardized Monitoring Framework – Compliance Cycles and Period



#### **Monitoring Waivers**

The SMF allows States to grant waivers to water systems to reduce the sampling frequencies to once every 3, 6 or 9 years for inorganic compounds, synthetic organic compounds, and volatile organic compound. Waivers of sampling requirements are granted for specified contaminants based on both a vulnerability assessment and the analytical results of previous sampling. The vulnerability assessment may be based on a determination that either the contaminant has not been used in the area or that the system is not susceptible to contamination.



### **Analytical Method**

An analytical method is a procedure that determines the concentration of a contaminant in a water sample.

#### Analytical methods generally describe:

- How to collect, preserve, and store the sample.
- Procedures to concentrate, separate, identify, and quantify contaminants present in the sample.
- Quality control criteria the analytical data must meet.
- How to report the results of the analysis.

#### In general, an analytical method

- Is applicable to routine analyses of samples.
- Is suitable for measuring the drinking water contaminant in the concentration range of interest.
- Provides data with the necessary accuracy and precision to demonstrate compliance or meet monitoring objectives in a wide variety of drinking water matrices.
- Includes instructions for all aspects of the analysis from sample collection to data reporting.
- Incorporates appropriate quality control criteria so that acceptable method performance is demonstrated during the analysis of samples.

# Drinking Water Analysis Chart

ANALYSIS	METHOD	HOLDING
		TIME
Inorganic Compounds (IOC) 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
		44 -
Lead and Copper	Pb	14 days
	EPA 200.7 for Cu	
Public or Individual Water Source Testing	1	
Nitrate	SM-4500 NO3 D	48 hours
Total Coliform & E. Coli	SM-9223 B	30 Hours
Metals Analysis on Drinking Water (per element)		
GFAA	EPA 200.9	6 months
(AS, PD, SD, SE, II)	EBA 200 7	6 months
7n)	LFA 200.7	0 11011115
CVAA (Ha)	EPA 245.1	6 months
Primary Pollutant Metals	GFAA/ICP/CVAA	6 months
Drinking Water Analysis		
PH	FPA 150 1	
Acidity	SM-2310 B (4b)	14 days
Alkalinity (Bicarbonate & Carbonate)	SM-2320 B (4a)	14 days
BOD	SM-5210 B	48 hours
Calcium	EPA 200.7	6 months
Chloride	SM-4500 CI	8 days
Chlorine, total	SM-4500 CI	5 hours
Color	SM-2120 B	8 hours
COD	EPA 410.4 (7.3)	28 days
Cyanide	EPA 335.2 (8.7)	28 days
Dissolved Oxygen	SM-4500 O C	8 hours
Fluoride	SM-4500 F C	28 days

Hardness	SM-2340 B	6 months
Magnesium	EPA 200.7	6 months
Nitrogen, ammonia	SM-4500 NH3 E	28 days
	SM-4500 NH3 H	
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
Drinking Water Analysis		
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
	1	I

ORGANICS		
Semi-volatile Organics in Water (SOC)*	(various)	7 days
Volatile Organics	(various)	7 days
Trihalomethanes*	EPA 501.1	7 davs
		·
Gross Alpha & Bata (Radionuclides)*	(various)	7 days
BOD	SM-5210 B	48
		hours
COD	EPA 410.4(7.3)	28 days
Oil and Grease	EPA 413.1(1.2)	28 days
Hardness W/digestion	SM-2340 B	6
		months
Nitrogen, TKN	EPA 351.4	28 days
Nitrogen, ammonia	SM-4500 NH3 F	28 days
Nitrogen, Total Organic	SM-4500 NoraNH3	28 days
Nitrogen, nitrate	SM-4500 NO3	48
	D	hours
Nitrogen, nitrite	SM-4500 NO2	48
	В	hours
Phosphorous, ortho	SM-4500 P E	. 48
		hours
Sulfate	SM-4500 SO4 E	28 days
Solids, dissolved	SM-2540	7 days
Solids, settle able	SM-2540 F	7 days
Solids, suspended	SM-2540 D	7 days
Solids, total	SM-2540 B	7 days
Solids, volatile	SM-2540 E	7 days
Total Organic Carbon	EPA 415.1	28 days
РН	EPA 150.1	

Metals (per element)		
ICP	EPA 200.7	6
(Ag, Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Sb,		months
GFAA	EPA 200.9	6 months
(As, Pb, Ba, Se, Tl)		
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

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	Minimum	Maximum	Storage &
	Туре	Size	Holding Time	Preservation
Acidity	P or G <sup>B</sup>	100ml	24 hrs/14 days	refrigerate
Alkalinity	P or G	200ml	24 hrs/14 days	refrigerate
BOD (5 day)	P or G	1L	6 hrs/48 hrs	refrigerate
Boron	Р	100ml	28 days/6 months	
Chloride	P or G	250ml	28 days	
Chlorine, residual	P or G	500ml	0.5 hr/stat	analyze on site ASAP
COD	P or G	500ml	28 days/28 days	analyze on site ASAP
Color	P or G	500ml	48 hrs/48 hrs	refrigerate
Coliform, Total	P or G	125ml	30 hrs	refrigerate
Conductivity	P or G	500ml	48 hrs/48 hrs	refrigerate
Cyanide, Total	P or G	500ml	28 days/28 days	add NaOH to pH>12
				refrigerate in dark
Fluoride	Р	300ml	28days/ 28 days	
Hardness	P or G	100ml	6 months/6 months	add HNO₃ to pH<2
Metals, general	P <sup>A</sup> or G <sup>A</sup>	250ml	6 months/6 months	add HNO₃ to pH<2
Furnace	P <sup>A</sup> or G <sup>A</sup>	250ml	6 months/6 months	
Flame	P <sup>A</sup> or G <sup>A</sup>	250ml	6 months/6 months	
Mercury	P <sup>A</sup> or G <sup>A</sup>	500ml	28 days/28 days	add HNO₃ to pH<2
Nitrogen	P or G	500ml	7 days/ 28 days	ASAP or add H <sub>2</sub> SO4 to pH<2 &
Ammonia				refrigerate

Nitrate	P or G	100ml	48 hrs/48	ASAP &
			hrs	refrigerate
Nitrate + Nitrite	P or G	200ml	48 hrs/28	ASAP &
			days	refrigerate
Nitrite	P or G	100ml	none/48 hrs	ASAP &
				refrigerate
TKN	P or G	500ml	7 days/28	add H <sub>2</sub> SO <sub>4</sub> to
			days	pH<2
Oxygen,	G (BOD)	300ml		
dissolved				
Electrode			0.5 hrs/stat	ASAP on site
Winkler			8hrs/8 hrs	ASAP on site
рН	P or G	50ml	2 hrs/stat	ASAP on site
Phosphate,	G <sup>A</sup>			
Ortho		100ml	48hrs	filter ASAP
				refrigerate
Total		100ml	28 days/28	refrigerate
			days	
Solids,	P or G			
Dissolved		250ml	7 days	refrigerate
Settleable		1L	48 hrs	refrigerate
Suspended		250ml	7 days	refrigerate
Total		250ml	7 days	refrigerate
Volatile		250ml	7 days	refrigerate
Silica	Р	200ml	28 days/28	refrigerate
			days	
Sulfate	P or G	100ml	28 days/28	refrigerate
			days	
Turbidity	P or G	100ml	24 hrs/48	ASAP/refrigerate,
			hrs	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.

# **Common Laboratory Testing Procedures**



This lab equipment is used for testing parameters in water such as Metals, Pesticides and Hydrocarbons. Often geotechnical water testing that is performed to support characterization regarding the fate and transport of contaminants in soils and sediments. Information such as the grain size distribution provides insight into the absorption, accumulation and movement of contaminants as it may relate to various particle sizes.





Top Photo: Extraction is a process used to concentrate trace levels of materials, in this case metals. Some metals are able to be complexed with an organic chelating agent. The organic chelating agent, Ammonium pyrrolidine dithiocarbamate (APDC), chemically binds the metals in the water. APDC is easily dissolved in the nonpolar organic solvent, methyl isobutyl ketone (MIBK). Because MIBK is nonpolar, it will not dissolve in water and will separate from the water like oil and water.

Bottom Photo: Atomic absorption requires the presence of ground state metal atoms (Me°). The initial process which takes place in an atomic absorption spectrophotometer is to create a population of ground state atoms. This is accomplished in a variety of ways, usually classified as flame and non-flame. The simplest and most common method uses a flame to produce these atoms.





Vapor atomic fluorescence spectroscopy (CVAFS) analytical techniques were designed by the EPA for the analysis of Mercury at low and sub parts per trillion (ppt) concentrations. Low detection limits were developed to support risk assessment, Mercury bioaccumulation in fish is a heightened concern. Thirty-nine states have issued fish consumption advisories due to mercury contamination. Mercury is a toxic pollutant across most regulatory programs (air, water, hazardous waste & pollution prevention). It is persistent and harmful to human health and the environment at relatively low levels.





This lab's Quality Assurance Quality Control (QAQC) methods includes spikes, performance samples, replicates, detection limits and blanks.





Prepared samples stored for metal analysis.





Top Photo: This form shows a typical ion chromatography run will have a standard curve consisting of 4 or 5 points for each ion of interest. A combined ion stock standard is used. The correlation coefficient of the standard curve for each ion should be >.998. The coefficient is calculated by plotting the peak area against the standard concentration using a linear fit.

Bottom Photo: Some labs have the luxury of automatic filling dilution water for BOD bottles. If the BOD bottle is filled too rapidly, excessive agitation and bubbling may result in supersaturated water. This device also has the capability of measuring the oxygen level.



### **Collection of Surface Water Samples**

Representative samples may be collected from rivers, streams and lakes if certain rules are followed:

- 1. Watch out for flash floods! If a flooding event is likely and samples must be obtained, always go in two-person teams for safety. Look for an easy route of escape.
- 2. Select a sampling location at or near a gauging station, so that stream discharge can be related to water-quality loading. If no gauging station exists, then measure the flow rate at the time of sampling, using the streamflow method described below.
- 3. Locate a straight and uniform channel for sampling.
- 4. Unless specified in the sampling plan, avoid sampling locations next to confluences or point sources of contamination.
- 5. Use bridges or boats for deep rivers and lakes where wading is dangerous or impractical.
- 6. Do not collect samples along a bank, as they may not be representative of the surface water body as a whole.
- 7. Use appropriate gloves when collecting the sample.

#### Streamflow Measurement

Before collecting water quality samples, record the stream's flow rate at the selected station. The flow rate measurement is important for estimating contaminant loading and other impacts.

The first step in streamflow measurement is selecting a cross-section. Select a straight reach where the stream bed is uniform and relatively free of boulders and aquatic growth. Be certain that the flow is uniform and free of eddies, slack water and excessive turbulence.

After the cross-section has been selected, determine the width of the stream by stringing a measuring tape from bank-to-bank at right angles to the direction of flow. Next, determine the spacing of the verticals. Space the verticals so that no partial section has more than 5 per cent of the total discharge within it.

At the first vertical, face upstream and lower the velocity meter to the channel bottom, record its depth, then raise the meter to 0.8 and 0.2 of the distance from the stream surface, measure the water velocities at each level, and average them. Move to the next vertical and repeat the procedure until you reach the opposite bank. Once the velocity, depth and distance of the cross-section have been determined, the mid-section method can be used for determining discharge. Calculate the discharge in each increment by multiplying the averaged velocity in each increment by the increment width and averaged depth.

(Note that the first and last stations are located at the edge of the waterway and have a depth and velocity of zero.) Add up the discharges for each increment to calculate total stream discharge. Record the flow in liters (or cubic feet) per second in your field book.

#### **Composite Sampling**

Composite sampling is intended to produce a water quality sample representative of the total stream discharge at the sampling station. If your sampling plan calls for composite sampling, use an automatic type sampler.



### **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.

Handle the samples as little as possible in the field. Each custody sample requires a chain of custody record and may require a seal. If you do not seal individual samples, then seal the containers in which the samples are shipped.

When the samples transfer possession, both parties involved in the transfer must sign, date and note the time on the chain of custody record. If a shipper refuses to sign the chain-of-custody you must seal the samples and chain of custody documents inside a box or cooler with bottle seals or evidence tape. The recipient will then attach the shipping invoices showing the transfer dates and times to the custody sheets. If the samples are split and sent to more than one laboratory, prepare a separate chain of custody record for each sample. If the samples are delivered to after-hours night drop-off boxes, the custody record should note such a transfer and be locked with the sealed samples inside sealed boxes.



Using alcohol to disinfect a special sample tap before obtaining a sample.

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Chain of Custody Example.
# **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.

# **Key Concepts**

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  $MgCl_2$ , which consists of magnesium cations  $Mg^{2+}$  and chloride anions  $Cl^-$ ; or sodium oxide  $Na_2O$ , which consists of sodium cations  $Na^+$  and oxide anions  $O^{2-}$ . 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., NaCl) are very soluble in water, others (e.g., SiO<sub>2</sub>) 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  $H_2O$ ,  $NH_3$ ,  $CI^-$ , and  $CN^-$ . 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  $[Co((OH)_2Co(NH_3)_4)_3]^{6+}$ , an early demonstration that chirality is not inherent to organic compounds. A topical theme within this specialization is supramolecular coordination chemistry.

• **Examples:** [Co(EDTA)]<sup>-</sup>, [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, TiCl<sub>4</sub>(THF)<sub>2</sub>.

#### 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, O<sub>2</sub>, 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 SiO<sub>2</sub>, SnCl<sub>4</sub>, and N<sub>2</sub>O. Many main group compounds can also be classed as "organometallic", as they contain organic groups, e.g.,  $B(CH_3)_3$ ). 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  $S_4N_4$ , diborane  $B_2H_6$ , silicones, buckminsterfullerene  $C_{60}$ .

### 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., TiCl<sub>4</sub>) 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,  $H_2$ , and  $N_2$ . 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 (C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>CH<sub>3</sub>, Ferrocene Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, Molybdenum hexacarbonyl Mo(CO)<sub>6</sub>, Diborane B<sub>2</sub>H<sub>6</sub>, Tetrakis(triphenylphosphine)palladium(0) Pd[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub>

#### **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:** Fe<sub>3</sub>(CO)<sub>12</sub>, B<sub>10</sub>H<sub>14</sub>, [Mo<sub>6</sub>Cl<sub>14</sub>]<sup>2-</sup>, 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, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>

#### **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,  $Cu^{II}_{2}(OAc)_{4}(H_{2}O)_{2}$  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  $NH_3$  is pyramidal whereas  $CIF_3$  is T-shaped.

For the transition metals, crystal field theory allows one to understand the magnetism of many simple complexes, such as why  $[Fe^{III}(CN)_6]^{3-}$  has only one unpaired electron, whereas  $[Fe^{III}(H_2O)_6]^{3+}$  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  $[M(H_2O)_6]^{n+}$ :

$$[M(H_2O)_6]^{n+} + 6 H_2O^* \rightarrow [M(H_2O^*)_6]^{n+} + 6 H_2O$$

where H<sub>2</sub>O\* denotes isotopically enriched water, e.g., H<sub>2</sub><sup>17</sup>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:

 $[MnO_4]^- + [Mn^*O_4]^{2-} \rightarrow [MnO_4]^{2-} + [Mn^*O_4]^{-}$ 

#### **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.

## **Characterization of Inorganic Compounds**

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 <sup>1</sup>H and <sup>13</sup>C many other "good" NMR nuclei (e.g., <sup>11</sup>B, <sup>19</sup>F, <sup>31</sup>P, and <sup>195</sup>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.

- o 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 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 cryogens. Solids are typically prepared using tube furnaces, the reactants and products being sealed in containers, often made of fused silica (amorphous SiO<sub>2</sub>) but sometimes more specialized materials such as welded Ta tubes or Pt "boats". Products and reactants are transported between temperature zones to drive reactions.

# **pH Section**



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

The pH scale is traceable to a set of standard solutions whose pH is established by international agreement. 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.

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

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



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Mathematically, pH is 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 concept of p[H] was first introduced by Danish chemist Søren Peder Lauritz Sørensen at the Carlsberg Laboratory 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:  $p_{H}$ .

#### Alkalinity

Alkalinity is the name given to 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

## pH Definition and Measurement

CONCENTRATION OF HYDROGEN IONS COMPARED TO DISTILLED H2O	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	100 (100 (100 (100 (100 (100 (100 (100	"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

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

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

This definition was adopted because ion-selective electrodes, which are used to measure pH, respond to activity.

Ideally, electrode potential, *E*, follows the Nernst equation, which, for the hydrogen ion can be written as

$$E = E^o + \frac{RT}{F} \ln (a_H +) = E^o - \frac{2.303RT}{F} pH$$

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<sup>+</sup> number of electrons transferred is one. It follows that electrode potential is proportional to pH when pH is defined in terms of activity.

Precise measurement of pH is presented in International Standard ISO 31-8 as follows: A galvanic cell is set up to measure the electromotive force (E.M.F.) 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 hydrogenion selective electrode is a standard hydrogen electrode.

Reference electrode | concentrated solution of KCI || 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.



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 
$$\overline{2.303RT/F}$$
 the "Nernstian slope".

To apply this process in practice, 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 are used in order to accommodate the fact that the "slope" may differ slightly from ideal.

To implement this approach to calibration, 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. 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 therefore pH is a dimensionless quantity.

#### pH Indicators

Indicators may be used to measure pH, by making use of the fact that their color changes with pH. 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. More precise measurements are possible if the color is measured spectrophotometrically, using a colorimeter of 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.

#### рОН

pOH is sometimes used as a measure of the concentration of hydroxide ions, 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

$$[OH^{-}] = \frac{K_W}{[H^+]}$$
  
where K<sub>W</sub> is the self-ionization constant of water. Taking logarithms  
pOH = pK<sub>W</sub> - pH

So, at room temperature pOH  $\approx$  14 – 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 mol dm<sup>-3</sup> acid) and above about 10.5 (ca. 0.0003 mol dm<sup>-3</sup> alkali) requires special procedures because, when using the glass electrode, the Nernst law breaks down under those conditions. Various factors contribute to this. It cannot be assumed that liquid junction potentials are independent of pH.

Also, extreme pH implies that the solution is 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 Na<sup>+</sup> and K<sup>+</sup> in the solution. Specially constructed electrodes are available which partly overcome these problems. Runoff from 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,  $a_{H}^{+}$ , can be defined as:

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

where  $\mu_{H^+}$  is the chemical potential of the hydrogen ion,  $\mu^{\circ}_{H^+}$  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 a salt such as sodium chloride is slightly different from that of pure water, even though the salt is neither acidic nor basic. This is because 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. For example, 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. However, pH measurement is 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 ( $\sim 0.1$ ) compared to that of seawater ( $\sim 0.7$ ), 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, and the new pH scale is referred to as the **total scale**, often denoted as  $pH_T$ .

# 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.

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

The pH of a solution containing a weak acid requires the solution of a quadratic equation.

The pH of a solution containing a weak base may require the solution of a cubic equation.

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

$$2H_2O \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

with a dissociation constant, K<sub>w</sub> defined as

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

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

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



# STATES OF MATTER

## **Wastewater Priory Pollutants Section**



## Wastewater/Pretreatment Sampling General Information

In accordance with the Clean Water Act and General Pretreatment Program Regulations, the POTW conducts a variety of sampling activities which must be closely coordinated.

Each of these activities is briefly described below.

#### Permit Application Policy Example

All industrial users that require a permit must be sampled to determine the characteristics of the wastes to be discharged into the POTW's sewer system.

Prior to the issuance of a permit for existing industrial users, the POTW samples the user's effluent, and performs the analyses required by the applicable discharge standards (i.e., Categorical standards or local limits).



- ✓ For new industrial users, estimates of the wastes to be discharged into the POTW's sewer system must be submitted along with the permit application.
- ✓ No sampling would be performed at these new facilities, since they do not presently discharge wastes into the sewer system.

✓ A four-day sampling program is usually conducted at each site to collect both composite and grab (for pollutants not amenable to composite sampling) samples as needed.

#### Sewer System Evaluation Policy Example

On a regular basis, selected locations in the sewer system are sampled to develop background data for purposes of updating the local limits, and to screen areas for higher than **"background"** pollutant levels. In addition, problem areas are sampled on an as needed basis to determine potential sources of POTW Code violations that either occur on a frequent basis, or are the result of a slug load to the sewer system. To monitor sewers for background information, the sampling program would typically be conducted over a four-day period. In instances where the intent is to determine sources of pollutants and/or slug loads, the length of the program would vary.

#### Multi-City Users (Metering Stations) Policy Example

All wastewater, which is transported to the POTW Treatment Plant from the Multi-City users, is analyzed for pollutants of concern to the Industrial Pretreatment Program. The sampling program is conducted over a five-day period to obtain four days of sampling data at each sewer location (i.e., a metering station) on a quarterly basis. Once the sampling dates have been determined, the Water Quality Inspector will notify, in writing, the Sub-regional Organizational Group (**SROG**) or equivalent representative for that City of the dates when the sampling will be conducted.

#### Sampling Safety Policy Example

Upon arrival at the site, safety is the priority. A visual inspection must be completed prior to any entry. The site must be free of any obstructions or hazards which may cause injury when entering sampling area. If there are any problems detected, the SROG or equivalent representative and the Water Quality Inspector should be notified, and no entry should be attempted until the problem has been corrected.

#### Metering and Sampling Stations Qualify As Confined Spaces

If all safety criteria have been met, prepare equipment for the site. Check the assignment sheet to determine what parameters are required to be sampled, which in turn determines the type of tubing to be used, (i.e. Tygon or Teflon).

The sampler must be completely assembled before performing QA/QC procedures. After QA/QC is complete, a sufficient amount of weight must be attached to the tubing to keep the strainer submerged in the effluent for proper siphoning of the sample, without allowing the strainer to hit the bottom of the flume. Make sure the intake tubing does not kink.f the metering station has a flow meter, you may connect either their cable or a POTW cable to the sampler from the flow meter.

Occasionally, you will set up a flow meter to have a comparison reading. Determine the pulse rate and proper setting from the flow, and program the sampler. After entering the data into the sampler, wait to make sure the equipment is pulling samples. After the initial set-up of the sampling equipment, samples will be collected during the remainder of the sampling period.

Split samples may be requested by the SROG or equivalent representative. If the volume of the sample is adequate, these may be given, provided the representative supplies the containers and allows the POTW Inspector to pour off the samples.

Upon exiting the confined space, continue to follow the confined space entry procedures as outlined by OSHA Standards. When you return to the sampling vehicle, you must immediately perform field tests and preserve the samples according to the techniques set forth in by Standard Methods or the State/Federal Rule.

All paper work must be filled out completely before the sampling crew's departure. This paperwork includes the chain of custody which is turned in to the laboratory with the samples, "*Metering Station Field Observation Form*" or equivalent form that remains with the sampling site file, and the Multi-City Metering Station Sample Record of which the original is given to the Water Quality Inspector and the copy is given to the SROG or equivalent representative. If there is not a representative at the site, these copies will be turned over to the Water Quality Inspector with the originals at the end of the week.

# Remember, all paperwork should be completed prior to leaving site.





The National Pretreatment Program is unique in that the General Pretreatment Regulations require all large POTWs (i.e., those designed to treat flows of more than 5 million gallons per day) and smaller POTWs with significant industrial discharges to establish local pretreatment programs. These local programs must enforce all national pretreatment standards and requirements in addition to any more stringent local requirements necessary to protect site-specific conditions at the POTW.



Many industries have a need to treat water to obtain very high quality water for demanding purposes. Water treatment produces organic and mineral sludges from filtration and sedimentation. Ion exchange using natural or synthetic resins removes calcium, magnesium and carbonate ions from water, replacing them with hydrogen and hydroxyl ions.

Regeneration of ion exchange columns with strong acids and alkalis produces a wastewater rich in hardness ions which are readily precipitated out, especially when in admixture with other wastewater.

Toxic materials including many organic materials, metals (such as zinc, silver, cadmium, thallium, etc.) acids, alkalis, non-metallic elements (such as arsenic or selenium) are generally resistant to biological processes unless very dilute. Metals can often be precipitated out by changing the pH or by treatment with other chemicals. Many, however, are resistant to treatment or mitigation and may require concentration followed by landfilling or recycling. Dissolved organics can be *incinerated* within the wastewater by Advanced Oxidation Process.

# List of WWT/Pretreatment Acronyms used in this Course

#### Acronym Full Phrase

AA	Approval Authority
AO	Administrative Order
BAT	Best Available Technology Economically Achievable
BCT	Best Conventional Pollutant Control Technology
BMP	Best Management Practices
BMR	Baseline Monitoring Report
BOD5	5-day Biochemical Oxygen Demand
BPJ	Best Professional Judgment
BPT	Best Practicable Control Technology Currently Available
CA	Control Authority
CFR	Code of Federal Regulations
CIU	Categorical Industrial User
CSO	Combined Sewer Overflow
CWA	Clean Water Act (formerly referred to as the Federal Water Pollution
	Control Act or Federal Water Pollution Control Act Amendments of 1972)
	Pub. L. 92-500. as amended by Pub. L. 95-217. Pub. L. 95-576. Pub. L.
	96-483. Pub. L. 97-117. and Pub. L. 100-4. 33 U.S.C. 1251 et seg.
CWF	Combined Wastestream Formula
CWT	Centralized Waste Treater
DMR	Discharge Monitoring Report
DSE	Domestic Sewage Exclusion
DSS	Domestic Sewage Study
ELG	Effluent Limitations Guideline
EPA	Environmental Protection Agency
EPCRA	Emergency Preparedness and Community Right to Know Act
ERP	Enforcement Response Plan
FDF	Fundamentally Different Factors
FR	Federal Register
FWA	Flow Weighted Average
GPD	Gallons per Day
IU	Industrial User
LEL	Lower Explosive Limit
MAHL	Maximum Allowable Headworks Loading
MAIL	Maximum Allowable Industrial Loading
MGD	Million Gallons per Day
NAICS	North American Industry Classification System (replaces SIC coding in 1998)
NOV	Notice of Violation
NPDES	National Pollutant Discharge Elimination System
NRDC	Natural Resources Defense Council
NSPS	New Source Performance Standard
O&G	Oil and Grease

O&M	Operations and Maintenance
OCPSF	Organic Chemicals, Plastics, and Synthetic Fibers
P2	Pollution Prevention
PCI	Pretreatment Compliance Inspection
PCS	Permit Compliance System
PIRT	Pretreatment Implementation Review Task Force
POTW	Publicly Owned Treatment Works
PSES	Pretreatment Standards for Existing Sources
PSNS	Pretreatment Standards for New Sources
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
SDS	Safety Data Sheet
SIC	Standard Industrial Classification
SIU	Significant Industrial User
SPCC	Spill Prevention Control and Countermeasures
SNC	Significant Noncompliance
SSO	Sanitary Sewer Overflow
SUO	Sewer Use Ordinance
TCLP	Toxicity Characteristic Leaching Procedure
TIE	Toxicity Identification Evaluation
TOMP	Toxic Organic Management Program
TRE	Toxicity Reduction Evaluation
TRI	Toxic Release Inventory
TSS	Total Suspended Solids
TTO	Total Toxic Organics
USC	United States Code
UST	Underground Storage Tank
WET	Whole Effluent Toxicity
WWTP	Wastewater Treatment Plant



### WWT Glossary

This glossary includes a collection of terms used in this course and an explanation of each term.

#### Act or "the Act" [40 CFR §403.3(b)]

The Federal Water Pollution Control Act, also known as the Clean Water Act, as amended, 33 USC 1251*et.seq.* 

#### **Approval Authority** [40 CFR §403.3(c)]

The Director in an NPDES State with an approved State Pretreatment Program and the appropriate EPA Regional Administrator in a non-NPDES State or State without an approved pretreatment program.

#### Approved POTW Pretreatment Program or Program [40 CFR §403.3(d)]

A program administered by a POTW that meets the criteria established in 40 CFR Part 403 and which has been approved by a Regional Administrator or State Director.

#### Approved State Pretreatment Program

A program administered by a State that meets the criteria established in 40 CFR §403.10 and which has been approved by a Regional Administrator

#### **Approved/Authorized State**

A State with an NPDES permit program approved pursuant to section 402(b) of the Act and an approved State Pretreatment Program.

#### **Baseline Monitoring Report (BMR)** [paraphrased from 40 CFR §403.12(b)]

A report submitted by categorical industrial users (CIUs) within 180 days after the effective date of an applicable categorical standard, or at least 90 days prior to commencement of discharge for new sources, which contains specific facility information, including flow and pollutant concentration data. For existing sources, the report must also certify as to the compliance status of the facility with respect to the categorical standards.

#### 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.

#### Blowdown

The discharge of water with high concentrations of accumulated solids from boilers to prevent plugging of the boiler tubes and/or steam lines. In cooling towers, blowdown is discharged to reduce the concentration of dissolved salts in the recirculating cooling water.

#### Bypass [40 CFR §403.17(a)]

The intentional diversion of wastestreams from any portion of an Industrial User's treatment facility.

#### Categorical Industrial User (CIU)

An industrial user subject to National categorical pretreatment standards.

#### Categorical Pretreatment Standards [40 CFR § 403.6 and 40 CFR Parts 405-471]

Limitations on pollutant discharges to POTWs promulgated by the EPA in accordance with Section 307 of the Clean Water Act, that apply to specific process wastewater discharges of particular industrial categories.

#### 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.

#### 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.

#### Clean Water Act (CWA)

The common name for the Federal Water Pollution Control Act. Public law 92-500; 33 U.S.C. 1251 et seq.; legislation which provides statutory authority for both NPDES and Pretreatment Programs.

#### Code of Federal Regulations (CFR)

A codification of Federal rules published annually by the Office of the Federal Register National Archives and Records Administration. Title 40 of the CFR contains the regulations for *Protection of the Environment*.

#### Combined Sewer Overflow (CSO)

A discharge of untreated wastewater from a combined sewer system at a point prior to the headworks of a publicly owned treatment works. CSOs generally occur during wet weather (rainfall or snowfall). During periods of wet weather, these systems become overloaded, bypass treatment works, and discharge directly to receiving waters.

#### **Combined Wastestream Formula (CWF)** [paraphrased from 40 CFR §403.6(e)]

Procedure for calculating alternative discharge limits at industrial facilities where a regulated wastestream from a categorical industrial user is combined with other wastestreams prior to treatment.

#### **Compliance Schedule**

A schedule of remedial measures included in a permit or an enforcement order, including a sequence of interim requirements (for example, actions, operations, or milestone events) that lead to compliance with the CWA and regulations.

#### **Composite Sample**

Sample composed of two or more discrete samples. The aggregate sample will reflect the average water quality covering the compositing or sample period.

#### **Concentration-based Limit**

A limit based upon the relative strength of a pollutant in a wastestream, usually expressed in mg/l.

#### **Continuous Discharge**

A discharge that occurs without interruption during the operating hours of a facility, except for infrequent shutdowns for maintenance, process changes or similar activities.

#### **Control Authority** [paraphrased from 40 CFR § 403.12(a)]

A POTW with an approved pretreatment program or the approval authority in the absence of a POTW pretreatment program.

#### **Conventional Pollutants**

BOD, TSS, fecal coliform, oil and grease, and pH

#### **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.

#### **Detection Limit**

The minimum concentration of an analyte (substance) that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero as determined by the procedure set forth in 40 CFR Part 136, Appendix B.

#### **Development Document**

Detailed report of studies conducted by the U.S. EPA for the purpose of establishing effluent guidelines and categorical pretreatment standards.

#### Dilute Wastestream [paraphrased from 40 CFR §403.6(e)(1)(i)]

For purposes of the combined wastestream formula, the average daily flow (at least a 30-day average) from : (a) boiler blowdown streams, non-contact cooling streams, storm water streams, and demineralized backwash streams; provided, however, that where such streams contain a significant amount of a pollutant, and the combination of such streams, prior to treatment, with an industrial user's regulated process wastestream(s) will result in a substantial reduction of that pollutant, the Control Authority, upon application of the industrial user, may exercise its discretion to determine whether such stream(s) should be classified as diluted or unregulated. In its application to the Control Authority, the industrial user must provide engineering, production,

sampling and analysis, and such other information so the control authority can make its determination; or (b) sanitary wastestreams where such streams are not regulated by a categorical

pretreatment standard; or (c) from any process wastestreams which were, or could have been, entirely exempted from categorical pretreatment standards pursuant to paragraph 8 of the NRDC v. Costle Consent

Decree (12 ERC 1833) for one more of the following reasons (see Appendix D of 40 CFR Part 403):

a. the pollutants of concern are not detectable in the effluent from the industrial user (paragraph(8)(a)(iii));

b. the pollutants of concern are present only in trace amounts and are neither causing nor likely to cause toxic effects (paragraph (8)(a)(iii));

c. the pollutants of concern are present in amounts too small to be effectively deduced by technologies known to the Administrator (paragraph (8)(a)(iii)); or

d. the wastestream contains only pollutants which are compatible with the POTW (paragraph (8)(b)(I)).

#### Effluent Limitations Guideline

Any effluent limitations guidelines issued by the EPA pursuant to Section 304(b) of the CWA. These regulations are published to adopt or revise a national standard prescribing restrictions on quantities, rates, and concentrations of chemical, physical, biological, and other constituents which are discharged from point sources, in specific industrial categories (e.g., metal finishing, metal molding and casting, etc.).

#### **Enforcement Response Plan** [paraphrased from 40 CFR §403.8(f)(5)]

Step-by-step enforcement procedures followed by Control Authority staff to identify, document, and respond to violations.

#### **Existing Source**

Any source of discharge, the construction or operation of which commenced prior to the publication by the EPA of proposed categorical pretreatment standards, which will be applicable to such source if the standard is thereafter promulgated in accordance with Section 307 of the Act.

#### Federal Water Pollution Control Act (FWPCA)

The title of Public law 92-500; 33 U.S.C. 1251 et seq., also known as the Clean Water Act (CWA), enacted October 18, 1972.

#### Flow Weighted Average Formula (FWA) [paraphrased from 40 CFR §403.6(e)]

A procedure used to calculate alternative limits where wastestreams regulated by a categorical pretreatment standard and nonregulated wastestreams combine after treatment but prior to the monitoring point.

#### Flow Proportional Composite Sample

Combination of individual samples proportional to the flow of the wastestream at the time of sampling.

#### Fundamentally Different Factors [paraphrased from 40 CFR §403.13]

Case-by-case variance from categorical pretreatment standards based on the factors considered by the EPA in developing the applicable category/subcategory being fundamentally different than factors relating to a specific industrial user.

#### **General Prohibitions** [40 CFR §403.5(a)(1)]

No user shall introduce into a POTW any pollutant(s) which cause pass through or interference.

#### **Grab Sample**

A sample which is taken from a wastestream on a one-time basis with no regard to the flow of the wastestream and without consideration of time. A single grab sample should be taken over a period of time not to exceed 15 minutes.

#### **Indirect Discharge or Discharge** [40 CFR §403.3(g)]

The introduction of pollutants into a POTW from any non-domestic source regulated under section 307(b), (c), or (d) of the Act.

#### Industrial User (IU) or User [40 CFR §403.3(h)]

A source of indirect discharge.

#### Industrial Waste Survey

The process of identifying and locating industrial users and characterizing their industrial discharge.

#### Inhibition Concentration

Estimate of the toxicant concentration that would cause a given percent reduction (e.g., IC25) in a nonlethal biological measurement of the test organisms, such as reproduction or growth.

#### **Interference** [paraphrased from 40 CFR §403.3(i)]

A discharge which, alone or in conjunction with a discharge or discharges from other sources, both: (1)inhibits or disrupts the POTW, its treatment processes or operations, or its sludge processes, use or disposal; and (2) therefore is a cause of a violation of any requirement of the POTW's NPDES permit (including an increase in the magnitude or duration of a violation) or of the prevention of sewage sludge use or disposal in compliance with ... [applicable] statutory provisions and regulations or permits issued there under (or more stringent State or local regulations)

#### Local Limits [paraphrased 40 CFR § 403.5(c)]

Specific discharge limits developed and enforced by POTWs upon industrial or commercial facilities to implement the general and specific discharge prohibitions listed in 40 CFR  $\S$ 403.5(a)(1) and (b).

#### Monthly Average

The arithmetic average value of all samples taken in a calendar month for an individual pollutant parameter. The monthly average may be the average of all grab samples taken in a given calendar month, or the average of all composite samples taken in a given calendar month.

#### National Pollutant Discharge Elimination System (NPDES)

The national program for issuing, modifying, revoking and reissuing, terminating, monitoring and enforcing discharge permits from point sources to waters of the United States, and imposing and enforcing pretreatment requirements, under sections 307, 402, 318, and 405 of the CWA.

#### National Pretreatment Standard or Pretreatment Standard or Standard

*[40 CFR §403.3(j)]* Any regulation containing pollutant discharge limits promulgated by the EPA in accordance with section 307(b) and (c) of the Act, which applies to Industrial Users. This term includes prohibitive discharge limits established pursuant to §403.5.

#### **New Source** [40 CFR §403.3(k)]

Any building, structure, facility or installation from which there is or may be a discharge of pollutants, the construction of which commenced after the publication of proposed Pretreatment Standards under section 307(c) of the Act which will be applicable to such source if such standards are thereafter promulgated in accordance with that section *provided that*:

(a) The building, structure, facility or installation is constructed at a site at which no other discharge source is located; or

(b) The building, structure, facility or installation totally replaces the process or production equipment that causes the discharge of pollutants at an existing source; or

(c) The production or wastewater generating processes of the building, structure, facility, or installation are substantially independent of an existing source at the same site. In determining whether these are substantially independent, factors such as the extent to which the new facility is integrated with the existing plant, and the extent to which the new facility is engaged in the same general type of activity as the existing source, should be considered.

Construction on a site at which an existing source is located results in a modification rather than a new source if the construction does not create a new building, structure, facility, or installation meeting the criteria of paragraphs (k)(1)(ii), or (k)(1)(iii) of this section but otherwise alters, replaces, or adds to existing processor production equipment.

Construction of a new source, as defined under this paragraph has commenced if the owner or operator has:

(i) Begun, or caused to begin as part of a continuous onsite construction program:

(A) Any placement, assembly, or installation of facilities or equipment; or

(B) Significant site preparation work including clearing, excavation, or removal of existing buildings, structures, or facilities which is necessary for the placement, assembly, or installation of new source facilities or equipment, or

(C) Entered into a binding contractual obligation for the purchase of facilities or equipment which are intended to be used in its operation within a reasonable time. Options to purchase or contracts which can be terminated or modified without substantial loss, and contracts for feasibility, engineering, and design studies do not constitute a contractual obligation under this paragraph.

#### 90-Day Final Compliance Report [40 CFR §403.12(d)]

A report submitted by categorical industrial users within 90 days following the date for final compliance with the standards. This report must contain flow measurement (of regulated process streams and other streams), measurement of pollutants, and a certification as to whether the categorical standards are being met.

#### **Nonconventional Pollutants**

Any pollutant that is neither a toxic pollutant nor a conventional pollutant (e.g., manganese, ammonia, etc.)

#### Non-Contact Cooling Water

Water used for cooling which does not come into direct contact with any raw material, intermediate product, waste product, or finished product. The only pollutant contributed from the discharge is heat.

#### Non-Regulated Wastestream

Unregulated and dilute wastestreams (not regulated by categorical standards).

#### **Pass Through** [40 CFR §403.3(n)]

A discharge which exits the POTW into waters of the United States in quantities or concentrations which, alone or in conjunction with a discharge or discharges from other sources, is a cause of a violation of any requirement of the POTW's NPDES permit (including an increase in the magnitude or duration of a violation).

#### **Periodic Compliance Report** [paraphrased from 40 CFR §403.12(e) & (h)]

A report on compliance status submitted by categorical industrial users and significant noncategorical industrial users to the control authority at least semiannually (once every six months).

#### Point Source [40 CFR 122.2]

Any discernible, confined, and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, well, discrete fixture, container, rolling stock concentrated animal feeding operation vessel, or other floating craft from which pollutants are or may be discharged.

#### Pollutant [40 CFR 122.2]

Dredged spoil, solid waste, incinerator residue, filter backwash, sewage, garbage, sewage sludge, munitions, chemical wastes, biological materials, radioactive materials (except those regulated under the Atomic Energy Act of 1954, as amended (42 U.S.C. 2011 et seq.)), heat, wrecked or discarded equipment, rock, sand, cellar dirt, and industrial, municipal and agricultural waste discharged into water.

#### **Pretreatment** [paraphrased from 40 CFR §403.3(q)]

The reduction of the amount of pollutants, the elimination of pollutants, or the alteration of the nature of pollutant properties in wastewater prior to or in lieu of discharging or otherwise introducing such pollutants into a POTW.

#### **Pretreatment Requirements** [40 CFR §403.3(r)]

Any substantive or procedural requirement related to Pretreatment, other than a National Pretreatment Standard, imposed on an Industrial User.

#### Pretreatment Standards for Existing Sources (PSES)

Categorical Standards and requirements applicable to industrial sources that began construction prior to the publication of the proposed pretreatment standards for that industrial category. (see individual standards at 40 CFR Parts 405-471.)

#### Pretreatment Standards for New Sources (PSNS)

Categorical Standards and requirements applicable to industrial sources that began construction after the publication of the proposed pretreatment standards for that industrial category. (see individual standards at 40 CFR Parts 405-471.)

#### **Priority Pollutant**

Pollutant listed by the Administrator of the EPA under Clean Water Act section 307(a). The list of the current 126 Priority Pollutants can be found in 40 CFR Part 423 Appendix A.

#### **Process Wastewater**

Any water which, during manufacturing or processing, comes into contact with or results from the production or use of any raw material, intermediate product, finished product, byproduct, or waste product.

#### **Production-Based Standards**

A discharge standard expressed in terms of pollutant mass allowed in a discharge per unit of product manufactured.

#### Publicly Owned Treatment Works (POTW) [40 CFR §403.3(o)]

A treatment works as defined by section 212 of the Act, which is owned by a State or municipality (as defined by section 502(4) of the Act). This definition includes any devices or systems used in the storage, treatment, recycling, and reclamation of municipal sewage or industrial wastes of a liquid nature. It also includes sewers, pipes or other conveyances only if they convey wastewater to a POTW Treatment Plant.

The term also means the municipality as defined in section 502(4) of the Act, which has jurisdiction over the Indirect Discharges to and the discharges from such a treatment works.

#### **Regulated Wastestream**

For purposes of applying the combined wastestream formula, a wastestream from an industrial process that is regulated by a categorical standard.

#### **Removal Credit** [paraphrased from 40 CFR §403.7]

Variance from a pollutant limit specified in a categorical pretreatment standard to reflect removal by the POTW of said pollutant.

#### **Representative Sample**

A sample from a wastestream that is as nearly identical as possible in composition to that in the larger volume of wastewater being discharged and typical of the discharge from the facility on a normal operating day.

#### Sanitary Sewer Overflow (SSO)

Untreated or partially treated sewage overflows from a sanitary sewer collection system.

#### Self-Monitoring

Sampling and analyses performed by a facility to ensure compliance with a permit or other regulatory requirements.

#### Sewer Use Ordinance (SUO)

A legal mechanism implemented by a local government entity which sets out, among others, requirements for the discharge of pollutants into a publicly owned treatment works.

#### **Significant Industrial User (SIU)** [paraphrased from 40 CFR §403.3(t)]

(1) All users subject to Categorical Pretreatment Standards under 40 CFR 403.6 and 40 CFR chapter I, subchapter N; and (2) Any other industrial user that: discharges an average of 25,000 gallons per day or more of process wastewater to the POTW (excluding sanitary, noncontact cooling and boiler blowdown wastewater); contributes a process wastestream which makes up 5 percent or more of the average dry weather hydraulic or organic capacity of the POTW treatment plant; or is designated as such by the Control Authority as defined in 40 CFR 403.12(a) on the basis that the industrial user has a reasonable potential for adversely affecting the POTW's operation or for violating any pretreatment standard or requirement (in accordance with 40 CFR 403.8(f)(6)].

#### Significant Noncompliance (SNC) [40 CFR §403.8(f)(2)(vii)]

Industrial user violations meeting one or more of the following criteria:

1) Chronic violations of wastewater discharge limits, defined here as those in which sixty-six percent or more of all of the measurements taken during a six month period exceed (by any magnitude) the daily maximum limit or the average limit for the same pollutant parameter;

2) Technical Review Criteria (TRC) violations, defined here as those in which thirty-three percent or more of all of the measurements for each pollutants parameter taken during a six-month period equal or exceed the product of the daily maximum limit or the average limit multiplied by the applicable TRC (TRC=1.4 for BOD, TSS, fats, oil, and grease, and 1.2 for all other pollutants except pH);

3) Any other violation of a pretreatment effluent limit (daily maximum or longer-term average) that the Control Authority determines has caused, alone or in combination with other dischargers, interference or pass through (including endangering the health of POTW personnel or the general public);

4) Any discharge of a pollutant that has caused imminent endangerment to human health, welfare or to the environment or has resulted in the POTW's exercise of its emergency authority under paragraph (f)(1)(vi)(B) of this section to halt or prevent such a discharge;

5) Failure to meet, within 90 days after the schedule date, a compliance schedule milestone contained in a local control mechanism or enforcement order for starting construction, completing construction, or attaining final compliance;

6) Failure to provide, within 30 days after the due date, required reports such as baseline monitoring reports, 90-day compliance reports, periodic self-monitoring reports, and reports on compliance with compliance schedules;

7) Failure to accurately report noncompliance;

8) Any other violation or group of violations which the Control Authority determines will adversely affect the operation or implementation of the local pretreatment program.

#### Slug Discharge [40 CFR §403.8(f)(2)(v)]

Any discharge of a non-routine, episodic nature, including but not limited to, an accidental spill or a noncustomary batch discharge.

#### **Specific Prohibitions** [40 CFR §403.5(b)]

The following pollutants shall not be introduced into a POTW:

1) Pollutants which create a fire or explosion hazard in the POTW, including but not limited to, wastestreams with a closed cup flashpoint of less than 140 degrees Fahrenheit or 60 degrees Centigrade using the test methods specified in 40 CFR Part 261.21;

2) Pollutants which will cause corrosive structural damage to the POTW, but in no case discharges with pH lower than 5.0, unless the works is specifically designed to accommodate such discharges;

3) Solid or viscous pollutants in amounts which will cause obstruction to the flow in the POTW resulting in interference;

4) Any pollutant, including oxygen-demanding pollutants (BOD, etc.) Released in a discharge at a flow rate and/or concentration which will cause interference with the POTW;

5) Heat in amounts which will inhibit biological activity in the POTW resulting in interference, but in no case heat in such quantities that the temperature at the POTW treatment plant exceeds 40°C (104°F) unless the Approval Authority, upon request of the POTW, approves alternative temperature limits;

6) Petroleum oil, nonbiodegradable cutting oil, or products of mineral oil origin in amounts that will cause interference or pass through;

7) Pollutants which result in the presence of toxic gases, vapors, or fumes within the POTW in a quantity that may cause acute worker health and safety problems;

8) Any trucked or hauled pollutants, except at discharge points designated by the POTW.

#### Standard Industrial Classification (SIC)

A system developed by the U.S. Office of Management and Budget that is used to classify various types of business entities. Effective in 1998, the SIC scheme is replace by the North American Industry Classification System (**NAICS**), although the EPA has not yet implemented this change.

#### **Storm Water**

Rain water, snowmelt, and surface runoff and drainage.

#### Time Proportional Composite Sample

A sample consisting of a series of aliquots collected from a representative point in the discharge stream at equal time intervals over the entire discharge period on the sampling day.

#### **Toxic Pollutant**

Any pollutant listed as toxic under section 307(a)(1) of the CWA, or in the case of sludge use or disposal practices, any pollutant identified in regulations implementing section 405(d) of the CWA.

#### **Toxicity Reduction Evaluation**

A site-specific study conducted in a stepwise process designed to identify the causative agent(s) of effluent toxicity, isolate the sources of toxicity, evaluate the effectiveness of toxicity control options, and then confirm the reduction in effluent toxicity.

#### **Toxicity Test**

A procedure to determine the toxicity of a chemical or an effluent using living organisms. A toxicity test measures the degree of effect on exposed test organisms of a specific chemical or effluent.

#### **Toxicity Identification Evaluation**

Set of procedures to identify the specific chemicals responsible for effluent toxicity.

#### **Unregulated Wastestream**

For purposes of applying the combined wastestream formula, a wastestream not regulated by a categorical standard nor considered a dilute wastestream.

#### **Upset** [paraphrased from 40 CFR §403.16(a)]

An exceptional incident in which there is unintentional and temporary noncompliance with categorical Pretreatment Standards because of factors beyond the reasonable control of the Industrial User. An Upset does not include noncompliance to the extent caused by operational error, improperly designed treatment facilities, inadequate treatment facilities, lack of preventative maintenance, or careless or improper operation.

#### 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.



TREATMENT OF SEWAGE DIAGRAM

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#### 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.
## Clean Water Act (Wastewater Information)

#### 33 U.S.C. s/s 1251 et seq. (1977)

The Clean Water Act is a 1977 amendment to the Federal Water Pollution Control Act of 1972, which set the basic structure for regulating discharges of pollutants to waters of the United States.

The law gave the EPA the authority to set effluent standards on an industry basis (technologybased) and continued the requirements to set water quality standards for all contaminants in surface waters. The CWA makes it unlawful for any person to discharge any pollutant from a point source into navigable waters unless a permit (**NPDES**) is obtained under the act.

The 1977 amendments focused on toxic pollutants. In 1987, the CWA was reauthorized and again focused on toxic substances, authorized citizen suit provisions, and funded sewage treatment plants (**POTWs**) under the Construction Grants Program.

The CWA provides for the delegation by the EPA of many permitting, administrative, and enforcement aspects of the law to state governments. In states with the authority to implement CWA programs, the EPA still retains oversight responsibilities.

In 1972, Congress enacted the first comprehensive national clean water legislation in response to growing public concern for serious and widespread water pollution. The Clean Water Act is the primary federal law that protects our nation's waters, including lakes, rivers, aquifers and coastal areas.

Lake Erie was dying. The Potomac River was clogged with blue-green algae blooms that were a nuisance and a threat to public health. Many of the nation's rivers were little more than open sewers and sewage frequently washed up on shore. Fish kills were a common sight. Wetlands were disappearing at a rapid rate.

Today, the quality of our waters has improved dramatically as a result of a cooperative effort by federal, state, tribal and local governments to implement the pollution control programs established in 1972 by the Clean Water Act.

The Clean Water Act's primary objective is to restore and maintain the integrity of the nation's waters. This objective translates into two fundamental national goals:

- eliminate the discharge of pollutants into the nation's waters, and
- achieve water quality levels that are fishable and swimmable.

The Clean Water Act focuses on improving the quality of the nation's waters. It provides a comprehensive framework of standards, technical tools and financial assistance to address the many causes of pollution and poor water quality. This includes municipal and industrial wastewater discharges, polluted runoff from urban and rural areas, and habitat destruction.

#### For example, the Clean Water Act:

requires major industries to meet performance standards to ensure pollution control; charges states and tribes with setting specific water quality criteria appropriate for their waters and developing pollution control programs to meet them; provides funding to states and communities to help them meet their clean water infrastructure needs; protects valuable wetlands and other aquatic habitats through a permitting process that ensures development and other activities are conducted in an environmentally sound manner.

After 25 years, the Act continues to provide a clear path for clean water and a solid foundation for an effective national water program.

#### In 1972:

Only a third of the nation's waters were safe for fishing and swimming. Wetlands losses were estimated at about 460,000 acres annually.

Agricultural runoff resulted in the erosion of 2.25 billion tons of soil and the deposit of large amounts of phosphorus and nitrogen into many waters. Sewage treatment plants served only 85 million people.

#### Today:

Two-thirds of the nation's waters are safe for fishing and swimming. The rate of annual wetlands losses is estimated at about 70,000-90,000 acres according to recent studies.

The amount of soil lost due to agricultural runoff has been cut by one billion tons annually, and phosphorus and nitrogen levels in water sources are down. Modern wastewater treatment facilities serve 173 million people.

#### The Future:

All Americans will enjoy clean water safe for fishing and swimming.

We will achieve a net gain of wetlands by preventing additional losses and restoring hundreds of thousands of acres of wetlands.

Soil erosion and runoff of phosphorus and nitrogen into watersheds will be minimized, helping to sustain the nation's farming economy and aquatic systems.

The nation's waters will be free of the effects of sewage discharges.



Wastewater Treatment Headworks

## **Wastewater Priory Pollutants**

The concentrations of various substances in water in dissolved, colloidal or suspended form are typically low but vary considerably. Priority Pollutants refer to a list of 126 specific pollutants that includes heavy metals and specific organic chemicals. The priority pollutants are a subset of "toxic pollutants" as defined in the Clean Water Act (USA). These 126 pollutants were assigned a high priority for development of water quality criteria and effluent limitation guidelines because they are frequently found in wastewater.

Each POTW with an approved pretreatment program must develop local limits for arsenic, cadmium, chromium, copper, cyanide, lead, mercury, nickel, silver and zinc or demonstrate that limits are not necessary for these pollutants. The POTW must also identify all other pollutants of concern and evaluate the need for limits for these pollutants.

A pollutant of concern is defined as any pollutant limited in the POTW's NPDES permit or found in the collection system in sufficient quantity to have a reasonable potential to cause pass through or interference at the treatment plant, pose a threat to worker health and safety, or to cause other problems within the collection system or at the treatment plant, such as explosions or obstruction of wastewater flow.

The priority pollutant scans performed periodically by POTWs with approved pretreatment programs are useful in identifying pollutants of concern. POTWs with multiple plants may wish to develop local limits for each plant or after calculating the limits for each plant choose the most stringent as uniform local limits across all plants.

Local limits are most often associated with the control of toxic pollutants. However, if a POTW has experienced violations of their NPDES permit effluent limits for conventional pollutants (such as BOD, TSS, ammonia, phosphorus, or oil and grease), or has experienced operational problems due to these pollutants, the POTW should investigate the need for local limits for conventional pollutants as well.

Many POTWs have surcharge programs for conventional pollutants. A surcharge program should not be confused with local limits for these pollutants. In addition to a surcharge program, which is generally triggered by specific pollutant concentrations, a POTW should set absolute upper limits for conventional pollutants in its sewer use ordinance (SUO) or industrial user (IU) permits, based on total plant capacity.

**Nutrients**: Carbon, nitrogen and phosphorus are substances that are excreted by humans and thus found in wastewater. Excess nutrients can stimulate the growth of algae and other aquatic plants. When these plants die and decompose, they may reduce the amount of oxygen in the water. This condition, called hypoxia, can affect the survival of fish and other aquatic organisms.

Nutrients can also get into wastewater from industrial discharges, common household detergents and cleaners, runoff from streets and lawns and air pollutants that fall to the ground. Treatment plants cannot remove all nutrients from the wastewater. They can be reduced by controlling pollution that comes from lawns, farmland, streets and construction sites.

## Many of the heavy metals, pesticides, and other chemicals listed here are on the priority pollutant list:

- Heavy Metals (Total and Dissolved): "Heavy Metal" in the water treatment field refers to heavy, dense, metallic elements that occur only at trace levels in water, but are very toxic and tend to accumulate.
  - o Arsenic
  - o Cadmium
  - o Chromium
  - Lead in industry or in households
  - o Mercury
  - o **Zinc**
- Pesticides: Pesticides comprise a large class of compounds of concern. Typical pesticides and herbicides include DDT, Aldrin, Chlordane, Endosulfan, Endrin, Heptachlor, and Diazinon. Surprisingly, concentrations of pesticides in urban runoff may be equal or greater than the pesticides in agricultural runoff.
- Polycyclic Aromatic Hydrocarbons (PAHs): Polycyclic Aromatic Hydrocarbons include a family of semi-volatile organic pollutants such as naphthalene, anthracene, pyrene, and benzo(a)pyrene. There are typically two main sources of PAHs: spilled or released petroleum products (from oil spills or discharge of oil production brines) and combustion products that are found in urban runoff.
- Polychlorinated biphenyls (PCBs): Polychlorinated biphenyls are organic chemicals that formerly had widespread use in electrical transformers and hydraulic equipment. This class of chemicals is extremely persistent in the environment and has been proven to bioconcentrate in the food chain, thereby leading to environmental and human health concerns in areas such as the Great Lakes.

## Key features of the list of priority pollutants and its relationship to the list of toxic pollutants:

- 1. The Priority Pollutants are a set of chemical pollutants EPA regulates, and for which EPA has published analytical test methods.
- 2. The Priority Pollutant list makes the list of toxic pollutants more usable, in a practical way, for the purposes assigned to EPA by the Clean Water Act. For example, the Priority Pollutant list is more practical for testing and for regulation in that chemicals are described by their individual chemical names. The list of toxic pollutants, in contrast, contains open-ended groups of pollutants, such as "chlorinated benzenes." That group contains hundreds of compounds; there is no test for the group as a whole, nor is it practical to regulate or test for all of these compounds.

#### Derivation

Starting with the list of toxic pollutants, EPA used four criteria to select and prioritize specific pollutants:

- 1. We included all pollutants specifically named on the list of toxic pollutants;
- 2. There had to be a chemical standard available for the pollutant, so that testing for the pollutant could be performed;
- 3. The pollutant had to have been reported as found in water with a frequency of occurrence of at least 2.5%, and
- 4. The pollutant had to have been produced in significant quantities, as reported in Stanford Research Institute's 1976 Directory of Chemical Producers, USA.

#### Number of Entries

Originally, there were 129. When three pollutants were removed from the list of toxic pollutants in 1981 they were also removed from the Priority Pollutant list.

- 1. Entry numbers 17, 49, and 50 were removed.
- 2. The last number on the list is still 129, although there are 126 entries.

#### Publication

Why is the Priority Pollutant list published at 40 CFR 423, Appendix A, rather than at section 401, or some other, more general section?

- 1. One of the first industrial categories for which EPA developed effluent regulations was the Steam Electric Power Generating Point Source Category. The Priority Pollutant list was included to support regulations for that category.
- 2. Although the other sections within part 423 apply only to Steam Electric Power Generating, the Priority Pollutant list in Appendix A is not limited in terms of its relevance to that one industrial category.
- 3. Some users find it helpful to think of Appendix A to Part 423 as a convenient storage place for the list, or as a matter of convenience for citation.

#### List of Wastewater Toxic Pollutants

Priority pollutants are a set of chemical pollutants we regulate, and for which we have developed analytical test methods. The current list of 126 Priority Pollutants, shown below, can also be found in Appendix A to 40 CFR Part 423.

- 1. Acenaphthene
- 2. Acrolein
- 3. Acrylonitrile
- 4. Benzene
- 5. Benzidine
- 6. Carbon tetrachloride
- 7. Chlorobenzene
- 8. 1,2,4-trichlorobenzene
- 9. Hexachlorobenzene
- 10. 1,2-dichloroethane
- 11. 1,1,1-trichloreothane
- 12. Hexachloroethane
- 13. 1,1-dichloroethane
- 14. 1,1,2-trichloroethane
- 15. 1,1,2,2-tetrachloroethane
- 16. Chloroethane
- 17. REMOVED
- 18. Bis(2-chloroethyl) ether
- 19. 2-chloroethyl vinyl ethers
- 20. 2-chloronaphthalene
- 21. 2,4,6-trichlorophenol
- 22. Parachlorometa cresol
- 23. Chloroform
- 24. 2-chlorophenol
- 25. 1,2-dichlorobenzene
- 26. 1,3-dichlorobenzene
- 27. 1,4-dichlorobenzene

- 28. 3,3-dichlorobenzidine
- 29. 1,1-dichloroethylene
- 30. 1,2-trans-dichloroethylene
- 31. 2,4-dichlorophenol
- 32. 1,2-dichloropropane
- 33. 1,2-dichloropropylene
- 34. 2,4-dimethylphenol
- 35. 2,4-dinitrotoluene
- 36. 2,6-dinitrotoluene
- 37. 1,2-diphenylhydrazine
- 38. Ethylbenzene
- 39. Fluoranthene
- 40. 4-chlorophenyl phenyl ether
- 41. 4-bromophenyl phenyl ether
- 42. Bis(2-chloroisopropyl) ether
- 43. Bis(2-chloroethoxy) methane
- 44. Methylene chloride
- 45. Methyl chloride
- 46. Methyl bromide
- 47. Bromoform
- 48. Dichlorobromomethane
- 49. REMOVED
- 50. REMOVED
- 51. Chlorodibromomethane
- 52. Hexachlorobutadiene
- 53. Hexachlorocyclopentadiene
- 54. Isophorone

- 55. Naphthalene
- 56. Nitrobenzene
- 57. 2-nitrophenol
- 58. 4-nitrophenol
- 59. 2,4-dinitrophenol
- 60. 4,6-dinitro-o-cresol
- 61. N-nitrosodimethylamine
- 62. N-nitrosodiphenylamine
- 63. N-nitrosodi-n-propylamine
- 64. Pentachlorophenol
- 65. Phenol
- 66. Bis(2-ethylhexyl) phthalate
- 67. Butyl benzyl phthalate
- 68. Di-N-Butyl Phthalate
- 69. Di-n-octyl phthalate
- 70. Diethyl Phthalate
- 71. Dimethyl phthalate
- 72. benzo(a) anthracene
- 73. Benzo(a)pyrene
- 74. Benzo(b) fluoranthene
- 75. Benzo(k) fluoranthene
- 76. Chrysene
- 77. Acenaphthylene
- 78. Anthracene
- 79. Benzo(ghi) perylene
- 80. Fluorene
- 81. Phenanthrene
- 82. Dibenzo(,h) anthracene
- 83. Indeno (1,2,3-cd) pyrene
- 84. Pyrene
- 85. Tetrachloroethylene
- 86. Toluene
- 87. Trichloroethylene
- 88. Vinyl chloride
- 89. Aldrin
- 90. Dieldrin
- 91. Chlordane
- 92. 4,4-DDT

- 93. 4,4-DDE
- 94. 4,4-DDD
- 95. Alpha-endosulfan
- 96. Beta-endosulfan
- 97. Endosulfan sulfate
- 98. Endrin
- 99. Endrin aldehyde
- 100. Heptachlor
- 101. Heptachlor epoxide
- 102. Alpha-BHC
- 103. Beta-BHC
- 104. Gamma-BHC
- 105. Delta-BHC
- 106. PCB-1242 (Arochlor 1242)
- 107. PCB-1254 (Arochlor 1254)
- 108. PCB-1221 (Arochlor 1221)
- 109. PCB-1232 (Arochlor 1232)
- 110. PCB–1248 (Arochlor 1248)
- 111. PCB-1260 (Arochlor 1260)
- 112. PCB-1016 (Arochlor 1016)
- 113. Toxaphene
- 114. Antimony
- 115. Arsenic
- 116. Asbestos
- 117. Beryllium
- 118. Cadmium
- 119. Chromium
- 120. Copper
- 121. Cyanide, Total
- 122. Lead
- 123. Mercury
- 124. Nickel
- 125. Selenium
- 126. Silver
- 127. Thallium
- 128. Zinc
- 129. 2,3,7,8-TCDD

## **Types of POTW's Wastewater Samples**

#### General

There are four types of samples that are collected by the POTW's Sampling Section: grab, time proportional composites, flow proportional composites, and hand composites. The sampling method used depends largely on the types of analyses to be run, and the nature of the wastestream being sampled. Each sampling method is described in this section.

Most POTW's will define the sampling methods which must be used by industrial users (**IUs**) to obtain representative samples to show compliance with their permits: **Example** 

- (1) A grab sample is an individual sample collected in less than 15 minutes without regard for flow or time of day. pH, cyanide, oil and grease, sulfide, and volatile organics must be collected as grab samples.
- (2) 24-hour flow proportional composite samples where feasible. The POTW may waive this requirement if the IU demonstrates that this method is not feasible. Samples would then be taken by means of time proportional composite sampling methods or by hand composite where the industrial User (IU) can demonstrate that this will provide a representative sample of the effluent being discharged.

The volume of sample to be collected by any of these methods is dependent on the number

and types of analyses that must be performed.

#### Wastewater Grab Samples

Grab samples are individual samples collected in less than 15 minutes without regard to flow or time of day. Grab samples are normally taken manually, but can be pumped. Oil and grease samples and purgeable organics are exceptions and must be taken manually.

A grab sample is usually taken when a sample is needed to:



- (1) Provide information about an instantaneous concentration of pollutants at a specific time.
- (2) Quantify the pollutants in a non-continuous discharge (e.g., batch discharge).
- (3) Corroborate composite samples if the waste is not highly variable.
- (4) Monitor parameters not amenable to compositing such as pH, temperature, dissolved oxygen, chlorine, purgeable organics and sulfides, oil and grease, coliform bacteria, and sulfites.



The Refrigerated Automatic Sampler will have a Data programmer that will allow you to set the time to collect the sample or samples. This machine can also measure the amount of the sample. These can also be used for the collection of composite samples. Sometimes you will see a pH probe with real-time readings sent to the Operator's Command Center. This is a common sight for most wastewater plants and SIUs.



# Collecting Procedure for Water/Wastewater Grab Samples *Policy Example*

Lower dipper or mouth of the bottle into water just below surface. In some cases, you will need to rinse the bottle or dipper three times in the sample before obtaining the sample.

Retrieve collected sample to clean processing area.

Rinse the outside of the bottle 3 times to remove contamination.

Pour the sample into the required laboratory bottle.

You may need to filter the sample, this is true with some water and wastewater samples.

Filtering (for ortho-P and NOx samples). Some surface water virus samples need to be filtered.

- Secure caps tightly.
- > Bottle preservation is performed in the truck or lab before sampling.
- > Secure sample container caps tightly.
- > Label the sample containers and place them in an iced cooler before storage.

#### **Timed Composites**

Timed samples are usually taken in instances where the intention is to characterize the wastes over a period of time without regard to flow, or where the flow is fairly constant. Timed composite samples consist of a series of equal volume grab samples taken at regular intervals. Usually the interval is 15 minutes with a maximum sampling duration of 24 hours.

However, other intervals can be used and may be more appropriate under some circumstances. Samplers are available which can take up to 10 discreet samples per bottle, for a total of 240 discreet samples. The sampler may be programmed to take any number of samples into one composite bottle which has a 2.5-gallon capacity.

#### Flow Proportional Composites

Flow proportional composite samples consist of: a series of grab samples whose volumes are equal in size and proportion to the flow at the time of sampling. Samples are taken at varying time intervals, or continuous samples taken over a period of time based on the flow. Wherever possible, flow proportional sampling is recommended because it most accurately reflects the nature of the wastestream. Equal volume samples taken at varying time intervals are most often collected by the sampling inspectors. A flow measuring device should be used in conjunction with the automatic sampler.

This sampling method is used for all sampling activities except for instances where grab samples are required or time proportional sampling is more expedient and can provide the same accuracy as flow proportional sampling (i.e., constant flow levels).

## Hand Compositing

Hand compositing is a series of time proportional grab samples which are collected and composited by hand. Provided the sample volumes are equal and are collected at even intervals, the results should be the same as if done by an automatic sampler (i.e., flow proportional composite sampling).

A specific instance where this sampling method may be used is in metal plating shops which have batch discharges from the treatment tank. Provided the tank contains a homogeneous mixture, a minimum of four grab samples are taken of equal amounts and at evenly spaced intervals of time during discharge, to accurately represent the entire tank.

This should represent the waste characteristics of the entire batch discharged to the sewer. One hand composite per batch discharged would be equivalent to a 24-hour composite sample taken at other types of facilities. The sampling data would be compared with the average daily categorical standards or local limits where applicable.



Parshall Fume and Ultrasonic Flow Meter Notice the debris and most POTW's will write a NOV for uncleanness.



## Pre-Sampling Procedures Example

To ensure acceptable analytical results, numerous steps must be followed before a sampling program can be initiated:

- (1) Sampling equipment must be clean and be in good working order.
- (2) Sampling site must be selected.
- (3) Types of analyses must be determined.
- (4) Proper sample containers must be selected and prepared.

#### Wastewater Sampling Equipment

The POTW may use one or more of the following portable samplers, ISCO Ultra-Sonic flow meters, SIGMA Depth Sensor samplers, and SIGMA pH Probe samplers. Safety equipment and other necessary equipment are also used.

The equipment that is kept in the sampling vehicle is dependent on the types of sampling activities planned each week, while the equipment stored in the storeroom is for back-up needs and future sampling demands.

Each sampling vehicle should be equipped with at least one sampler and one flow meter more than is needed for the particular sampling period. For example, three scheduled flow proportionate sampling sites would require a vehicle to be equipped with four samplers and four flow meters. At least one spare battery for each type of equipment taken into the field should also be placed in the sampling vehicle.

Ancillary equipment, such as supports, harnesses, blowers, etc., that must be carried in each vehicle will depend on the nature of the sampling location.

In order to keep the equipment in good working order, it should be maintained and cleaned on a regular basis. Routine maintenance and cleaning procedures should be written into the procedures.

#### Sampling Equipment Maintenance Policy Example

Basic maintenance for samplers includes: periodic calibration, general equipment checking, and replacement of the internal desiccant and fuses. Routine cleaning should be done as covered in SOP or equivalent.

Basic maintenance of the flow meters includes: periodic replacement of the internal desiccant, plotter paper, ribbon, fuses, and any broken re-roll spool assemblies. **Note**: on this assembly there are two tabs on the sides of this piece which are extremely thin and easily broken.

The Nicad and Gel Cell batteries need to be recharged on a regular basis.

Any battery that reads less than 12.50 when checked should not be installed or left on any of the sampling equipment. At the battery charging station, areas are set aside for batteries that need to be charged and batteries already charged.

To prolong battery life, batteries should be charged for a maximum of 24 hours, in accordance with the procedures described in the manufacturer's operations and maintenance manuals.

It is important to note that charged Nicad batteries, if left unused for a long time, are nevertheless slowly discharging. Gel cell batteries are generally more stable. Voltage readings should be taken **before** the charged batteries are taken into the field to be sure that they still have a full charge.

When a sampler, flow meter, or ancillary equipment needs more specific repairs, the manufacturer representative should be contacted and arrangements made for repair or replacement of the equipment.

#### **Cleaning Automatic Samplers Policy Example**

Samplers, sample jars, grab beakers, and all other equipment used in collecting samples must be cleaned between their uses at each site, to avoid the possibility of cross contamination. Latex or nitrile gloves or equivalent should be worn to protect against infections and acid burns. The following steps should be taken to ensure the proper cleaning of the sampling equipment.

- (1) Break down the sampler and lay the three components in a row.
- (2) Place the strainers and weights in a plastic bucket.
- (3) Set the glass composite jars and Teflon caps off to the side, to be cleaned separately from the samplers.
- (4) Pour a small amount of diluted (1:128) O-Syl disinfectant and MICRO soap into each sampler component, the bucket containing the strainers and weights, and the composite jars.
- (5) To clean the sampler components:
  - (a) Partially fill the sampler bases and cover with water.
  - (b) Use a brush to scrub the inside and outside of each sampling component. Using a small bottle brush, thoroughly scrub the inside of the intake tube and the float housing of the sampler head (these are critical areas since they come in contact with the sample).
  - (c) Rinse off the soap with fresh water.
  - (d) Stack each component so that it will dry quickly and thoroughly.
  - (e) Reassemble the sampler after the components are dry, and store it in the proper compartment of the sampling van. Leave the sampler lid loose so moisture won't be trapped.
  - (f) Clean the strainers and weights in the bucket. Empty the contents of the bucket and rinse the bucket, strainers, and weights. After they have dried, place them in the proper storage areas of the sampling van.
  - (g) Drain the wastewater tank of the sampling van into the sewer drain.
  - (h) Refill the fresh-water tank on the sampling van with potable water.

## Sampler Bottle Cleaning and Preparation Policy Example

- (1) Fill each jar with O-Syl (same dilution as used in the sampler disinfection), MICRO soap, and fresh water.
- (2) Thoroughly scrub the inside and outside of the jars until they are sparkling clean. Make sure that all oil and grease are removed.
- (3) Rinse the jars with fresh water.
- (4) Pour a small amount of 1:1 nitric acid into one jar, and securely place the proper Teflon cap on the jar. Swirl the nitric acid throughout the jar, remove the lid, and pour the nitric acid into the next jar. Repeat this procedure until all the bottles have been treated. Rinse bottles with water after the acid wash. **NOTE:** Wear safety glasses or a full-face shield to protect your eyes.
- (5) Place jars in the drying oven. If jars are to air dry use Acetone to clean the bottles the same way as stated in (4) above. Let the jars and caps dry completely.
- (6) Place the jars, with their caps on loosely, in their respective places on the sampling van.

#### Selection of Pretreatment Sampling Site

In order to ensure the collection of valid samples, a representative sampling site must be selected. For industrial sampling, the sites are designated in the permit.

#### Industrial Users - Permitted/Nonpermitted Example

The sampling points within an industry varies with each industry depending on the nature of the process and location of pretreatment facilities. Therefore, exact locations must be identified on a case by case basis. However, the following general principles apply in all cases:

(1) A permanent sampling location(s) must be identified for use by the POTW and the IU.

All permitted industries are required to install a sampling vault. The location of the vault is designated by the enforcement inspector. The enforcement inspector responsible for an individual company or site is responsible for providing directions (**maps**) of the specific sampling points, as well as current copies of permits and the name of the contact person and phone number. This information needs to be kept current in the sampling file. Locations of sampling points need to be compared to what is listed on the currant permit. If sampling points that the POTW is using do not agree with permit location, do not sample -refer to Chief Inspector or Supervisor.

- (2) The sampling location should be easily accessible and relatively free of safety hazards.
- (3) For categorical industries, there should be, if possible, no discharge present other than that from the regulated process.

If other wastestreams are combined with the regulated wastestream prior to the sampling location, the combined wastestream formula will need to be utilized. The sampling crew must be aware of lower limits to correctly show analysis on chain of custody.

- (4) If the rate of industrial process discharge flow is needed (i.e., where mass limitations are applied), the sampling location will need to be located where the flow of the wastestream is known or can be measured or estimated and flow rates for the other wastestreams obtained.
- (5) In instances where sampling must be performed in the sewer outside of the building, the IU must install a sampling vault in accordance with Code.

#### Sample Type and Analyses

Different sample volumes are required for various analyses. In addition, the laboratory has developed standard volumes for routine analyses performed on industrial waste samples as follows:

- (1) BOD/COD/TSS (1000-2000 ml, plastic) or equivalent
- (2) Heavy metals (500-2000 ml, plastic) or equivalent
- (3) Cyanide (2000 ml, plastic) or equivalent
- (4) Oil and grease (1000 ml, level-one glass) or equivalent

#### **Selection and Preparation of Sample Containers**

The selection of a sample container is based on the parameter to be measured. The inspector should be familiar with the type of sampling containers and preservatives that are needed.

It is essential that the sample containers be made of chemically resistant material, and do not affect the concentrations of the pollutants to be measured.

In addition, sample containers should have a closure (i.e., leak proof/resistant, Teflon lined) that protects the sample from contamination and be properly labeled before leaving the sampling site.

#### Wastewater Sample Preservation

Wastewater usually contains one or more unstable pollutants that require immediate analysis or preservation until an analysis can be made.

Sample preservation is needed for composite samples, for example, which may be stored for as long as 24 hours prior to transferring them to the laboratory.

Recommended preservatives and holding times that should be used for specific pollutants are presented in the front of this section.

## Quality Assurance/Quality Control Policy *Example*

Quality Assurance/Quality Control (**QA/QC**) measures taken by the sampling crew include equipment blanks, trip blanks, split samples and duplicate samples. Equipment blanks and trip blanks are routine QA/QC measures.

Split samples are taken for Local Limits (pretreatment) sampling and when requested by an industry or laboratory. Split samples requested by an industry are analyzed by their lab at their expense.

Duplicate samples are run when requested by a Supervisor or Project Leader.

The laboratory prepares all trip blanks/travel blanks used by the sampling crews. This is performed in the laboratory rather than in the field in order to assure that there is no field contamination in the blanks.

Any contamination detected in the blanks would result from field exposure which could in turn affect collected samples.

#### Chain of Custody

Documentation of all pertinent data concerning the collection, preservation and transportation of samples is critical to the overall success of the Wastewater Sampling Program. If sampling is performed for the Pretreatment program, any sampling data may be used as evidence in court proceedings against a noncompliant industrial user. In this case documentation becomes critical. This form is a legal document and is of major importance in a court hearing. Specific procedures with regard to chain of custody are outlined below:

- (1) The sampling crew takes a sufficient supply of pre-numbered Industrial Waste Lab Reports, (custody forms) and sample containers into the field.
- (2) The sampling crew fills in the sampling form at the time of sample collection, and returns the form to the lab along with the collected sample. Specific information to be completed on the form includes:
  - (a) CODE: The company ID number assigned by supervisor.
  - (b) SITE No.: The sampling point ID number assigned by supervisor.
  - (c) DATE SAMPLED: From Date sampling began To Date sample is pulled. If it is a grab sample, only the date the sample was taken will be entered with the other line crossed out.
  - (d) SUBMITTED BY: This will have a preprinted truck number. The sampling crew will write in their initials on the blank line which follows.
  - (e) LABEL: A letter is checked and the type of analysis to be performed.
  - (f) PRESERVATIVE: The method of preservation used. See page 115 to see which preservatives to use.

- (g) TYPE OF SAMPLE: Check off whether flow proportional, timed composite, hand composite, or grab sample.
- (h) TIME: The time frame needed for collection of the sample. A starting time for sample collection, an ending time, and a total time in hours and quarter hours is recorded, such as 23.25 hours. On a grab sample only, the end time, which is the time the sample was taken, will be entered and the other two lines will be crossed out.
- (i) RELINQUISHED BY: This is the signature of the person that relinquishes sample to lab personnel, or to any other person taking custody of the sample.
- (j) DATE: Date sample is submitted to the laboratory or relinquished to another person.
- (k) NOTES TO LAB: Includes any special notes to the lab, such as special analysis required of the sample, a letter code which is assigned to the entity being tested the amount of flow if sample is flow proportional, grab sample pH and temperature, and/or actual sample temperature.
- (I) FIELD TEST: Results of any field tests including sample pH, hexavalent chromium, dissolved sulfides, copper, and residual chlorine.
- (m) RESULTS: The appropriate box(es) need to be checked to correspond to the label designation chosen above.
- (3) When the sampling is completed at a site, the sampling crew labels the bottles with the label letter designation. The samples are sealed with chain of custody seals and placed in an ice chest for transportation to the lab.
- (4) The sampling crew submits the samples and the chain of custody form to the laboratory.
- (5) The laboratory logs the samples and assigns a Lab Reference Number to the sample. The sample is tracked by means of this number.
- (6) Laboratory personnel sign and date the form, and return it to the sampling crew who makes two copies of the form. One copy is for the sampling crew files and the other is for data entry. The original form is returned to the laboratory. It is also important to note that the sampling vehicle should be kept locked at all times when the sampling crew is not in the vehicle, or in full view of the vehicle.

## Equipment Maintenance Cleaning Techniques Example

It is important to keep all equipment used for sampling clean to reduce the risk of cross contamination.

Is your automatic sampler and equipment clean?

All components of an automatic sampler need to be clean prior to setup, since contamination can occur.

Automatic sampler - Each section should be clean, especially the inlet tube.

Intake tubing - Cleaned or new Tygon or Teflon should be used according to the samples you are collecting.

- Intake line strainer Clean or stainless steel or Teflon.
- > Pump tubing Clean or new medical grade silicone tubing.

Composite bottle - Generally glass is used for this and it's extremely important that it is clean.

Automatic sampling equipment - all components of an automatic sampler should be cleaned using phosphate free soap and rinsed thoroughly prior to setup.

#### Follow safety procedures (goggles, gloves, etc...) When cleaning equipment!

Composite bottles used in the automatic sampler need to be cleaned prior to setup.

- 1. Rinse bottle and cap with tap water to remove any residual contaminants.
- 2. Wash bottle and cap with a phosphate free soap and tap water.
- 3. Rinse bottle and cap with tap water to flush off any soap.

4. Add 1:1 nitric acid to bottle, cap and shake to cover entire inside of bottle and cap. Pour out 1:1 nitric acid.

- 5. Triple rinse bottle and cap with analyte free water.
- 6. Allow bottle and cap to dry.
- 7. Store Bottle with cap loosely screwed onto bottle to keep contaminants out.

#### Tubing - clean or new

Using clean tubing (intake and pump) for each sampling event will eliminate the need to clean the tubing. If tubing is not going to be changed before a sampling event, then the tubing will need to be washed.

1. Pump clean tap water through tubing, using the automatic sampler pump to transfer water from one container to another.

2. Place tubing into another container that has a phosphate free soap in it and pump the soapy water through the tubing 3 or 4 times while catching the discharge in a separate container.

- 3. Pump clean tap water through tubing to rinse out soap.
- 4. Add 1:1 nitric acid to clean tap water and pump this solution through tubing 3 or 4 times.
- 5. Pump analyte-free water through tubing until all residual acid has been removed.
- 6. Keep tubing in a clean place until next sampling event.

## **Regular Maintenance Includes the Following**

#### **Automatic Sampler**

- Washing
- Drying
- Change desiccant
- Check full bottle shut-off float
- Recharge battery

#### Flowmeter

- Washing
- Drying
- Change plotter paper
- Change printer ribbon
- Change desiccant
- Recharge battery

#### Record keeping - keep a record of cleaning dates. What was cleaned, and when.



A modern wastewater treatment facility may have up to 10 different sampling sites. These may include Local Limits, QA/QC, Influent, Outfall, Chlorine, and many more sites to maintain compliance and to ensure that the plant is running efficiently.

## **Proper Sample Handling Example**

The proper handling of water quality samples also includes wearing gloves. Gloves not only protect field personnel, but also prevent potential contamination to the water sample. Always wear powderless, disposable gloves. When sampling for inorganics, wear latex gloves. Nitrile gloves are appropriate for organics.

The following sections provide a field reference for chain of custody procedures, sampling surface water and ground water, and further provides procedures for measuring field parameters and handling water-quality samples.

Use chain-of-custody procedures when coolers and containers are prepared, sealed and shipped. They will remain sealed until used in the field. When making arrangements with the laboratory, make sure you request



enough containers, including those for blank and duplicate samples. Order extra sample bottles to allow for breakage or contamination in the field.

Some samples require low-temperature storage and/or preservation with chemicals to maintain their integrity during shipment and before analysis in the laboratory. The most common preservatives are hydrochloric, nitric, sulfuric and ascorbic acids, sodium hydroxide, sodium thiosulfate, and biocides. Many laboratories provide pre-preserved bottles filled with measured amounts of preservatives. Although most federal and state agencies allow the use of pre-preserved sample containers, some may require either cool temperatures or added preservatives in the field.

When the containers and preservatives are received from the laboratory, check to see that none have leaked. Be aware that many preservatives can burn eyes and skin, and must be handled carefully. Sampling bottles should be labeled with type of preservative used, type of analysis to be done and be accompanied by a Safety Data Sheets (Formerly Material Safety Data Sheet) (**SDS**).

Make sure you can tell which containers are pre-preserved, because extra care must be taken not to overfill them when collecting samples in the field. Check with the laboratory about quality control procedures when using pre-preserved bottles. Coolers used for sample shipment must be large enough to store containers, packing materials and ice. Obtain extra coolers, if necessary. Never store coolers and containers near solvents, fuels or other sources of contamination or combustion. In warm weather, keep coolers and samples in the shade.

#### **Field Parameters**

Measure and record the field parameters of temperature, electrical conductivity, pH and dissolved oxygen in an undisturbed section of streamflow. Other parameters may be measured, if desired.



Sample Station commonly found at most water or wastewater treatment plants. This tap will allow the operator to obtain Grab Samples for pH, Temperature, COD, Bacterial, ORP, OUP, Organics and Inorganic field parameters.



## TESTING THE pH OF WATER

pH Meter pH scale is between 0-14; 0 being Acid and 14 being Base.

92 Chemical Contaminants 201 1<sup>st</sup> Edition TLC (928) 468-0665

## QA/QC Field Procedures for Plant Sampling *Example*

#### **Duplicate Sampling Procedure**

The purpose of Duplicate Samples is to check the laboratory's ability to reproduce analytical results. Duplicate Samples are to be collected using these steps:

- 1. Determine amount of sample needed. If a flow proportion sample is required, then base the amount of sample needed on the current flow reading. If a flow-proportion sample is not required, then use the predetermined amount for the sampling site.
- 2. Collect sample using a grab type sampler or a sampling head.
- 3. Measure the amount determined in Step 1 using a graduated cylinder or other accurate measuring device.
- 4. Pour measured sample into sample container that is not marked as the Duplicate Sample.
- 5. Measure same amount as in Step 1
- 6. Pour second measured quantity into sample container marked for Duplicate Sample.
- 7. Process both samples using standard procedures and submit both samples to laboratory.

#### Split Sampling Procedure

The purpose of Split Samples is to check analytical procedures by having the samples analyzed by two different laboratories. Split Samples are to be collected using these steps:

- 1. Determine amount of sample needed. If a flow proportion sample is required, then base the amount of sample needed on the current flow reading. If a flow-proportion sample is not required, then use the predetermined amount for the sampling site.
- 2. Collect sample using a grab type sampler or a sampling head.
- 3. Measure the amount determined in Step 1 using a graduated cylinder or other accurate measuring device.
- 4. Pour measured sample into sample container that is not marked as the Split Sample.
- 5. Measure same amount as in Step 1
- 6. Pour second measured quantity into sample container marked for Split Sample.
- 7. Process both samples using standard procedures and submit both samples to the laboratory. The laboratory will be responsible for submitting the samples to the outside laboratory that will be analyzing the Split Sample.

#### Trip Blank Procedure

The purpose of Trip Blanks is to determine if the sample bottles have been adequately cleaned, and if sample contamination occurs between the time sample bottles leave the laboratory to the time that samples are returned to the lab.

Trip blanks are prepared by the laboratory using bottles supplied by the sampler. They are picked up by the person who begins the sampling day. Trip blanks are placed in the cooler which contains the other samples and remain there until the samples are turned into the laboratory.

## Field Equipment Blank Procedure

The purpose of Field Equipment Blanks is to test the procedure for cleaning the sample measuring container to determine if cross contamination between sample sites has occurred. These Blanks are needed only at sites where flow-proportion samples are taken. Follow these steps when collecting a Field Equipment Blank:

- 1. Collect Field Equipment Blank **AFTER** collecting a sample and **BEFORE** moving to the next sampling location.
- 2. After collecting sample, triple rinse sample measuring container, usually a graduated cylinder, using distilled water.
- 3. Open a sealed bottle of High distilled water.
- 4. Pour the distilled water into the sample measuring container that was just rinsed.
- 5. Pour the distilled water from sample measuring device into sample bottles labeled for the Field Equipment Blanks.
- 6. Repeat Steps 3 through 5 until all Field Equipment Blank sample bottles have been filled.
- 7. Process samples using standard procedures and submit to laboratory.

An equipment blank is distilled water which has been collected in a composite sample bottle or a series of discrete bottles from an automatic sampler. Equipment blanks are used to evaluate the reliability of composite samples collected in the field.

The data produced from the equipment blank indicates the performance of the sample collection system, which involves the cleaning of sampling equipment, and accessories, preservation techniques, and handling of samples.

The objective is to demonstrate that the samples are not contaminated by inadequate cleaning of equipment, contaminated preservation additives or sample collection techniques, and to provide documented records on Quality Assurance Practices.

Procedures to be followed in collecting the equipment blanks are outlined below. (Also see QA/QC check list, example).

- (1) The sampler is to be assembled completely in the manner determined by the parameters the crew will be sampling (i.e. if sampling for organics, Teflon suction tubing must be used at that site). The composite jar inside the sampler must always be rinsed out thoroughly with distilled water.
- (2) Program the sampler to collect the proper amount of distilled water that is representative of the sample parameters that will be collected at that site. Grab samples are excluded. Pump distilled water through the strainer and intake tubing prior to filling the sampler bottle. Then, place the strainer into as many fresh, uncontaminated bottles of distilled water as needed to collect the necessary volume of sample.
- (3) If the sampler is set up in the discrete mode, the crew must then transfer the collected samples into the field composite bottle and shake to mix thoroughly.

- (4) Transfer the sample from the field composite bottle into its respective lab sample bottles. Test and preserve the samples as appropriate for the parameters being analyzed.
- (5) Follow the chain of custody procedures outlined in SOP for turning the samples in to the laboratory. All paperwork must be completed at this time, and all bottles must be marked accordingly. Custody seals must be used. The crew must note the sampling activity in a logbook that is kept specifically for documenting preparation of equipment blanks and/or any other QA activities.

#### Wastewater Sampling Procedures/Techniques

#### General Guidelines

In general, the following guidelines should be observed in conducting sampling activities:

- (1) Samples being collected must be representative of the wastestream being tested.
- (2) Samples shall be collected in uncontaminated containers and preserved properly.
- (3) Samples should be of sufficient volume for the required analyses.
- (4) Samples should be stored in a manner which does not alter the properties of the sample prior to chain of custody transfer.
- (5) Samples should be properly and completely identified by marking them with the proper information.
- (6) Sample lines should be as short as possible and the smallest practical diameter to facilitate purging, reduce lag time, and give adequate consideration to maximum transport velocity. Also, they should have sufficient strength to prevent structural failure.
- (7) Sample lines should be pitched downward at least 10 percent to prevent settling or separation of solids contained by the sample.
- (8) Samples should be delivered as quickly as possible to the laboratory.

#### Specific Techniques

Sampling techniques in addition to the above general guidelines must also recognize differences in sampling methodology, preservation, and analytical methods.

The following sections specify techniques that differ by pollutant group and discuss such factors as sampling methodology (e.g., composite, grab, etc.), type of container, preservation and holding time.

## Sampling Techniques for Volatile Organics

Volatile organics are analyzed in accordance with EPA methods 601, 602, and 603.

Due to the volatility of these compounds, only grab samples can be taken. If a composite sample is needed, individual grab samples must be collected and composited in the laboratory prior to analysis.

The procedures that must be followed in taking these samples are outlined below.

**NOTE:** Gloves, clothing, face, and eye protection must be worn when handling volatile organics.

In addition, the sampling crew must thoroughly clean those parts of the body that have been exposed to these materials.

- (1) For each sampling date, the lab will also provide two additional bottles to be used as a backup in case of breakage. These sampling vials are only good for one week. If any are unused, they must be returned to the lab for disposal.
- (2) The lab will provide one sample trip blank per sampling date. This bottle is to be kept on ice until the samples are submitted to the lab. At least one day prior to sampling, go to the lab and request the sample bottles (40 ml vials) for the specific sampling site, as indicated by the sampling plan. The laboratory will arrange to have the appropriate number of sample bottles prepared, based on the number of analyses to be performed. The sampling crew should make sure that all bottles are provided for these samples by the lab technicians.
- (3) Collect the sample in a clean glass beaker. Test for chlorine with the Hach test kit. If there is any chlorine residual, neutralize the chlorine with sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) and retest for chlorine. Repeat until there is no chlorine residual. Make notes on chain of custody sheet if extra amounts of sodium thiosulfate are required for neutralization.
- (4) Remove the vials from the ice. There will be two empty vials for the 601 sample and two vials with HCl for the 602. The HCl will already have been measured into the vials by the lab personnel.
- (5) Fill the vial to just overflowing in such a manner that no air bubbles pass through the sample as the vial is being filled. This is accomplished by pouring the sample from the beaker into the vial along the side of the vial to minimize the possibility of entrapping air in the sample. Do not rinse out or overfill the vials, this will wash out the preservative in the vial.
- (6) Seal the vial so that no air bubbles are entrapped in it. Remember to put the Teflon side of the cap facing down onto the vial.

- (7) To be sure there are no air bubbles, turn the vial upside down and tap it against the palm of the hand. Check to see if there are air bubbles along the sides or bottom of the vial. If there are bubbles, unseal the vial, top off the vial, and reseal. Check the vial again for the presence of bubbles.
- (8) All samples must be maintained at 4°C from the time of collection until the time of extraction. Custody seals must be placed on all samples, and all paper work must be filled out properly.
- (9) Return the sample bottles and QA/QC bottles to the laboratory the same day the sample is collected.

## Acid/Base/Neutral Extractable Organics and Pesticides Example

Acid extractable organics are analyzed in accordance with EPA methods 604 and 625. Base/neutral extractable organics are analyzed in accordance with EPA method 625, or individual methods for various groups of compounds including EPA methods 605, 606, 607, 609, 611, and 612. Pesticides are analyzed in accordance with EPA method 608.

The procedures that must be followed in taking these samples are outlined below.

- (1) Samples must be collected in certified clean one-gallon amber glass bottles with Teflon lids.
- (2) Travel blanks or QA/QC bottles may not be required with the samples.
- (3) Grab samples must be collected in amber glass bottles. They do not have to be completely filled, but must be a minimum of 1/3 to 1/2 full. Bottles should not be prewashed with samples prior to filling.
- (4) For composite sampling, glass composite bottles must be used and precleaned. Teflon tubing must be used for the suction piping. The pump tubing must be medium grade silicone rubber.
- (5) The composite bottle in the sampler must be kept refrigerated (putting ice in the sampler) at 4°C. If amber glass is not used, (i.e. 2 1/2-gallon clear composite sampler bottle,) the sample must be protected from the light during collection and compositing. The compositing must be done in the field, (i.e. when discrete sampling has been used).
- (6) All samples must be iced at 4°C from the time of collection until extraction.
- (7) The sample should be checked for the presence of chlorine using field test kits that provide results in accordance with EPA methods 330.4 and 330.5. If chlorine is determined to be present, 80 mg of sodium thiosulfate should be added to each bottle. The sample must be retested for chlorine. This procedure must be repeated until there is no residual of chlorine shown. The amount of sodium thiosulfate added must be noted on the chain of custody if in excess of 80 mg.
- (8) All necessary paperwork must be completed at sampling site. All bottles must be properly labeled, and have custody seal.

## Conventional Pollutants Figure 1

- Biochemical Oxygen Demand (BOD)
- Total Suspended Solids (TSS)
- Fecal Coliform
- ≻ pH
- Oil and Grease (O&G)



A small wastewater treatment operator's lab.

#### **Physical-Chemical Treatment**

Physical-chemical treatment (to remove dissolved metals and organics), and disinfection (to kill any remaining pathogens). After treatment is complete, effluent is discharged to the receiving stream, typically a creek, river, lake, estuary or ocean. Some POTWs may apply treated effluent directly to golf courses, parkland, or croplands.

Both primary and secondary treatment processes generate waste solids, known as sewage sludge or biosolids. Sludges from the treatment process may be used productively (i.e., as fertilizer or soil conditioner), disposed of in a landfill or incinerated in a dedicated sewage sludge incinerator with the ash also disposed of in a landfill.

As described above, POTWs are designed to treat typical household wastes and biodegradable commercial and biodegradable industrial wastes. The Clean Water Act (**CWA**) and the EPA define the contaminants from these sources as conventional pollutants.

Conventional pollutants are identified in Figure 1 above and include those specific pollutants that are expected to be present in domestic discharges to POTWs.

Commercial and industrial facilities may, however, discharge toxic pollutants that the treatment plant is neither designed for nor able to remove.

## Sampling Techniques for Heavy Metals

- (1) Generally, all metal samples collected are to be composite samples, i.e., flow/composite, time/composite, or hand composite.
- (2) For composite sampling, place the lid on the bottle and agitate the bottle to completely mix the composite sample.
- (3) Transfer the required amount from the composite container to either a 500 ml or 2000 ml clean plastic bottle. Check the pH of the sample as described in Section 8.7.2.5.
  - **Note:** For inductively coupled plasma (**ICP**) metal analysis, a 500 ml clean plastic bottle is required. For extra metals or metals by furnace, a 2000 ml clean plastic bottle is required.
- (4) Add nitric acid (1:1 solution) to the sample to reduce the pH to below 2.0. Usually, 2 ml/500 ml is sufficient. Recheck the pH to be sure it is below 2.0. Make a note on the lab sheet if more than two ml of acid is required to bring the pH below 2.0.
- (5) Label the sample bottle with the corresponding IW number and proper analysis code letter. Attach the custody seal to the sample, then store in the ice chest until transferred to the laboratory. Fill out the IW lab sheet with all the pertinent information, being careful to include all required parameters and the type of analysis required, e.g., ICP/furnace.
- (6) When a grab sample is necessary, rinse out the receiving sample bottle with an aliquot of the sample stream at least three times. Then fill the sample bottle and proceed with steps two through four described above.
- (7) When a split sample is requested (i.e., one for the samplers and one for the user), the composite sample is prepared as described in item one. Providing there is sufficient sample, a portion is transferred into the bottle provided by the user.
- (8) If more than one site is sampled per day, a clean composite container (i.e., two and one half-gallon glass jar), must be used at each site.
- (9) If a discreet sampler is being used, at the time of collection combine all the samples that have been collected into a single clean composite bottle. Then follow the preceding steps one through four, and refer to step six if a split is requested.

## Cyanide

To assure that the sample can be analyzed for cyanide, no chlorine can be present in the sample. Procedures for taking cyanide samples are as follows:

- (1) This sample is normally a grab sample. The cyanide sample is a composite sample when collected as part of Priority Pollutants or Plant Sampling at the waste treatment plants.
  - (a) In the sampling file, check the industries' wastewater discharge permit and locate all cyanide (CN) sampling sites. If the sampling sites are located in a confined space, follow Confined Space procedures before collecting the sample or samples.
  - (b) Collect 2000 ml (maximum), 1000 ml (minimum), of CN sample into a type C plastic bottle.

**NOTE:** 2000 ml is the standard, but for batch dischargers 1000 ml is adequate.

- (c) Test the cyanide sample for pH and temperature with the pH meter. Record the results on the custody sheet (Industrial Waste (IW) lab sheet).
- (d) Test for chlorine with **Hach Total Chlorine Test Kit** (the instructions ate located in the kit)
- (e) If chlorine is present in the CN sample, neutralize it with Ascorbic Acid  $(C_6H_8O_6)$ . For ascorbic acid neutralization, add  $C_6H_8O_6$ , a few crystals at a time, until five mls of sample in the test tube produces no color. Then add an additional 0.06 g of  $C_6H_8O_6$  for each liter of sample volume.
- (f) Once all Cl<sub>2</sub> has been neutralized, preserve the sample with Sodium Hydroxide (NaOH) and raise the pH to >12. Verify the >12 pH with a pH meter or pH test strips.
- (g) Mark on the side of the CN sample bottle the Lab sheet number (using a water proof marker), and place a corresponding custody seal across the sample bottle tightened cap. Place a Cyanide label on the bottle if cyanide is suspected of being present in the sample.
- (h) Store the CN sample in the ice at 4°C and transport it to the laboratory.

## **Total Sulfides**

- (1) The Total Sulfide sample is collected as a grab sample only. Use a clean 500 ml plastic bottle to collect the sample. This sample may be pumped into the sample container or collected directly from the discharge side of the sampling device.
- (2) Preserve the sample with 1 ml of 2N Zinc Acetate ( $C_4H_6O_4Zn$ ) and then add Sodium Hydroxide (NaOH) to raise the pH > 9.
- (3) Label and seal the sample with a custody seal. Cool to  $4^{\circ}$ C.

## Oil and Grease/TPH

Oil and grease samples are collected as two separate samples:

**METHOD 413.1** (Oil and Grease). Non-volatile hydrocarbons: vegetable oils, animal fats, waxes, soaps, and related matters.

**METHOD 418.1** (TPH). Extractable petroleum hydrocarbons: light fuels and mineral oils.

- (1) This is a grab sample only. The bottle used to take the sample must be the same bottle given to the laboratory for analysis. Do not pump or transfer the wastewater sample into the bottle. Obtain a level one clean 1000 ml glass bottle, do not use a pre-preserved bottle because you will lose the preservative when collecting the sample.
- (2) Collect the sample by placing the bottle neck down (up-side down) into the effluent stream below the surface. This should be as close to the discharge pipe or point as physically possible. Turn the bottle, allowing the bottle to fill, while keeping the bottle below the surface. Remove the filled bottle and cap it. Never skim the surface of the effluent stream.
- (3) Preserve the sample using five ml of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) for method 413.1 or hydrochloric acid (HCL) for method 418.1 (6:1 Ratio) to a pH of less than two. Reference 42 of methods 418.1 and 41 of methods 413.1. When more than five ml of HCL is used to lower the pH to less than two, make note of how much additional acid is used, and record this on the lab sheet. Also indicate required analyses method on lab sheet.
- (4) After making sure the sample is well mixed and preserved, seal and attach the proper identification (custody) label to the bottle. Then attach a custody seal across the lid. Store all samples at 4°C.
- (5) Under no circumstances are Inspectors to collect an oil and grease sample or any other grab sample for IUs.
- (6) All samples must be taken from a good representative flow. If there is any question as to whether there is sufficient flow for a representative sample, do not collect any sample. Make the necessary notes in the file report as to why no sample was obtained.

## BOD/COD/SS

- (1) 24-hour composite sampling is always used for this test. Agitate the bottle to completely mix the composite sample. Do not allow the solids to settle out before you pour off the sample.
- (2) When more than one sample is being taken from a composite bottle, the BOD/COD/SS is taken first. The lab needs 1000 ml if the sample is cloudy or has solids. If the sample is clear, you must collect 2000 ml. Transfer the appropriate volume to the sample bottle.
- (3) Take the pH/temperature of the sample with either pH paper and a thermometer, or the pH meter carried on the sampling trucks.
- (4) Label the sample bottle and place a custody seal over the lid. Store on ice at  $4^{\circ}$ C.
- (5) Should split samples be requested, they are given when it is sure there is enough sample for POTW requirements. Users must provide their own sample containers and allow POTW's staff to pour off samples.



Rotating Bar Screens The Wastewater Headworks is a key compliance sampling location.



**Wastewater related samples**. Above the operator is taking a wastewater sample for COD and TKN using a polypropylene plastic bottle. Below, the operator is using an amber class bottle for EPA Method 8151 Herbicides. This bottle also can be used for other applications such as EPA Method 1664 for Oil and grease along with other analysis that need to be protected from light.





**VOC bottles.** There are several types of analysis that are part of the EPA Method 8260 for Volatile Organics and Volatile Organic Compounds (VOCs). The above photograph shows glass vials that are clear and depending on the Method the vials may also be amber. Depending on the sample method the operator must take precautions not to empty out the preservative that is in the sample bottle as shown above. Some operator may want to add the preservative (acid) themselves.



The 250 ml amber glass bottle as shown above will be used to analyze Chlorinated Herbicides. This method can also determine parent acids and salts and esters of these acids, for example Pentachlorophenol (PCP). Operators of small and rural water and wastewater system use cheaper methods to determine how the treatment process is producing. The sample kit's shown above is an example of how Nitrate and Ammonia Nitrogen can be measured however it does not meet regulatory requirements or methods

## **IOC Section**

# **Periodic Table of the Elements**

	1 IA	New Original		Alkali	metals		Act	inide serie	es	c	Solid							18 VIIIA	
1	H Hydrogen 1.00794	2 IIA		Alkali	ne earth m	netals	Poo	or metals		Br	Liquid		13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	2 4 He Helium 4.002602	Ì
2	3 Li 5.941	4 2 Be Dorytium 9.012182	Lanthanide series		Nonmetals Noble gases		F Gas Tc Synthetic		5 3 B Doron 10.811	6 2 C Corbon 12.0107	7 3 N Néregon 14.00674	8 3 Origen 15 9994	9 7 F F 18.9994032	10 2 Ne Ncon 20.1797	K L				
3	11 Na Sodum 22.969770	12 2 Mg Magnesium 24.8050	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 - VIIIB	10	11 IB	12 IIB	13 2 Al Auminum 26.981538	14 2 Si Silicon 29.0855	15 P Phosphorus 30.970761	16 2 S Sutur 32.066	17 CI 20453	18 2 Ar Argon 39.948	11 × 12
4	19 K Potassium 39.0983	20 28 Ca Calcnum 40.078	21 28 Sc 2 5candium 44 955910	22 28 Ti 10 10 2 Titanium 47.867	23 28 11 Vanadum 50 5415	24 28 Cr 13 Chromum 51.9961	25 28 13 Manganese 54 936049	26 28 Fe 14 tran 55 8457	27 15 Co 15 Cobuit 56 933200	28 3 Ni 18 56 6934	29 28 Cu 18 Copper 63 546	30 28 Zn 19 2000 65:409	31 18 Ga 18 0atium 69 723	32 Ge Germanium 72.64	33 19 As 19 Arsenic 74.92160	34 ta Se ta Setenium 78.96	35 18 Br 19 Bronne 79.904	36 1 Kr 1 Nypton 83 798	N.L.M.Y
5	37 Rb Rubidum 85.4678	38 28 Sr Strortjum 87.62	39 Y 10 92 92 93 93 93 93 93 93 93 93 93 93 93 93 93	40 28 Zr 10 27rconium 91.224	41 10 Nb 10 92 90638	42 Mo 95.94	43 TC Technetum (98)	44 28 Ru 18 Ruthenium 18 101.07	45 20 10 10 10 10 10 10 10 10 10 10 10 10 10	46 28 Pd 10 Patadium 106 42	47 Ag	48 28 19 28 28 28 28 28 28 28 28 28 28 28 28 28	49 2 In 18 100 3 100	50 50 Sn 118.710	51 20 <b>Sb</b> Antimony 121.760	52 10 10 10 10 10 10 10 10 10 10 10 10 10	53 6 100ne 126.90447	54 1 Xe 1 Xenon 131.293	KIMNO
6	55 Cs Cesium 132.90545	56 28 Ba 18 Barium 2 137,327	57 to 71	72 28 Hf 18 Hamum 2 178.49	73 78 Ta Tartalum 12 160.5479	74 28 W 18 Tungsten 2 163.84	75 28 Re 18 Prienkam 2 186 207	76 20 0s 10 0straum 2 190.23	77 28 Ir 192 192 217	78 28 Pt 18 Platinum 1 195.078	79 38 Au 17 Gold 1 196 96655	80 28 Hg 18 Mercury 2 200.59	81 20 TI 10 7hallium 3 204 3899	82 28 Pb 18 Lead 4 207.2	83 18 Bi 18 Bismuth 5 206 98038	84 28 Po 187 Potonium 16 (209)	85 Television Astachner (210)	86 28 Rn 27 Radon 8 (222)	1002212
7	87 1 Francium 1 (223)	88 28 Ra 18 Radum 8 (226) 2	89 to 103	104 Rf 327 RatisetterStart 10 (261)	105 28 D 5 322 Dubnium 11 (262) 2	106 28 S.g. 322 Sestorgium 12 (266) 22	107 28 Bh 18 Botrium 13 (264) 2	108 28 Hs 18 Hassium 18 (269) 2	109 <sup>28</sup> Mt <sup>58</sup> Methenum <sup>55</sup> (268) <sup>2</sup>	110 28 DS 322 Damstadium 17 (271)	111 2 Rg 12 Roentgenium 18 (272) 1	112 18 Uub 18 Ununbium 18 (205) 22	113 Uut Unurthum (284)	114 Uuq Ununquadhum (299)	115 Uup Viordeintum (200)	116 Uuh Ununhesum (292)	117 UUS Ununseptum	118 Ulio Ununoctum	CADELORO
				Atomic masses in parentheses are those of the most stable or common isotope.															
					Design Copyright & 1997 Michael Dagdi (michael@oxyshi.com). Hdp./lwwi.dayah.com/periodic/														
Note: The subgroup numbers 1- 15 were adopted in 1994 by the International Union of Pure and Applied Chernistry. The names of elements 112-115 are the Latin equivalents of those numbers.				57 2 La 18 Lanthanum 2 138.9055	58 20 Ce 10 Cenum 27 140.116	59 78 18 18 19 19 19 19 19 19 19 19 19 19 19 19 19	60 28 Nd 22 Neodymaum 2 144.24	61 2 Pm 18 Promethum 2 (145)	62 2 <b>Sm</b> 5amarium 2 150.36	63 28 Europium 25 151 964	64 2 Gd 35 Gadosnaum 2 157.25	65 2 <b>Tb</b> 18 Terbum 2 158.92534	66 28 Dy 28 Dysprosium 2 162,500	67 29 Hotmium 29 164 93032	68 2 Er 10 Ertsium 2 167 259	69 2 <b>Tm</b> 31 Thulium 2 168.93421	70 2 <b>Yb</b> 18 Ytterbium 2 173.04	71 2 Lu 32 Lutetium 2 174.967	
				89 8 Ac 10 Actinium 9 (227) 2	90 29 Th 16 32 Thorium 232,0381 2	91 22 Pa 18 Protectedury 9 231.03588 2	92 28 U 18 Uranium 238.02891 2	93 2 Np 18 Neptunium 92 (237) 2	94 28 Pu 100 Plutonium 88 (244) 24	95 2 Am 18 Americium 25 (243) 27	96 2 Cm 18 Cunum 25 (247) 2	97 2 Bk 10 Berkelium 8 (247) 2	98 28 Cf 32 Californium 8 (251) 2	99 2 Elis 18 Einsteinium 8 (252) 2	100 3 5 18 727 Fermum 8 (257) 3	101 2 Mcd 32 Mendelevium 8 (258) 2	102 2 No 10 Nobelium 22 (259) 2	103 <sup>2</sup> Ln <sup>18</sup> Lawrenckum <sup>9</sup> (262) <sup>2</sup>	



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> MCL or TT <sup>1</sup> (mg/L) <sup>2</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		
Antimony	0.006	0.006	Increase in blood cholesterol; decrease in blood sugar	Discharge from petroleum refineries; fire retardants; ceramics; electronics; solder		
Arsenic	0 <sup><u>7</u></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		
Asbestos (fiber >10 micrometers)	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		
Barium	2	2	Increase in blood pressure	Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits		
Beryllium	0.004	0.004	Intestinal lesions	Discharge from metal refineries and coal- burning factories; discharge from electrical, aerospace, and defense industries		
Cadmium	0.005	0.005	Kidney damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints		
Chromium (total)	0.1	0.1	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits		
			Short term exposure: Gastrointestinal distress			
Copper	1.3	TT <sup>z</sup> ; Action Level=1.3	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		

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## 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		
Cyanide (as free cyanide)	0.2	0.2	Nerve damage or thyroid problems	Discharge from steel/metal factories; discharge from plastic and fertilizer factories		
Fluoride	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		
Lead	zero	TT <sup>z</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	Corrosion of household plumbing systems; erosion of natural deposits		
			Adults: Kidney problems; high blood pressure			
Mercury (inorganic)	0.002	0.002	Kidney damage	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands		
Nitrate (measured as Nitrogen)	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		
Nitrite (measured as Nitrogen)	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		
Selenium	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		
# 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
Thallium	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.

# **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

sites - N	o. of s	ites		
d) (stan	dard n	nonitoring)	(reduced l	monitoring)
100	50			
60	30			
40	20			
20	10			
10	5			
5	5			
	sites - N d) (stan 100 60 40 20 10 5	sites - No. of s d) (standard n 100 50 60 30 40 20 20 10 10 5 5 5	sites - No. of sites d) (standard monitoring) 100 50 60 30 40 20 20 10 10 5 5 5	sites - No. of sites d) (standard monitoring) (reduced 1 100 50 60 30 40 20 20 10 10 5 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</td>
 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.

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# WATER QUALITY BROKEN DOWN INTO 3 BROAD CATEGORIES

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



# TURBIDITY (ntu's) PARAMETERS FOR WATER QUALITY

# **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





**BASIC WATER CYCLE** 

# 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  $(Sb_2S_3)$ . 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,  $Sb_2O_3$ . 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 (SbH<sub>3</sub>) 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 R3m 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, <sup>121</sup>Sb with a natural abundance of 57.36% and <sup>123</sup>Sb with a natural abundance of 42.64%. It also has 35 radioisotopes, of which the longest-lived is <sup>125</sup>Sb with a half-life of 2.75 years. In addition, 29 metastable states have been characterized. The most stable of these is <sup>124</sup>Sb with a half-life of 60.20 days, which has an application in some neutron sources. Isotopes that are lighter than the stable <sup>123</sup>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  $(Sb_2S_3)$  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  $(Sb_4O_6)$  is formed when antimony is burnt in air. In the gas phase, this compound exists as  $Sb_4O_6$ , but it polymerizes upon condensing. Antimony pentoxide  $(Sb_4O_{10})$  can only be formed by oxidation by concentrated nitric acid. Antimony also forms a mixed-valence oxide, antimony tetroxide  $(Sb_2O_4)$ , 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 Sb(OH)<sub>3</sub> is unknown, but the conjugate base sodium antimonite ([Na<sub>3</sub>SbO<sub>3</sub>]<sub>4</sub>) forms upon fusing sodium oxide and Sb<sub>4</sub>O<sub>6</sub>. Transition metal antimonites are also known. Antimonic acid exists only as the hydrate HSb(OH)<sub>6</sub>, forming salts containing the antimonate anion Sb(OH)–6. Dehydrating metal salts containing this anion yields mixed oxides. Many antimony ores are sulfides, including stibnite (Sb<sub>2</sub>S<sub>3</sub>), pyrargyrite (Ag<sub>3</sub>SbS<sub>3</sub>), 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 [Sb<sub>6</sub>S<sub>10</sub>]<sup>2–</sup> and [Sb<sub>8</sub>S<sub>13</sub>]<sup>2–</sup>.

# Halides

Antimony forms two series of halides,  $SbX_3$  and  $SbX_5$ . The trihalides  $SbF_3$ ,  $SbCl_3$ ,  $SbBr_3$ , and  $Sbl_3$  are all molecular compounds having trigonal pyramidal molecular geometry. The trifluoride  $SbF_3$  is prepared by the reaction of  $Sb_2O_3$  with HF:

 $Sb_2O_3 + 6 HF \rightarrow 2 SbF_3 + 3 H_2O$ 

It is Lewis acidic and readily accepts fluoride ions to form the complex anions SbF-4 and SbF2-5. Molten SbF<sub>3</sub> is a weak electrical conductor. The trichloride SbCl<sub>3</sub> is prepared by dissolving Sb<sub>2</sub>S<sub>3</sub> in hydrochloric acid:

 $Sb_2S_3 + 6 \text{ HCl} \rightarrow 2 \text{ SbCl}_3 + 3 \text{ H}_2S$ 

The pentahalides  $SbF_5$  and  $SbCl_5$  have trigonal bipyramidal molecular geometry in the gas phase, but in the liquid phase,  $SbF_5$  is polymeric, whereas  $SbCl_5$  is monomeric.  $SbF_5$  is a powerful Lewis acid used to make the super acid fluoroantimonic acid ("HSbF<sub>6</sub>").

Oxyhalides are more common for antimony than arsenic and phosphorus. Antimony trioxide dissolves in concentrated acid to form oxoantimonyl compounds such as SbOCI and (SbO)<sub>2</sub>SO<sub>4</sub>.

# Antimonides, hydrides, and organoantimony compounds

Compounds in this class generally are described as derivatives of Sb<sup>3-</sup>. Antimony forms antimonides with metals, such as indium antimonide (InSb) and silver antimonide (Ag<sub>3</sub>Sb). The alkali metal and zinc antimonides, such as Na<sub>3</sub>Sb and Zn<sub>3</sub>Sb<sub>2</sub>, are more reactive. Treating these antimonides with acid produces the unstable gas stibine, SbH<sub>3</sub>:

$$Sb^{3-} \textbf{+} 3 \ H^{\scriptscriptstyle +} \rightarrow SbH_3$$

Stibine can also be produced by treating Sb<sup>3+</sup> 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  $Sb(C_6H_5)_3$  (triphenylstibine),  $Sb_2(C_6H_5)_4$  (with an Sb-Sb bond), and cyclic  $[Sb(C_6H_5)]_n$ . Pentacoordinated organoantimony compounds are common, examples being  $Sb(C_6H_5)_5$  and several related halides.

# History

Antimony(III) sulfide,  $Sb_2S_3$ , 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 28 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 As3-4 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  $As_2O_3$  ("white arsenic") and  $As_2O_5$ , 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 As(OH)<sub>3</sub>.

A broad variety of sulfur compounds of arsenic are known. Orpiment  $(As_2S_3)$  and realgar  $(As_4S_4)$  are somewhat abundant and were formerly used as painting pigments. In  $As_4S_{10}$ , arsenic has a formal oxidation state of +2 in  $As_4S_4$ , 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 (AsF<sub>5</sub>) 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 distinct bulk properties. Other arsenic alloys include the II-IV semiconductor cadmium arsenide.

# **Occurrence and Production**

Minerals with the formula MAsS and MAs<sub>2</sub> (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 Ascontaining 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 arseniccontaining 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 "pressuretreated" 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).

Arsenic Level in Tap Water (in parts per billion, or ppb)	Approximate Total Cancer Risk (assuming 2 liters consumed/day)		
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		

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.

# 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 included 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 (µg/kg/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 arsenicexposed 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  $4.3 \times 10^{-3} (\mu g/m^3)^{-1}$ . EPA estimates that, if an individual were to continuously breathe air containing inorganic arsenic at an average of 0.0002  $\mu g/m^3 (2 \times 10^{-7} \text{ mg/m}^3)$  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  $0.002 \ \mu g/m^3 (2 \times 10^{-6} \ m g/m^3)$  would result in not greater than a one-in-a-hundred thousand increased chance of developing cancer, and air containing  $0.02 \ \mu g/m^3 (2 \times 10^{-5} \ m g/m^3)$  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 (mg/kg/d)<sup>-1</sup> 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  $AsH_3$ , 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 arsenibetaine, 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 (socalled "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 IN DRINKING WATER**

# **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 (CICH=CHAsCl<sub>2</sub>), 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 reddishbrown 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 of0.2 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  $\mu$ g/day. Values about 1000  $\mu$ g 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 (Fe<sub>3</sub>O<sub>4</sub>) nanocrystals. Using the high specific surface area of Fe<sub>3</sub>O<sub>4</sub> 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  $3 \mu g/L$ . 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 singlehome 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.



# TASTE AND ODOR CHLORINE ORGANICS INORGANICS BIOLOGICALS BOTTLED WATER Image: Chlorine Image:

TYPES OF WATER QUALITY FILTRATION TECHNOLOGIES AND EFFECTIVE USES

# 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 have 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 uses 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.

## **Common Asbestos Questions**

## IS ASBESTOS CURRENTLY USED IN ANY NEW PRODUCTS?

Probably not. As you can imagine there has been tremendous liability for any company that manufactured asbestos-containing materials. Manufacturers have found substitutes for asbestos, thus it is not likely that you would encounter new products that contain asbestos. Manufacturers started to phase out the use of asbestos in products during the mid-1970s to early-1980s.

## WHAT IS A CARCINOGEN? IS ASBESTOS A CARCINOGEN?

A carcinogen is a substance capable of causing cancer. Asbestos is a recognized carcinogen. If fact, asbestos is one of a few substances recognized as being a "*true*" human carcinogen.

## HOW ABOUT DOSE-RESPONSE? WHAT DOES THIS MEAN AND HOW IMPORTANT IS IT?

Understanding the concept of dose-response is extremely important in the role of environmental contaminants. The term "**dose**" applies to a person's exposure to a substance. Dose is a measure of how much of a substance a person's body absorbs. In this case, the number of fibers that are in the air, and how much time is spent breathing these fibers. The term "**response**" refers to a health outcome from the dose and generally refers to disease.

Many people are under the false impression that any exposure to an environmental contaminant can cause harm and should be avoided. However, it is impossible to live in a world without contaminants. We are exposed to pollutant, allergens, contaminants and toxic materials every day in our lives in the water we drink, the food we eat and the substances we encounter. Generally these contaminants are found in extremely small quantities and do not pose a threat to our health. Even when we are exposed to higher levels there are mechanisms in the body for detoxification of the contaminants.

It is only when we are exposed to high concentrations (**dose**) for long periods of time that health problems (**response**) become likely. The terms "**high**" and "**long**" vary for each particular substance in the environmental. If exposure can't be avoided, an employees' exposure to asbestos should be for a short duration and at very low levels. This will lower their risk of disease. Even a single exposure to high levels of asbestos most likely would not be a problem.

## HOW CAN ASBESTOS HURT ME?

Unless the asbestos is disturbed, it does not present a hazard. Generally it is necessary to inhale the asbestos fibers for a prolonged period of time before any damaged occurs.

## WHAT CAN I DO TO PROTECT MYSELF AGAINST ASBESTOS?

First and foremost it is important to recognize asbestos or the many products that may contain asbestos. Asbestos was often used for insulation purposes. It generally appears as small fibers that break lengthwise and generally not in half. If you encounter asbestos, or a material that you think contains asbestos, contact your supervisor.

At the present time no UT employees are trained to remove or handle asbestos. Since asbestos is primarily a hazard to the lungs, avoid breathing it. If it is impossible to avoid, or if you feel safer, a respirator equipped with HEPA filters is acceptable. Another method of controlling exposure is to use good dust control procedures. Water is frequently used to control dust.

## ARE THERE ANY ACUTE SYMPTOMS OF ASBESTOS EXPOSURE?

Generally there are no short-term (**acute**) symptoms of asbestos exposure, until the exposure level is extremely high. Inhalation of extremely high levels of asbestos can result in shortness of breath, chest or abdominal pain and irritation of the skin and mucous membranes.

## HOW IS ASBESTOS MEASURED IN THE AIR?

The number of asbestos fibers in the air can be measured by a process known as air sampling or, as it is sometimes called, air monitoring. Basically it is simple. Air is drawn through a small filter where the fibers are trapped. The volume of air sampled is calculated based on the flow rate of the pump and the how long the pump operates. After the sample is collected the filter is sent to a laboratory where the number of fibers are counted.

Note that only fibers are counted. There are other airborne fibers, similar to asbestos that can cause the sample to be artificially high. The laboratory reports the results as the number of fibers per volume of air. Generally the volume of air is expressed as cubic centimeters or cc. Thus, the results are expressed at fibers/cc. There are other lab procedures that can more precisely determine which fibers are asbestos.

## 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 Explained**

**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  $\beta\alpha\rho\dot{\nu}\varsigma$  (*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  $1.8 \times 10^{-5/\circ}$ 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 g·cm<sup>-3</sup>) is again intermediate between those of strontium (2.36 g·cm<sup>-3</sup>) and radium (~5 g·cm<sup>-3</sup>).

## **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:

Ba + 2 ROH  $\rightarrow$  Ba(OR)<sub>2</sub> + H<sub>2</sub>↑ (R is an alkyl or a hydrogen atom)

Additionally, barium reacts with ammonia to form complexes such as  $Ba(NH_3)_6$ .

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,  $g\!\cdot\!cm^{-3}$ 

 
 O<sup>2-</sup>
 S<sup>2-</sup>
 F<sup>-</sup>
 CI<sup>-</sup>
 SO2-4
 CO2-3
 O2-2
 H<sup>-</sup>

 Ca<sup>2+[9]</sup>
 3.34
 2.59
 3.18
 2.15
 2.96
 2.83
 2.9
 1.7

 Sr<sup>2+[10]</sup>
 5.1
 3.7
 4.24
 3.05
 3.96
 3.5
 4.78
 3.26

 Ba<sup>2+[11]</sup>
 5.72
 4.3
 2.1
 1.9
 4.49
 4.29
 4.96
 4.16

 Zn<sup>2+[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 CO<sub>2</sub> 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-live 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 Ba<sup>2+</sup> 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 Explained**

**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  $J \cdot kg^{-1} \cdot K^{-1}$ ) and thermal conductivity (216  $W \cdot m^{-1} \cdot K^{-1}$ ), 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 (11.4×10<sup>-6</sup> K<sup>-1</sup>), 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 ~0.01 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 <sup>9</sup>Be also undergoes a (n,2n) neutron reaction with neutron energies over about 1.9 MeV, to produce <sup>8</sup>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:

9 4Be + n  $\rightarrow$  2(4 2He) + 2n

Neutrons are liberated when beryllium nuclei are struck by energetic alpha particles producing the nuclear reaction

9 4Be + 4 2He  $\rightarrow$  12 6C + n , where 4 2He is an alpha particle and 12 6C is a carbon-12 nucleus.

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, <sup>9</sup>Be, and therefore beryllium is a monoisotopic element.

Plot showing variations in solar activity, including variation in <sup>10</sup>Be concentration. Note that the beryllium scale is inverted, so increases on this scale indicate lower <sup>10</sup>Be levels

Radioactive cosmogenic <sup>10</sup>Be is produced in the atmosphere of the Earth by the cosmic ray spallation of oxygen. <sup>10</sup>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, <sup>10</sup>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 <sup>10</sup>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 <sup>10</sup>Be by the reaction of fast neutrons with <sup>13</sup>C in the carbon dioxide in air. This is one of the indicators of past activity at nuclear weapon test sites. The isotope <sup>7</sup>Be (half-life 53 days) is also cosmogenic, and shows an atmospheric abundance linked to sunspots, much like <sup>10</sup>Be.

<sup>8</sup>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 <sup>4</sup>He nuclei and the very low concentrations of available beryllium-8.

The British astronomer Sir Fred Hoyle first showed that the energy levels of <sup>8</sup>Be and <sup>12</sup>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 <sup>7</sup>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 <sup>13</sup>Be which decays through neutron emission. It has a half-life of  $2.7 \times 10^{-21}$  s. <sup>6</sup>Be is also very short-lived with a half-life of  $5.0 \times 10^{-21}$  s. The exotic isotopes <sup>11</sup>Be and <sup>14</sup>Be are known to exhibit a nuclear halo. This phenomenon can be understood as the nuclei of <sup>11</sup>Be and <sup>14</sup>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 <sup>9</sup>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  $(Be_4Si_2O_7(OH)_2)$ , beryl  $(Al_2Be_3Si_6O_{18})$ , chrysoberyl  $(Al_2BeO_4)$  and phenakite  $(Be_2SiO_4)$ . 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.



Beryllium hydrolysis as a function of pH Water molecules attached to Be are omitted

The beryllium atom has the electronic configuration [He]  $2s^2$ . The two valence electrons give beryllium a +2 oxidation state and the 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 acetylacetone. 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  $[Be(H_2O)_4]^{2+}$  ion.

 $[Be(H_2O)_4]^{2+} + H_2O \rightleftharpoons [Be(H_2O)_3(OH)]^+ + H_3O^+$ 

Other products of hydrolysis include the trimeric ion  $[Be_3(OH)_3(H_2O)_6]^{3+}$ . Beryllium hydroxide,  $Be(OH)_2$ , 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. BeF<sub>2</sub> has a silica-like structure with corner-shared BeF<sub>4</sub> tetrahedra. BeCl<sub>2</sub> and BeBr<sub>2</sub> have chain structures with edge-shared tetrahedra. All beryllium halides have a linear monomeric molecular structure in the gas phase.

Beryllium difluoride,  $BeF_2$ , 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).  $BeF_2$  has many similarities to  $SiO_2$  (quartz) a mostly covalently bonded network solid.  $BeF_2$  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,  $BeF_2$  has much lower electrical conductivity when in solution or when molten than would be expected if it were fully ionic.

## Beryllium Oxide

Beryllium oxide, BeO, is a white refractory solid, which has the wurtzite crystal structure and a thermal conductivity as high as in some metals. BeO is amphoteric. Salts of beryllium can be produced by treating  $Be(OH)_2$  with acid. Beryllium sulfide, selenide and telluride are known, all having the zincblende structure.

## Beryllium Nitride

Beryllium nitride,  $Be_3N_2$  is a high-melting-point compound which is readily hydrolyzed. Beryllium azide,  $BeN_6$  is known and beryllium phosphide,  $Be_3P_2$  has a similar structure to  $Be_3N_2$ . 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  $Be_5B$ ,  $Be_4B$ ,  $Be_2B$ ,  $BeB_2$ ,  $BeB_6$  and  $BeB_{12}$ . Beryllium carbide,  $Be_2C$ , 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).



**DIAGRAM OF AN ATOM** 

# 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.

 $Cd + CdCl_2 + 2 \text{ AlCl}_3 \rightarrow Cd_2(\text{AlCl}_4)_2$ 

## 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 <sup>113</sup>Cd (beta decay, half-life is 7.7 × 10<sup>15</sup> years) and <sup>116</sup>Cd (two-neutrino double beta decay, half-life is 2.9 × 10<sup>19</sup> years). The other three are <sup>106</sup>Cd, <sup>108</sup>Cd (both double electron capture), and <sup>114</sup>Cd (double beta decay); only lower limits on their half-life times have been set. At least three isotopes – <sup>110</sup>Cd, <sup>111</sup>Cd, and <sup>112</sup>Cd – are stable.

Among the isotopes that do not occur naturally, the most long-lived are <sup>109</sup>Cd with a half-life of 462.6 days, and <sup>115</sup>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 <sup>113m</sup>Cd ( $t_{1/2}$  = 14.1 years), <sup>115m</sup>Cd ( $t_{1/2}$  = 44.6 days), and <sup>117m</sup>Cd ( $t_{1/2}$  = 3.36 hours).

The known isotopes of cadmium range in atomic mass from 94.950 u (<sup>95</sup>Cd) to 131.946 u (<sup>132</sup>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, <sup>113</sup>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.



**BASICS OF AN ATOM** 

# 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" ( $\chi \rho \dot{\omega} \mu \alpha$ ), 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 (FeCr<sub>2</sub>O<sub>4</sub>). 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  $\mu$ g/liter, and in rivers and lakes 26  $\mu$ g/liter to 5.2 mg/liter. Chromium is mined as chromite (FeCr<sub>2</sub>O<sub>4</sub>) 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  $\mu$ g/liter of total chromium of which 30  $\mu$ g/liter is present as Cr(VI).

## Isotopes

Naturally occurring chromium is composed of three stable isotopes; <sup>52</sup>Cr, <sup>53</sup>Cr and <sup>54</sup>Cr with <sup>52</sup>Cr being the most abundant (83.789% natural abundance). 19 radioisotopes have been characterized with the most stable being <sup>50</sup>Cr with a half-life of (more than) 1.8×10<sup>17</sup> years, and <sup>51</sup>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.

<sup>53</sup>Cr is the radiogenic decay product of <sup>53</sup>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 <sup>26</sup>Al and <sup>107</sup>Pd for the early history of the solar system. Variations in <sup>53</sup>Cr/<sup>52</sup>Cr and Mn/Cr ratios from several meteorites indicate an initial <sup>53</sup>Mn/<sup>55</sup>Mn ratio that suggests Mn-Cr isotopic composition must result from in-situ decay of <sup>53</sup>Mn in differentiated planetary bodies. Hence <sup>53</sup>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 (<sup>43</sup>Cr) to 67 u (<sup>67</sup>Cr). The primary decay mode before the most abundant stable isotope, <sup>52</sup>Cr, is electron capture and the primary mode after is beta decay. <sup>53</sup>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  $Cr^{3+}$  ion has a similar radius (63 pm) to the  $Al^{3+}$  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  $Cr^{3+}$  replaces  $Al^{3+}$  in corundum (aluminum oxide,  $Al_2O_3$ ), 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 [CrCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]Cl. Closely related compounds have different colors: pale green [CrCl(H<sub>2</sub>O)<sub>5</sub>]Cl<sub>2</sub> and the violet [Cr(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>.

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 (Cr(OH)<sub>3</sub>) is amphoteric, dissolving in acidic solutions to form  $[Cr(H_2O)_6]^{3+}$ , and in basic solutions to form  $[Cr(OH)_6]^{3-}$ . It is dehydrated by heating to form the green chromium(III) oxide (Cr<sub>2</sub>O<sub>3</sub>), 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 (CrO2-4) and dichromate ( $Cr_2O_7^{2-}$ ) anions, which exist in equilibrium:

Chromium(VI) halides are known also and include the hexafluoride  $CrF_6$  and chromyl chloride ( $CrO_2Cl_2$ ).

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  $(Na_2CrO_4)$ 

 $Cr_2O2-7 + 14 H_3O^+ + 6 e^- \rightarrow 2 Cr^{3+} + 21 H_2O (\epsilon_0 = 1.33 V)$ 

They are, however, only moderately oxidizing at high pH:  $CrO2-4 + 4 H_2O + 3 e^- \rightarrow Cr(OH)_3 + 5 OH^- (\epsilon_0 = -0.13 V)$ 

Chromium(VI) compounds in solution can be detected by adding an acidic hydrogen peroxide solution. The unstable dark blue chromium(VI) peroxide ( $CrO_5$ ) is formed, which can be stabilized as an ether adduct  $CrO_5 \cdot OR_2$ .

Chromic acid has the hypothetical formula  $H_2CrO_4$ . It is a vaguely described chemical, despite many well-defined chromates and dichromates are known. The dark red chromium(VI) oxide  $CrO_3$ , 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 ( $CrF_5$ ). This red solid has a melting point of 30 °C and a boiling point of 117 °C. It can be synthesized by treating chromium metal with fluorine at 400 °C and 200 bar pressure.

The peroxochromate(V) is another example of the +5 oxidation state. Potassium peroxochromate  $(K_3[Cr(O_2)_4])$  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 150–170 °C.

Compounds of chromium(IV) (in the +4 oxidation state) are slightly more common than those of chromium(V). The tetrahalides,  $CrF_4$ ,  $CrCl_4$ , and  $CrBr_4$ , can be produced by treating the trihalides ( $CrX_3$ ) 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,  $CrCl_2$ , 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 ( $Cr_2(O_2CCH_3)_4$ ), 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) 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.

174 Chemical Contaminants 201 1<sup>st</sup> Edition TLC (928) 468-0665

# 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 *cyprium* (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. <sup>63</sup>Cu and <sup>65</sup>Cu are stable, with <sup>63</sup>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 <sup>67</sup>Cu with a half-life of 61.83 hours. Seven metastable isotopes have been characterized, with <sup>68m</sup>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  $\beta^+$ . <sup>64</sup>Cu, which has a half-life of 12.7 hours, decays both ways.

<sup>62</sup>Cu and <sup>64</sup>Cu have significant applications. <sup>64</sup>Cu is a radiocontrast for X-ray imaging, and complexed with a chelate can be used for treating cancer. <sup>62</sup>Cu is used in <sup>62</sup>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.

 $2 \ Cu^{2+} + 4 \ I^- \rightarrow 2 \ Cul \ + \ I_2$ 

## **Coordination Chemistry**

Copper, like all metals, forms coordination complexes with ligands. In aqueous solution, copper(II) exists as  $[Cu(H_2O)_6]^{2+}$ . 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:

$$Cu^{2+} + 2 OH^{-} \rightarrow Cu(OH)_{2}$$

Aqueous ammonia results in the same precipitate. Upon adding excess ammonia, the precipitate dissolves, forming tetraamminecopper(II):

$$Cu(H_2O)_4(OH)_2 + 4 \text{ NH}_3 \rightarrow [Cu(H_2O)_2(NH_3)_4]^{2+} + 2 H_2O + 2 OH^-$$

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,  $KCuO_2$ , a blue-black solid. The best studied copper(III) compounds are the cuprate superconductors. Yttrium barium copper oxide (YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>) 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, K<sub>3</sub>CuF<sub>6</sub> and Cs<sub>2</sub>CuF<sub>6</sub>, 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:

 $2 \text{ HO}_2 \rightarrow \text{H}_2\text{O}_2 \textbf{+} \text{O}_2$ 

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.
# 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<sub>3</sub>CN, 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, cyanohydridins 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 CN· 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 oxygendeficient 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  $[M(CN)_6]^{3-}$  (M = Ti, V, Cr, Mn, Fe, Co), which are octahedral in shape;
- the tetracyanides,  $[M(CN)_4]^{2-}$  (M = Ni, Pd, Pt), which are square planar in their geometry;
- the dicyanides  $[M(CN)_2]^-$  (M = Cu, Ag, 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" ( $\{Fe(CN)_6\}^{4-}$ ) 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 [NiFe]-hydrogenases proceeds from carbamoylphosphate, which converts to cysteinyl thiocyanate, the  $CN^-$  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, CH<sub>3</sub>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.

- $RX + CN^- \rightarrow RCN + X^-$  (nucleophilic substitution) followed by
- 1. RCN + 2 H<sub>2</sub>O  $\rightarrow$  RCOOH + NH<sub>3</sub> (hydrolysis under reflux with mineral acid catalyst), or
- 2 RCN + LiAlH<sub>4</sub> + (second step) 4 H<sub>2</sub>O → 2 RCH<sub>2</sub>NH<sub>2</sub> + LiAl(OH)<sub>4</sub> (under reflux in dry ether, followed by addition of H<sub>2</sub>O)

## Manufacture

The principal process used to manufacture cyanides is the Andrussow process in which gaseous hydrogen cyanide is produced from methane and ammonia in the presence of oxygen and a platinum catalyst.

$$2 \text{ CH}_4 + 2 \text{ NH}_3 + 3 \text{ O}_2 \rightarrow 2 \text{ HCN} + 6 \text{ H}_2\text{O}$$

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  $(CH_3)_3SiCN$  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 ( $Fe^{3+}$ ) to compete with cyanide cytochrome  $a_3$  (so that cyanide will bind to the antidote rather that 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 coxidation, converts the amine into a colored 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

Many communities add fluoride to their drinking water to promote dental health. Each community makes its own decision about whether or not to add fluoride. The EPA has set an enforceable drinking water standard for fluoride of 4 mg/L (some people who drink water containing fluoride in excess of this level over many years could develop bone disease, including pain and tenderness of the bones). The EPA has also set a secondary fluoride standard of 2 mg/L to protect against dental fluorosis.

# 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: <u>http://www.cdc.gov/fluoridation/</u>

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<sup>-</sup> 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 (Na<sub>3</sub>AlF<sub>6</sub>) is a pesticide that can leave fluoride on agricultural commodities. Cryolite was originally utilized in the preparation of aluminum.
- Sulfuryl fluoride (SO<sub>2</sub>F<sub>2</sub>) 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 polytetrafluorethylene (Teflon), polychlorotrifluoroethylene (moisture barriers), efavirenz (pharmaceutical used for treatment of HIV), fluoxetine (an antidepressant), 5-fluorouracil (an anticancer drug), hydrochlorofluorocarbons and hydrofluorcarbons (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 ( $H_2SiF_6$ ) and its salt sodium hexafluorosilicate ( $Na_2SiF_6$ ) 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 <sup>18</sup>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.

191 Chemical Contaminants 201 1st Edition TLC (928) 468-0665 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 ( $Na_2SiF_6$ ), the median lethal dose ( $LD_{50}$ ) 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 (≥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 (≥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<sup>-5</sup> 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  $Pb_3O_4$ ).

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  $(NH_4)_2S/(NH_4)_2S_2$  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.

 $2 \text{ PbO} + \text{PbS} \rightarrow 3 \text{ Pb} + \text{SO}_2$ 

# 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  $Pb(NO_3)_2$ . 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  $Pb_3(OH)_2(CO_3)_2$  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  $^{\circ}$ C (210  $^{\circ}$ 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  $R_2PbCl_2$  in the presence of HCl (a by-product of the previous reaction) leads to the complete mineralization to give  $PbCl_2$ . 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)

 $\begin{array}{l} PbO_2 + 4 \ H^+ + SO2 - \\ 4 + 2e^- \rightarrow PbSO_4 + 2 \ H_2O \end{array}$ 

# Anode (Oxidation)

Pb + SO2-4  $\rightarrow$  PbSO<sub>4</sub> + 2e<sup>-</sup>

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 of 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 PbO<sub>2</sub>) 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  $(1.0 \ \mu g/g)$  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 handto-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.



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 °C and boiling point of 356.73 °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 <sup>202</sup>Hg being the most abundant (29.86%). The longest-lived radioisotopes are <sup>194</sup>Hg with a half-life of 444 years, and <sup>203</sup>Hg with a half-life of 46.612 days. Most of the remaining radioisotopes have half-lives that are less than a day. <sup>199</sup>Hg and <sup>201</sup>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 ( 2) 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  $\gamma\delta\rho\alpha\rho\gamma\mu\rho\sigma\varsigma$  (*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, Hg2+2.

Stable derivatives include the chloride and nitrate. Treatment of Hg(I) compounds complexation with strong ligands such as sulfide, cyanide, etc. induces disproportionation to Hg<sup>2+</sup> and elemental mercury. Mercury(I) chloride, a colorless solid also known as calomel, is really the compound with the formula Hg<sub>2</sub>Cl<sub>2</sub>, 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 Hg2+ 3(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  $Ag^+$  does. Best known is mercury(II) chloride, an easily sublimating white solid. HgCl<sub>2</sub> forms coordination complexes that are typically tetrahedral, e.g. HgCl<sub>2</sub>–4.

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 °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, HgS, which occurs in nature as the ore cinnabar and is the brilliant pigment vermillion. Like ZnS, HgS crystallizes in two forms, the reddish cubic form and the black zinc blende form. Mercury(II) selenide (HgSe) and mercury(II) telluride (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  $(Hg_2N^+)$ , the one-dimensional polymer (salts of HgNH+2) n), and "fusible white precipitate" or  $[Hg(NH_3)_2]Cl_2$ . Known as Nessler's reagent, potassium tetraiodomercurate(II) (Hgl2-4) 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 HgR<sub>2</sub>, which are often volatile, or 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  $CH_3HgX$ , 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, diaperrash 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<sub>2</sub>) 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 °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 ng /(1 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  $0.7-42 \ \mu g/m^3$ . A study has shown that acute exposure (4 – 8 hours) to calculated elemental mercury levels of 1.1 to 44 mg/m<sup>3</sup> 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  $NO_3^-$  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 RONO<sub>2</sub> 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  $N_2$  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 electroders 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  $NO_2^-$ , is a symmetric anion with equal N-O bond lengths and a O-N-O bond angle of approximately 120°. 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  $NO_2$  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:

NO + NO<sub>2</sub> + 2NaOH (or Na<sub>2</sub>CO<sub>3</sub>)  $\rightarrow$  2NaNO<sub>2</sub> + H<sub>2</sub>O ( or CO<sub>2</sub>)

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,  $N_2O_3$ , which is formally the anhydride of nitrous acid:

 $2NH_3 + H_2O + N_2O_3 \rightarrow 2NH_4NO_2$ 

This compound may decompose explosively on heating. In organic chemistry nitrites are used in diazotization reactions.

#### Structure

The nitrite ion has a symmetrical structure ( $C_{2v}$  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:

 $HNO_2 \rightleftharpoons H^+ + NO_2^-; pK_a = ca. 3.3 at 18 °C$ 

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:

3HNO<sub>2</sub> (aq) <sup>⇐</sup>H<sub>3</sub>O<sup>+</sup> + NO<sub>3</sub><sup>-</sup> + 2NO

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 is 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 $E^0/V$  $NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O$ +0.94 $2HNO_2 + 4H^+ + 4e^- \rightleftarrows H_2N_2O_2 + 2H_2O$ +0.86 $N_2O_4 + 2H^+ + 2e^- \rightleftharpoons 2HNO_2$ +1.065 $2HNO_2 + 4H^+ + 4e^- \rightleftarrows N_2O + 3H_2O$ +1.29

The data can be extended to include products in lower oxidation states. For example:

$$H_2N_2O_2 + 2H^+ + 2e^- \rightleftharpoons N_2 + 2H_2O; E^0 = 2.65V$$

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):

$$5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 5NO_3^- + 2Mn^{2+} + 3H_2O$$

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:

$$HNO_2 + N_2H_5^+ \rightarrow HN_3 + H_2O + H_3O^+$$

which can also further react with nitrite:

$$HNO_2 + HN_3 \rightarrow N_2O + N_2 + H_2O$$

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,  $[Co(NH_3)_5(ONO)]^{2+}$ ; it is metastable and isomerizes to the yellow nitro complex  $[Co(NH_3)_5(NO_2)]^{2+}$ . An example of chelating nitrite (3) was found in  $[Cu(bipy)_2(O_2N)]NO_3$  - "bipy" is the bidentate ligand 2,2'bypyridyl, 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 redcolored azo dye upon treatment of a NO<sub>2</sub><sup>-</sup>-containing sample with sulfanilic acid and naphthyl-1amine 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 C-NO<sub>2</sub> group. Nitrites have the general formula 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 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 devises because its electrical conductivity varies with light.

Naturallv 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 water at 0.05 mg/l. in

# 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 Se2+ 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 [Se(OH)<sub>3</sub>]<sup>+</sup>.CIO- 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 (~10<sup>-9</sup> to 10<sup>-12</sup> S·cm<sup>-1</sup>) of its highly purified form. This is comparable to or less than that of bromine (7.95×10<sup>-12</sup> S·cm<sup>-1</sup>), 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 Se<sup>2–</sup>, SeO2– 3 and SeO2– 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  $\sigma \epsilon \lambda \eta v \eta$  *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 unsoluble in  $CS_2$ . 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  $(SeO_2)$  and selenium trioxide  $(SeO_3)$ . Selenium dioxide is formed by the reaction of elemental selenium with oxygen:

 $Se_8 + 8 O_2 \rightarrow 8 SeO_2$ 

It is a polymeric solid that forms monomeric  $SeO_2$  molecules in the gas phase. It dissolves in water to form selenous acid,  $H_2SeO_3$ . Selenous acid can also be made directly by oxidizing elemental selenium with nitric acid:

 $3 \text{ Se} + 4 \text{ HNO}_3 + \text{H}_2\text{O} \rightarrow 3 \text{ H}_2\text{SeO}_3 + 4 \text{ NO}$ 

Unlike sulfur, which forms a stable trioxide, selenium trioxide is thermodynamically unstable and decomposes to the dioxide above 185 °C:

 $2 \text{ SeO}_3 \rightarrow 2 \text{ SeO}_2 + \text{O}_2 (\Delta \text{H} = -54 \text{ kJ/mol})$ 

Selenium trioxide is produced in the laboratory by the reaction of anhydrous potassium selenate  $(K_2SeO_4)$  and sulfur trioxide  $(SO_3)$ .

Salts of selenous acid are called *selenites*. These include silver selenite ( $Ag_2SeO_3$ ) and sodium selenite ( $Na_2SeO_3$ ).

Hydrogen sulfide reacts with aqueous selenous acid to produce selenium disulfide:

$$H_2SeO_3 + 2 H_2S \rightarrow SeS_2 + 3 H_2O$$

Selenium disulfide consists of 8-membered rings of a nearly statistical distribution of sulfur and selenium atoms. It has an approximate composition of  $SeS_2$ , with individual rings varying in composition, such as  $Se_4S_4$  and  $Se_2S_6$ . Selenium disulfide has been use in shampoo as an antidandruff agent, an inhibitor in polymer chemistry, a glass dye, and a reducing agent in fireworks. Selenium trioxide may be synthesized by dehydrating selenic acid,  $H_2SeO_4$ , which is itself produced by the oxidation of selenium dioxide with hydrogen peroxide:

 $SeO_2 + H_2O_2 \rightarrow H_2SeO_4$ 

Hot, concentrated selenic acid is capable of dissolving gold, forming gold(III) selenate.

#### Halogen Compounds

lodides 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:

 $Se_8 + 24 \ F_2 \rightarrow 8 \ SeF_6$ 

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:

 $Al_2Se_3 + 6 H_2O \rightarrow Al_2O_3 + 6 H_2Se$ 

Alkali metal selenides react with selenium to form polyselenides, Se2-x, 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  $[((CH_3)_3Si)_2N]_2Se$ .

Selenium reacts with cyanides to yield selenocyanates:

8 KCN + Se<sub>8</sub>  $\rightarrow$  8 KSeCN

#### **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 ( $R_2Se$ , analogues of thioethers), diselenides ( $R_2Se_2$ , 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  $\sigma \epsilon \lambda \eta v \eta$  *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 ( $\mu$ 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.

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1 1																		2
11																		11-
н																		не
1.0079												-						4.0026
lithium	beryllium												boron	carbon	nitrogen	oxygen	fluorine	neon
3	4												5	6	1	8	9	10
Li	Be												В	C	N	0	F	Ne
6.941	9.0122												10.811	12.011	14.007	15.999	18.998	20.180
sodium	magnesium												aluminium	silicon	phosphorus	sulfur	chlorine	argon
11	12												13	14	15	16	17	18
Na	Mg												AI	Si	Ρ	S	CI	Ar
22.990	24.305												26.982	28.086	30.974	32.065	35.453	39.948
potassium	calcium		scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc	gallium	germanium	arsenic	selenium	bromine	krypton
19	20		21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	Ca		So	Ti		Cr	Mn	Fo	Co	Ni	CII	7n	Ga	Go	Λc	So	Br	K r
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39.098	40.078		44.956	47.867	50.942	51.996	54.938	55.845	58.933	58.693	63,546	65.39	69.723	72.61	74.922	78.96	79.904	83.80
39.098 rubidium	40.078 strontium		44.956 yttrium	47.867 zirconium	50.942 niobium	51.996 molybdenum	54.938 technetium	55.845 ruthenium	58.933 rhodium	58,693 palladium	63,546 silver	65.39 cadmium	69.723	72.61	74.922 antimony	78.96 tellurium	79.904 Iodine	83.80 xenon
39.098 rubidium 37	40.078 strontium 38		44.956 yttrium 39	47.867 zirconium <b>40</b>	50.942 niobium 41	51.996 molybdenum 42	54.938 technetium 43	55.845 ruthenium 44	58.933 rhodium 45	58.693 palladium <b>46</b>	63.546 silver 47	65.39 cadmium 48	69.723 Indium 49	72.61 tin 50	74.922 antimony 51	78.96 tellurium 52	79.904 iodine 53	83.80 xenon 54
39,098 rubidium 37 Rb	40.078 strontium 38 Sr		44.956 yttrium 39 Y	47.867 zirconium 40 Zr	50.942 niobium 41 Nb	51.996 molybdenum 42 Mo	54.938 technetium 43 TC	<sup>55.845</sup> ruthenium 44 Ru	58.933 rhodium 45 Rh	58.693 palladium 46 Pd	63.546 silver 47 Ag	eadmium 48 Cd	69.723 Indium 49	72.61 50 Sn	74.922 antimony 51 Sb	78.96 tellurium 52 Te	79.904 iodine 53	83.80 xenon 54 Xe
39,098 rubidium 37 <b>Rb</b> 85,468	40.078 strontium 38 Sr 87.62 badium		44.956 yttrium 39 Y 88.906	47.867 zirconium 40 <b>Zr</b> 91.224 bofnium	50.942 niobium 41 Nb 92.906	51.996 molybdenum 42 Mo 95.94 hungsten	54.938 technetium 43 TC [98]	55.845 ruthenium 44 Ru 101.07	58.933 rhodium 45 Rh 102.91	58.693 palladium 46 Pd 106.42	63.546 silver 47 Ag 107.87	65.39 cadmium 48 Cd 112.41	69.723 indium 49 In 114.82	72.61 tin 50 Sn 118.71	74.922 antimony 51 Sb 121.76	78.96 telurium 52 Te 127.60	79.904 iodine 53 126.90	83.80 xenon 54 Xe 131.29
39.098 rubidium 37 Rb 85.468 caesium 55	40.078 strontium 38 Sr 87.62 barlum 56	57-70	44.956 yttrium 39 Y 88.906 lutetium 71	47.867 zirconium 40 Zr 91.224 hafnium 72	50.942 nioblum 41 Nb 92.906 tantalum 73	51,996 molybdenum 42 Mo 95.94 tungsten 74	54.938 technetium 43 TC [98] rhenium 75	55.845 ruthenium 44 Ru 101.07 osmium 76	58.933 rhodium 45 Rh 102.91 iridium 77	58.693 palladium 46 Pd 106.42 platinum 78	63,546 silver 47 Ag 107.87 gold 79	65.39 cadmium 48 Cd 112.41 mercury 80	69.723 indium 49 In 114.82 thallium 81	72.61 tin 50 Sn 118.71 lead 82	74.922 antimony 51 Sb 121.76 bismuth 83	78.96 tellurium 52 Te 127.60 potonium 84	79.904 iodine 53 126.90 astatine 85	83.80 xenon 54 Xe 131.29 radon 86
39.098 rubidium 37 Rb 85.468 caesium 55	40.078 strontium 38 Sr 87.62 barium 56	57-70	44.956 yttrium 39 Y 88.906 lutetium 71	47.867 zirconium 40 Zr 91.224 hafnium 72	50.942 niobium 41 Nb 92.906 tantalum 73 T	51.996 molybdenum 42 Mo 95.94 tungsten 74	54.938 technetium 43 TC [98] rhenium 75	55.845 ruthenium 44 Ru 101.07 osmium 76	58.933 rhodium 45 Rh 102.91 iridium 77	58,693 palladium 46 Pd 106,42 platinum 78	63.546 silver 47 Ag 107.87 gold 79	65.39 cadmium 48 Cd 112.41 mercury 80	69.723 indium 49 In 114.82 thatilium 81	72.61 tin 50 Sn 118.71 lead 82	74.922 antimony 51 Sb 121.76 bismuth 83	78.96 teiturium 52 Te 127.60 polonium 84	79.904 Iodine 53 126.90 astatine 85	83.80 xenon 54 Xe 131.29 radon 86
39,098 rubidium 37 <b>Rb</b> 85,468 caesium 55 <b>Cs</b>	40.078 strontium 38 Sr 87.62 barium 56 Ba	57-70 <del>X</del>	44.956 yttrlum 39 Y s8.906 lutetium 71 Lu	47.867 zirconium 40 Zr 91.224 hatnium 72 Hf	50.942 niobium 41 Nb 92.906 tantalum 73 Ta	51.996 molybdenum 42 Mo 95.94 tungsten 74 W	54.938 technetium 43 <b>TC</b> [98] thenium 75 <b>Re</b>	55.845 ruthenium 44 Ru 101.07 osmium 76 OS	58,933 rhodium 45 Rh 102,91 iridium 77 Ir	58,693 palladium 46 Pd 106,42 platinum 78 Pt	63,546 silver 47 Ag 107,87 gold 79 Au	65.39 cadmium 48 Cd 112.41 mercury 80 Hg	69,723 indium 49 In 114,82 thallium 81 TI	72.61 tin 50 Sn 118.71 lead 82 Pb	74.922 antimony 51 Sb 121.76 bismuth 83 Bi	78.96 teTurium 52 Te 127.80 polonium 84 PO	79.904 iodine 53 126.90 astatine 85 At	83.80 xenon 54 Xe 131.29 radon 86 Rn
39,098 rubidium 37 <b>Rb</b> 85,468 caesium 55 <b>Cs</b> 132,91	40.078 strontium 38 Sr 87.62 barium 56 Ba 137.33	57-70 <del>X</del>	44.956 yttrium 39 Y 88.906 lutetium 71 Lu 174.97	47.867 zirconium 40 Zr 91.224 hafnium 72 Hf 178.49	50.942 niobium 41 Nb 92.906 tantalum 73 Ta 180.95	51.996 molybdenum 42 MO 95.94 tungsten 74 W 183.84	54.938 technetium 43 Tcc 1989 thenium 75 <b>Rec</b> 186.21	55.845 ruthenium 44 Ru 101.07 osmium 76 OS 190.23	58,933 rhodium 45 Rh 102,91 iridium 77 Ir 192,22	58,693 palladium 46 Pd 106,42 platinum 78 Pt 195,08	63.546 silver 47 Ag 107.87 gold 79 Au 196.97	65.39 cadmium 48 Cd 112.41 mercury 80 Hg 200.59	69,723 indium 49 In 114,82 thailium 81 TI 204,38	72.61 tin 50 Sn 118.71 lead 82 Pb 207.2	74.922 antimony 51 Sbb 121.76 bismuth 83 Bi 208.98	78.96 tellurium 52 Te 127.60 polonium 84 PO [209]	79.904 iodine 53 <b>I</b> 126.90 astatine 85 <b>At</b> [210]	83.80 xenon 54 Xe 131.29 radon 86 Rn [222]
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39.098 rubidium 37 <b>Rb</b> 85.468 caesium 55 <b>Cs</b> 132.91 francium 87	40.078 strontium 38 Sr barium 56 Baa 137.33 radium 88	57-70 ★ 89-102	44.956 yttrihum 39 Y 88.906 luteritum 71 Lu 174.97 lawrencium 103	47.867 zirconium 40 Zrr 91.224 hatinium 72 Hff 178.49 rutherfordium 104	50.942 niobium 41 <b>Nbb</b> 92.906 tantalum 73 <b>Ta</b> 180.95 dubnium 105	51.996 molybdenum 42 MOO 95.94 tungsten 74 W 183.84 seaborgium 106	54.938 technetium 43 Tcc 1981 thenium 75 Ree 186.21 bohrium 107	55.845 ruthenium 44 Ru 101.07 osmium 76 OS 190.23 hassium 108	58.933 rhodlum 45 <b>Rh</b> 102.91 kidium 77 <b>Ir</b> 192.22 meitnentum 109	58,693 palladium 46 Pd 106,42 platinum 78 Pt 195,08 ununnilium 110	63,546 silver 47 Ag gold 79 Au 196,97 unununium 111	65.39 cadmium 48 Cd 112.41 mercury 80 Hg 200.59 ununblum 112	69.723 Indium 49 In 114.82 thallium 81 TI 204.38	72.61 111 50 <b>Sn</b> 1118.71 Iead 82 <b>Pb</b> 207.2 ununquadum 114	74.922 antimony 51 Sbb 121.76 bismuth 83 Bi 208.98	78.96 telurium 52 Tee 127.60 potonium 84 PO [209]	79.904 iodine 53 126.90 astatine 85 At [210]	83.80 xenon 54 Xee 131.29 radon 86 Rn [222]
39.098 rubidum 37 <b>Rb</b> 85.468 caesium 55 <b>Cs</b> 132.91 francium 87 <b>Fr</b>	40.078 stronthum 38 Sr 87.62 barium 56 Baa 137.33 radium 88 Ra	57-70 ★ 89-102 ★ ★	44.956 yttrihum 39 Y B8.906 lutefilum 71 LU 174.97 lawrencium 103 Lr	47.867 zirconium 40 Zrr 91.224 hatinium 72 Hff 178.49 rutherfordium 104 Rff	v 50.942 niobium 41 Nb 92.906 tantalum 73 Ta 180.95 dubnium 105 Db	51.996 motybdenum 42 Moo 95.94 tungsten 74 W 183.84 seaborgium 106 Sg	technetium 43 Tcc 98 thenium 75 Ree 186.21 bohrium 107 Bh	55.845 ruthenium 44 Ruu 101.07 osmilum 76 OS 190.23 hassium 108 HS	58.933 rhodlum 45 Rh 102.91 kidium 77 Ir 192.22 metherium 109 Mt	58,693 palladium 46 Pd 106,42 platinum 78 Pt 195,08 ununnilium 110 Uun	63,546 silver 47 Ag gold 79 Au 196,97 unununium 111 Uuu	65.39 cadmium 48 Cd 112.41 mercury 80 Hg 200.59 ununblum 112 Uub	69.723 Indium 49 In 114.82 thatlium 81 TI 204.38	72.61 1118.71 118.71 16ad 82 Pb 207.2 ununquadum 114 Uuq	74.922 antimony 51 Sbb 121.76 bismuth 83 Bi 208.98	78.96 telurium 52 Te 127.80 polonium 84 PO [209]	79.904 iodine 53 126.90 astatine 85 <b>At</b> [210]	83.80 xenon 54 Xee 131.29 radon 86 Rn [222]
139.098 rubidum 37 Rb 85.468 caesium 55 CS 132.91 francium 87 Fr [223]	40.078 stronitum 38 Sr 87.02 barlum 56 Ba 137.33 radium 88 Ra [226]	57-70 ★ 89-102 ★ ★	44.956 yttrilum 39 Y s8.906 lutetium 71 LU 174.97 lawrencium 103 LC [262]	47.867 zirconium 40 Zrr 91.224 hafnium 72 Hff 178.49 rutherfordium 104 Rff [261]	50.942 nibbium 41 Nb 92.906 tantalum 73 Ta 180.95 dubnium 105 Db [262]	51.996 molybdenum 42 Moo 95.94 tungsten 74 W 183.84 seaborgium 106 SG [266]	54.938 technetium 43 Tc 1981 rhenium 75 Re 186.21 bohnium 107 Bh 1264]	102 55.845 ruthenium 44 Ruu 101.07 osmium 76 OS 190.23 hassium 108 HS [269]	58.933 rhodium 45 Rh 102.91 irdium 77 Ir 192.22 meitnenium 109 Mt [268]	58.693 palladium 46 Pd 106.42 platinum 78 Pt 196.08 ununnilium 110 Uun [271]	63,546 silver 47 Ag 107.87 gold 79 Au 196.97 unununium 111 Uuuu [272]	65.39 cadmium 48 Cd 112.41 mercury 80 Hg 200.59 ununblum 112 Uub	69.723 indum 49 In 114.82 thalilum 81 TI 204.38	72.61 111 50 Sn 118.71 16ad 82 Pb 207.2 Ununquadium 114 Uuq [289]	74.922 antimony 51 Sbb 121.76 bismuth 83 Bi 208.98	78.96 teTurium 52 Te 127.60 potonium 84 PO [209]	79.904 iodine 53 I 126.90 astatine 85 At [210]	83.80 xenon 54 Xe 131.29 radon 86 Rn [222]

	lanthanum	cerium	praseodymium	neodymium	promethium	samarium	europium	gadolinium	terbium	dysprosium	holmium	erbium	thulium	ytterbium
*Lanthanide series	5/	58	59	60	61	62	63	64	65	00	67	68	69	70
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
	138.91	140.12	140.91	144.24	[145]	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04
	actinium	thorium	protactinium	uranium	neptunium	plutonium	americium	curium	berkelium	californium	einsteinium	fermium	mendelevium	nobelium
* * Actinide series	89	90	91	92	93	94	95	96	97	98	99	100	101	102
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
	[227]	232.04	231.04	238.03	[237]	[244]	[243]	[247]	[247]	[251]	[252]	[257]	[258]	[259]

# 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 **TI** 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  $\theta \alpha \lambda \lambda \delta \varsigma$ , *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<sup>+</sup>) 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 TICI) 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. <sup>203</sup>Tl and <sup>205</sup>Tl are the only stable isotopes, and <sup>204</sup>Tl is the most stable radioisotope, with a half-life of 3.78 years.

<sup>202</sup>TI (half-life 12.23 days) can be made in a cyclotron, while <sup>204</sup>TI is made by the neutron activation of stable thallium in a nuclear reactor.

<sup>201</sup>TI (half-life 73 hrs), decays by electron capture, emitting Hg X-rays (~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.

<sup>208</sup>TI (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.<sup>126</sup>

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  $TI^{3+} + 3 e^- \rightarrow TI(s)$ . The thallium(III) oxide is a black solid which decomposes above 800 °C, forming the thallium(I) oxide and oxygen.

#### History

Thallium (Greek  $\theta \alpha \lambda \lambda \delta \varsigma$ , *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  $TICu_7Se_4$ , hutchinsonite  $TIPbAs_5S_9$ , and lorandite  $TIAsS_2$ . 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 highdensity 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 °C, some 20 °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  $(TI(CHO_2))$  and thallium(I) malonate  $(TI(C_3H_3O_4))$  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 g/cm<sup>3</sup> at 20 °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 mg per m<sup>2</sup> 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 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.

#### **Thallium Pollution**

According to the United States Environmental Protection Agency (EPA), man-made sources of thallium pollution include gaseous emission of cement factories, coal burning power plants, and metal sewers. The main source of elevated thallium concentrations in water is the leaching of thallium from ore processing operations.

Organic chemicals that are regulated in drinking water are a group of human-made chemical compounds and are components of a variety of pesticides and industrial and commercial products, including degreasers, paints, and petroleum distillates.



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# **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 SOCs 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 SOCs. The monitoring frequency can be adjusted through a waiver if SOCs 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, SOCs, and VOCs.

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 MCLs 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

# Volatile Organic Compounds (VOCs)

#### 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 sublimate from the liquid or solid form of the compound and enter the surrounding air.

An example is formaldehyde, with a boiling point of -19 °C (-2 °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 perchlorothylene in the dry cleaning process to reuse it in an effort to save money, they can't recapture it all. To avoid exposure to perchlorothylene, 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 manmade 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.

Volatile Organic Chemicals	MCL (ppb)	Potential Health Effects
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 Bromodichloromethane Chlorodibromomethane	100	Cancer
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

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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**



Germanium, left and Boron, right





# WATER QUALITY INDICATORS

### **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 amphoterism. 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 metalloidal', showing metalloidal character, or having metalloid-like or some metalloid(al) or metallic properties.

#### Allotropes

Some allotropes of the elements exhibit more pronounced metallic, metalloidal 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

Н								He
Li	Be		В	С	N	0	F	Ne
Na	Mg		AI	Si	Р	S	CI	Ar
K	Ca	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Cd	In	Sn	Sb	Те	I	Xe
Cs	Ba	Hg	ΤI	Pb	Bi	Po	At	Rn
Fr	Ra	Cn	Uut	FI	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.



## WATER MOLECULE

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 microrganisms 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:
  - o Actinium
  - o Thorium
  - o Uranium
  - o Radium
  - $\circ$   $\;$  The transuraniums, such as plutonium, americium, etc.
  - o 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

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## 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 lifebiological 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)

Non toxic Low toxic		ty	Moderate to high toxicity				
Aluminum	Magnesium	Barium	Praseodymium	Actinium	Indium	Polonium	Uranium
Bismuth	Manganese	Cerium	Promethium	Antimony	Iridium	Radium	Vanadium
Calcium	Molybdenum	Dysprosium	Rhenium	Beryllium	Lead	Ruthenium	Zinc
Cesium	Potassium	Erbium	Rhodium	Boron	Mercury	Silver	Zirconium
Iron	Strontium	Europium	Samarium	Cadmium	Nickel	Tantalum	
Lithium	Rubidium	Gadolinium	Scandium	Chromium	Niobium	Thallium	
	Sodium	Gallium	Terbium	Cobalt	Osmium	Thorium	
		Germanium	Thulium	Copper	Palladium	Titanium	
		Gold	Tin	Hafnium	Platinum	Tungsten	
		Holmium	Ytterbium				
		Neodymium	Yttrium				

[Metals that normally do not exist as dissolved species in natural waters or are very rare in crustal rocks are in italics]

 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

[µg/L, microgram per liter; µg/g, microgram per gram; >, greater than; <, less than; --, no guideline available]

	Cadmium	Chromium	Copper	Lead	Mercury	Uranium
Drinking water, in µg/L <sup>1</sup>	5	100	<sup>2</sup> 1,000	15	2	<sup>3</sup> 20
Water supporting aquatic life, in µ.g/L <sup>4</sup>	12	100	20	100	0.05	-
Natural sediments, nonpolluted, in $\mu g/g^5$		<25	<25	<40	<1	-
Natural sediments, moderately polluted, in µ.g/g <sup>5</sup>		25 to 75	25 to 50	40 to 60		-
Natural sediments, heavily polluted, in $\mu g/g^5$	>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 ( $Sb_2S_3$ ). 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,  $Sb_2O_3$ . 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 (SbH<sub>3</sub>) 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 R3m 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, <sup>121</sup>Sb with a natural abundance of 57.36% and <sup>123</sup>Sb with a natural abundance of 42.64%. It also has 35 radioisotopes, of which the longest-lived is <sup>125</sup>Sb with a half-life of 2.75 years. In addition, 29 metastable states have been characterized. The most stable of these is <sup>124</sup>Sb with a half-life of 60.20 days, which has an application in some neutron sources. Isotopes that are lighter than the stable <sup>123</sup>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 ( $Sb_2S_3$ ) 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. Vásaros & 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 At<sup>+</sup> and AtO<sup>+</sup> 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 (XAt), astatates (XAtO<sub>3</sub>), 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.

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TEST REPORT: WATER COMPANY 123 ANYWHERE ST. SOMEWHERE, AZ 85001	D A <u>F</u>	RINKING V NALYSIS F OR MODEL :	VATER RESULTS RO103TDS
IND THIS CONTAMINANT WAS NOT DETECTED AT OR ABOVE CON ND SNO BACTERIA SUBMITTED NBR NO BACTERIA REQU THE MCL (Maximum Contaminant Level) OR AN ESTABLISHE ** BACTERIA RESULTS MAY BE INVALID DUE TO LACK OF COLLE THE 30-HOUR HOLDING TIMES	UR STATED DETECTIO IRED D GUIDELINE HAS BEE CTION INFORMATION	ON LEVEL	THIS CONTAMINANT PLE HAS EXCEEDED
ANALYSIS PERFORMED: P - PRESSURE A - ABSENCE EP - E.C.	MCL (mg/l)	Det. Level	Level Detected
TOTAL COLIFORM	Р	Р	А
INORGANIC CHEMICALS - Metals			
Aluminum Arsenic Barium Cadmium	0.2 0.05 2 0.005	0.1 0.020 0.30 0.002	ND ND ND
Chromium Copper Iron	0.1 1.3 0.3	0.010 0.004 0.020	
Manganese Mercury Nickel	0.05 0.002 0.1	0.004 0.001 0.02	
Selenium Silver Sodium Zinc	0.05 0.1  5	0.02 0.02 1.0 0.004	
INORGANIC CHEMICALS - Other, and Physic	cal Factors		
Alkalinity (Total as CaCO)		0.1	ND
Fluoride Nitrate as N Nitrite as N	4 10 1	0.5 0.5 0.5	
Sulfate Hardness (suggested limit - 100) pH (Standard Units)	250 6.5 - 8.5	5.0 10	ND ND 7.7
Total Dissolved Solids Turbidity (Turbidity Units)	500 1.0	20 0.1	ND ND
ORGANIC CHEMICALS - Trihalomethanes:			
Bromoform	0.080	0.004	ND

# WATER ANALYSIS REPORT

Chemical Contaminants 201 11/1/2017 TLC (928) 468-0665

### 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 28 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 As3– 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  $As_2O_3$  ("white arsenic") and  $As_2O_5$ , 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 As(OH)<sub>3</sub>.

A broad variety of sulfur compounds of arsenic are known. Orpiment  $(As_2S_3)$  and realgar  $(As_4S_4)$  are somewhat abundant and were formerly used as painting pigments. In  $As_4S_{10}$ , arsenic has a formal oxidation state of +2 in  $As_4S_4$ , 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 (AsF<sub>5</sub>) 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 distinct bulk properties. Other arsenic alloys include the II-IV semiconductor cadmium arsenide.

#### **Occurrence and Production**

Minerals with the formula MAsS and MAs<sub>2</sub> (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.

Arsenic Level in Tap Water (in parts per billion, or ppb)	Approximate Total Cancer Risk (assuming 2 liters consumed/day)
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 included 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 (µg/kg/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 noobserved-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  $4.3 \times 10^{-3} (\mu g/m^3)^{-1}$ . EPA estimates that, if an individual were to continuously breathe air containing inorganic arsenic at an average of  $0.0002 \ \mu g/m^3 (2 \times 10^{-7} \ m g/m^3)$  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  $0.002 \ \mu g/m^3 (2 \times 10^{-6} \ m g/m^3)$  would result in not greater than a one-in-a-hundred thousand increased chance of developing cancer, and air containing  $0.02 \ \mu g/m^3 (2 \times 10^{-5} \ m g/m^3)$  would result in not greater than a one-in-a-fundred thousand increased chance of developing cancer, and air containing  $0.02 \ \mu g/m^3 (2 \times 10^{-5} \ m g/m^3)$  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 (mg/kg/d)<sup>-1</sup> 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.

## **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 lowabundance 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<sup>+</sup>) 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 ( $C_6H_5$ ) $_4$ <sup>-</sup>) 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, isoelectronic with N<sub>2</sub>, is not isolable in condensed form, but  $B_2F_4$  and  $B_4Cl_4$  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  $\delta^{11}$ 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  $3.5 \times 10^{-22}$  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  ${}^{10}B(OH)_4$  ion onto clays. It results in solutions enriched in  ${}^{11}B(OH)_3$  and therefore may be responsible for the large  ${}^{11}B$  enrichment in seawater relative to both oceanic crust and continental crust; this difference may act as an isotopic signature. The exotic  ${}^{17}B$  exhibits a nuclear halo, i.e. its radius is appreciably larger than that predicted by the liquid drop model.

The <sup>10</sup>B isotope is good at capturing thermal neutrons. Natural boron is about 20% <sup>10</sup>B and 80% <sup>11</sup>B. The nuclear industry enriches natural boron to nearly pure <sup>10</sup>B. The less-valuable by-product, depleted boron, is nearly pure <sup>11</sup>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-BF<sub>3</sub>) 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 <sup>10</sup>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, <sup>10</sup>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, <sup>10</sup>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, <sup>6</sup>Li and <sup>10</sup>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 <sup>10</sup>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 <sup>11</sup>B and contains almost no <sup>10</sup>B. <sup>11</sup>B is largely immune to radiation damage. Depleted boron is a by-product of the nuclear industry.

<sup>11</sup>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 <sup>11</sup>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% B<sub>2</sub>O<sub>3</sub>, 80% SiO<sub>2</sub>, and 2% Al<sub>2</sub>O<sub>3</sub>, 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 laserassisted 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 wellknown "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 ( $B_2O_3$ ), liquid (BBr<sub>3</sub>), or gaseous boron sources ( $B_2H_6$  or BF<sub>3</sub>). However, after 1970s, it was mostly replaced by ion implantation, which relies mostly on BF<sub>3</sub> 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 (Nd<sub>2</sub>Fe<sub>14</sub>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  $B_2O_3$  with carbon in the electric furnace:

 $2 B_2 O_3 + 7 C \rightarrow B_4 C + 6 CO$ 

Boron carbide's structure is only approximately  $B_4C$ , 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  $B_{12}C_3$  (i.e., with  $B_{12}$  dodecahedra being a motif), but with less carbon as the suggested  $C_3$  units are replaced with B-C chains, and there are smaller ( $B_6$ ) 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 ReB<sub>2</sub> 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.
- AlMgB<sub>14</sub> + TiB<sub>2</sub> 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 (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>•10 H<sub>2</sub>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) H<sub>3</sub>BO<sub>3</sub> 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 pharamaceutical 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 in 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.  $MgB_2$  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.

## **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 Ag<sub>8</sub>GeS<sub>6</sub>.

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 (GeCl<sub>4</sub>), 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 ( $Ge(C_2H_5)_4$ ), 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<sup>10</sup>, 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 (GeF <sub>4</sub>) 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 ([GeO]<sup>2–3</sup>). 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 Ge<sub>2</sub>Cl<sub>6</sub>, and +3 and +1 observed on the surface of oxides, or negative oxidation states in germanes, such as –4 in GeH<sub>4</sub>.

Germanium cluster anions (Zintl ions) such as  $Ge_4^{2^-}$ ,  $Ge_9^{4^-}$ ,  $Ge_9^{2^-}$ ,  $[(Ge_9)_2]^{6^-}$  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  $O_3^-$ .

Two oxides of germanium are known: germanium dioxide (GeO<sub>2</sub>, germania) and germanium monoxide, (GeO). The dioxide, GeO<sub>2</sub> can be obtained by roasting germanium disulfide (GeS<sub>2</sub>), 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 GeO<sub>2</sub> 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,  $Bi_4Ge_3O_{12}$ , (BGO) is used as a scintillator.

Binary compounds with other chalcogens are also known, such as the disulfide (GeS<sub>2</sub>), diselenide (GeSe<sub>2</sub>), and the monosulfide (GeS), selenide (GeSe), and telluride (GeTe). GeS<sub>2</sub> 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 (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  $Gel_4$  is a solid,  $GeF_4$  a gas and the others volatile liquids. For example, germanium tetrachloride,  $GeCl_4$ , 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.  $GeCl_4$  is used in the production of organogermanium compounds. All four dihalides are known and in contrast to the tetrahalides are polymeric solids. Additionally  $Ge_2Cl_6$  and some higher compounds of formula  $Ge_nCl_{2n+2}$  are known. The unusual compound  $Ge_6Cl_{16}$  has been prepared that contains the  $Ge_5Cl_{12}$  unit with a neopentane structure.

Germane (GeH<sub>4</sub>) is a compound similar in structure to methane. Polygermanes compounds that are similar to alkanes—with formula  $Ge_nH_{2n+2}$  containing up to five germanium atoms are known. The germanes are less volatile and less reactive than their corresponding silicon analogues. GeH<sub>4</sub> reacts with alkali metals in liquid ammonia to form white crystalline MGeH<sub>3</sub> which contain the GeH<sub>3</sub><sup>-</sup> 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 ( $Ge(C_2H_5)_4$ ). Organogermanes of the type R<sub>4</sub>Ge (where R is an alkyl) such as tetramethylgermane ( $Ge(CH_3)_4$ ) and tetraethylgermane are accessed through the cheapest available germanium precursor germanium tetrachloride and alkyl nucleophiles.

Organic germanium hydrides such as isobutylgermane  $((CH_3)_2CHCH_2GeH_3)$  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, germylenes (similar to carbenes), and germynes (similar to carbynes). The organogermanium compound 2-carboxyethylgermasesquioxane 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 (GeO<sub>2</sub>) 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. 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 spectroscopes 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 (SiO<sub>2</sub>) and germanium dioxide (GeO<sub>2</sub>), the silica stationary phase in some gas chromatography columns can be replaced by GeO<sub>2</sub>.

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.

# **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 rosecolored Po<sup>2+</sup> 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 Po<sup>2–</sup> 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 Po<sup>2–</sup> 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  $LD_{50}$  for <sup>210</sup>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 <sup>210</sup>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  $\mu$ Sv/Bq if ingested, and 2.5  $\mu$ Sv/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,  $\mu$ Ci), about 50 nanograms (ng), or inhaling 1.8 MBq (48  $\mu$ Ci), 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>  $\mu$ Ci/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  $T_2O$ ).

<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. G

loves 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 Ålexander Litvinenko, a Russian dissident, in 2006 was announced as due to <sup>210</sup>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 <sup>210</sup>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 <sup>210</sup>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 <sup>210</sup>Po as a source of charged particles for neutralizing static electricity. In USA, the devices with no more than 500  $\mu$ Ci of (sealed) <sup>210</sup>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  $\mu$ 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 <sup>210</sup>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  $W \cdot m^{-1} \cdot K^{-1}$ , 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 nm (5.430710 Å).

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 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 threedimensional 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 SiO<sub>2</sub> + 2 C  $\rightarrow$  Si + 2 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:  $SiO_2 + C \rightarrow SiO + CO$  or  $SiO + 2 C \rightarrow SiC + CO$ . However, provided the concentration of  $SiO_2$  is kept high, the silicon carbide can be eliminated by the chemical reaction

 $2 \text{ SiC} + \text{SiO}_2 \rightarrow 3 \text{ Si} + 2 \text{ CO}.$ 

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 (99.9999999%), 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 resolidified, 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 highpurity zinc vapors at 950 °C, producing silicon by SiCl<sub>4</sub> + 2 Zn  $\rightarrow$  Si + 2 ZnCl<sub>2</sub>. 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 HSiCl<sub>3</sub>  $\rightarrow$  Si + 2 HCl + SiCl<sub>4</sub>. 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, Mg<sub>2</sub>Si through high melting refractory compounds such as molybdenum disilicide, MoSi<sub>2</sub>.
- Silicon carbide, 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, SiH<sub>4</sub>, is a pyrophoric gas with a similar tetrahedral structure to methane, CH<sub>4</sub>. 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,  $Si_nH_{2n+2}$  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, SiX<sub>4</sub>, 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, (SiF<sub>2</sub>)<sub>n</sub>.
- 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*, Si(OH)<sub>4</sub>.
- Under the right conditions monosilicic acid readily polymerizes to form more complex silicic acids, ranging from the simplest condensate, disilicic acid (H<sub>6</sub>Si<sub>2</sub>O<sub>7</sub>) to linear, ribbon, layer and lattice structures which form the basis of the many silicate minerals and are called *polysilicic acids* {Si<sub>x</sub>(OH)<sub>4-2x</sub>}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, SiS<sub>2</sub> is a polymeric solid (unlike its carbon analogue the liquid CS<sub>2</sub>).
- Silicon forms a nitride, Si<sub>3</sub>N<sub>4</sub> 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 SiH<sub>n</sub>X<sub>3-n</sub> ligands, SiX<sub>3</sub> ligands, and Si(OR)<sub>3</sub> 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 polydimethysilylene (SiMe<sub>2</sub>)<sub>n</sub>. Polycarbosilane, [(SiMe<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>]<sub>n</sub> with a backbone containing a repeating -Si-Si-C unit, is a precursor in the production of silicon carbide fibers.

# **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,  $(CH_3)_2Te$ , 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  $(Te(OH)_6)$ . 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, <sup>122</sup>Te, <sup>123</sup>Te, <sup>124</sup>Te, <sup>125</sup>Te and <sup>126</sup>Te, are stable. The other three, <sup>120</sup>Te, <sup>128</sup>Te and <sup>130</sup>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 <sup>128</sup>Te). This makes <sup>128</sup>Te the isotope with the longest half-life among all radionuclides, which is approximately 160 trillion (10<sup>12</sup>) 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 <sup>106</sup>Te to <sup>110</sup>Te being able to undergo this mode of decay.<sup>[6]</sup> The atomic mass of tellurium (127.60 g·mol<sup>-1</sup>) exceeds that of the following element iodine (126.90 g·mol<sup>-1</sup>).

#### 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  $\mu$ g/kg. In comparison, even the rarest of the lanthanides have crustal abundances of 500  $\mu$ g/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  $AuTe_2$ ), petzite,  $Ag_3AuTe_2$ , and sylvanite,  $AgAuTe_4$ . 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,  $AuSb_2$ , and bismuthide maldonite,  $Au_2Bi$ , 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, NiTe<sub>2</sub>). 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.

$$M_2Te + O_2 + Na_2CO_3 \rightarrow Na_2TeO_3 + 2 M + CO_2$$

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.

$$HTeO-3 + OH^- + H_2SO_4 \rightarrow TeO_2 + SO2-4 + 2 H_2O$$

The reduction to the metal is done either by electrolysis or by reacting the tellurium dioxide with sulfur dioxide in sulfuric acid.

$$TeO_2 + 2 SO_2 + 2H_2O \rightarrow Te + SO2-4 + 4 H^+$$

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,  $Te_n^{2-}$ . The -2 oxidation state is exhibited in binary compounds with many metals, such as zinc telluride, ZnTe, formed by heating tellurium with zinc. Decomposition of ZnTe with hydrochloric acid yields hydrogen telluride (H<sub>2</sub>Te), a highly unstable analogue of the other chalcogen hydrides, H<sub>2</sub>O, H<sub>2</sub>S and H<sub>2</sub>Se:

 $ZnTe + 2 \text{ HCl} \rightarrow ZnCl_2 + H_2Te$ 

 $H_2Te$  is unstable, whereas salts of its conjugate base [TeH]<sup>-</sup> are stable.

#### Halides

The +2 oxidation state is exhibited by the dihalides,  $TeCl_2$ ,  $TeBr_2$  and  $Tel_2$ . 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:

 $Te + X_2 + 2 X^- \rightarrow TeX2-4$ 

where X is Cl, Br, or I. These anions are square planar in geometry. Polynuclear anionic species also exist, such as the dark brown Te 2I2– 6, and the black Te 4I2–14.

Fluorine forms two halides with tellurium: the mixed-valence  $Te_2F_4$  and  $TeF_6$ . In the +6 oxidation state, the  $-OTeF_5$  structural group occurs in a number of compounds such as  $HOTeF_5$ ,  $B(OTeF_5)_3$ ,  $Xe(OTeF_5)_2$ ,  $Te(OTeF_5)_4$  and  $Te(OTeF_5)_6$ . The square antiprismatic anion TeF2-

8 is also attested. The other halogens do not form halides with tellurium in the +6 oxidation state, but only tetrahalides (TeCl<sub>4</sub>, TeBr<sub>4</sub> and Tel<sub>4</sub>) in the +4 state, and other lower halides (Te<sub>3</sub>Cl<sub>2</sub>, Te<sub>2</sub>Cl<sub>2</sub>, Te<sub>2</sub>Br<sub>2</sub>, Te<sub>2</sub>I and two forms of TeI). In the +4 oxidation state, halotellurate anions are known, such as TeCl2–6 and Te<sub>2</sub>Cl2– 10.

Halotellurium cations are also attested, including Tel+3, found in Tel<sub>3</sub>AsF<sub>6</sub>.

## Oxocompounds

Tellurium monoxide was first reported in 1883 as a black amorphous solid formed by the heat decomposition of  $TeSO_3$  in vacuum, disproportionating into tellurium dioxide,  $TeO_2$  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,  $\beta$ -TeO<sub>3</sub>, is obtained by thermal decomposition of Te(OH)<sub>6</sub>. 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 Te<sup>4+</sup>, OH<sup>-</sup> and O-2. Tellurium also exhibits mixed-valence oxides, Te<sub>2</sub>O<sub>5</sub> and Te<sub>4</sub>O<sub>9</sub>. The tellurium oxides and hydrated oxides form a series of acids, including tellurous acid  $(H_2TeO_3)$ , orthotelluric acid  $(Te(OH)_6)$  and metatelluric acid  $((H_2TeO_4)_n)$ . The two forms of telluric acid form *tellurate* salts containing the TeO2–4 and TeO6–6 anions, respectively. Tellurous acid forms *tellurite* salts containing the anion TeO2–3. Other tellurium cations include TeF2+8, which consists of two fused tellurium rings and the polymeric TeF2+7.

## Zintl cations

When tellurium is treated with concentrated sulfuric acid, it forms red solutions containing the Zintl ion, Te2+4. The oxidation of tellurium by  $AsF_5$  in liquid  $SO_2$  also produces this square planar cation, as well as with the trigonal prismatic, yellow-orange Te4+6:

4 Te + 3 AsF<sub>5</sub>  $\rightarrow$  Te2+ 4(AsF-6)<sub>2</sub> + AsF<sub>3</sub> 6 Te + 6 AsF<sub>5</sub>  $\rightarrow$  Te4+ 6(AsF-6)<sub>4</sub> + 2 AsF<sub>3</sub>

Other tellurium Zintl cations include the polymeric Te2+7 and the blue-black Te2+ 8, which consists of two fused 5-membered tellurium rings. The latter cation is formed by the reaction of tellurium with tungsten hexachloride:

 $\begin{array}{l} 8 \text{ Te } + 2 \text{ WCl}_6 \rightarrow \text{Te2+} \\ 8(\text{WCl-6})_2 \end{array}$ 

Interchalcogen cations also exist, such as  $Te_2Se_2+6$  (distorted cubic geometry) and  $Te_2Se_2+$ 

8. These are formed by oxidizing mixtures of tellurium and selenium with  $AsF_5$  or  $SbF_5$ .

## Organotellurium compounds

Tellurium does not readily form analogues of alcohols and thiols, with the functional group –TeH and are called tellurols. The –TeH functional group is also attributed to using the prefix *tellanyl*-. Like H<sub>2</sub>Te, these species are unstable with respect to loss of hydrogen. Telluraethers (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 *antimonalischer 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.

Element	Allotropes
Tin:	<ul> <li>grey tin (alpha tin)</li> <li>white tin (beta tin)</li> <li>rhombic tin (gamma tin)</li> <li>sigma tin</li> </ul>
Iron:	<ul> <li>ferrite (alpha iron) - forms below 770°C (the Curie point, T<sub>c</sub>); the iron becomes magnetic in its alpha form; BCC</li> <li>beta - forms below 912°C; BCC crystal structure</li> <li>gamma - forms below 1,394°C; FCC crystal structure</li> <li>delta - forms from cooling down molten iron below 1,538°C; BCC crystal structure</li> <li>epsilon - forms at high pressures</li> </ul>

## 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	- 15		-		273	5	121		05)	20		1	0.7	205	0.50	20	65	helium
H I																		
1.0079																		4.0026
lithium	beryllium	1											boron	carbon	nitrogen	oxygen	fluorine	neon
3	4												5	6	7	8	9	10
Li	Be												В	C	N	0	F	Ne
6.941	9.0122												10.811	12.011	14.007	15.999	18.998	20.180
sodium	magnesium												aluminium	silicon	phosphorus	sulfur	chlorine	argon
	12												13	14	15	16	11/	18
Na	Mq												AI	SI	Ρ	S	C	Ar
22.990	24.305									_			26.982	28.086	30.974	32.065	35.453	39.948
potassium	calcium		scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc	gallium	germanium	arsenic	selenium	bromine	krypton
19	20		21	22	23	24	25	26	21	28	29	30	31	32	33	34	35	36
									-									
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
<b>K</b> 39.098	Ca 40.078		<b>Sc</b> 44.956	<b>Ti</b> 47.867	50.942	<b>Cr</b> 51.996	<b>Mn</b> 54.938	<b>Fe</b>	<b>Co</b> 58.933	Ni 58.693	Cu 63,546	<b>Zn</b> 65.39	Ga 69.723	<b>Ge</b> 72.61	<b>As</b> 74.922	<b>Se</b> 78.96	<b>Br</b> 79.904	<b>Kr</b> 83.80
K 39.098 rubidium 37	Ca 40.078 strontium 38		44.956 yttrium	47.867 zirconium	50.942 niobium	51.996 molybdenum	54.938 technetium	Fe 55.845 ruthenium	58.933 rhodium	58.693 palladium	63.546 silver	Zn 65.39 cadmium	Ga 69.723 Indium	72.61	As 74.922 antimony	78.96 tellurium	Br 79.904 Iodine	83.80 xenon
K 39.098 rubidium 37	Ca 40.078 strontium 38		44.956 yttrium 39	47.867 zirconium 40	50.942 niobium 41	51.996 molybdenum 42	Mn 54.938 technetium 43	Fe 55.845 ruthenium 44	Co 58.933 rhodium 45	Ni 58.693 palladium 46	63.546 silver 47	Zn 65.39 cadmium 48	Ga 69.723 indium 49	Ge 72.61 tin 50	As 74.922 antimony 51	Se 78.96 telurium 52	8r 79.904 Iodine 53	83.80 xenon 54
8 39.098 rubidium 37 Rb	Ca 40.078 strontium 38 Sr		Sc 44.956 yttrium 39 Y	Ti 47.867 zirconium 40 Zr	V 50.942 niobium 41 Nb	Cr 51.996 molybdenum 42 Mo	Mn 54.938 technetium 43 TC	Fe 55.845 ruthenium 44 Ru	Co 58.933 rhodium 45 Rh	Ni 58,693 palladium 46 Pd	Cu 63.546 silver 47 Ag	Zn 65.39 cadmium 48 Cd	Ga 69.723 Indium 49 In	Ge 72.61 tin 50 Sn	As 74.922 antimony 51 Sb	Se 78.96 tellurium 52 Te	Br 79.904 todine 53 I	Кг <sup>83.80</sup> 54 Хе
839.098 rubidium 37 Rb 85.468	Ca 40.078 strontium 38 Sr 87.62		SC 44.956 yttrium 39 Y 88.906	47.867 zirconium 40 Zr 91.224	V 50.942 nioblum 41 Nb 92.906	Cr 51.996 molybdenum 42 Mo 95.94	Mn 54.938 technetium 43 TC [98]	Fe 55.845 ruthenium 44 Ru 101.07	Co 58,933 rhodium 45 Rh 102,91	Ni 58,693 palladium 46 Pd 106,42	63,546 silver 47 Ag 107,87	Zn 65,39 cadmium 48 Cd 112,41	Ga 69.723 Indium 49 In	Ge 72.61 tin 50 Sn 118.71	As 74.922 antimony 51 Sb 121.76	Se 78.96 tellurium 52 Te 127.60	Br 79.904 iodine 53 I 126.90	Kr <sup>83.80</sup> xenon 54 Xe 131.29
K 39.098 rubidium 37 Rb 85.468 caesium 55	Ca 40.078 strontlum 38 Sr 87.62 barlum 56	57-70	44.956 yttrium 39 Y 88.906 lutetium 71	Ti 47.867 zirconium 40 Zr 91.224 hafnium 72	50.942 nioblum 41 Nb 92.906 tantalum 73	51.996 molybdenum 42 Mo 95.94 tungsten 74	Mn 54.938 technetium 43 Tc [98] rhenium 75	Fe 55.845 ruthenium 44 Ru 101.07 osmium 76	Co 58.933 rhodium 45 Rh 102.91 iridium 77	Ni 58,693 palladium 46 Pd 106.42 platinum 78	Cu 63,546 silver 47 Ag 107.87 gold 79	Zn 65.39 cadmium 48 Cd 112.41 mercury 80	Ga 69,723 Indium 49 In 114.82 thallium 81	Ge 72.61 tin 50 Sn 118.71 lead 82	As 74.922 antimony 51 Sb 121.76 bismuth 83	Se 78.96 teturium 52 Te 127.60 polonium 84	Br 79.904 iodine 53 1 126.90 astatine 85	Kr 83.80 xenon 54 Xe 131.29 radon 86
K 39,098 rubidium 37 Rb 85,468 caesium 55	Ca 40.078 strontium 38 Sr 87.62 barium 56 D o	57-70	44.956 yttrium 39 Y 88.906 lutetium 71	47.867 zirconlum 40 Zr 91.224 hafnium 72	50.942 niobium 41 Nb 92.906 tantalum 73	61.996 molybdenum 42 Mo 95.94 tungsten 74	Mn 54.938 technetium 43 Tc [98] thenium 75 Do	Fe 55.845 ruthenium 44 Ru 101.07 osmium 76	Co 58,933 rhodium 45 Rh 102.91 iridium 77	Ni 58,693 palladium 46 Pd 106.42 platinum 78	63,546 silver 47 Ag 107.87 gold 79	Zn 65.39 cadmium 48 Cd 112.41 mercury 80	Ga 69,723 indium 49 In 114.82 thailium 81	Ge 72.61 tin 50 Sn 118.71 lead 82 De	As 74.922 antimony 51 Sb 121.76 bismuth 83	84	<b>Br</b> 79.904 iodine <b>53</b> <b>1</b> 126.90 astatine <b>85</b>	83.80 xenon 54 Xee 131.29 radon 86
к 39,098 rubidium 37 <b>Rb</b> 85,468 саевішт 55 <b>Cs</b>	Ca 40.078 strontlum 38 Sr 87.62 barlum 56 Ba	57-70 ★	Sc 44.956 yttrlum 39 Y 88,906 lutetium 71 Lu	Ti 47.867 Zirconlum 40 Zr 91.224 hafnium 72 Hf	50.942 niobium 41 Nb 92.906 tantalum 73 Ta	Cr 51.996 molybdenum 42 Moo 95.94 tungsten 74 W	Mn 54.938 technetium 43 Tc 198 thenium 75 Re	Fe 55.845 ruthenium 44 Ru 101.07 osmilum 76 Os	Co 58.933 rhodlum 45 Rh 102.91 iridlum 77 Ir	Ni 58.693 palladium 46 Pd 106.42 platinum 78 Pt	Cu 63.546 silver 47 Ag 107.87 gold 79 Au	Zn 65.39 cadmium 48 Cd 112.41 mercury 80 Hg	Ga 69.723 indium 49 In 114.82 thallium 81 TI	Ge 72.61 tin 50 Sn 118.71 lead 82 Pb	As 74.922 antimony 51 Sb 121.76 bismuth 83 Bi	Se 78.96 telurium 52 Te 127.60 polonium 84 PO	Br 79.904 1001ne 53 1 126.90 astatine 85 At	Kr 83.80 xenon 54 Xe 131.29 radon 86 Rn
K 39,098 rubidium 37 Rb 85,468 caesium 55 CS 132,91	Ca 40.078 strontlum 38 Sr 87.62 barlum 56 Ba 137.33	57-70 ★	Sc 44.956 yttrlum 39 Y 88,906 lutetium 71 Lu 174.97	Ti 47.867 Zirconlum 40 Zr 91.224 hafnium 72 Hf Hf 178.49	V 50.942 nibbium 41 Nb 92.906 tantalum 73 Ta 180.95	Cr 51.996 molybdenum 42 Moo 95.94 tungsten 74 W 183.84	Mn 54.938 technetium 43 Tc 1981 rhenium 75 <b>Re</b> 186.21	Fe 55.845 ruthenium 44 Ru 101.07 osmium 76 Os 190.23	Co 58.933 rhodlum 45 Rh 102.91 iridium 77 Ir 192.22	Ni 58.693 palladium 46 Pd 106.42 platinum 78 Pt 195.08	Cu 63.546 silver 47 Ag 107.87 gold 79 Au 196.97	Zn 65.39 cadmium 48 Cd 112.41 mercury 80 Hg 200.59	Ga 69.723 indium 49 In 114.82 thailium 81 TI 204.38	Ge 72.61 tin 50 Sn 118.71 lead 82 Pb 207.2	As 74.922 antimony 51 Sb 121.76 bismuth 83 Bi 208.98	Se 78.96 telurium 52 Te 127.60 polonium 84 PO [209]	Br 79.904 iodine 53 I 126.90 astatine 85 At [210]	Kr 83.80 xenon 54 Xe 131.29 radon 86 Rn [222]
K 39,098 rubidium 37 Rb 85,468 caesium 55 CS 132,91 francium 87	Ca 40.078 strontum 38 Sr 87.62 barlum 56 Ba 137.33 radium 88	57-70 ★ 89-102	Sc 44.956 yttrium 39 Y 88.906 lutetium 71 Lu 174.97 lawrencium 103	Ti 47.867 zirconium 40 Zr 91.224 hafnium 72 Hf 178.49 rutherfordium 104	V 50.942 niobium 41 Nb 92.906 tantalum 73 Ta 180.95 dubnium 105	Cr 51.996 molybdenum 42 Mo 95.94 tungsten 74 W 183.84 seaborgium 106	Mn 54.938 technetium 43 TC 198] rhenium 75 Re 186.21 bohnium 107	Fe 55.845 ruthenium 44 Ru 101.07 osmium 76 OS 190.23 hassium 108	Co 58,933 rhodium 45 Rh 102,91 iridium 77 Ir 192,22 meitnenium 109	Ni 58,693 palladium 46 Pd 106,42 platinum 78 Pt 195,08 ununnilium 110	Cu 63,546 silver 47 Ag 107.87 gold 79 Au 196.97 unununium 111	Zn 65.39 cadmium 48 Cd 112.41 mercury 80 Hg 200.59 ununbium 112	Ga 69.723 Indium 49 In 114.82 thallium 81 TI 204.38	Ge 72.61 110 50 Sn 118.71 lead 82 Pb 207.2 ununquadium 114	As 74.922 antimony 51 Sb 121.76 bismuth 83 Bi 208.98	Se 78.96 tellurlum 52 Te 127.60 potonium 84 PO [203]	Br 79.904 iodine 53 I 126.90 astatine 85 At [210]	Kr 83.80 xenon 54 Xe 131.29 radon 86 Rn [222]
K 39.098 rubidum 37 Rb 85.468 caesium 55 CS 132.91 francium 87	Ca 40,078 strontum 38 Sr 87.62 barlum 56 Ba 137.33 radium 88	57-70 ★ 89-102	Sc 44.956 yttrium 39 Y 88.906 lutetium 71 Lu 174.97 lawrencium 103	Ti 47.867 zirconium 40 Zr 91.224 hatnium 72 Hf 178.49 rutherfordium 104	V 50.942 niobium 41 Nb 92.906 tantalum 73 Ta 180.95 dubnium 105	Cr 51.996 molybdenum 42 Mo 95.94 tungsten 74 W 183.84 seaborgium 106	Mn 54.938 technetium 43 TC 198 rhenium 75 Re 186.21 bohnium 107	Fe 55.845 ruthenium 44 Ru 101.07 osmium 76 OS 190.23 hassium 108	Co 58,933 rhodium 45 Rh 102,91 iridium 77 Ir 192,22 meitnenium 109	Ni 58,693 palladium 46 Pd 106,42 platinum 78 Pt 195,08 ununnilium 110	Cu 63,546 silver 47 Ag 107.87 gold 79 Au 196.97 ununnium 111	Zn 65.39 cadmium 48 Cd 112.41 mercury 80 Hg 200.69 ununbium 112	Ga 69,723 Indium 49 In 114.82 thallium 81 TI 204.38	Ge 72.61 lin 50 Sn 118.71 lead 82 Pb 207.2 ununquadium 114	As 74.922 antimony 51 Sb 121.76 bismuth 83 Bi 208.98	Se 78.96 tellurlum 52 Te 127.60 potonilum 84 PO [209]	Br 79.904 iodine 53 I 126.90 astatine 85 At [210]	Kr 83.80 xenon 54 Xe 131.29 radon 86 Rn [222]
K 39.098 rubidum 37 Rb 85.468 caesium 55 CS 132.91 francium 87 Fr	Ca 40.078 strontum 38 Sr 87.62 barlum 56 Ba 137.33 radium 88 Ra	57-70 ★ 89-102 ★ ★	Sc 44.956 yttrlum 39 Y 88.906 lutetium 71 Luu 174.97 lawrendum 103 Lr	Ti 47.867 zirconlum 40 Zr 91.224 hatnium 72 Hff 178.49 rutherforcium 104 Rf	V 50.942 nibbium 41 NB 92.906 tantalum 73 Ta 180.95 dubnium 105 Db	Cr 51.996 molybdenum 42 Mo 95.94 tungsten 74 W 183.84 seaborgium 106 Sg	Mn 54,938 technetium 43 Tc 198 menum 75 Ree 186.21 bohrium 107 Bh	Fe 55.845 ruthenlum 44 Ru 101.07 osmium 76 OS 190.23 hassium 108 HS	Co 58,933 rhodlum 45 Rh 102,91 iridlum 77 Ir 192,22 meitnerium 109 Mt	Ni 58,693 palladium 46 Pd 106,42 platinum 78 Pt 196,08 ununnilium 110 Uun	Cu 63.546 silver 47 Ag 107.87 gold 79 Au 196.97 ununnium 111 Uuu	Zn 65.39 cadmium 48 Cd 112.41 mercury 80 Hg 200.59 ununbium 112 Uub	Ga 69,723 Indium 49 In 114,82 Italium 81 TI 204,38	Ge 72.61 Un 50 Sn 118.71 lead 82 Pb 207.2 ununquadum 114 Uuq	As 74.922 antimony 51 Sb 121.76 bismuth 83 Bi 208.98	Se 78.96 telurium 52 Te 127.60 potonium 84 PO [209]	Br 79.904 Iodine 53 I 126.90 astatine 85 At [210]	Kr 83.80 xenon 54 Xe 131.29 radon 86 Rn [22]

*Lanthanida series	lanthanum 57	cerium 58	praseodymium 59	neodymium 60	promethium 61	samarium 62	europium 63	gadolinium <b>64</b>	terbium 65	dysprosium 66	holmium 67	erbium 68	thulium 69	ytterbium 70
Lanthaniae series	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
	138.91	140.12	140.91	144.24	[145]	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04
* * Actinide series	actinium 89	thorium 90	protactinium 91	uranium 92	neptunium 93	plutonium 94	americium 95	curium 96	berkelium 97	californium 98	einsteinium 99	fermium 100	mendelevium 101	nobelium 102
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
	[227]	232.04	231.04	238.03	[237]	[244]	[243]	[247]	[247]	[251]	[252]	[257]	[258]	[259]

PARAMETER	ANALYZE SAMPLE WITHIN (max. holding time)
CHLORINE	15 MINUTES
DISSOLVED OXYGEN	15 MINUTES
NITRATE	48 HOURS
рН	15 MINUTES
PHOSPHATE	FILTER WITHIN 15 MINUTES; ANALYZE WITHIN 48 HOURS
TURBIDITY	48 HOURS

SAMPLE HOLDING TIME REQUIREMENTS (Per Federal Regulations)

# **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,  $O_2$  and ozone,  $O_3$ ), 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  $P_4$  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  $\dot{\alpha}\lambda\lambda\sigma\tau\rho\sigma\pii\alpha$  (*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

## Element

Allotropes	
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- Diamond an extremely hard, transparent crystal, with the carbon atoms arranged in a tetrahedral lattice. A poor electrical conductor. An excellent thermal conductor.
- Lonsdaleite also called hexagonal diamond.
- 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.

Carbon

- Linear acetylenic carbon (Carbyne)
- Amorphous carbon
- Fullerenes, including Buckminsterfullerene, aka "buckyballs", such as C<sub>60</sub>.
- Carbon nanotubes allotropes of carbon with a cylindrical nanostructure.
- White phosphorus crystalline solid P<sub>4</sub>
- Red phosphorus polymeric solid
- Scarlet phosphorus
- Phosphorus: Violet phosphorus
  - Black phosphorus semiconductor, analogous to graphite
  - Diphosphorus
  - dioxygen, O<sub>2</sub> colorless (faint blue)
  - Ozone, O<sub>3</sub> blue
    - Tetraoxygen, O<sub>4</sub> metastable
    - Octaoxygen, O<sub>8</sub> red
  - Sulfur has a large number of allotropes, second only to carbon
    - "Red selenium," cyclo-Se<sub>8</sub>
- Selenium:

Oxygen:

Sulfur:

- Red selenium, cyclo-5
   Cray selenium, nelymari
- Gray selenium, polymeric Se
- Black selenium

Metalloids	
Element	Allotropes
Boron:	<ul> <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><li>Amorphous silicon</li><li>crystalline silicon, Diamond cubic structure</li></ul>
Arsenic:	<ul> <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> <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> <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> <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, Tl, 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.

# **Allotropes Described Section**

# 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 Al<sup>3+</sup> 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  $Al_2(SO_4)_3$ . Aluminum sulfate is mainly used as a flocculating agent in the purification of drinking water and waste water treatment plants, and also in paper manufacturing.

Aluminum sulfate is sometimes referred to as a type of alum. Alums are a class of related compounds typified by  $AB(SO_4)_2$ ·12H<sub>2</sub>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 Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•16H<sub>2</sub>O and octadecahydrate Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•18H<sub>2</sub>O are the most common. The heptadecahydrate, whose formula can be written as [Al(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•5H<sub>2</sub>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:

 $AI_2(SO_4)_3$  + 6 NaHCO<sub>3</sub>  $\rightarrow$  3 Na<sub>2</sub>SO<sub>4</sub> + 2 AI(OH)<sub>3</sub> + 6 CO<sub>2</sub>

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 hoselines. 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. The system then returned to full-time chlorination, starting with a low distribution system residual of0.2 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.

# **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 Ca<sup>2+</sup> 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 highintensity 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 calciumwater 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 g/cm<sup>3</sup>, 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 (Ca<sup>2+</sup>) 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 °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 (CaCO<sub>3</sub>) is one of the common compounds of calcium. It is heated to form quicklime (CaO), which is then added to water (H<sub>2</sub>O). This forms another material known as slaked lime (Ca(OH)<sub>2</sub>), 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 (<sup>40</sup>Ca, <sup>42</sup>Ca, <sup>43</sup>Ca and <sup>44</sup>Ca), plus two more isotopes (<sup>46</sup>Ca and <sup>48</sup>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 <sup>41</sup>Ca, which has a half-life of 103,000 years. Unlike cosmogenic isotopes that are produced in the atmosphere, <sup>41</sup>Ca is produced by neutron activation of <sup>40</sup>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. <sup>41</sup>Ca has received much

attention in stellar studies because it decays to <sup>41</sup>K, a critical indicator of solar-system anomalies.

Ninety-seven percent of naturally occurring calcium is in the form of <sup>40</sup>Ca. <sup>40</sup>Ca is one of the daughter products of <sup>40</sup>K decay, along with <sup>40</sup>Ar. While K-Ar dating has been used extensively in the geological sciences, the prevalence of <sup>40</sup>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, <sup>40</sup>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 <sup>44</sup>Ca/<sup>40</sup>Ca) in a sample compared to the same ratio in a standard reference material. <sup>44</sup>Ca/<sup>40</sup>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 paleooceanography. 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 <sup>44</sup>Ca/<sup>40</sup>Ca rises. Soft tissue <sup>44</sup>Ca/<sup>40</sup>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 <sup>44</sup>Ca/<sup>40</sup>Ca tends to rise when the rate of removal of Ca<sup>2+</sup> 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 <sup>44</sup>Ca/<sup>40</sup>Ca corresponds to falling seawater Ca<sup>2+</sup> concentration, and falling <sup>44</sup>Ca/<sup>40</sup>Ca corresponds to rising seawater Ca<sup>2+</sup> concentration. In 1997 Skulan and DePaolo presented the first evidence of change in seawater <sup>44</sup>Ca/<sup>40</sup>Ca over geologic time, along with a theoretical explanation of these changes.

More recent papers have confirmed this observation, demonstrating that seawater Ca<sup>2+</sup> 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  $Ca^{2+}$  into surface water. This  $Ca^{2+}$  eventually is transported to the ocean where it reacts with dissolved  $CO_2$  to form limestone. Some of this limestone settles to the sea floor where it is incorporated into new rocks. Dissolved  $CO_2$ , 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  $(HCO_3)$  that forms when  $CO_2$  reacts with water at seawater pH:

 $\begin{array}{l} \mathsf{Ca}^{2+} + 2\mathsf{HCO-} \\ 3 \rightarrow \mathsf{CaCO}_3 \text{ (limestone)} + \mathsf{CO}_2 + \mathsf{H}_2\mathsf{O} \end{array}$ 

Note that at ocean pH most of the  $CO_2$  produced in this reaction is immediately converted back into HCO-3. The reaction results in a net transport of one molecule of  $CO_2$  from the ocean/atmosphere into the lithosphere.

The result is that each  $Ca^{2+}$  ion released by chemical weathering ultimately removes one  $CO_2$  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  $CO_2$  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 (CaCO<sub>3</sub>) liberates equimolar amounts of Ca<sup>2+</sup> and CO<sub>2</sub>, it has no net effect on the CO<sub>2</sub> content of the atmosphere and ocean. The weathering of silicate rocks like granite, on the other hand, is a net CO<sub>2</sub> sink because it produces abundant Ca<sup>2+</sup> but very little CO<sub>2</sub>.

#### 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 (CaCO<sub>3</sub>) 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 (Ca(OH)<sub>2</sub>) (also known as limewater) is used to detect the presence of carbon dioxide by being bubbled through a solution. It turns cloudy where CO<sub>2</sub> is present.
- Calcium arsenate (Ca<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>) is used in insecticides.
- Calcium carbide (CaC<sub>2</sub>) is used to make acetylene gas (for use in acetylene torches for welding) and in the manufacturing of plastics.
- Calcium chloride (CaCl<sub>2</sub>) 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 (Ca(C<sub>6</sub>H<sub>11</sub>NHSO<sub>3</sub>)<sub>2</sub>) was used as a sweetening agent but is no longer permitted for use because of suspected cancer-causing properties.
- Calcium gluconate  $(Ca(C_6H_{11}O_7)_2)$  is used as a food additive and in vitamin pills.
- Calcium hypochlorite (Ca(OCl)<sub>2</sub>) is used as a swimming pool disinfectant, as a bleaching agent, as an ingredient in deodorant, and in algaecide and fungicide.
- Calcium permanganate (Ca(MnO<sub>4</sub>)<sub>2</sub>) is used in liquid rocket propellant, textile production, as a water sterilizing agent and in dental procedures.
- Calcium phosphate (Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) 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  $(Ca_3P_2)$  is used in fireworks, rodenticide, torpedoes and flares.
- Calcium stearate (Ca(C<sub>18</sub>H<sub>35</sub>O<sub>2</sub>)<sub>2</sub>) 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 (CaSO<sub>4</sub>·2H<sub>2</sub>O) is used as common blackboard chalk, as well as, in its hemihydrate form better known as Plaster of Paris.
- Calcium tungstate (CaWO<sub>4</sub>) is used in luminous paints, fluorescent lights and in X-ray studies.
- Hydroxylapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH), but is usually written Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) 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 (LD<sup>50</sup>) 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 CaCO<sub>3</sub> (=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 CaCO<sub>3</sub> (=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 Ca<sup>2+</sup> and Mg<sup>2+</sup>. 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:

$$CaCO_3 + CO_2 + H_2O \leftrightarrows Ca^{2+} + 2HCO_3^{--}$$

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 ( $Ca^{2+}$ ,  $Mg^{2+}$ ) and carbonate and bicarbonate anions ( $CO_3^{2-}$ ,  $HCO_3^{-}$ ).

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:

$$2 C_{17}H_{35}COO^{-} + Ca^{2+} \rightarrow (C_{17}H_{35}COO)_2Ca$$

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 (CaCO<sub>3</sub>), magnesium hydroxide (Mg(OH)<sub>2</sub>), and calcium sulfate (CaSO<sub>4</sub>). 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 (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 Ca<sup>2+</sup> 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 Ca<sup>2+</sup> and Mg<sup>2+</sup>, 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 (°dH), parts per million (ppm, mg/L, or American degrees), grains per gallon (gpg), English degrees (°e, e, or °Clark), or French degrees (°f). The table below shows conversion factors between the various units.

#### Hardness unit conversion.

	mmol/L	ppm, mg/L	dGH, °dH	gpg	°e, °Clark	°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, °dH	5.608	0.05603	1	0.9591	0.7986	0.5603
gpg	5.847	0.05842	1.043	1	0.8327	0.5842
°e, °Clark	7.022	0.07016	1.252	1.201	1	0.7016
°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 (CaCO<sub>3</sub>) that, when dissolved in a unit volume of pure water, would result in the same total molar concentration of  $Mg^{2+}$  and  $Ca^{2+}$ . 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 CaCO<sub>3</sub> (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 CaCO<sub>3</sub> or 40.08 mg/L Ca<sup>2+</sup>.
- A degree of General Hardness (dGH or 'German degree (°dH, deutsche Härte)' is defined as 10 mg/L CaO or 17.848 ppm.
- A *Clark degree (°Clark)* or *English degrees (°e or e)* is defined as one grain (64.8 mg) of CaCO<sub>3</sub> per Imperial gallon (4.55 liters) of water, equivalent to 14.254 ppm.
- A *French degree* (°*F or f*) is defined as 10 mg/L CaCO<sub>3</sub>, 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:

LSI = pH (measured) — 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:

- RSI = 2 pHs pH (measured)
- For 6,5 < RSI < 7 water is considered to be approximately at saturation equilibrium with calcium carbonate
- For RSI > 8 water is under saturated and, therefore, would tend to dissolve any existing solid CaCO3
- For 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 CH+ 3, 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 CO<sub>2</sub> forms a medium-strength *carbonic acid* H<sub>2</sub>CO<sub>3</sub>.

# 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 (**FI**).

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.

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# 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  $R_c$  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 (M	S IPa)	BH (Brinell)
Iron whiskers	11	000	
Ausformed steel	(hardened) 29	930	850–1200
Martensitic steel	20	)70	600
Bainitic steel	13	380	400
Pearlitic steel	12	200	350
Cold-worked iron	69	90	200
Small-grain iron	34	10	100
Carbon-containing iron	14	10	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 bodycentered 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.

#### Isotopes

Naturally occurring iron consists of four stable isotopes: 5.845% of <sup>54</sup>Fe, 91.754% of <sup>56</sup>Fe, 2.119% of <sup>57</sup>Fe and 0.282% of <sup>58</sup>Fe. Of these stable isotopes, only <sup>57</sup>Fe has a nuclear spin (-1/2). The nuclide <sup>54</sup>Fe is predicted to undergo double beta decay, but this process had never been observed experimentally for these nuclei, and only the lower limit on the half-life was established:  $t_{1/2}$ >3.1×10<sup>22</sup> years.

<sup>60</sup>Fe is an extinct radionuclide of long half-life (2.6 million years). It is not found on Earth, but its ultimate decay product is the stable nuclide nickel-60.

Much of the past work on measuring the isotopic composition of Fe has focused on determining

<sup>60</sup>Fe variations due to processes accompanying nucleosynthesis (i.e., meteorite studies) and ore formation. In the last decade however, advances in mass spectrometry technology have allowed the detection and quantification of minute, naturally occurring variations in the ratios of the stable isotopes of iron.

Much of this work has been driven by the Earth and planetary science communities, although applications to biological and industrial systems are beginning to emerge.

The most abundant iron isotope <sup>56</sup>Fe is of particular interest to nuclear scientists as it represents the most common endpoint of nucleosynthesis. It is often cited, falsely, as the isotope of highest binding energy, a distinction which actually belongs to nickel-62. Since <sup>56</sup>Ni is easily produced from lighter nuclei in the alpha process in nuclear reactions in supernovae (see silicon burning process), nickel-56 (14 alpha particles) is the endpoint of fusion chains inside extremely massive stars, since addition of another alpha particle would result in zinc-60, which requires a great deal more energy. This nickel-56, which has a half-life of about 6 days, is therefore made in quantity in these stars, but soon decays by two successive positron emissions within supernova decay products in the supernova remnant gas cloud, first to radioactive cobalt-56, and then stable iron-56. This last nuclide is therefore common in the universe, relative to other stable metals of approximately the same atomic weight.

In phases of the meteorites *Semarkona* and *Chervony Kut* a correlation between the concentration of <sup>60</sup>Ni, the daughter product of <sup>60</sup>Fe, and the abundance of the stable iron isotopes could be found which is evidence for the existence of <sup>60</sup>Fe at the time of formation of the Solar System. Possibly the energy released by the decay of <sup>60</sup>Fe contributed, together with the energy released by decay of the radionuclide <sup>26</sup>Al, to the remelting and differentiation of asteroids after their formation 4.6 billion years ago. The abundance of <sup>60</sup>Ni present in extraterrestrial material may also provide further insight into the origin of the Solar System and its early history.

Nuclei of iron atoms have some of the highest binding energies per nucleon, surpassed only by the nickel isotope <sup>62</sup>Ni. This is formed by nuclear fusion in stars. Although a further tiny energy gain could be extracted by synthesizing <sup>62</sup>Ni, conditions in stars are unsuitable for this process to be favored. Elemental distribution on Earth greatly favors iron over nickel, and also presumably in supernova element production.

Iron-56 is the heaviest stable isotope produced by the alpha process in stellar nucleosynthesis; elements heavier than iron and nickel require a supernova for their formation. Iron is the most abundant element in the core of red giants, and is the most abundant metal in iron meteorites and in the dense metal cores of planets such as Earth.

#### 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 (Fe<sub>3</sub>O<sub>4</sub>) or hematite (Fe<sub>2</sub>O<sub>3</sub>), 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 ("Fp2")			
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 ( $K_2FeO_4$ ) 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 ( $Fe_4(Fe[CN]_6)_3$ ). The latter is used as the traditional "blue" in blueprints.

The iron compounds produced on the largest scale in industry are iron(II) sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O) and iron (III) chloride (FeCl<sub>3</sub>). The former is one of the most readily available sources of iron(II), but is less stable to aerial oxidation than Mohr's salt ((NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>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 ( $Fe_3O_4$ ), and iron (III) oxide ( $Fe_2O_3$ ). 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 ( $FeS_2$ ), 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.

Fe + 2 HX  $\rightarrow$  FeX<sub>2</sub> + H<sub>2</sub>

Iron reacts with fluorine, chlorine, and bromine to give the corresponding ferric halides, ferric chloride being the most common:

2 Fe + 3 
$$X_2 \rightarrow$$
 2 Fe $X_3$  (X = F, Cl, Br)

#### Iron Coordination and Organometallic Compounds

Several cyanide complexes are known. The most famous example is Prussian blue,  $(Fe_4(Fe[CN]_6)_3)$ . 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, Fe(CO)<sub>5</sub>, which is used to produce carbonyl iron powder, a highly reactive form of metallic iron.

# Oxygen

**Oxygen** is a chemical element with symbol **O** and atomic number 8. Its name derives from the Greek roots  $\delta\xi\omega\varsigma$  (oxys) ("acid", literally "sharp", referring to the sour taste of acids) and - $\gamma\delta\nu\sigma\varsigma$  (-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<sub>2</sub>. 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 kJ mol<sup>-1</sup>. 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.

Trioxygen (O<sub>3</sub>) 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<sub>2</sub> combines with atomic oxygen made by the splitting of O<sub>2</sub> 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<sub>4</sub>) 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<sub>2</sub> to 20 GPa, is in fact a rhombohedral O<sub>8</sub> 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  $O_2$  for every 2 molecules of  $N_2$ , 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 ( $-182.95 \,^{\circ}$ C,  $-297.31 \,^{\circ}$ F), and freezes at 54.36 K ( $-218.79 \,^{\circ}$ C,  $-361.82 \,^{\circ}$ 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  $0.1\% O_2$  by volume) and Venus have far lower concentrations. However, the  $O_2$  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  $O_2$  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  $O_2$  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  $O_2$  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  $Na_4SiO_4$ ,  $Na_2SiO_3$ , and  $Na_2Si_2O_5$  are used as detergents and adhesives.

Oxygen also acts as a ligand for transition metals, forming metal– $O_2$  bonds with the iridium atom in Vaska's complex, with the platinum in  $PtF_6$ , 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 (R-OH); ethers (R-O-R); ketones (R-CO-R); aldehydes (R-CO-H); carboxylic acids (R-COOH); esters (R-COO-R); acid anhydrides (R-CO-O-CO-R); and amides (R-C(O)-NR<sub>2</sub>). 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 ( $(CH_3)_2CO$ ) and phenol ( $C_6H_5OH$ ) 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  $O_2$ . 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 (PO3–4) groups in the biologically important energycarrying 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.

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# 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 – hence its name given from Greek mythology, Φωσφόρος meaning "light-bearer" (Latin *Lucifer*), referring to the "Morning Star", the planet Venus. 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<sub>4</sub> molecules, in which each atom is bound to the other three atoms by a single bond. This P<sub>4</sub> tetrahedron is also present in liquid and gaseous phosphorus up to the temperature of 800 °C when it starts decomposing to P<sub>2</sub> 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<sub>4</sub> 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(α)	white(β)	violet	black
Symmetry	Body-centered cubic	Triclinic	Monoclinic	Orthorhombic
Pearson symbol		aP24	mP84	oS8
Space group	l43m	P1 No.2	P2/c No.13	Cmca No.64
Density (g/cm³)	1.828	1.88	2.36	2.69
Bandgap (eV)	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.

• <sup>33</sup>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 SiO<sub>2</sub>, and coke (impure carbon) to produce vaporized  $P_4$ . 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:

$$4 \text{ Ca}_{5}(\text{PO}_{4})_{3}\text{F} + 18 \text{ SiO}_{2} + 30 \text{ C} \rightarrow 3 \text{ P}_{4} + 30 \text{ CO} + 18 \text{ CaSiO}_{3} + 2 \text{ CaF}_{2}$$

Side products from this production include ferrophosphorus, a crude form of  $Fe_2P$ , 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):

 $2 \text{ Ca}_3(\text{PO}_4)_2 + 6 \text{ SiO}_2 + 10 \text{ C} \rightarrow 6\text{CaSiO}_3 + 10 \text{ CO} + \text{P}_4$ 

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	$HH_2PO_2$	Hypophosphorous acid	1	acid, salts
+3	$H_2HPO_3$	Phosphorous acid	2	acid, salts
+3	HPO <sub>2</sub>	metaphosphorous acid	1	salts
+3	H <sub>3</sub> PO <sub>3</sub>	(ortho)phosphorous acid	3	acid, salts
+5	(HPO <sub>3</sub> ) <sub>n</sub>	metaphosphoric acids	n	salts (n=3,4,6)
+5	H(HPO <sub>3</sub> ) <sub>n</sub> OH	l polyphosphoric acids	n+2	acids, salts (n=1- 6)
+5	$H_5P_3O_{10}$	tripolyphosphoric acid	3	salts
+5	$H_4P_2O_7$	pyrophosphoric acid	4	acid, salts
+5	H <sub>3</sub> PO <sub>4</sub>	(ortho)phosphoric acid	3	acid, salts

#### Phosphorus (V) Compounds Oxides

The most prevalent compounds of phosphorus are derivatives of phosphate ( $PO_4^{3-}$ ), 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:

 $H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- K_{a1} = 7.25 \times 10^{-3}$  $H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-} K_{a2} = 6.31 \times 10^{-8}$  $HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-} K_{a3} = 3.98 \times 10^{-13}$ 

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  $HPO_4^{2-}$  and  $H_2PO_4^{-}$ . For example, the industrially important trisodium triphosphate (also known as sodium tripolyphosphate, STPP) is produced industrially on a megaton scale via this condensation reaction:

 $2 \text{ Na}_2[(HO)PO_3] + \text{Na}[(HO)_2PO_2] \rightarrow \text{Na}_5[O_3P-O-P(O)_2-O-PO_3] + 2 H_2O$ Phosphorus pentoxide (P<sub>4</sub>O<sub>10</sub>) 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 (HPO<sub>4</sub><sup>2-</sup>).

 $PCI_5$  and  $PF_5$  are common compounds. Both are volatile and pale or colorless. The other two halides,  $PBr_5$  and  $PI_5PI_5$  are unstable. The pentachloride and pentafluoride adopt trigonal bipyramidal molecular geometry and are Lewis acids. With fluoride,  $PF_5$  forms  $PF_6^-$ , an anion that is isoelectronic with  $SF_6$ . The most important oxyhalide is phosphorus oxychloride ( $POCI_3$ ), 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  $(PNCl_2)_n$  exist mainly as rings such as the trimer hexachlorophosphazene. The phosphazenes arise by treatment of phosphorus pentachloride with ammonium chloride:  $PCl_5 + NH_4Cl \rightarrow 1/n (NPCl_2)_n + 4 HCl$  The chloride groups can be replaced by alkoxide (RO<sup>-</sup>) 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<sub>3</sub>) and its organic derivatives (PR<sub>3</sub>) are structural analogues with ammonia (NH<sub>3</sub>) but the bond angles at phosphorus are closer to 90° 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  $PCI_3$  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:

 $P_4 \textbf{+} \textbf{6} \textbf{Cl}_2 \rightarrow \textbf{4} \textbf{PCl}_3$ 

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  $PCI_3$  serves as a source of  $P^{3+}$  in routes to organophosphorus (III) compounds. For example it is the precursor to triphenylphosphine:

$$PCI_3$$
 + 6 Na + 3  $C_6H_5CI \rightarrow P(C_6H_5)_3$  + 6 NaCl

Treatment of phosphorus trihalides with alcohols and phenols gives phosphites, e.g. triphenylphosphite:

$$\mathsf{PCI}_3 + 3 \ \mathsf{C}_6\mathsf{H}_5\mathsf{OH} \to \mathsf{P}(\mathsf{OC}_6\mathsf{H}_5)_3 + 3 \ \mathsf{HCI}$$

Similar reactions occur for phosphorus oxychloride, affording triphenylphosphate:

$$OPCI_3 + 3 C_6H_5OH \rightarrow OP(OC_6H_5)_3 + 3 HCI$$

# 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<sup>3-</sup>. Phosphides arise by reaction of metals with red phosphorus. Salts of P<sup>3-</sup> 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:

 $Ca_3P_2 + 6 H_2O \rightarrow 2 PH_3 + 3 Ca(OH)_2$ 

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 devises 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 ma/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 Se2+ 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 [Se(OH)<sub>3</sub>]<sup>+</sup>.CIO- 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 (~10<sup>-9</sup> to  $10^{-12} \text{ S} \cdot \text{cm}^{-1}$ ) of its highly purified form. This is comparable to or less than that of bromine (7.95×10<sup>-12</sup> S·cm<sup>-1</sup>), 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 Se<sup>2–</sup>, SeO2–

3 and SeO2- 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  $\sigma \epsilon \lambda \eta v \eta$  *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 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 unsoluble in  $CS_2$ . 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  $(SeO_2)$  and selenium trioxide  $(SeO_3)$ . Selenium dioxide is formed by the reaction of elemental selenium with oxygen:

 $Se_8 + 8 \text{ O}_2 \rightarrow 8 \text{ SeO}_2$ 

It is a polymeric solid that forms monomeric  $SeO_2$  molecules in the gas phase. It dissolves in water to form selenous acid,  $H_2SeO_3$ . Selenous acid can also be made directly by oxidizing elemental selenium with nitric acid:

 $3 \text{ Se} + 4 \text{ HNO}_3 + \text{H}_2\text{O} \rightarrow 3 \text{ H}_2\text{SeO}_3 + 4 \text{ NO}$ 

Unlike sulfur, which forms a stable trioxide, selenium trioxide is thermodynamically unstable and decomposes to the dioxide above 185 °C:

 $2 \text{ SeO}_3 \rightarrow 2 \text{ SeO}_2 + \text{O}_2 (\Delta \text{H} = -54 \text{ kJ/mol})$ 

Selenium trioxide is produced in the laboratory by the reaction of anhydrous potassium selenate ( $K_2SeO_4$ ) and sulfur trioxide ( $SO_3$ ).

Salts of selenous acid are called *selenites*. These include silver selenite  $(Ag_2SeO_3)$  and sodium selenite  $(Na_2SeO_3)$ .

Hydrogen sulfide reacts with aqueous selenous acid to produce selenium disulfide:

$$H_2SeO_3 + 2 H_2S \rightarrow SeS_2 + 3 H_2O$$

Selenium disulfide consists of 8-membered rings of a nearly statistical distribution of sulfur and selenium atoms. It has an approximate composition of  $SeS_2$ , with individual rings varying in composition, such as  $Se_4S_4$  and  $Se_2S_6$ . Selenium disulfide has been use 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:

$$SeO_2 + H_2O_2 \rightarrow H_2SeO_4$$

Hot, concentrated selenic acid is capable of dissolving gold, forming gold(III) selenate.

# Halogen Compounds

lodides of selenium are not well known. The only stable chloride is selenium monochloride  $(Se_2Cl_2)$ , 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 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:

 $Se_8 + 24 \ F_2 \rightarrow 8 \ SeF_6$ 

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  $H_2Se$ . It is a strongly odiferous, toxic, and colorless gas. It is more acidic than  $H_2S$ . 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:

 $Al_2Se_3 + 6 H_2O \rightarrow Al_2O_3 + 6 H_2Se$ 

Alkali metal selenides react with selenium to form polyselenides, Se2-x, 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:

 $8 \text{ KCN} + \text{Se}_8 \rightarrow 8 \text{ KSeCN}$ 

### 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 ( $R_2Se_2$ , analogues of thioethers), diselenides ( $R_2Se_2$ , 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  $\sigma \epsilon \lambda \eta v \eta$  *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 ( $\mu$ 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.
## 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 sulfurcontaining 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 (oxygenalternative) 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 sublimes easily. At 95.2 °C, below its melting temperature, cyclo-octasulfur changes from  $\alpha$ -octasulfur to the  $\beta$ -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  $\beta$ -octasulfur 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  $S_8$ , several other rings are known. Removing one atom from the crown gives  $S_7$ , which is more deeply yellow than  $S_8$ . HPLC analysis of "elemental sulfur" reveals an equilibrium mixture of mainly  $S_8$ , but with  $S_7$  and small amounts of  $S_6$ . Larger rings have been prepared, including  $S_{12}$  and  $S_{18}$ .

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  $\delta$ S-34 values of co-genetic minerals. The differences between minerals can be used to estimate the temperature of equilibration.

The  $\delta$ C-13 and  $\delta$ S-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 <sup>34</sup>S of ecosystem components. Rocky Mountain lakes thought to be dominated by atmospheric sources of sulfate have been found to have different  $\delta^{34}$ 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 (FeS), but there are exceptions, with carbonaceous chondrites containing free sulfur, sulfates and other sulfur compounds. The distinctive colors of Jupiter's volcanic moon lo 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 22×16×11 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 lo, 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. Eventually the surface-borne deposits played out, and miners excavated veins that ultimately dotted the Sicilian landscape with labyrinthine mines. Mining was unmechanized and labor-intensive, with pickmen freeing the ore from the rock, and mine-boys or *carusi* carrying baskets of ore to the surface, often through a mile or more of tunnels. Once the ore was at the surface, it was reduced and extracted in smelting ovens.

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:

 $R-S-R + 2 H_2 \rightarrow 2 RH + H_2S$ 

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:

 $3 \text{ } O_2 \texttt{+} 2 \text{ } H_2S \rightarrow 2 \text{ } SO_2 \texttt{+} 2 \text{ } H_2O$ 

 $SO_2 \texttt{+} \texttt{2} \texttt{H}_2S \rightarrow \texttt{3} \texttt{S} \texttt{+} \texttt{2} \texttt{H}_2O$ 

#### 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:

H₂S ⇄HS⁻ + H⁺

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:

 $2 \text{ Na} + S_8 \rightarrow Na_2S_8$ 

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,  $H_2S_x$  where x = 2, 3, and 4. Ultimately reduction of sulfur gives sulfide salts:

16 Na +  $S_8 \rightarrow 8 Na_2S$ 

The interconversion of these species is exploited in the sodium-sulfur battery. The radical anion  $S_3^-$  gives the blue color of the mineral lapis lazuli.

With very strong oxidants,  $S_8$  can be oxidized, for example, to give bicyclic  $S_8^{2+}$ .

#### Oxides and Oxyanions

The principal sulfur oxides are obtained by burning sulfur:

$$S + O_2 \rightarrow SO_2$$

 $2 \text{ SO}_2 \textbf{+} \text{ O}_2 \rightarrow 2 \text{ SO}_3$ 

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  $SO_n^{2-}$ . Sulfur dioxide and sulfites (SO2-3) are related to the unstable sulfurous acid (H<sub>2</sub>SO<sub>3</sub>). Sulfur trioxide and sulfates (SO2-

4) are related to sulfuric acid. Sulfuric acid and SO<sub>3</sub> combine to give oleum, a solution of pyrosulfuric acid ( $H_2S_2O_7$ ) in sulfuric acid.

Peroxides convert sulfur into unstable such as  $S_8O$ , a sulfoxide. Peroxymonosulfuric acid ( $H_2SO_5$ ) and peroxydisulfuric acids ( $H_2S_2O_8$ ), made from the action of SO<sub>3</sub> on concentrated  $H_2O_2$ , and  $H_2SO_4$  on concentrated  $H_2O_2$  respectively.

Thiosulfate salts (S<sub>2</sub>O<sub>2</sub>-3), sometimes referred as "hyposulfites", used in photographic fixing (HYPO) and as reducing agents, feature sulfur in two oxidation states. Sodium dithionite, (S<sub>2</sub>O<sub>2</sub>-4), contains the more highly reducing dithionite anion. Sodium dithionate (Na<sub>2</sub>S<sub>2</sub>O<sub>6</sub>) is the first member of the polythionic acids (H<sub>2</sub>S<sub>n</sub>O<sub>6</sub>), 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 (SOCl<sub>2</sub>) is a common reagent in organic synthesis.

#### Pnictides

An important S–N compound is the cage tetrasulfur tetranitride (S<sub>4</sub>N<sub>4</sub>). Heating this compound gives polymeric sulfur nitride ((SN)<sub>x</sub>), which has metallic properties even though it does not contain any metal atoms. Thiocyanates contain the SCN<sup>-</sup> group. Oxidation of thiocyanate gives thiocyanogen, (SCN)<sub>2</sub> with the connectivity NCS-SCN. Phosphorus sulfides are numerous, the most important commercially being the cages  $P_4S_{10}$  and  $P_4S_3$ .

#### 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 (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 FeS<sub>2</sub>. The upgrading of these ores, usually by roasting, is costly and environmentally hazardous. Sulfur corrodes many metals via the process called tarnishing.

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, SnO<sub>2</sub>.

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.

β-tin (the metallic form, or white tin), which is stable at and above room temperature, is malleable. In contrast, α-tin (nonmetallic form, or gray tin), which is stable below 13.2 °C (56 °F), is brittle. α-tin has a diamond cubic crystal structure, similar to diamond, silicon or germanium. α-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, α-tin and β-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 <sup>120</sup>Sn (at almost a third of all tin), <sup>118</sup>Sn, and <sup>116</sup>Sn, while the least abundant one is <sup>115</sup>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 <sup>115</sup>Sn, <sup>117</sup>Sn and <sup>119</sup>Sn, is among the easiest elements to detect and analyze by NMR spectroscopy, and its chemical shifts are referenced against SnMe<sub>4</sub>.

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 <sup>126</sup>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 <sup>100</sup>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 <sup>121m</sup>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 (SnO<sub>2</sub>), 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: SnF<sub>4</sub>, SnCl<sub>4</sub>, SnBr<sub>4</sub>, and Snl<sub>4</sub>. The three heavier members are volatile molecular compounds, whereas the tetrafluoride is polymeric. All four halides are known for Sn(II) also: SnF<sub>2</sub>, SnCl<sub>2</sub>, SnBr<sub>2</sub>, and Snl<sub>2</sub>. 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  $SnCl_4$  whereas the reaction of hydrochloric acid and tin gives  $SnCl_2$  and hydrogen gas.

Alternatively SnCl<sub>4</sub> and Sn combine to stannous chloride via a process called comproportionation:

 $SnCl_4 \textbf{+} Sn \rightarrow 2 \; SnCl_2$ 

Tin can form many oxides, sulfides, and other chalcogenide derivatives. The dioxide  $SnO_2$  (cassiterite) forms when tin is heated in the presence of air.  $SnO_2$  is amphoteric, which means that it dissolves in both acidic and basic solutions. There are also stannates with the structure  $[Sn(OH)_6]^{2-}$ , like  $K_2[Sn(OH)_6]$ , although the free stannic acid  $H_2[Sn(OH)_6]$  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 (SnH<sub>4</sub>), where tin is in the +4 oxidation state, is unstable. Organotin hydrides are however well known, e.g. tributyltin hydride (Sn(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>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 tincarbon 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 ( $(C_2H_5)_2Snl_2$ ), 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:

 $SnCl_4 + 4 RMgBr \rightarrow R_4Sn + 4 MgBrCl$ 

The mixed halide-alkyls, which are more common and more important commercially than the tetraorgano derivatives, are prepared by redistribution reactions:

 $SnCl_4 + R_4Sn \rightarrow 2 SnCl_2R_2$ 

Divalent organotin compounds are uncommon, although more common than related divalent organogermanium and organosilicon compounds. The greater stabilization enjoyed by Sn(II) is attributed to the "inert pair effect". Organotin(II) compounds include both stannylenes (formula:  $R_2Sn$ , as seen for singlet carbenes) and distannylenes ( $R_4Sn_2$ ), which are roughly equivalent to alkenes. Both classes exhibit unusual reactions.

## **Metals Section**

A **metal** (from Greek " $\mu$ έταλλον" – *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:

4 Na +  $O_2 \rightarrow 2$  Na<sub>2</sub>O (sodium oxide) 2 Ca +  $O_2 \rightarrow 2$  CaO (calcium oxide) 4 Al + 3  $O_2 \rightarrow 2$  Al<sub>2</sub>O<sub>3</sub> (aluminum oxide).

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.

## **Special Treatment and Filtration Section**



The conventional water treatment process utilizes a coagulation process which involves adding iron or aluminum salts, such as aluminum sulfate, ferric sulfate, ferric chloride or polymers, to the water. These chemicals are called coagulants, and have a positive charge. The positive charge of the coagulant neutralizes the negative charge of dissolved and suspended particles in the water. When this reaction occurs, the particles bind together, or coagulate (this process is sometimes also called flocculation). The larger particles, or floc, are heavy and quickly settle to the bottom of the water supply. This settling process is called sedimentation.



#### **BASIC WATER TREATMENT**

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# Point-of-Use Units

Under the Arsenic Rule, systems have another approach available for achieving compliance. This approach involves system-installed and maintained POU devices on a single tap in each customer's household. If you choose this approach, your system will have to arrange for regular inspection and maintenance of the devices. You, not the homeowner, are responsible for maintaining the POU device.

Either system staff or service providers under contract with the system must regularly inspect and service each device. You will need to establish and maintain an especially good working relationship with your customers if you choose POU devices. Your employees or contractors will need to enter customers' homes on a regular basis. Customers may be willing to accept this inconvenience because POU devices may be much less expensive than central treatment.

Currently, EPA considers only activated alumina and reverse osmosis POU devices to be POU SSCTs for arsenic removal. Point-of-use reverse osmosis treatment unit EPA is developing guidance on how to implement a POU compliance strategy. You should consult with your State to determine whether a POU compliance strategy can work for you.

#### Central Treatment

- ✓ All water treated
- ✓ Less expensive for large communities
- ✓ Capital costs very high, but equipment lasts a long time
- ✓ Little customer involvement
- ✓ Does not require access to individual homes
- ✓ Some technologies require a highly trained operator
- ✓ Waste disposal may be expensive

#### Point-of-Use Units

- ✓ Treats water at the individual taps where the unit is installed
- ✓ Can be less expensive for small communities
- ✓ Capital costs low, but media and membranes may require frequent replacement
- ✓ Much customer involvement and support necessary
- ✓ Requires access to individual homes
- ✓ Does not require a highly trained operator; maintenance can be contracted out
- ✓ Waste disposal typically not a problem

## Synthetic Organic Chemicals

Synthetic organic chemicals (**SOC**) include all man-made organics, some of which are volatile organic compounds (**VOC**). Activated carbon can substantially reduce many VOCs such as benzene, trichlorethane and carbon tetrachloride. Activated carbon also removes SOCs such as Alachlor, EDB and toluene. The EPA is establishing limits for these chemicals in public drinking water supplies.

Before recommending treatment, water suspected of containing any of these and other substances must be analyzed to determine their concentrations and whether they exceed the EPA standards.

Activated carbon beds compact with use so they may need occasional backwashing, however, backwash carbon as little as possible to prevent loss of the fragile material. Also, contaminant-laden carbon may migrate toward the bottom of the bed during backwash and reduce filter performance. When operating a carbon filter or system on turbid water supplies, remove suspended particles with a depth filter before treating it with activated carbon. A carbon filter typically backwashes at 10 gpm/ft (25 m/hr) for about 10 minutes, followed by a 5 minute downflow rinse.

Over a period of several months to two years, the carbon's adsorption capacity diminishes. The exhausted carbon bed should be replaced with fresh carbon. The old carbon should be hauled to an approved disposal facility.



#### ACTIVATED CARBON ABSORBS GASES AND CHEMICALS



WATER PHASE DIAGRAM



FILTRATION (WATER PASSES THROUGH FILTERS TO PURIFY THE WATER)

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## **Small Water Filters**

Water filters generally come in two forms. Portable ion exchange water filters, and reverse osmosis water filters. Both are used for "*point of use*" drinking water, that is, to filter out harmful or unwanted particles before the water is used for human consumption.

Reverse Osmosis works by forcing the water through a semi-permeable membrane that stops certain particles from passing through.

Portable water filters work using a cartridge containing activated carbon and ion exchange resin. The carbon absorbs and helps reduce the levels of chlorine and chlorine compounds, as well as pesticides, color and other organic substances. This improves taste and appearance. The ion exchange resin works to reduce temporary hardness.

## **Activated Carbon Filtration**

Activated carbon has been used for many years to solve water problems. In the beginning, its use was more art than science. Today, however, we understand more about what activated carbon can remove and how it removes impurities. Activated carbon quickly and effectively removes chlorine from water.

The presence of organic matter in water can cause color, taste, and odor complaints. Activated carbon adsorbs organic matter in its extensive network of pores. The adsorption process takes time, so service rates should be limited to 5 gpm/ft (12m/hr) or less for these applications.



A handful of GAC. Basically, just burnt coconut shells. This is used to remove tastes and odors and other long chained organic compounds from drinking water.

## **Membrane Configurations**



## **Electric-Driven Processes**

There are two membrane processes that purify a water stream by using an electric current to move ions across a membrane. These processes are:

- Electrodialysis
- Electrodialysis reversal



# FILTRATION SPECTRUM

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



# NANOFILTRATION

## **Membrane Filtration Processes**

In 1748, the French physicist Nollet first noted that water would diffuse through a pig bladder membrane into alcohol. This was the discovery of osmosis, a process in which water from a dilute solution will naturally pass through a porous membrane into a concentrate solution. Over the years, scientists have attempted to develop membranes that would be useful in industrial processes, but it wasn't until the late 1950s that membranes were produced that could be used for what is known as reverse osmosis. In reverse osmosis, water is forced to move through a membrane from a concentrate solution to a dilute solution.

Since that time, continual improvements and new developments have been made in membrane technology, resulting in ever-increasing uses in many industries. In potable water treatment, membranes have been used for desalinization, removal of dissolved inorganic and organic chemicals, water softening, and removal of the fine solids.

In particular, membrane technology enables some water systems having contaminated water sources to meet new, more stringent regulations. In some cases, it can also allow secondary sources, such as brackish groundwater, to be used. There is great potential for the continuing wide use of membrane filtration processes in potable water treatment, especially as technology improves and costs are reduced.

## **Description of Membrane Filtration Processes**

In the simplest membrane processes, water is forced through a porous membrane under pressure, while suspended solid, large molecules, or ions are held back or rejected.

## **Types of Membrane Filtration Processes**

The two general classes of membrane processes, based on the driving force used to make the process work, are:

- Pressure-driven processes
- Electric-driven processes

### **Pressure-Driven Processes**

The four general membrane processes that operate by applying pressure to the raw water are:

- Microfiltration
- Ultrafiltration
- Nanofiltration
- Reverse Osmosis



#### Microfiltration

Microfiltration (**MF**) is a process in which water is forced under pressure through a porous membrane. Membranes with a pore size of 0.45  $\mu$ m are normally used; this size is relatively large compared with the other membrane filtration processes. This process has not been generally applicable to drinking water treatment because it either does not remove substances that require removal from potable water, or the problem substances can be removed more economically using other processes. The current primary use of MF is by industries to remove very fine particles from process water, such as in electronic manufacturing. In addition, the process has also been used as a pretreatment for other membrane processes. In particular, RO membranes are susceptible to clogging or filter binding unless the water being processed is already quite clean.

However, in recent years, microfiltration has been proposed as a filtering method for particles resulting from the direct filtration process. Traditionally, this direct filtration process has used the injection of coagulants such as alum or polymers into the raw water stream to remove turbidity such as clay or silts. The formed particles were then removed by rapid sand filters. The use of filter aids to improve filtering efficiency, especially for small particles that could contain bacterial and protozoan life are recommended.

#### Ultrafiltration

Ultrafiltration (**UF**) is a process that uses a membrane with a pore size generally below 0.1  $\mu$ m. The smaller pore size is designed to remove colloids and substances that have larger molecules, which are called high-molecular-weight materials. UF membranes can be designed to pass material that weigh less than or equal to a certain molecular weight. This weight is called the molecular weight cutoff (**MWC**) of the membrane. Although UF does not generally work well for removal of salt or dissolved solids, it can be used effectively for removal or most organic chemicals.

#### Nanofiltration

Nanofiltration (**NF**) is a process using membranes that will reject even smaller molecules than UF. The process has been used primarily for water softening and reduction of total dissolved solids (**TDS**). NF operates with less pressure that reverse osmosis and is still able to remove a significant proportion of inorganic and organic molecules. This capability will undoubtedly increase the use of NF for potable water treatment.

#### **Reverse Osmosis**

Reverse Osmosis (**RO**) is a membrane process that has the highest rejection capability of all the membrane processes. These RO membranes have very low MWC pore size that can reject ions at very high rates, including chloride and sodium. Water from this process is very pure due to the high reject rates. The process has been used primarily in the water industry for desalinization of seawater because the capital and operating costs are competitive with other processes for this service. The RO also works most organic chemicals, and radionuclides and microorganisms. Industrial water uses such as semiconductor manufacturing is also an important RO process.

RO is discussed in more detail later.

## Primary Water Treatment Alternatives Ballasted Flocculation



In an effort to enhance the effectiveness of primary treatment, a ballasted flocculation unit uses many minute particles, which attract and hold materials together. Coagulating chemicals are also added to further clump particles together. The larger, heavier particles settle out of the wastewater rapidly.

This unit may significantly improve solids and organic

material removal compared to conventional primary treatments.

#### Fuzzy Filter



Wastewater flows from the bottom of this machine to the top through lots of fuzzy pink balls that pick up most of the solid particles. This technology is typically used as an advanced treatment and has not been adapted to primary treatment elsewhere. If it is successful, it could dramatically reduce the size, or footprint, of the primary treatment process.

#### Secondary Treatment Alternative Biological Aerated Filtration

Primary treated wastewater and air are injected at the bottom of this unit. It moves to the



top through lots of granules. The granules both separate solids and provide a surface for biological activity to take place. Biological Aerated Filtration can provide secondary treatment quality without taking up as much space. In addition, this technology can be adapted to function as a nitrogen removal process (nitrificationdenitrification) which may be important if reclaimed water is used in the future to augment stream flow.

## Advanced Secondary Treatment Alternative

#### **Membrane Bioreactors**



This unit combines an activated sludge secondary treatment bioreactor and a microfiltration membrane. Membranes are submerged in the aeration tank and water is drawn through the membrane with a low-pressure vacuum, leaving the solids in the aeration tank. The Membrane Bioreactor can convert screened sewage to clean effluent in a single process - eliminating the need for separate primary, secondary and advanced treatment. It produces a very high quality effluent meeting Class A criteria

(after disinfection). This technology has the potential to significantly reduce plant footprint while producing improved effluent quality.

## **Advanced Treatment Alternatives**

#### **Fuzzy Filter**

This upflow filtration process was described above as a primary treatment alternative. The porosity of the filter bed can be altered by how compressed the fuzzy pink balls (media) are. In an advanced treatment application the loading rate on a fuzzy filter can be 5 times higher than typical sand filtration. This would result in a substantially smaller footprint.

#### Microfiltration



Microfiltration membranes (such as MEMBRANE

BIOREACTORS) are used for physical separation of small particles from liquids. Membranes can be classified according to their pore size. There are four main types of membranes (listed from largest pore size to smallest): microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Membranes are designed to operate in a pressure or vacuum mode.

In pressure membranes, the wastewater to be treated is forced down the center of the

spaghetti-like membrane and is pushed through the walls in an 'inside-out' direction.

For vacuum membranes, wastewater is drawn from the outside of the membrane into the hollow core where it is collected. Microfiltration membranes can be designed as strands, sheets or plates depending on the manufacturer and application. Microfiltration membranes can be used for direct filtration of secondary effluent or as pretreatment for reverse osmosis membranes (see next page). Microfiltration has the potential to



produce better effluent quality when compared to standard sand filtration technologies.

## **Reverse Osmosis Process**

Osmosis is a natural phenomenon in which a liquid - water in this case - passes through a semi-permeable membrane from a relatively dilute solution toward a more concentrated solution. This flow produces a measurable pressure, called osmotic pressure. If pressure is applied to the more concentrated solution, and if that pressure exceeds the osmotic pressure, water flows through the membrane from the more concentrated solution toward the dilute solution.

This process, called reverse osmosis, or RO, removes up to 98% of dissolved minerals, and virtually 100% of colloidal and suspended matter. RO produces high quality water at low cost compared to other purifications processes.



The membrane must be physically strong to stand up to high osmotic pressure - in the case of sea water, 2500 kg/m. Most membranes are made of cellulose acetate or polyamide composites cast into a thin film, either as a sheet or fine hollow fibers. The membrane is constructed into a cartridge called a reverse osmosis module.

After filtration to remove suspended particles, incoming water is pressurized with a pump to 200 - 400 psi (1380 - 2760 kPa) depending on the RO system model. This exceeds the water's osmotic pressure. A portion of the water (**permeate**) diffuses through the membrane leaving dissolved salts and other contaminants behind with the remaining water where they are sent to drain as waste (**concentrate**).

Pretreatment is important because it influences permeate quality and quantity. It also affects the module's life because many water-borne contaminants can deposit on the membrane and foul it. Generally, the need for pretreatment increases as systems become larger and operate at higher pressures, and as permeate quality requirements become more demanding. Because reverse osmosis is the principal membrane filtration process used in water treatment, it is described here in greater detail.

To understand Reverse Osmosis, one must begin by understanding the process of osmosis, which occurs in nature. In living things, osmosis is frequently seen. The component parts include a pure or relatively pure water solution and a saline or contaminated water solution, separated by a semi-permeable membrane, and a container or transport mechanism of some type.



OSMOSIS

The semi-permeable membrane is so designated because it permits certain elements to pass through, while blocking others. The elements that pass through include water, usually smaller molecules of dissolved solids, and most gases. The dissolved solids are usually further restricted based on their respective electrical charge.

In osmosis, naturally occurring in living things, the pure solution passes through the membrane until the osmotic pressure becomes equalized, at which point osmosis ceases. The osmotic pressure is defined as the pressure differential required to stop osmosis from occurring. This pressure differential is determined by the total dissolved solids content of the saline solution, or contaminated solution on one side of the membrane. The higher the content of dissolved solids, the higher the osmotic pressure. Each element that may be dissolved in the solution contributes to the osmotic pressure, in that the molecular weight of the element affects the osmotic pressure.

Generally, higher molecular weights result in higher osmotic pressures. Hence the formula for calculating osmotic pressure is very complex. However, approximate osmotic pressures are usually sufficient to design a system.

Common tap water as found in most areas may have an osmotic pressure of about 10 PSI (Pounds per Square Inch), or about 1.68 Bar. Seawater at 36,000 PPM typically has an osmotic pressure of about 376 PSI (26.75 Bar).

Thus, to reach the point at which osmosis stops for tap water, a pressure of 10 PSI would have to be applied to the saline solution, and to stop osmosis in seawater, a pressure of 376 PSI would have to be applied to the seawater side of the membrane.

Several decades ago, U.S. Government scientists had the idea that the principles of osmosis could be harnessed to purify water from various sources, including brackish water and seawater. In order to transform this process into one that purifies water, osmosis would have to be reversed, and suitable synthetic membrane materials would have to be developed. Additionally, ways of configuring the membranes would have to be engineered to handle a continuous flow of raw and processed water without clogging or scaling the membrane material.

These ideas were crystallized, and fueled by U.S. Government funding, usable membrane materials and designs resulted. One of the membrane designs was the spiral wound membrane element. This design enabled the engineers to construct a membrane element that could contain a generous amount of membrane area in a small package, and to permit the flow of raw water to pass along the length of the membrane. This permits flows and pressures to be developed to the point that ample processed or purified water is produced, while keeping the membrane surface relatively free from particulate, colloidal, bacteriological or mineralogical fouling.

The design features a perforated tube in the center of the element, called the product or permeate tube. Wound around this tube are one or more "**envelopes**" of membrane material, opening at the permeate tube. Each envelope is sealed at the incoming and exiting edge. Thus, when water penetrates or permeates though the membrane, it travels, aided by a fine mesh called the permeate channel, around the spiral and collects in the permeate tube. The permeate or product water is collected from the end of each membrane element, and becomes the product or result of the purification process.

Meanwhile, as the raw water flows along the "**brine channel**" or coarse medium provided to facilitate good flow characteristics, it gets more and more concentrated. This concentrated raw water is called the reject stream or concentrate stream. It may also be called brine if it is coming from a salt water source. The concentrate, when sufficient flows are maintained, serves to carry away the impurities removed by the membrane, thus keeping the membrane surface clean and functional. This is important, as buildup on the membrane surface, called fouling, impedes or even prevents the purification process.

The membrane material itself is a special thin film composite (**TFC**) polyamide material, cast in a microscopically thin layer on another, thicker cast layer of Polysulfone, called the microporous support layer. The microporous support layer is cast on sheets of paper-like material that are made from synthetic fibers such as polyester, and manufactured to the required tolerances.

Each sheet of membrane material is inspected at special light tables to ensure the quality of the membrane coating, before being assembled into the spiral wound element design.

To achieve Reverse Osmosis, the osmotic pressure must be exceeded, and to produce a reasonable amount of purified water, the osmotic pressure is generally doubled. Thus with seawater osmotic pressure of 376 PSI, a typical system operating pressure is about 800 PSI. Factors that affect the pressure required include raw water temperature, raw water TDS (Total Dissolved Solids), membrane age, and membrane fouling. The effect of temperature is that with higher temperatures, the salt passage increases, flux (permeate



flow) increases, and operating pressure required is lower. With lower temperatures, the inverse occurs, in that salt passage decreases (reducing the TDS in the permeate or product water), while operating pressures increase. Or, if operating pressures do not increase, then the amount of permeate or product water is reduced. In general, Reverse Osmosis (**R**/**O**) systems are designed for raw water temperatures of 25° C (77° F). Higher temperatures or lower temperatures can be accommodated with appropriate adjustments in the system design.

Membranes are available in "*standard rejection*" or "*high rejection*" models for seawater and brackish water. The rejection rate is the percentage of dissolved solids rejected, or prevented from passing through the membrane. For example, a membrane with a rejection rate of 99% (usually based on Na (Sodium)) will allow only 1% of the concentration of dissolved solids to pass through into the permeate. Hence, product water from a source containing 10,000 PPM would have 100 PPM remaining.

Of course, as the raw water is processed, the concentrations of TDS increase as it passes along the membrane's length and usually multiple membranes are employed, with each membrane in series seeing progressively higher dissolved solids levels.

Typically, starting with seawater of 36,000 PPM, standard rejection membranes produce permeate below 500 PPM, while high rejection membranes under the same conditions produce drinking water TDS of below 300 PPM.

There are many considerations when designing R/O systems that competent engineers are aware of. These include optimum flows and pressures, optimum recovery rates (the percentage of permeate from a given stream of raw water), prefiltration and other pretreatment considerations, and so forth.

Membrane systems in general cannot handle the typical load of particulate contaminants without prefiltration. Often, well designed systems employ multiple stages of prefiltration, tailored to the application, including multi-media filtration and one or more stages of cartridge filtration. Usually the last stage would be 5m or smaller, to provide sufficient protection for the membranes.

R/O systems typically have the following components: A supply pump or pressurized raw water supply, prefiltration in one or more stages, chemical injection of one or more pretreatment agents may be added, a pressure pump suited to the application, sized and driven appropriately for the flow and pressure required, a membrane array including one or more membranes installed in one or more pressure tubes (also called pressure vessels, R/O pressure vessels, or similar), various gauges and flow meters, a pressure regulating valve, relief valve(s) and/or safety pressure switches, and possibly some form of post treatment.

Post treatment should usually include a form of sterilization such as Chlorine, Bromine, Ultra-Violet (**U-V**), or Ozone. Other types of post treatment may include carbon filters, pH adjustment, or mineral injection for some applications.



Packaged portable skid unit complete with treatment, instrumentation, UV, and softening.

Some very low cost R/O systems may dispense with most of the controls and instruments. However, systems installed in critical applications should be equipped with a permeate or product flow meter, a reject, concentrate or brine flow meter, multiple pressure gauges to indicate the pressure before and after each filtration device, and the system operation pressure in the membrane loop, preferably both before and after the membrane array. Another feature found in better systems is a provision to clean the membranes in place, commonly known as a "*Clean In Place*" (CIP) system. Such a system may be built right into the R/O system or may be provided as an attachment for use as required.

Reverse Osmosis has proved to be the most reliable and cost effective method of desalinating water, and hence its use has become more and more widespread. Energy consumption is usually some 70% less than for comparable evaporation technologies. Advancements have been made in membrane technology, resulting in stable, long lived membrane elements.

Component parts have been improved as well, reducing maintenance and down time. Additional advancements in pretreatment have been made in recent years, further extending membrane life and improving performance. Reverse Osmosis delivers product water or permeate having essentially the same temperature as the raw water source (an increase of 1° C or 1.8° F may occur due to pumping and friction in the piping). This is more desirable than the hot water produced by evaporation technologies. R/O Systems can be designed to deliver virtually any required product water quality. For these and other reasons, R/O is usually the preferred method of desalination today.

Reverse osmosis, also known as hyperfiltration, is the finest filtration known. This process will allow the removal of particles as small as ions from a solution. Reverse osmosis is used to purify water and remove salts and other impurities in order to improve the color, taste, or properties of the fluid. It can be used to purify fluids such as ethanol and glycol, which will pass through the reverse osmosis membrane, while rejecting other ions and contaminants from passing. The most common use for reverse osmosis is in purifying water. It is used to produce water that meets the most demanding specifications that are currently in place.

Reverse osmosis uses a membrane that is semi-permeable, allowing the fluid that is being purified to pass through it, while rejecting the contaminants that remain. Most reverse osmosis technology uses a process known as cross-flow to allow the membrane to continually clean itself. As some of the fluid passes through the membrane the rest continues downstream, sweeping the rejected species away from the membrane. The process of reverse osmosis requires a driving force to push the fluid through the membrane, and the most common force is pressure from a pump. The higher the pressure, the larger the driving force. As the concentration of the fluid being rejected increases, the driving force required to continue concentrating the fluid increases.

Reverse osmosis is capable of rejecting bacteria, salts, sugars, proteins, particles, dyes, and other constituents that have a molecular weight of greater than 150-250 daltons. The separation of ions with reverse osmosis is aided by charged particles. This means that dissolved ions that carry a charge, such as salts, are more likely to be rejected by the membrane than those that are not charged, such as organics.

The larger the charge and the larger the particle, the more likely it will be rejected. Reverse Osmosis, when properly configured with sediment, carbon and/or carbon block technology, produces pure water that is clearly the body's choice for optimal health. It is the best tasting because it is oxygen-rich.

A Reverse Osmosis System removes virtually all: bad taste, odor, turbidity, organic compounds, herbicides, insecticides, pesticides, chlorine and THM's, bacteria, virus, cysts, parasites, arsenic, heavy metals, lead, cadmium, aluminum, dissolved solids, sodium, calcium, magnesium, inorganic dead dirt minerals, fluoride, sulfates, nitrates, phosphates, detergents, radioactivity and asbestos.



## Electrodialysis

Electrodialysis (**ED**) is a process in which ions are transferred through a membrane as a result of direct electric current applied to the solution. The current carries the ions through a membrane from the less concentrated solution to the more concentrated one.

#### Electrodialysis Reversal

Electrodialysis Reversal (**EDR**) is a process similar to ED, except that the polarity of the direct current is periodically reversed. The reversal in polarity reverses the flow of ions between demineralizing compartments, which provides automatic flushing of scale-forming materials from the membrane surface. As a result, EDR can often be used with little or no pretreatment of feedwater to prevent fouling. So far, ED and EDR have been used at only a few locations for drinking water treatment.



Nanofiltration Unit

### Ozone in Cooling Water Treatment Learn how to use the strong points of ozone to your advantage and avoid the pitfalls. By Mario C. Uy

When commercial ozone generators were first introduced for cooling water treatment, they were marketed as a stand-alone treatment, a cure-all, a panacea. We now know this isn't true. Because there have been many misconceptions regarding ozone, this article is intended to review the basics of ozone, its true capabilities and limitations and its potential benefits in cooling water treatment applications.

#### What is Ozone?

Ozone  $(O_3)$  is formed by combining three atoms of oxygen. The air we breathe contains two atoms of oxygen (O) in the molecular form of O<sub>2</sub>. When sufficient energy is applied to the molecular O<sub>2</sub>, such as the discharge of electricity during a thunderstorm or strong UV radiation from the sun, some of the molecular O<sub>2</sub> will split into two individual oxygen atoms.



When the individual oxygen atoms merge with other oxygen molecules ( $O_2$ ), they form  $O_3$ . Ozone is a very unstable molecule and will revert back to  $O_2$  quickly.

#### Capabilities

Ozone is a very powerful oxidizing biocide, viricide, fungicide, sporicide, disinfectant and sterilizer. It kills microorganisms on contact by cellular lysis and cytoplasmic dispersion – it directly ruptures the cell walls of the microorganisms, which results in an instantaneous death.

By comparison, chlorine kills bacteria by diffusing through the cell wall and then oxidizing the enzymes within the cell. Ozone kills microorganisms including *E. Coli, Legionella, Pneumophilia, Streptococcus Facalis Bacillus, Clostridium,* amoebae cysts, *Giardia, Cryptosporidium, Pseudomonas*, etc. It also eradicates fungi, mold and yeast.

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#### What is the Significance of Ozone?

Ozone is a very powerful oxidant, even more powerful than chlorine. Below is a table comparing the oxidizing potential of ozone to other oxidizing agents.

Oxidizing agent	Oxidation potential (volts)	Power relative to chlorine	
Fluorine (F <sub>2</sub> )	3.06	2.25	
Ozone (O <sub>3</sub> )	2.07	1.52	
Hydrogen Peroxide (H <sub>2</sub> O <sub>2</sub> )	1.77	1.30	
Potassium Permanganate (KMnO <sub>4</sub> )	1.67	1.23	
Chlorine (Cl <sub>2</sub> )	1.36	1.00	
Chlorine Dioxide(ClO <sub>2</sub> )	1.27	0.93	
Bromine (Br <sub>2</sub> )	1.09	0.80	

This table is courtesy of CEC the Ozone Company.

#### In Addition, Ozone:

Oxidizes and mitigates pollutants from water Ozone (O<sub>3</sub>) Molecule and wastewater.

0

0

- Breaks down volatile organic compounds (VOC) such as, phenols, benzene, pesticides and other aromatic hydrocarbons.
- Breaks down inorganic compounds such as cyanides, sulfides, nitrites.
- Removes color.
- Bleaches.
- Removes taste and odor.
- Removes soluble iron and manganese indirectly by converting them to filterable insoluble solids.

Ozone is very friendly to the environment. The extra atom of oxygen makes ozone very unstable.

While it has a half-life of about 20 minutes in clean water, its half-life in dirty water is even shorter as it is consumed by the microorganisms, VOCs and other compounds.

Because it breaks down to oxygen, ozone does not leave any toxic or carcinogenic byproducts. It does not impart any taste, odor, color or solids.

By comparison, chlorine forms carcinogenic by-products, such as trihalomethanes (THM) and other halogenated compounds. When added to water, chlorine hydrolyzes to hypochlorous acid and then to hypochlorite ion, both of which can linger on and adversely affect our hydrological system.

Since ozone reverts to oxygen very quickly it cannot be packaged and stored. Thus it must be generated on-site. In turn, this on-site generation eliminates any hazards associated with transportation, storing and handling.
#### **Commercial Production**

Ozone is produced commercially in the same way it is formed naturally by lightning or UV radiation from the sun. The commercial lightning method is called corona discharge. Dried air or oxygen is passed through an electrified field (corona) generated by a high voltage between positive and negative grids.

The high voltage splits the molecular oxygen into atomic oxygen. Some of the atomic oxygen merge with molecular oxygen to form ozone, while other oxygen atoms simply recombine to form O2. A fraction of oxygen in the air is transformed into ozone. When ambient air is used as a feed gas, you can get ozone between 1 and 2 percent by weight in air. When oxygen is used as a feed gas, you can get ozone between 6 and 12 percent by weight.



Natural UV radiation is simulated commercially by UV lamps. Air is passed through a chamber between the UV lamp and a shield. UV light can create or destroy ozone depending on the UV wavelength. Wavelengths of 185 nanometers (nm) are required for the generation of ozone and 254 nm for the destruction of ozone. This method produces a very low level of ozone and is usually suitable for small applications. In addition to these methods, ozone may also be made through electrolytic and chemical reactions.

#### Potential Health Hazards

According to the EPA, "the same chemical properties that allow high concentrations of ozone to react with organic material outside the body give it the ability to react with similar organic material that makes up the body.

"When inhaled, ozone can damage the lungs. Relatively low amounts can cause chest pain, coughing, shortness of breath, and throat irritation. Ozone may worsen chronic respiratory diseases such as asthma and compromise the ability of the body to fight respiratory infections."

The EPA makes a distinction between ozone in the upper and lower atmosphere. Ozone in the upper atmosphere, referred to as stratospheric ozone, helps filter out damaging ultraviolet radiation from the sun. Conversely, ozone in the lower atmosphere, – the air we breathe – can be harmful to the respiratory system.

OSHA has issued a threshold limit value (**TLV**) on ozone exposure to 0.1 ppm over eight hours per day and five days per week, or 0.3 ppm for a 15-minute continuous exposure.

Because of the potential health hazards, it is crucial to destroy any excess ozone in a safe way.

#### How is Ozone Injected?

Ozone is typically injected into water via a venturi. A side stream water pump is typically used to create the vacuum on the venturi with a static mixer installed after it to ensure adequate mixing, distribution and proper contact between the ozone and water.

Another less popular alternative is the diffuser method, where ozone is injected under pressure through diffusers creating bubble columns – much like air diffusers in aquariums.

#### Destroying Ozone

Ozone can be destroyed by catalytic conversion units, activated carbon filters, thermal destructors or by ultraviolet radiation.

Catalytic conversion is the most popular method of ozone destruction. Activated carbon filtration decomposes ozone but carbon is also consumed in the process. There's also a risk of fire as carbon could ignite under high exothermic conditions.

In thermal destruction, ozone is destroyed by heating it in excess of 300 degrees Celsius. Ultraviolet radiation decomposes ozone at the wavelength of 254 nanometers.

#### Early Misconceptions

In cooling water applications, the most common problems encountered are scale deposition, corrosion, fouling and microbiological (bacteria, algae, fungi, etc.) growth. Today, there's an even greater threat - the emergence of pathogenic bacteria like *Legionella* 

#### Pneumophilia.

Microbial is a concern because it contributes to and amplifies deposition, corrosion and fouling by acting as a nucleation point or catalyst for these problems. The effect of microbial on scale deposition and fouling is one of the early misconceptions of ozone.

Early applications showed that ozone also removed mineral deposits. Later, it was found that this removal was only true where the deposits were held in a bio-matrix. It is like the steel structure of a building that holds up all the bricks. By destroying the steel structure at strategic points, the whole building implodes.

Comparing this to the bio-induced deposits, the bio-matrix held the deposits together, acting like glue. When the ozone destroyed the bio-matrix, the attached crystals became dispersed.

Not understanding this phenomenon fully, some ozone manufacturers began marketing them as scale inhibitor. Needless to say, ozone failed to prevent mineral deposits under other conditions, such as super saturation, excessive hardness, and alkalinity.

Because microorganisms also induce other problems such as corrosion and fouling, ozone was also marketed early on as a corrosion and fouling inhibitor, under similar biological pretext. Likewise, ozone failed to prevent these problems under non-biological conditions.

Traditionally, non-oxidizing biocides and oxidizing biocides are used to control microbial. Typical non-oxidizing biocides are organo-sulfur compounds (carbamate based, thiocyanate), organotin, isothiazolone, organobromine (dibromonitrilopropionamide), organic thiocyano-azole (benzothiazole) glutaraldehyde and quaternary ammonia.

Typical oxidizing biocides are chlorine, bromine and chlorine dioxide. Most of these biocides have a long-term negative impact on the environment. As such, there is a growing pressure to reduce or restrict these biocides in the blowdown water, especially if the water is being discharged to a waterway.

In addition to the discharge burden, these biocides have to be stored, transported and handled, which increases potential health and injury risks to personnel.

#### Limitations

Because of its short life, ozone levels drop off rapidly as time progresses and as it moves away from the injection point, decreasing its disinfecting efficacy. In systems with long piping runs, ozone may not get far enough, leaving the farthest areas vulnerable to microbiological growth.

This situation may be remedied by injecting ozone at various strategic points throughout the water system. A bio-dispersant can be added to penetrate and disperse the sessile bacteria (growing on surfaces) so that they can become planktonic (floating in water), thus enabling the bacteria to be transported to the ozone injection point for destruction.

Increasing the ozone level at the injection point to raise residual levels downstream is not a good solution. The higher ozone concentration may destroy the water treatment chemicals, increase corrosion near the injection area and destroy seals, gaskets, etc.

Ozone does not do a good job penetrating biofilm. It may burn the surface of the biofilm, protecting the microorganisms underneath from further destruction. Therefore, they will survive and will likely continue to cause localized corrosion.

This situation may be remedied by adding a good bio-dispersant to penetrate and disperse the biofilm, including the bacteria living under the biofilm.

Ozone does not discriminate in terms of what it oxidizes. If ozone is used as a disinfectant in water loaded with other non-biological organic matters, they will also consume ozone. As such, there may not be enough ozone left to accomplish the intended disinfection.

The remedy is to generate more ozone to supply the total ozone demand. However, this increases costs in both operating and capital. As such, ozone may not be cost effective for these types of applications.

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Ozone generator and control panel.



### **Ultraviolet Radiation**

The enormous temperatures on the sun create ultraviolet (**UV**) rays in great amounts, and this radiation is so powerful that all life on earth would be destroyed if these rays were not scattered by the atmosphere and filtered out by the layers of ozone gas that float some 20 miles above the earth.

This radiation can be artificially produced by sending strong electric currents through various substances. A sun lamp, for example, sends out UV rays that when properly controlled result in a suntan. Of course, too much will cause sunburn.

## Open contact chamber, beautiful green light that can burn your eyes.

The UV lamp that can be used for the



disinfection of water depends upon the low-pressure mercury vapor lamp to produce the ultraviolet energy. A mercury vapor lamp is one in which an electric arc is passed through an inert gas. This in turn will vaporize the mercury contained in the lamp; and it is a result of this vaporization that UV rays are produced.



Enclosed lamp system, this one is on wastewater effluent.

The lamp itself does not come into contact with the water, the lamp is placed inside a quartz tube, and the water is in contact with the outside of the quartz tube. Quartz is used in this case since practically none of the UV rays are absorbed by the quartz, allowing all of the rays to reach the water. Ordinary glass cannot be used since it will absorb the UV rays, leaving little for disinfection.

The water flows around the quartz tube. The UV sterilizer will consist of a various number of lamps and tubes, depending upon the quantity of water to be treated. As water enters the sterilizer, it is given a tangential flow pattern so that the water spins over and around the quartz sleeves. In this way the microorganisms spend maximum time and contact with the outside of the quartz tube and the source of the UV rays.

The basic design flow of water of certain UV units is in the order of 2.0 gpm for each inch of the lamp. Further, the units are designed so that the contact or retention time of the water in the unit is not less than 15 seconds.

Most manufacturers claim that the UV lamps have a life of about 7,500 hours, which is about 1 years' time. The lamp must be replaced when it loses about 40% to 50% of its UV output; in any installation this is determined by means of a photoelectric cell and a meter that shows the output of the lamp. Each lamp is outfitted with its own photoelectric cell, and with its own alarm that will be activated when the penetration drops to a present level.

Ultraviolet radiation is an excellent disinfectant that is highly effective against viruses, molds, and yeasts and it is safe to use. It adds no chemicals to the water, it leaves no residual, and it does not form THMs. It is used to remove traces of ozone and chloramines from the finished water. Alone, UV radiation will not remove precursors, but in combination with ozone, it is said to be effective in the removal of THM precursors and THMs.



UV Trains and SCADA display.

The germicidal effect of UV is thought to be associated with its absorption by various organic components essential to the cell's functioning. For effective use of ultraviolet, the water to be disinfected must be clean, and free of any suspended solids. The water must also be colorless and must be free of any colloids, iron, manganese, taste, and odor.

These are conditions that must be met. Also, although a water may appear to be clear, such substances as excesses of chlorides, bicarbonates, and sulfates affect absorption of the ultraviolet ray. These parameters will probably require at least filtration of one type or another. The UV manufacturer will of course stipulate which pretreatment may be necessary.

Removal of Disinfection By-products						
Disinfectant	Disinfectant By- product	Disinfectant By-product Removal				
Chlorine (HOCI)	Trihalomethane (THM)	Granular Activated Carbon (GAC), resins, controlled coagulation, aeration.				
	Chloramine Chlorophenol	GAC-UV GAC				
Chloramine (NH <sub>x</sub> Cl <sub>y</sub> )	Probably no THM Others?	GAC UV?				
Chlorine dioxide (CIO <sub>2</sub> )	Chlorites Chlorates	Use of Fe2+ in coagulation, RO, ion- exchange				
Permanganate (KMnO <sub>4</sub> )	No THMs					
Ozone (O <sub>3</sub> )	Aldehydes, Carboxylics, Phthalates	GAC				
Ultraviolet (UV)	None known	GAC				

The table indicates that most of the disinfectants will leave a by-product that is or would possibly be inimical to health. This may aid with a decision as to whether or not precursors should be removed before these disinfectants are added to water.

If it is decided that removal of precursors is needed, research to date indicates that this removal can be attained through the application of controlled chlorination plus coagulation and filtration, aeration, reverse osmosis, nanofiltration, GAC or combinations of others processes.

In conclusion, the literature is replete with the pursuit of newer processes, or combination of known processes, or the search for new methods for removal of the DBPs. These will all require laboratory, pilot plant, and field experience research will be more than a "*labor of love*."



Hydrogen Molecules Water Molecules H<sub>2</sub>O Oxygen Molecules H H H

## **Types of POU Home Treatment Methods**

This section discusses the principal types of **POE** and **POU** home treatment devices.

#### Water Softeners

Home-type water softeners generally use the ion exchange process. In addition to reducing hardness, they remove some other impurities. But at the same time, they increase the salt level in the treated water.

Coarse salt is typically used for regeneration, and most units are furnished with a time clock to operate the regeneration cycle automatically in the middle of the night on set days of the week.

Softeners are normally classified as POE devices because they are often installed to treat all water to the building. In other instances, softeners are connected to treat only the hot-water supply to a building.

Softener with brine tank on right



#### Physical Filters

Physical filters are rather like strainers in that they are intended to remove suspended matter from the water. Some can remove material as small as cysts, large bacteria, and asbestos fibers. Most units are designed to remove only larger particles such as grit, dirt, and rust.

The filter unit may be made of fabric, fiber, ceramic, screening, diatomaceous earth, or other materials. Physical filters are most often used as a prefilter ahead of other treatment devices.

#### Activated Carbon Filters

As detailed before, activated carbon can remove many organic chemical contaminants from water – provided there is sufficient contact time with the water. Carbon filters can remove most taste, odors, and color as well as synthetic organic chemical such as pesticides and volatile organic chemicals (**VOCs**).

Carbon also effectively removes radon and chlorine from water. It does not effectively remove microorganisms. As a matter of fact, if there are any microorganisms in the source of water, they can actually thrive by feeding on the organic material that has previously been retained on the carbon particles.

The carbon in filters will eventually become loaded with contaminants so that the unit will no longer function. If a carbon unit is used after this point, it will periodically start to discharge quantities of organics into the effluent. As a result, the water being used from the unit may, at times, have a higher level of organics that the influent. Unfortunately, there is no definite way of determining when carbon is exhausted. The life of the carbon in a unit depends on such factors as the concentration and types of contaminants in the water, the quantity of granular activated carbon (**GAC**) in the treatment unit, and the amount of water put through the unit. It is strongly recommended that when a GAC treatment unit is used, the carbon be changed frequently.

#### **Reverse Osmosis**

A reverse osmosis (**RO**) unit cannot be used by itself for water treatment. Some membranes will be destroyed by exposure to chlorine, and the efficiency of a membrane can be fouled by suspended matter in the influent water. For this reason, an RO module is always preceded by pre-filters.

As discussed before, RO units must be operated under pressure. Home-type RO units do not work very efficiently because they must operate on water system pressure, so about 75 percent of the water introduced to the unit is usually piped to waste.

Small RO units produce a very small flow, so the treated water is piped to a diaphragm pressure tank, which supplies water to a separate faucet. RO is effective in removing most inorganics, salts, metals, and organics having larger molecules. Although RO is known to effectively remove *Giardia lambia* cysts, bacteria, and viruses, it is not recommended for use on microbiologically unsafe water.

#### **Ultraviolet Disinfection**

Although the use of ultraviolet (**UV**) light is not cost effective for the treatment of any sizable quantities of water, it can be practically applied for home treatment use. Units consist of a UV light source enclosed in a protective transparent sleeve, mounted so that water can flow past the light. UV light destroys bacteria and inactivates viruses. However, its effectiveness against spores and cysts is questionable. Both dissolved solids and turbidity adversely affect the performance of UV disinfection. The most common operation problem is a buildup of dirt on the transparent shield, so units should frequently be inspected and cleaned.



## 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. Diets should be rich in electrolytes as the aggressive nature of distilled water can "**leach**" electrolytes from the body.

#### **Special Treatment**

Special treatment units for home use are also available for removal of methane, hydrogen sulfide, nitrate, fluoride, radon, and other objectionable contaminants. Most often, this type of treatment is used on private wells.

#### The Use of Point-of-Entry (POE) Treatment Instead of Central Treatment

Under recent US Environmental Protection Agency (**USEPA**) regulations, water systems with a source water exceeding a maximum contaminant level (**MCL**) can install **POE** devices on all water services (instead of providing central treatment) to satisfy the requirement of providing water to the public below the MCL. An example of where this might be a viable alternative is a system having water so hard that a large proportion of the customers have already installed home softeners. If the contaminant exceeding the MCL in the source water can be removed by ion exchange softening, the system might meet the federal requirements by ensuring that every customers has a softener installed.

At the same time, a number of problems must be overcome. It is difficult for the system to ensure that all drinking water furnished to the public is treated. Another problem is that the water system must have a plan for checking and maintaining all the units to ensure that they are always properly operated. It is expected that some very small systems may find this option workable under certain circumstances. The American Water Works Association has recommended that all treatment required for a public water supply be in the form of central treatment.



## **DESALINATION - DISTILLATION**



## MULTISTAGE FLASH DISTILLATION

408 Chemical Contaminants 201 11/1/2017 TLC (928) 468-0665

## **Reverse Osmosis Home Filtration Devices**

Reverse Osmosis home filtration devices are designed to fit neatly under almost any sink. The filter pack typically will slide to the back of the sink next to the garbage disposal. The tank tucks behind the plumbing and garbage disposal to the back of the sink. It uses very little of the sink's practical space.

The R/O connects to the cold water supply under the sink. First, water first passes through at a 1 micron sediment filter, which removes large particles that float in the water like silt, sand, rust, dirt, etc. We can see down to 40 microns (a human hair is about 80 microns and most bacteria is around 1 micron). This filter should be changed as needed by visually looking at it. (typically 6 months to 1 year).



Small under the sink home use unit.

Second, the water passes through a Bituminous granulated coal filter that removes chlorine, some pesticides, herbicides and toxic chemicals. This filter should be changed every 6 months religiously.

Both of the first two filters' main purpose is to protect the R/O membrane form chlorine and particles that can prematurely ruin the membrane. The R/O membrane is the heart of the system. It filters down to a molecular level (1/10,000/micron).

Water is basically forced through the membrane. The water that makes it through is the purified water and the water that doesn't make it is impure water and it is dumped down the drain. The water slows down to a drop at a time and is accumulated in a 3 gallon pressurized storage tank.

The water is then pushed out of the tank at about 40-60 psi through a 10 inch post coconut shell carbon filter designed to pick up anything missed by the previous filters insuring great taste on the way to the faucet. The faucet is an air gap faucet and meets all plumbing codes.

#### 1 micron sediment filter

A micron is a unit of measure. People can see down to 40 microns. Most Bacteria is between 1-5 microns. The sediment filter consists of a poly spun fiber and removes sediment down to 1 micron.

#### Bituminous granulated coal filter

This carbon filter has 56 cubic inches of carbon, which is more than any other filter made with similar dimensions on the market. We use two different types of carbon in our system (post carbon filter is a coconut shell carbon). Different types of carbon have different adsorption rates and different removal rates of toxic chemicals, so by using two types of carbon, we get the highest adsorption rates possible.

#### **R/O Membrane**

R/O membranes are generally made of Thin Film Composite. (**TFC for short**). There are basically two types of membranes on the market -TFC and CTA (**Cellulose Triacetate**).

TFC membranes are simply more durable because they are made out of a plastic type of material. CTA's are made with a paper type of material. Anyone who knows the R/O business in areas of hard water will only use TFC membranes because CTA customers will be buying membranes typically every 1 to 3 years (that gets expensive), whereas TFC membranes will typically last 3 to 5 years.



## **REVERSE OSMOSIS SYSTEM**

### Homeowner's Water Filtration Devices

**Carbon Block Filters** improve taste and odor, reduce turbidity, remove chlorine and THM's, remove organic chemicals, pesticides, herbicides, and insecticides, and may remove some bacteria, cysts and parasites, radioactivity and asbestos fibers. A carbon-block filter can also remove some heavy metals. They do not remove fluorides, viruses, dissolved solids such as salt, sodium, calcium/magnesium and inorganic minerals as well as phosphates and detergents. Manganese, iron, metallic dead dirt minerals, hydrogen sulfide/sulfates, arsenic, aluminum, dissolved lead, nitrates and heavy metals also remain in the water. (Some specially treated carbon block units have excellent lead removal.)

**Granular Activated Carbon Filters** improve taste and odor, reduce turbidity, remove chlorine and THM's, organic chemicals, pesticides, herbicides, and insecticides. They may control bacteria growth when silver-impregnated. Mercury and radioactivity may also be reduced by this type of filter. Granular Activated Carbon Filters do not remove fluorides, sulfates, nitrates, arsenic, aluminum, metallic dead dirt minerals, salts, sodium, heavy metals, lead, calcium, iron, magnesium, virus, bacteria, parasites, cysts, manganese, hydrogen sulfide or asbestos. Back flushing is often recommended for this type of filter. Bacteria may become a problem.



**KDF/Carbon Combination** is similar to a Granular Activated Carbon Filter with additional metal removal capabilities, including lead. Chlorine is converted to chloride by KDF (zinc/copper composite), extending the life of a carbon media bed.

This type of filtration helps to minimize biological activity. KDF/Carbon Filters do not remove salts, fluorides, sulfates, nitrates, arsenic, aluminum, dead dirt minerals, phosphates or detergents. They may or may not be effective at removing parasites, cysts, and asbestos.

### **EPA Water Treatment Processes**

Treating your water to reduce arsenic will be necessary if more cost-effective alternatives are not available. EPA has identified best available technologies (BATs) and small system compliance technologies (SSCTs) for removing arsenic from drinking water (40 CFR 141.62(c)&(d)).

BATs are technologies that have proven effective for large systems, and SSCTs are technologies that are effective and affordable for small systems. Systems are not required to use any specific technology. Systems can use technologies not listed as BATs or SSCTs if they are effective. Installing a BAT makes a system eligible for a general variance if, due to source water conditions, the system cannot achieve compliance. A general variance, if approved by the State, would allow the system to supply water with an arsenic level above the MCL for a certain period of time.

EPA anticipates that most small systems will use activated alumina (or another type of adsorptive media), reverse osmosis POU devices, or modified lime softening. For more information on these technologies. Most technologies may require pre-treatment (e.g., chlorination) to effectively remove arsenic from drinking water. The need for pre-treatment depends on source water quality.

You may also wish to consider promising technologies such as granular ferric hydroxide and modified activated alumina, which are not yet approved by EPA as BATs or SSCTs. EPA has developed the Arsenic Treatment Technology Design Manual for Small Systems (EPA 816-R-02-011), which examines these new technologies, as well as the BATs and SSCTs. This manual is available from EPA by calling the Safe Drinking Water Hotline at 1-800-426-4791 or by going on line at www.epa.gov/safewater.

#### Activated Alumina

Activated alumina (AA), an adsorptive medium, uses very small grains, which are packed into a large container. Water is then continuously passed through one or more containers. When AA is exhausted it is simply disposed of and replaced with fresh AA. AA can treat water containing up to 0.160 mg/L of arsenic.

#### **Reverse Osmosis**

Reverse osmosis uses high pressure to force water through a membrane with microscopic holes that prevents arsenic and other large contaminants from passing through. Some water is also not able to pass through the membrane and is wasted. Reverse osmosis can treat water containing up to 0.160 mg/L of arsenic.

#### Modified Lime Softening

The addition of lime to water causes calcium and magnesium to form solid particles, which can then be removed by clarification and filtration. Arsenic can join these particles and be removed along with them. Lime softening is very expensive and water systems are unlikely to install this technology only for arsenic removal. However, for water systems that use lime softening to reduce hardness, the process can be modified to increase arsenic removal. Modified lime softening can treat water containing up to 0.080 mg/L of arsenic.

### Arsenic Disposal and Related Information Section



In accordance with the Arsenic Rule, systems must demonstrate compliance with the revised arsenic maximum contaminant level (MCL) (10 ppb) at each entry point to the distribution system. Systems utilizing multiple sources will need to consider a mitigation strategy for each entry point to the distribution system that exceeds the revised MCL.

A system will need to optimize existing treatment or install new treatment if it has high arsenic sources and cannot achieve compliance through a non-treatment options such as blending, seasonal use of sources, or development of an alternative source. The system should first determine whether any of its existing treatment technology is capable of removing arsenic even though it may not be doing so currently.

Treatment may be accomplished at the wellhead, as a centralized treatment system (water pumped from several sources to a centralized location for treatment before entering the distribution system). Also, treatment located at the Point-of-Use (POU) or Point-of-Entry (POE) within a building or entering a building, respectively, may be appropriate in some situations.

	TASTE AND ODOR	CHLORINE	ORGANICS	INORGANICS	BIOLOGICALS
BOTTLED WATER		$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$
ULTRA VIOLET (UV)	$\bigcirc$	$\bigcirc$	$\bigcirc$		$\bigcirc$
CARBON FILTERS				$\bigcirc$	$\bigcirc$
REVERSE OSMOSIS SYSTEM	$\bigcirc$	$\bigcirc$			$\bigcirc$
N	PARTIAL				

TYPES OF WATER QUALITY FILTRATION TECHNOLOGIES AND EFFECTIVE USES



FILTRATION METHODS AND REMOVAL SIZES

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## **EPA Arsenic Waste Disposal**

#### What Do I Need to Consider When Deciding on a Waste Disposal Option?

All arsenic treatment technologies, other than zero-treatment options such as alternate source use and blending, produce waste in the form of liquid residuals (e.g., brine, concentrates, filter rinse, and backwash), solid residuals (e.g., spent media, membranes, and dewatered sludge), or both. These residuals contain concentrated arsenic and other contaminants that must be disposed of properly.

Certain raw water characteristics can affect a system's waste disposal options and should be considered when selecting an arsenic treatment technology.

#### Raw water characteristics that may affect disposal alternatives include:

- ✓ Excessively high or low pH.
- ✓ High concentrations of competing ions (including fluoride, sodium, sulfate, and chloride).
- ✓ High total suspended solids (TSS).
- High total dissolved solids (TDS).
- ✓ High concentrations of heavy metals (including arsenic, lead, chromium, and aluminum).
- ✓ High concentrations of radionuclides.

The type of waste generated depends on the arsenic treatment technology selected. The following table shows the liquid and solid waste residuals that will be produced by likely small system treatment technologies.

You should work with your State to determine the best waste disposal option for your system based on your treatment processes, the type of

✓ waste generated, and the contaminant levels in the waste streams.

#### Selecting a Technology to Treat Arsenic

When choosing a technology, remember:

1. It is usually easier and cheaper to modify an existing treatment system than to install new treatment.

2. If you choose carefully, you may be able to install one technology to achieve compliance with the Arsenic Rule and other new rules. For more information on EPA's current and proposed regulations see www.epa.gov/safewater/regs.html or call the Safe Drinking Water Hotline at 1-800-426-4791.

3. You may need additional training to learn how to operate and maintain a new treatment process.

4. Most treatment technologies are more effective when the source water is pre-treated.

5. You should consider all options for waste disposal when you are choosing a treatment technology.

6. You should always pilot test a treatment method before installing it. Technologies are highly dependent on system specific considerations.

7. Your State may be able to help you choose an appropriate treatment technology. For more information about treatment technologies and how they might work for you, ask your State or refer to:

- The Arsenic Treatment Technology Design Manual for Small Systems (EPA 816-R-02-011), available from EPA by calling the Safe Drinking Water Hotline at 1-800-426-4791.
- www.epa.gov/ogwdw000/ars/treat.html

#### Demonstration

EPA is conducting a demonstration program on the treatment of arsenic in drinking water. The Agency intends to identify and evaluate commercially available technologies, engineering options, or other approaches that cost-effectively help small systems (10,000 or fewer customers) meet the revised arsenic MCL. For more information on this program, see www.epa.gov/ORD/NRMRL/arsenic/.

#### Laboratory Testing

Certain analytical methods previously used by laboratories to measure arsenic concentrations are not sensitive enough to determine if your system is in compliance with the revised arsenic MCL of 0.010 mg/L. The methods that are no longer appropriate for compliance sampling are EPA method 200.7 and SM 3120B. The currently acceptable methods for compliance sampling are:

- ✓ EPA 200.8
- ✓ EPA 200.9
- ✓ SM 3113B
- ✓ SM 3114B
- ✓ ASTM D-2972-93B
- ✓ ASTM D-2972-93C

Contact your State if you are unsure about the method your lab normally uses.

### What Does Compliance Monitoring Involve? Monitoring Instructions

#### Routine Monitoring

If your monitoring results are at or below the revised MCL, you still must perform routine monitoring for arsenic at each sampling point (40 CFR 141.23(c)(1)):

- ✓ Once every 3 years during each nine year compliance cycle for ground water systems.
- ✓ Annually for surface water and GWUDI systems.

#### Waivers

Your State may issue you a waiver to reduce your monitoring frequency if your system historically has had arsenic levels below the revised MCL. Waivers allow you to take one sample during each 9-year compliance cycle. To be eligible for a waiver, you must have sampling results from three previous compliance periods (see Routine Monitoring, above) that (40 CFR141.23(c)):

- ✓ Were collected at each sampling point.
- ✓ All were analyzed using analytical methods approved by the Arsenic Rule.
- ✓ All have arsenic levels below 0.010 mg/L.

For example, the system described in the Arsenic Planning Worksheet monitored during the previous three compliance periods (i.e., in 1998, 2001, and 2004). The system also collected samples from each sampling point and analyzed them using approved analytical methods. Since all of the results were below 0.010 mg/L, this system may be eligible for a waiver. Note that, in 1992, the system used analytical method SM 3120B.

This method is not approved for compliance with the revised MCL, so the data from 1992 could not be used to satisfy the waiver eligibility requirements. In addition, the system did not sample from each sampling point in 1995. Therefore, these data do not meet the waiver requirements.

#### **Increased Monitoring**

Even if you are in compliance with the MCL, your State may require you to monitor more frequently (40 CFR 141.23(g)). Please contact your State for more information.

#### **Compliance Determination**

If the arsenic concentration in any of your samples exceeds 0.010 mg/L, your State may direct you to take a confirmation sample within 2 weeks (40 CFR 141.23(f)(1)). If the average of the initial sample and the confirmation sample is over 0.010 mg/L, you must begin quarterly monitoring at that sampling point (40 CFR 141.23(f)(3)&(c)(7)).

Calculate compliance with the MCL based on the running annual average, which is the sum of your results from the previous four quarters divided by the number of samples taken (40 CFR 141.23(i)(2)). You will be in violation when the running annual average exceeds 0.010 mg/L.

- You must divide the sum of the sample results from the previous four quarters by the number of samples taken. For example, if you failed to sample in one quarter, add the results from the other three quarters and divide by 3.
- During your first year of quarterly sampling, you will not yet have four quarters of results. In this case, you can assume the best case scenario when calculating the running annual average. Results for all future quarters (within the first year) can be entered as 0.0 mg/L.

#### Sampling and Reporting Notes

The four quarters are: Q1: January - March Q2: April - June Q3: July - September Q4: October - December

When you calculate your running annual average, use 0.0 mg/L for all samples with arsenic levels below what the analytical method can detect. If your State allows you to take more than the required number of samples, all of your samples will be averaged to determine compliance.

#### Monitoring and Reporting Violations

You have committed a monitoring and reporting (M&R) violation if:

- You fail to take a sample;
- You do not sample from each sampling point; or,
- You do not report your results to the State on time.

#### Maximum Contaminant Level Violations

If the running annual average of arsenic at a sampling point is greater than 0.010 mg/L, your system is in violation of the MCL (40 CFR 141.23(i)(1)). If you monitor once a year or less and the result from the initial sample (or the average of the results from the initial and confirmation samples) is greater than 0.010 mg/L but not more than 0.040 mg/L, your system has not yet violated the MCL.

Having a result greater than 0.010 mg/L will require you to collect quarterly samples. If your system has an MCL violation, you must continue quarterly sampling until your State determines that your system is reliably and consistently below the MCL.

#### **Reporting and Notification Requirements**

Keeping the State and your customers informed is part of your responsibility as a public water system. The State needs to know if your system poses any health risks so it can help you protect your customers. Informed customers are more likely to understand the need for a new treatment system, infrastructure changes, and rate increases.

#### If you have an M&R violation, you must (40 CFR 141.31(b) & 141.204):

- ✓ Report this violation to the State within 48 hours of when the violation occurs.
- ✓ Notify your customers within a year. You may be able to incorporate this information into your CCR instead of a separate notification.

#### If you have an MCL violation, you must (40 CFR 141.31(b) & 141.203):

- ✓ Report this violation to the State within 48 hours of receiving the lab results.
- ✓ Notify your customers within 30 days.

In both cases, you must send a copy of any public notice to the State. If you are *in compliance,* you must report your results and running annual average, if any, to the State within 10 days after the end of the month in which the sample was taken, or within 10 days of the end of the sampling period, whichever is shorter (40 CFR 141.31(a)).

In your annual *Consumer Confidence Report,* you must include a statement about arsenic if monitoring results exceed 0.005 mg/L (40 CFR141.153(d)(6) and 141.154(b)&(f)). See page 12 of this guide for more information.

#### **Monitoring Worksheets**

Depending on your source water and your previous arsenic results, you may be required to take samples quarterly, annually, once every 3 years, or once every 9 years.

#### These monitoring worksheets will help you:

- Collect the correct number of samples for each sampling period.
- Report monitoring results to your State on time.
- Collect appropriate confirmation samples.
- Know when your system is in violation of the arsenic MCL.
- Report MCL violations to your State and your customers on time.

Several copies of each worksheet are provided. The first copy is followed by instructions on how to complete it. The second copy is an example. The third is a blank worksheet that you can photocopy and use. Please note that your State may have a monitoring form of its own that must be used to submit sample results. If that is the case, the worksheets provided here **do not** replace the State form.

#### Appendix A: Sources for More Information on Arsenic

- ✓ The final text of the Arsenic Rule: EPA-815-Z-01-001 or Federal Register Vol. 66, No 14., pp. 6976-7066. The document is also available on line at www.epa.gov/safewater/ars/arsenic finalrule.html.
- ✓ The Arsenic Implementation Guidance, EPA-816-D-01-002: www.epa.gov/safewater/ars/implement.html (available September 2002).
- ✓ EPA's Safe Drinking Water Hotline: 1-800-426-4791

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## **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 statues, 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 water 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 longterm 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  $\mu$ 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  $\mu$ g/L in the source water to 3.5  $\mu$ 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  $\mu$ g/L and an average finished water concentration of 4.0  $\mu$ 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  $\mu$ g/L, and the lime softening plant reduced the average total arsenic concentration to 16.6  $\mu$ 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).

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

This report documents treatment plant information as well as results of sampling and analysis at two iron removal plants (referred to as Plants A and B). 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 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  $\mu$ 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  $\mu$ g/L to 3.0  $\mu$ 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  $\mu$ g/L to 11.9  $\mu$ 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  $\mu$ g/L of iron, while Plant B averaged 1,137  $\mu$ 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 longterm 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  $\mu$ g/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  $\mu$ g/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  $\mu$ g/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  $\mu$ g/L total arsenic) contained approximately 0.3 to 28.8  $\mu$ g/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  $\mu$ g/L) but no As(III), which was consistently removed to less than 5  $\mu$ g/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 CaCO3). 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 arsenicladen 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 pretreatment method for arsenic removal. Aeration has been referred to in the literature as a possible useful pre-treatment method to ensure that arsenic in is 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  $\mu$ g/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.

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  $\mu$ g/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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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 statues, 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 water 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 nontransient 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 yearround 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 Iagoons), 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 longterm 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  $\mu$ 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  $\mu$ g/L in the source water to 3.5  $\mu$ 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  $\mu$ g/L and an average finished water concentration of 4.0  $\mu$ 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  $\mu$ g/L, and the lime softening plant reduced the average total arsenic concentration to 16.6  $\mu$ 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).

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

This report documents treatment plant information as well as results of sampling and analysis at two iron removal plants (referred to as Plants A and B). 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 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  $\mu$ 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  $\mu$ g/L to 3.0  $\mu$ 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  $\mu$ g/L to 11.9  $\mu$ 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  $\mu$ g/L of iron, while Plant B averaged 1,137  $\mu$ 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 longterm 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  $\mu$ g/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  $\mu$ g/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  $\mu$ g/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  $\mu$ g/L total arsenic) contained approximately 0.3 to 28.8  $\mu$ g/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  $\mu$ g/L) but no As(III), which was consistently removed to less than 5  $\mu$ g/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 CaCO3). 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 arsenicladen 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.

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EPA 600-R-01-102

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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  $\mu$ g/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.

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  $\mu$ g/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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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 nontransient 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 yearround 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



**REMOVAL METHODS** 



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



## WATER SAMPLING FLOW CHART



## HOW TO TAKE A WATER SAMPLE



STANDARD PLATE COUNT PROCEDURE (Basic test used to detect general bacteria in samples)

446 Chemical Contaminants 201 11/1/2017 TLC (928) 468-0665

### **Common Water Quality and Sampling Statements**

#### These statements will be more explained in the previous chapters.

#### 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 chorine 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.

2. The sampling point should be a non-swivel faucet.

- 3. Remove any aerator or screen and flush.
- 4. It should not be a faucet that leaks, permitting water to run over the outside of the faucet.

5. Leaking faucets can promote bacterial growth.

6. If an outside faucet must be used, disconnect any hoses or other attachments and be sure to flush the line thoroughly.

7. 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 equals 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  $\mu$ m thick, and have 0.45  $\mu$ 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  $\mu$ 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 midpoint 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



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. A 99.99 percent reduction would be 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 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.  $Cl_2NH_3$  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.

### Glossary

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 Hammer: A pneumatic cylindrical hammering device containing a piston used on air rotary rigs. The air hammer's heavy piston moves up and down by the introduction of compressed air creating a hammering action on the bit.

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).

ALKANLINE 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 Al2(SO4)3~14H2O. It is a cationic polymer.

AMMONIA: A chemical made with Nitrogen and Hydrogen and used with chlorine to disinfect water.

AMMONIA: NH3 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.

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 NO3, 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 (6.02x10^23).

#### В

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).

Bentonite: High quality clay composed primarily of montmorillonite. Used to thicken drilling mud in mud rotary drilling and used to form seals in well construction or abandonment.

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.

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.

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 SOLTION : 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).

#### С

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 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.

CaOCI2.4H2O: 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 (CO32-) and bicarbonate (HCO3-) 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 CaCO3" – 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 NaHCO3 (baking soda), it would have a carbonate hardness of about 18 mg/L as CaCO3. If you had a liter of water containing 50 mg of Na2CO3, it would have a carbonate hardness of about 29 mg/L as CaCO3.

CARBONATE ROCK: Rock that is composed primarily of calcium carbonate.

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. Cl2 gas will settle on the floor.

CELL POTENIAL : 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.

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 LAW: Certain rules that pertain to the laws of nature and chemistry.

CHEMICAL OXIDIZER: KMnO4 or Potassium Permanganate is used for taste and odor control because it is a strong oxidizer which eliminates many organic compounds.

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 a 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 iodmetic 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 onetenth 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.

CIO2: 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.

COLLIOD : 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.

COMPLETION (WELL COMPLETION): Refers to the final construction of the well including the installation of pumping equipment.

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.

CONDUCTOR : Material that allows electric flow more freely.

CONTACT TIME, pH and LOW TURBIDITY: Factors which are important in providing good disinfection using chlorine.

CONTACT TIME: 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 algae and slime growth, Control mud ball formation, Improve coagulation, Precipate iron. The addition of chlorine to the water prior to any other plant treatment processes.

CONTROL TASTE AND ODOR PROBLEMS: KMnO4 Potassium permanganate is a strong oxidizer commonly used to control taste and odor problems.

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.

COVALENT BOND : Chemical bond that involves sharing electrons.

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.

CYANURIC ACID: White, crystalline, water-soluble solid, C3H3O3N3·2H2O, 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.

DECIBELS: The unit of measurement for sound.

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.

DELIQUESCENE : 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 TIME: The minimum detention time range recommended for flocculation is 5 – 20 minutes for direct filtration and up to 30 minutes for conventional filtration.

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 or SOLVATION : The spread of ions in a monosacharide.

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 electradodes.

DRY ACID: A granular chemical used to lower pH and or total alkalinity.

Е

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.

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.

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) 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.

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. Long-chain polymer flocculants, such as modified polyacrylamides, are manufactured and sold by the flocculant producing business. These can be supplied in dry or liquid form for use in the flocculation process. The most common liquid polyacrylamide is supplied as an emulsion with 10-40 % actives and the rest is a carrier fluid, surfactants and latex. Emulsion polymers require activation to invert the emulsion and allow the electrolyte groups to be exposed.

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.

FREE CHLORINE RESIDUAL: Regardless of whether pre-chloration 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.

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.

Н

H2SO4: 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 (CI), 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 CH2CICO2H. In the same manner, in dichloroacetic acid two chlorine atoms would take the place of two hydrogen atoms (CHCI2CO2H).

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 (Ca2+), and magnesium (Mg2+) metal cations, and sometimes other dissolved compounds such as bicarbonates and sulfates. Calcium usually enters the water as either calcium carbonate (CaCO3), in the form of limestone and chalk, or calcium sulfate (CaSO4), in the form of other mineral deposits. The predominant source of magnesium is dolomite (CaMg(CO3)2). 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 Ca2+ and Mg2+ ions) is read as parts per million or weight/volume (mg/L) of calcium carbonate (CaCO3) 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. HF: The molecular formula of Hydrofluoric acid.

HIGH TURBIDITY CAUSING INCREASED CHLORINE DEMAND: May occur or be caused by the inadequate disinfection of water.

HOMOPOLAR: Of uniform polarity; not separated or changed into ions; not polar in activity. Electricity. unipolar.

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: (H2SiF6) 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), peculation (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 (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.

L

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.

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.

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)); diseasecausing 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 COMPUND: 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.

#### Κ

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.

KINETIC ENERGY: 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, lacrimation.

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 : A 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.

Μ

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.1 It is recommended by the American Public Health Association in standard total coliform membrane filtration procedure for testing water, wastewater, and foods.2,3 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. M-ENDO BROTH: 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 : A substance possessing both the properties of metals and non-metals.

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 CH4. 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. METHLENE BLUE : A heterocyclic aromatic chemical compound with the molecular formula  $C_{16}H_{18}N_3SCI$ .

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.

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 it 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.

MURIATIC ACID: An acid used to reduce pH and alkalinity. Also used to remove stain and scale.

MYCOTOXIN: A toxin produced by a fungus.

Ν

NaOCI: Is the molecular formula of Sodium hypochlorite.

NaOH: Is the molecular formula of Sodium hydroxide.

NASCENT: Coming into existence; emerging.

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.

NH3: The molecular formula of Ammonia.

NH4+: 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 (N2) is one of the strongest in nature. The resulting difficulty of converting (N2) into other compounds, and the ease (and associated high energy release) of converting nitrogen compounds into elemental N2, have dominated the role of nitrogen in both nature and human economic activities.

NO3-: 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+, Fe3+, or Cl-). Normality accounts for any discrepancy between the concentrations of the various ionic species in a solution. For example, in a salt such as MqCl2, there are two moles of CI- for every mole of Mg2+, so the concentration of CI- as well as of Mg2+ 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+ or OH- ion. For example, 2 Normal sulfuric acid (H2SO4), means that the normality of H+ ions is 2, or that the molarity of the sulfuric acid is 1. Similarly for 1 Molar H3PO4 the normality is 3 as it contains three H+ 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.

#### 0

O3: 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 Al2O3 that protects the foil from further corrosion.

#### OXIDIZED:

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 (O3) is a triatomic molecule, consisting of three oxygen atoms. It is an allotrope of oxygen that is much less stable than the diatomic O2. 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, O3, 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 O3 = 3 O2.

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 PATHOGENS: Disease-causing pathogens; waterborne pathogens A pathogen may contaminate water and cause waterborne disease.

#### Ρ

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. 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.

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PITLESS ADAPTER: A fitting installed on a section of column pipe and well casing permitting piping from the well to be installed below grade. (Often requires a special permit for construction)

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. 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.

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.

POTENTIAL ENERGY: The energy that a body has by virtue of its position or state enabling it to do work.

Potentiometric surface: An imaginary surface representing the height a column of water will reach at any location within a confined aquifer. The measured surface of a confined aquifer related to the aquifer's pressure head.

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.

PRESIPATATE : Formation of a solid in a solution or inside another solid during a chemical reaction or by diffusion in a solid.

PRESISION : How close the results of multiple experimental trials are. See also accuracy. PREVENTION: To take action; stop something before it happens.

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  $(H^{+})$  to an atom, molecule, or ion.

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.

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.

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. Crystalgrade types of sodium fluoride should be fed with a saturator. Overfeeding must be prevented to protect public health when using a fluoridation system.

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 bryozoa, snails and annelid worms.

SCHRODINGER EQUATION: Quantum state equation which represents the behavior of an election around an atom.

SCROLL AND BASKET: The two basic types of centrifuges used in water treatment. 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.

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.

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.

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.

Slurry: A mixture of crushed rock and 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.

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 (Energy<sub>rest</sub> =  $mc^2$  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. Sulfate in drinking water currently has a secondary maximum contaminant level (SMCL) of 250 milligrams per liter (mg/L), based on aesthetic effects (i.e., taste and odor). This regulation is not a federally enforceable standard, but is provided as a guideline for States and public water systems. EPA estimates that about 3% of the public drinking water systems in the country may have sulfate levels of 250 mg/L or greater. The Safe Drinking Water Act (SDWA), as amended in 1996, directs the U.S. Environmental Protection Agency (EPA) and the Centers for Disease Control and Prevention (CDC) to jointly conduct a study to establish a reliable dose-response relationship for the adverse human health effects from exposure to sulfate in drinking water, including the health effects that may be experienced by sensitive subpopulations (infants and travelers).

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, S2-, which exists in strongly alkaline aqueous solutions formed from H2S or alkali metal salts such as Li2S, Na2S, and K2S. Sulfide is exceptionally basic and, with a pKa > 14, it does not exist in appreciable concentrations even in highly alkaline water, being undetectable at pH < ~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), HSconverts to H2S, 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 (H2S, NaSH, Na2S) 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 Ag2S. 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. 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.

#### Т

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 microgranular (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.

This reaction proceeds more rapidly with increasing temperature and decreasing pressure. Deflagration of ozone can be triggered by a spark, and can occur in ozone concentrations of 10 wt% or higher.

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. TITRATION: 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.

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  $N_2$ ). 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. 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.

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.

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.

VIRUSES: 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, Tm, 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.

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.

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. 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.

VOLUMETERIC ANALYSIS: See titration.

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 :  $H_2O$  : 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 of 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).

WAVE FUNCTION: A function describing the electron's position in a three-dimensional space. 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).

#### Х

X-RAY : Form of ionizing, electromagnetic radiation, between gamma and UV rays. X-RAY DIFFRACTION: A method for establishing structures of *crystalline* solids using singe 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.

Ζ

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.

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Chemical Name	Common Name	Chemical Formula
Aluminum hydroxide		AI(OH) <sub>3</sub>
Aluminum sulfate	Alum, liquid	AL <sub>2</sub> (SO <sub>4</sub> )3 . 14(H <sub>2</sub> O)
Ammonia		NH <sub>3</sub>
Ammonium		NH4
Bentonitic clay	Bentonite	
Calcium bicarbonate		Ca(HCO <sub>3</sub> )2
Calcium carbonate	Limestone	CaCO <sub>3</sub>
Calcium chloride		CaCl <sub>2</sub>
Calcium Hypochlorite	HTH	Ca(OCI) <sub>2</sub> . 4H <sub>2</sub> O
Calcium hydroxide	Slaked Lime	Ca(OH) <sub>2</sub>
Calcium oxide Calcium sulfate	Unslaked (Quicklime) Gypsum	CaO CaSO₄
Carbon Carbon dioxide	Activated Carbon	C CO <sub>2</sub>
Carbonic acid		H2CO <sub>3</sub>
Chlorine gas		Cl <sub>2</sub>
Chlorine Dioxide		CIO <sub>2</sub>
Copper sulfate	Blue vitriol	CuSO4 . 5H2O
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)₃
Ferrous sulfate	Copperas	FeSO <sub>4</sub> .7H <sub>2</sub> 0
Hydrofluorsilicic acid		H <sub>2</sub> SiF <sub>6</sub>
Hydrochloric acid Hydrogen sulfide	Muriatic acid	HCI H <sub>2</sub> S
Hypochlorous acid Magnesium bicarbonate		HOCL Mg(HCO₃)2
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(HCO₃)2
Manganous sulfate		MnSO <sub>4</sub>
Monochloramine		NH <sub>2</sub> Cl
Potassium bicarbonate		KHCO <sub>3</sub>

# **Common Water Treatment and Distribution Chemicals**

Potassium permanganate		KMnO <sub>4</sub>
Chemical Name	Common Name	Chemical Formula
Sodium carbonate	Soda ash	Na <sub>2</sub> CO <sub>3</sub>
Sodium chloride Sodium chlorite	Salt	NaCl NaClO <sub>2</sub>
Sodium fluoride Sodium fluorosilicate		NaF Na₂SiF <sub>6</sub>
Sodium hydroxide Sodium hypochlorite Sodium Metaphosphate	Lye Hexametaphosphate	NaOH NaOCI 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		$H_2SO_4$

# WATER TREATMENT CHEMICALS

CHEMICAL NAME	CHEMICAL USE IN WATER TREATMENT	
SULFURIC ACID		
ALUMINUM SULPHATE (Alum)	USED AS A COAGULANT	
FERRIC CHLORIDE	USED AS A COAGULANT	
CALCIUM HYDROXIDE (Lime)	AIDS IN THE FLOCCULATION PROCESS/ALSO USED AS pH CONTROL	
	USED FOR pH CONTROL	
SODIUM ALUMINATE	USED AS COAGULANT TO IMPROVE FLOCCULATION	
SODIUM HYPOCHLORITE (also known as Bleach)	USED AS A DISINFECTANT	
CHLORINE	USED AS A DISINFECTANT	

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	Iechnetium	+6
44	Rubidium	(+2), +3, +4, (+6), (+7), +8
45	Rhodium	(+2), (+3), +4, (+6)
46	Palladium	+2, +4, (+6)
4/	Silver	+1, (+2), (+3)
48		(+1), +2
49	Indium	(+1), (+2), +3
50	IIN	+2, +4

51	Antimony	-3, +3, (+4), +5
52	Tellurium	-2, (+2), +4, +6
53	lodine	-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
90 91	Thorium Protactinium	+4 +5

A. Reference: *Lange's Handbook of Chemistry, 8th Ed.*, Norbert A. Lange (Ed.), Handbook Publishers, Inc. 1952.

Common Used Products	Chemical Name
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

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