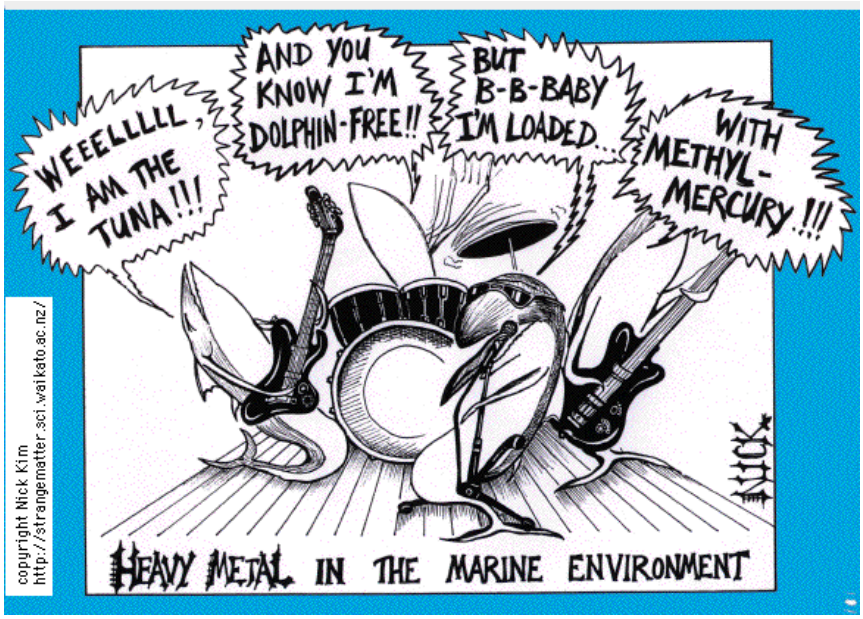
Lecture 7

TOXIC HEAVY METALS

http://www.theoldschoolhenstead.co.uk/Pupils/Mercurymetal/Mercury.htm

1



http://www.webelements.com

2

Heavy Metals

- Metallic elements that are denser than other common metals
- Mercury, lead, cadmium and arsenic (a semimetal) present the greatest environmental hazard - WHY?
  - Extensively used
  - Toxic
  - Widely distributed
- Ultimate sink for heavy metals are soils and sediments

3

Heavy Metals - Densities

TABLE 11-1 Densities of Some Important Heavy Metals and Other Substances

Substance	Density (g/cm^3)
Hg	13.5
Pb	11.3
Cu	9.0
Cd	8.7
Cr	7.2
Sn	5.8–7.3
As	5.8
Al	2.7
Mg	1.7
H_2O	1.0

Light metals

4

Toxic Heavy Metals: Hg, Pb, Cd and As

Toxicity of the heavy metals:

- Of the four, Hg is highly toxic in the elemental form
  - Exposure through inhalation of Hg vapor from liquid Hg
- All four are ***dangerous*** in the following ***form***:
  - Cations (e.g. from soluble compounds)
  - Organometallic (i.e. bonded to organic molecules)

5

Toxic Heavy Metals – Cont.

Q. Why are they toxic?

Mechanism of heavy metal toxicity

- Due to strong affinity of metal cations (M^{n+}) for sulfur

  Found in proteins (e. g. enzymes)
  - ***Sulfhydryl groups*****, - SH**, in many enzymes, react with ingested M^{n+}
  - Can deactivate the enzyme
    => stops or alters metabolic processes

6

Toxic Heavy Metals – Cont.

Drill: Write the balanced chemical reactions that correspond to the reaction of an Hg^{2+} ion (a) with H_2S and (b) with R-SH (where R is an organic group) to produce hydrogen ions and an organometallic product.

Is this what you got?

$$Hg^{2+} + 2\,H_2S \longrightarrow HS - Hg - SH + 2H^+$$

$$Hg^{2+} + 2\,RSH \longrightarrow RS - Hg - SR + 2H^+$$

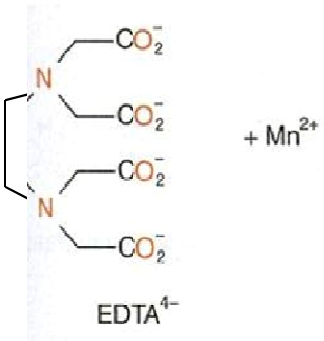
7

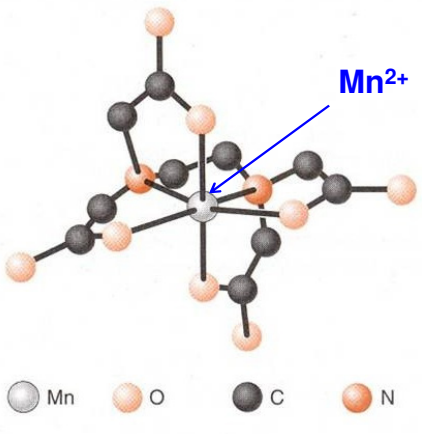
Chelation Therapy: Treatment of Heavy Metal Poisoning

- Utilizes a **chelating agent** that binds strongly to the metal cation

Ex. EDTA

Binds th/ > 1 site





6 binding sites (orange) = ***hexadentate***

Gk. "chela" = claw

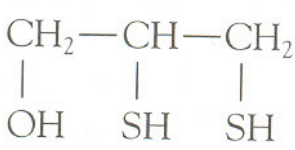
8

Source: D.C. Harris, "Quantitative Chemical Analysis." (6th ed., p. 259)

Treatment of Heavy Metal Poisoning (Cont.)

Medical treatment

- Administers a compound that binds to the metal more strongly than does the enzyme. Ex. BAL



British Anti-Lewisite

9

Toxic Heavy Metals

(1) Mercury

Toxic forms:

- Elemental (Hg liquid/vapor), and
- Compounds of mercury
  - Inorganic salts – ex. mercuric nitrate, $Hg(NO_3)_2$
  - Organometallic – ex. methylmercury

Mode of entry:

- Elemental Hg through inhalation
- Ingestion
- Transdermal: Hg (e.g. organomercury) can also enter the body by absorption through the skin
- Systemic: Once in the body, it is carried by the bloodstream to the brain

10

Toxic Heavy Metals: Mercury – *Cont.*

Effects of exposure:

Severity of health effects from mercury exposure depends on:

- the chemical form of mercury;
- the dose;
- the age of the person exposed (the fetus is the most susceptible);
- the duration of exposure;
- the route of exposure (inhalation, ingestion, dermal contact), and
- the health of the person exposed.

11

Toxic Heavy Metals: Mercury – *Cont.*

Effects of exposure:

(1) Elemental mercury effects

- Tremors;
- Emotional changes (e.g., mood swings, irritability, nervousness, etc.);
- Insomnia;
- Neuromuscular changes (such as weakness, muscle atrophy, twitching);
- Headaches;
- Disturbances in sensations; changes in nerve responses; performance deficits on tests of cognitive function.

At higher exposures there may be:

- Kidney damage,
- Respiratory failure, and
- Death

12

Toxic Heavy Metals: Mercury – *Cont.*

(2) Organomercury effects – Ex. Methylmercury

- Exposure in the womb (which can result from a mother's consumption of fish and shellfish that contain methylmercury), can adversely affect a baby's growing brain and nervous system.
- Impacts on *cognitive thinking*, *memory*, *attention*, *language*, and *fine motor* and *visual spatial skills* have been seen in children exposed to methylmercury in the womb.

13

Toxic Heavy Metals: Mercury – *Cont.*

(3) Inorganic mercury effects

High exposures to inorganic mercury may result in damage to:

- Gastrointestinal tract,
- Nervous system, and
- Kidneys

Reference: US EPA, "Mercury: Health Effects" available at http://www.epa.gov/hg/effects.htm

14

Mercury is the only common metal liquid at ordinary temperatures. Mercury is sometimes called ***quicksilver***. It rarely occurs free in nature and is found mainly in cinnabar ore (HgS) in Spain and Italy. It is a heavy, silvery-white liquid metal. It alloys easily with many metals, such as gold, silver, and tin. These alloys are called **amalgams**. Its ease in amalgamating with gold is made use of in the recovery of gold from its ores.

15

Image available at http://www.webelements.com

History: Mercury

- The first emperor of unified China, Qin Shi Huang, reportedly died of ingesting mercury pills that were intended to give him eternal life. [43]
- The phrase **mad as a hatter** is likely a reference to mercury poisoning, as mercury-based compounds were once used in the manufacture of felt hats in the 18th and 19th century.
  (The Mad Hatter character of Alice in Wonderland was almost certainly inspired by an eccentric furniture dealer, not by a victim of mad hatter disease.) [44]
- In 1810, two British ships salvaged a large load of elemental mercury from a wrecked Spanish vessel near Cadiz, Spain. The bladders containing the mercury soon ruptured. The element spread about the ships in liquid and vapor forms. The sailors presented with neurologic compromises: *tremor, paralysis,* and *excessive salivation* as well as *tooth loss, skin problems*, and *pulmonary* complaints.
- For years Abraham Lincoln took a common medicine of his time called "blue mass" which contained significant amounts of mercury.

16

History: Mercury – *Cont.*

- The term **Hunter-Russell syndrome** derives from a study of mercury poisoning among workers in a seed packing factory in Norwich, England in the late 1930s who breathed methylmercury used as a seed disinfectant and preservative.[48]
- Outbreaks of methylmercury poisoning occurred in Minamata, Japan during the 1950s due to industrial discharges of mercury into the Minamata bay. More than 600 people died due to what became known as Minamata disease. In 22 documented cases, pregnant women who consumed contaminated fish showed mild or no symptoms but gave birth to infants with severe developmental disabilities.[2]
- Widespread mercury poisoning occurred in rural Iraq in 1971-1972, when grain treated with a methylmercury-based fungicide intended for planting only was used by the rural population to make bread, causing at least 459 deaths (see Basra poison grain disaster). [49]

17

History: Mercury – *Cont.*

- On August 14, 1996, Karen Wetterhahn, a Dartmouth College chemistry professor, spilled a small amount of dimethylmercury on her latex glove. She began experiencing the symptoms of mercury poisoning five months later and, despite aggressive chelation therapy, died a few months later from brain malfunction due to mercury intoxication. [24][25]
- On March 19, 2008, Tony Winnett, 55, inhaled mercury vapors while trying to extract gold from computer parts (by using liquid mercury to separate gold from the rest of the alloy), and died ten days later. [51][52]
- In December 2008, actor Jeremy Piven was diagnosed with hydrargyria resulting from eating sushi twice a day for twenty years. [53]

Reference: Wikipedia, "Mercury poisoning: History" available at http://en.wikipedia.org/wiki/Mercury_poisoning#History

18

Mercury (Cont.)

Uses:

- $Hg_{(l)}$ in thermometers, barometers and sphygmomanometer
- $Hg_{(g)}$ is used in fluorescent bulbs and advertising signs
- The basis of dental amalgams and preparations
  (~ 50% Hg by mass plus other metals such as Ag, Sn and Cu)
  US FDA, "About Dental Amalgam Fillings", available at http://www.fda.gov/

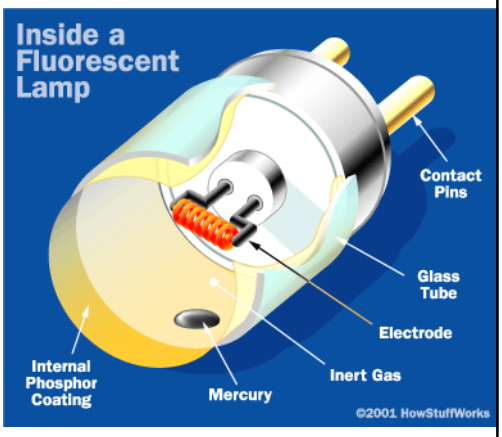
Mercury Sphygmomanometer
http://www.asia.ru/en/ProductInfo/1262315.htm

Dental amalgam: Image available at http://www.fda.gov/MedicalDevices/ProductsandMedicalProcedures/DentalProducts/DentalAmalgam/ucm171094.htm

19

Mercury (Cont.)

When lamp is on, current flows through the electrical circuit to the electrodes. There is a considerable voltage across the electrodes, so electrons will migrate through the inert gas from one end of the tube to the other. This energy changes cause some of the mercury in the tube to vaporize. As electrons and charged atoms collide with the gaseous mercury atoms, the Hg atoms undergo electronic excitation. When the electrons return to their ground state, they release energy in the form of light.



HowStuffWorks, ©1998-2011 HowStuffWorks, Inc. "How Fluorescent Lamps Work" by Tom Harris, available at http://home.howstuffworks.com/fluorescent-lamp2.htm

20

Mercury (Cont.)

Sources of Hg contamination of the environment:

NOTE: Mercury is a naturally-occurring element and exists mainly as cinnabar ore (HgS).

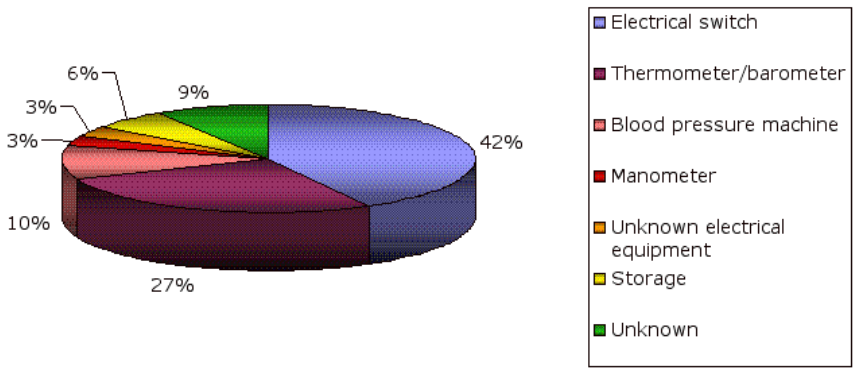
- Burning of coal and fuel oil (electric utilities; industries)

  Contains low levels of Hg

- Incineration of municipal waste that contain Hg
- Hg spills, e.g. from broken thermometers

21

Sources of Metallic Mercury Spills, New York HSEES (1/1/92 to 12/31/97)



http://acc6.its.brooklyn.cuny.edu/~scintech/mercury/alternatives_main.htm

22

Mercury (Cont.)

Q. Are you familiar with the origin of the expressio
"***mad as a hatter***"?

- Mercuric nitrate (source of Hg^{2+}) was used in hat-making in the old days
  - Made the fur fibers soaked in this solution rough and twisted

Easily mat together ←

- Workers in hat industry constantly exposed to Hg developed nervous disorder:
  - Muscle tremors
  - Depression, memory loss, irritability

Mad hatter: Images available at http://www.dominionpaper.ca/images/1982 and http://polarcoordinate.wordpress.com/2010/03/06/jabberwocky/

Mercury (Cont.)

Methylmercury toxicity

Methylmercury = more toxic than Hg^{2+}

- Soluble in fatty tissues of animals
  - ↗ **Bioaccumulates**
  - ↘ **Biomagnifies**

24

Toxic Heavy Metals
2) Lead

- Elemental form is not an environmental problem until it dissolves into **Pb^{2+}** (or the less stable Pb^{4+})

Mode of entry:

- Pb^{2+}: Usually through ingestion of contaminated water and food

Effects:

- Pb^{2+} can inhibit the synthesis of hemoglobin
- Adverse effect on the nervous systems (CNS and peripheral) and the kidneys
- Interferes with the normal development of children's brains
  - Behavioral effects, including lack of attentiveness
  - Possibly low IQ

25

Lead (Cont.)

http://www.espimetals.com/

Lead is a bluish-white lustrous metal. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. Alloys include pewter and solder. Tetraethyl lead ($PbEt_4$) is still used in some grades of petrol (gasoline) but is being phased out on environmental grounds.

26

Lead (Cont.)

Uses:

- Storage batteries, cable covering, plumbing, ammunition or lead shots ($Pb_{(s)}$ and PbO)
- Paints (*yellow* $PbCrO_4$, white $PbCO_3$)
  - Pre-1978 homes used lead-based paints
- Solder

Lead paint in Foyer

www.tennessee.gov/firstlady/photogallery/exec...

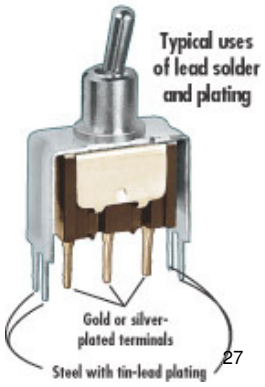


Image available at http://www.machinedesign.com/ASP/viewSelectedArticle.asp?strArticleId=56764&strSite=MDSite&catId=0

27

Lead (Cont.)

Sources of Pb contamination in the environment:

- Lead industries, mining and smelting
  - Air and dust emissions (processing or smelting of lead ores)
- Vehicle emissions (in many countries)
  - The U.S., Canada and Europe use unleaded gasoline
- Piping, fixtures and solder
  - Common source of Pb^{2+} in drinking water
- Leaching from landfills (discarded batteries and other Pb-containing products)

28

Toxic Heavy Metals
3. Cadmium

Image available at
www.webelements.com

Cadmium is a soft, bluish-white metal and is easily cut with a knife. It is similar in many respects to zinc. Cadmium and its compounds are highly toxic.

29

Cadmium (Cont.)

Mode of entry:

- Mostly through ingestion of contaminated food (in the form **Cd^{2+}**)
  - Seafood, organ meats have the highest levels among food

Effects:

- Cd is acutely toxic (lethal dose ~ 1 g)
  - Fortunately, low levels of Cd (as Cd^{2+}) is complexed by a sulfur-rich protein and is eliminated by urination
- Kidney disease may result from chronic exposure to high levels of Cd
  - Excess Cd (not complexed by proteins) is stored in the liver and kidneys

30

Cadmium (Cont.)

Uses:

- Rechargeable batteries (Nicad)
- Compounds of Cd are used as pigment
  - CdS and CdSe color plastics

Also used in paints* — Also used in TV screens

* Van Gogh's "Sunflower" was painted with CdS pigment (Baird, C. "Environmental Chemistry, 2nd ed.)

Sources of Cd contamination in the environment:

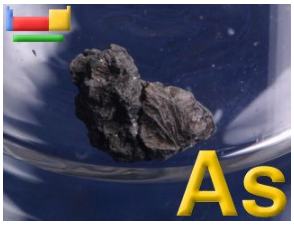
- Metal smelters (In nature Cd occurs with Zn, Pb and Cu)
- Coal burning
- Incineration of Cd-containing waste (plastics, batteries, etc.)

31

Toxic Heavy Metals
4) **Arsenic**

Historical perspective:

- Arsenic compounds (e.g. As_2O_3) used for murder and suicide from Roman times to Middle Ages



Elemental arsenic occurs in two solid modifications: yellow, and grey or metallic. The element is a steel grey, very brittle, crystalline, semimetallic (metalloid) solid. It tarnishes in air, and when heated rapidly oxidises to ***arsenous oxide*** which has a garlic odour. Arsenic and its compounds are **poisonous** as any reader of "who-done-it" books knows.
www.webelements.com

32

Arsenic (Cont.)

Mode of entry:

- Mostly through ingestion of ***contaminated water***
- As_2O_3 can be absorbed through the lungs and intestines

Effects:

- A known **carcinogen**
- Acute dose can be lethal
  - Causes gastrointestinal damage –severe vomiting; diarrhea
- Coagulates proteins and complexes with coenzymes
- Inhibits production of ATP

Note: As (III) is more toxic than As (V) – presumably due to stronger binding with S-containing proteins

33

Arsenic (Cont.)

Uses:

- Pesticides (compounds of As) – prior to use of organic pesticides
- Hardening and improving the sphericity of shots
- Doping agent in solid-state devices such as transistors

Sources of environmental contamination:

- From the continued use of its compounds as pesticide (e.g in CCA-treated wood)
- Unintended release during mining and smelting of gold, copper, etc.
- Lead and steel production
- Burning of coal (As is a contaminant)

34

Speciation and Toxicity of Metals

Speciation = chemical form of an element

- Affects toxicity of heavy metals

Relative toxicity and speciation

- **Methylmercury** > **$Hg_{(s)}$** (metallic; elemental)
- **Pb^{2+}** (soluble; ionic) > **$Pb_{(s)}$** (metallic; elemental)
- **As (III)**, like in arsenic oxide, As_2O_3 > **As (V)**, as in arsenic acid, $HAsO_4$

35

Chromium

Common oxidation states: **+3** and **+6**

Trivalent, Cr^{3+} (insoluble)

Hexavalent, Cr^{6+} (soluble)
(Subject of *Erin Brockovich*)

Relative toxicities

Cr^{6+} or Cr (VI) **(soluble, ionic)** **>** **Cr^{3+} or Cr (III)** **(insoluble)**

Ex. chromate ion, CrO_4^- ;
A suspected ***carcinogen***

Much less toxic than Cr (VI);
Acts as a ***trace element***

36

Chromium – Cont.

Uses of Chromium

- Electroplating
- Corrosion protection

} ***Chrome*** finish

- Leather tanning
  - Increases resistance to water, heat and bacteria
- Doping agent in solid-state devices such as transistors

Sources of contamination

- Industrial emissions (metal plating)
- Leaching from hazardous waste sites
- Leaching from CCA-treated wood (also a source of As contamination)
- Unintended release during mining and smelting of gold, copper and other metals

37

Major Contamination Problems with Heavy Metals

Mercury

- At the fishing village of Minamata, Japan (1950s)

Source of contamination:

- Hg-containing waste (PVC production) discharged into the bay
  - **Bioconversion** of Hg to methylmercury (more toxic form)
  - **Bioaccumulated** (moved up the food chain) at levels as high as 100 ppm in fish [vs. 0.5 ppm recommended limit of total Hg in fish in No. America] => Up to ***200x higher***!!!

Results of contamination:

- ***Death***: Hundreds; Thousand more suffer from various symptoms of Hg poisoning (numbness in the arms/legs, blurring or ***loss of vision***, irritability, etc)

38

Mercury (Cont.)

- Methylmercury could be passed on to the fetus (can cause severe brain damage)
- READ p. 527, bottom paragraph for more information on Hg contamination

Darthmouth College (1997) cancer researcher Karen Wetterhahn

- Died several months after 1-2 drops of dimethylmercury apparently seeped th/ her latex gloves (recommended protection at that time)

39

Major Contamination Problems … (Cont.)

Lead

- The 1845 Franklin Expedition to find a Northwest Passage across the Arctic is thought to have failed because all the members died from Pb poisoning. How?
  - Source of contamination = solder in the tin cans that held their food
  - Read "The Age of Lead" paragraph on page 681.

40

Major Contamination Problems … (Cont.)

Cadmium

- Acute environmental problem in the Jintsu River Valley region, Japan

Source of contamination:

- Contaminated (with Cd^{2+}) irrigation water drawn from the river, used for rice cultivation
- Zinc mining/smelting plant upstream = source of Cd^{2+}

Results of contamination

- Degenerative bone disease called *itai-itai* ("ouch-ouch") in 100s of people
  - Severe pain in the joints
  - Resulted from Cd^{2+} replacing Ca^{2+} in the bones

Porous bones; Easily fractured

41

Major Contamination Problems … (Cont.)

Arsenic (a metalloid)

- Arsenic's lethal effect when consumed in acute dose is due to ***gastrointestinal damage***

Causes severe vomiting and diarrhea

- Major problems from high levels of arsenic occur in the Bengal Delta
  - Up to 40 million people in Bangladesh and in the West Bengal region of India drink As-laced water
  - WHO called this the "largest mass poisoning of population in history."
  - Read p. 699 for more information
  - LD_{50} values for some common form of arsenic

42

Major Contamination Problems … (Cont.)

TABLE 15-3 LD_{50} Values for Some Common Forms of Arsenic

Name	Formula	LD_{50} (mg/kg)
Arsenous acid	H_3AsO_3	14
Arsenic acid	H_3AsO_4	20
Methylarsonic acid	$CH_3AsO(OH)_2$	700–1800
Dimethylarsonic acid	$(CH_3)_2AsO(OH)$	700–1800
Arsenocholine	$(CH_3)_3As^+CH_2CH_2OH$	6500
Arsenobetaine	$(CH_3)_3As^+CH_2COO^-$	>10,000

Source: X. C. Le, "Arsenic Speciation in the Environment," *Canadian Chemical News* (September 1999): 18.

Note that **arsenous acid**, an inorganic form of As, is the **most toxic** of the various forms of arsenic

43