Chapter 8

Toxicology: Poisons and Alcohol

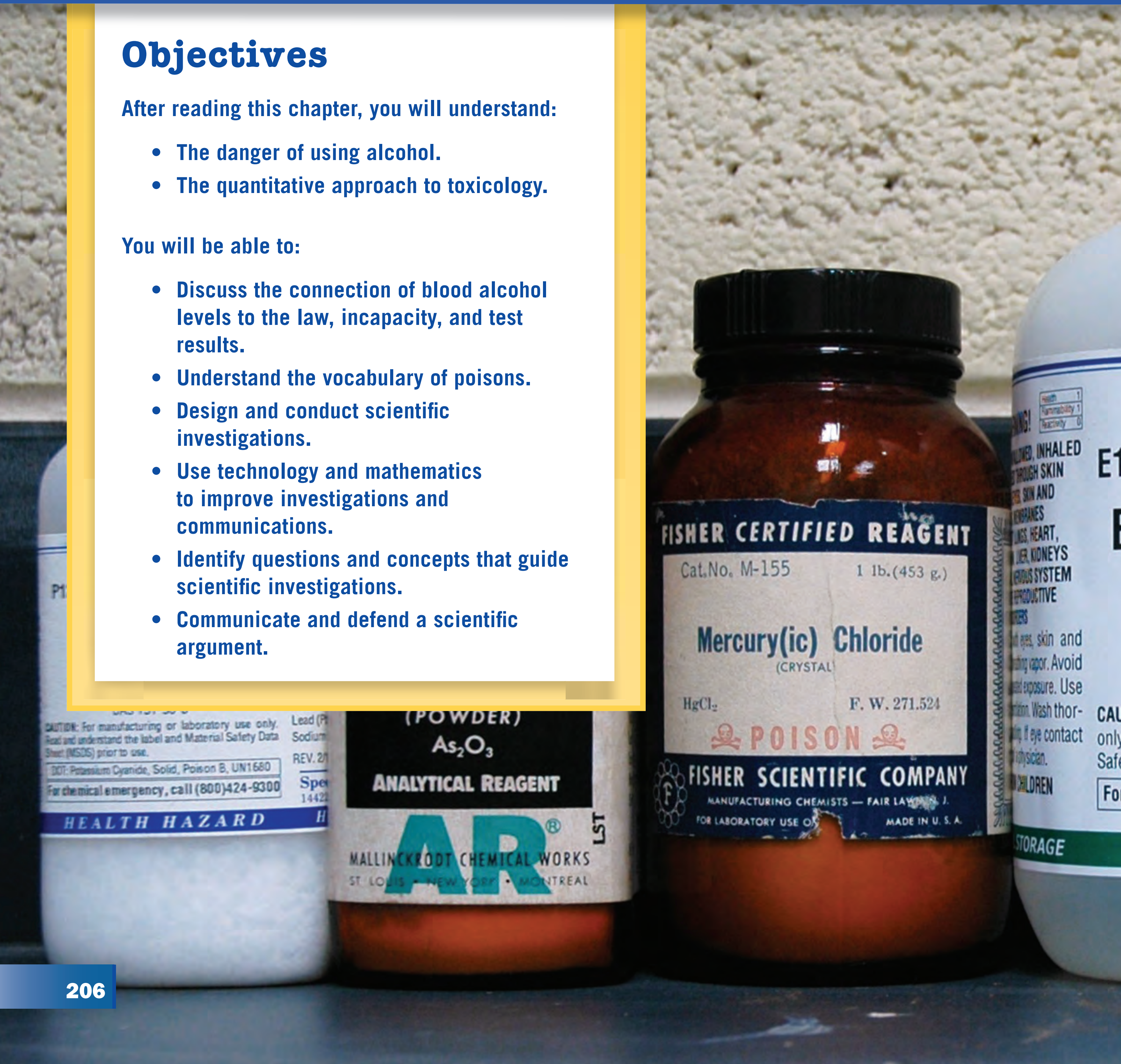
Objectives

After reading this chapter, you will understand:

- The danger of using alcohol.
- The quantitative approach to toxicology.

You will be able to:

- Discuss the connection of blood alcohol levels to the law, incapacity, and test results.
- Understand the vocabulary of poisons.
- Design and conduct scientific investigations.
- Use technology and mathematics to improve investigations and communications.
- Identify questions and concepts that guide scientific investigations.
- Communicate and defend a scientific argument.



“All substances are poisons. There is none which is not. The right dose differentiates a poison and remedy.”

—Paracelsus (1495–1541), Swiss physician and chemist

Teacher Note

The TRCD for this chapter includes a PowerPoint presentation, which is an overview of the chapter. It can be used as introductory material or at the end as a review.

The Study of Poisons

Was Paracelsus right? Take arsenic, for example: We all know that arsenic is poisonous, yet we take in compounds of arsenic through the water we drink and the foods we eat, because it is a naturally occurring substance. Some research indicates that trace amounts of arsenic affect humans in positive ways. Scientists know that arsenic deficiency stunts growth in chickens, rats, pigs, and goats.

Theophrastus Philippus Aureolus Bombastus von Hohenheim (1495–1541) was a Swiss antiestablishment, itinerant physician who stressed mineral and inorganic cures rather than the popular salves, pills, and infusions of natural products. He took the name Paracelsus, meaning "better than Celsus," an early Roman physician. Paracelsus essentially united medicine with chemistry.

In the past, arsenic compounds have been used as a remedy for everything from asthma to jealousy! Even in the early 20th century, an organic arsenic compound was used to treat syphilis until penicillin fortunately became available in the early 1940s. Arsenic is now used to treat a rare kind of cancer.

Is there anything for which Paracelsus's "rule" doesn't work? Scientists think of botulin, produced by the bacterium *Clostridium botulinum*, as the most deadly poison known (1 gram evenly spread out and inhaled would kill more than a million people), yet doctors are now using botulin to erase wrinkles and to prevent migraines. The term *hormesis* refers to the concept promoted by Paracelsus: that substances that kill at high doses are actually beneficial at low doses—the poison is in the dosage.

Class Discussion

Discuss with your class other substances for which "the dose is the poison," for example, oxygen, water, aspirin, alcohol, and other everyday substances.

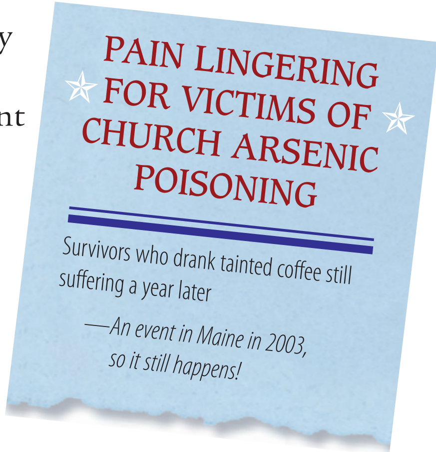
The History of Poisons

Prehistoric humans probably used poisons to kill their enemies. The earliest recorded use of poison was Socrates' execution in 339 BC with an extract of hemlock. During the European Renaissance, poisoning became an art, even an occupation or a hobby. Common poisons at the time came from plants such as hemlock, monkshood, belladonna, and toxic metal salts, with arsenic being by far the favorite. It left no trace, it was easy to get and use, and the symptoms looked like death by natural causes.

Poison hemlock is not an evergreen tree, but a plant related to the carrot. It contains an alkoloid similar to nicotine. Alkaloids are organic compounds, derived from amino acids, that especially affect the nervous system.

Forensic **toxicology** was developed in the 19th century. In 1814 Mathieu Orfila published *Traité des poisons*, the first systematic approach to the study of the chemistry of poisons. In 1836 a chemist named James Marsh developed a very sensitive and reliable test to detect arsenic in body tissues and fluids. Most of the important alkaloids present in plants were isolated in the 1800s. Now, with modern analytical instruments, it is easier than ever to find poisons, yet people still use them for murder and suicide.

toxicology: the study of the adverse effects of chemicals or physical agents on living organisms


PAIN LINGERING FOR VICTIMS OF CHURCH ARSENIC POISONING

Survivors who drank tainted coffee still suffering a year later

—An event in Maine in 2003, so it still happens!

Elements of Toxicology

As Paracelsus noted, dosage is an important part of toxicity, but other issues include (a) the chemical or physical form of the substance; (b) how it enters the body; (c) the body weight and physiological conditions of the victim, including age and sex; (d) the time period of exposure; and (e) whether other chemicals are present in the body or in the dose.

For example, arsenic is a metal, rather insoluble in stomach acid, and thus is not particularly poisonous. On the other hand, the compounds of arsenic trioxide (As_2O_3) and arsenic pentoxide (As_2O_5) are very poisonous. Arsenic can also be changed into a poisonous gas, arsine (AsH_3), which is used in the Marsh test.

We think of poisons as being swallowed, yet some substances are more toxic when injected, such as some recreational drugs. Other substances

In 1840, the Marsh test came to popular attention in the trial of Marie Lafarge, charged with killing her husband, who died after eating a slice of her cake. Their maid swore that she had seen Marie adding a white powder to his drink, and it was shown that she had twice bought arsenic oxide from the local pharmacy, supposedly to kill rats at her husband's forge. Application of the Marsh test to his body showed no arsenic present, though it was detected in food in the Lafarge house. Mathieu Orfila, appearing for the defense, claimed that the test was unreliable; however, when he himself applied the test to the body, he found arsenic. Marie was sentenced to life imprisonment. In 1852, suffering from tuberculosis, she was released by Napolean III, but she died that same year.

toxins: substances that cause injury to the health of a living thing on contact or absorption, typically by interacting with enzymes and receptors. The term is usually reserved for naturally produced substances that kill rapidly in small quantities.

chronic exposure: continuing exposure to toxins over a long period of time; thus chronic toxicity

acute toxicity: effects of a toxin occurring almost immediately (hours or days) after an exposure

synergism: combined effect of substances that exceeds the sum of their individual effects

antagonism: combined effect of substances that decreases their individual effects; the opposite of synergism

chelating agent: an organic compound that complexes with a metal to form a ring structure

can be adsorbed through the skin, such as some particularly nasty chemical warfare agents. Inhaling many common industrial chemicals causes health problems; exposure is regulated by government agencies.

As you will learn in the next section on alcohol, blood alcohol content (BAC) depends directly on body weight and the sex of the individual. Stomach contents can also be important. Infants are more susceptible to **toxins** than adults, and old age can also weaken the body's ability to fight poisons.

The time period of exposure to toxins is very important. Let's use arsenic again as an example: Small amounts ingested over time will actually help in building up a tolerance for the poison. Larger amounts over time **(chronic exposure)** will cause medical problems such as weakness, sluggishness, hair and weight loss, mental instability, and skin and liver cancer. **Acute toxicity** refers to a dose large enough to cause immediate problems, including death.

The product information that comes with some antihistamines and sedatives clearly says that they should not be taken with alcohol, which would make the effects of both stronger. The combination of two chemicals can increase (causing **synergism**) or decrease (causing **antagonism**) their individual effects. Taking a **chelating agent** after swallowing an arsenic compound decreases the effects of both. The chelate "ties up" the arsenic before it can do its damage by reacting with the sulfide linkages of enzymes.

A lady is lying in bed and she is dead. Beside the bed is a pool of liquid and two pieces of wood. How did she die?

Answer

poison Popsicle

Measuring Toxicity

Over the years, scientists have developed ways to measure toxicity; however, because of the variables involved, there is no sure way to measure poison levels in humans, even using the results of accidental human poisonings. Instead, scientists use standardized animal toxicity tests, most often by feeding a chemical to rats or mice.

LD_{50}: lethal dose for 50 percent of a given population

The term **LD_{50}** (or lethal dose) refers to the amount of a substance that kills half the test population, usually within four hours. It is given in milligrams (mg) of substance per kilogram (kg) of body weight. LD_{50} allows scientists to compare the toxicity of substances and even scale the amounts to different-sized animals. However, estimating lethal doses in humans based

Table 8.1: Toxicity Classes and Definitions

LD_{50} (rat, oral)	Correlation to Ingestion by a 150-Pound Adult Human	Toxicity
<1 mg/kg	a taste to a drop	extreme
1–50 mg/kg	a drop to a teaspoon	high
50–500 mg/kg	a teaspoon to an ounce	moderate
500–5,000 mg/kg	an ounce to a pint	slight
5–15 g/kg	a pint to a quart	practically nontoxic
>15 g/kg	more than 1 quart	relatively harmless

Because a single test may kill as many as 100 animals, the United States and other members of the Organization for Economic Cooperation and Development agreed in December 2000 to phase out the LD_{50} test in favor of alternatives that greatly reduce (or even eliminate) deaths of the test animals.

on those for lab mice, rats, or rabbits is very uncertain because resistance can be so different among species. For example, nicotine kills humans at 0.9 mg/kg, but a lethal dose of nicotine in dogs is 9.2 mg/kg; in pigeons, 75 mg/kg; and in rats, 53 mg/kg.

In spite of the uncertainties, lethal dose values are all we have now. Table 8.1 defines toxicity classes, and Table 8.2 gives a few toxicity values.

Note that the three most lethal compounds are natural products.

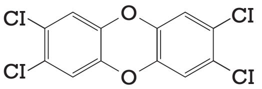
A distraught woman called a poison control center because she found her little daughter eating ants. She was reassured that the ants were not harmful. She calmed down and at the end of the conversation happened to mention that she had given her daughter some ant poison to kill the ants. Supposedly true!

Table 8.2: Some Lethal Dose Values

Material	LD_{50} mg/kg (rats, oral)	Material	LD_{50} mg/kg (rats, oral)
sucrose	29,700	zinc chloride	350
vitamin C	11,900	caffeine	192
magnesium chloride	8,100	nickel chloride	105
ethanol	7,060	cobalt chloride	80
methanol	5,628	nicotine	53
lead acetate (hydrate)	4,665	arsenic chloride	48
sodium bicarbonate	4,220	arsenic trioxide	14.6
bismuth chloride	3,334	arsenic pentoxide	8
aluminum chloride	3,311	sodium cyanide	6.4
sodium chloride	3,000	mercuric chloride	1
manganese chloride	1,484	VX (nerve agent)	0.060, skin contact
arsenic metal	763	ricin	0.020
cupric chloride	584	dioxin	0.020
antimony chloride	525	botulin toxin	0.000005–0.00005

In December 2004, doctors confirmed that Viktor Yushchenko, the Ukrainian presidential candidate running against the old-line Russian establishment, was suffering from dioxin poisoning. This isotope of dioxin (TCDD) is as toxic as ricin, so one drop of the pure substance would undoubtedly have killed him. Unlike ricin, however, the fat-soluble dioxin is more of a chronic poison; thus, he may have been fed small amounts of the material over time. Doctors found blood levels of dioxin 6,000 times higher than normal. One symptom of dioxin poisoning is the outbreak of facial cysts, which were quite evident in photographs of Yushchenko. TCDD was one of the contaminants found in Agent Orange, a chemical defoliant that caused many medical problems in Vietnam War veterans.

The dioxin referred to in Table 8.2 is a generic term for a class of compounds. The most poisonous dioxin is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD).



Clostridium botulinum is one of the most poisonous substances known to man. Some studies estimate an LD_{50} for humans of 0.000001 mg/kg. If this is true, only a few hundred grams could theoretically kill every human on earth! Yet, it is used in BOTOX™ therapy. Injection of a dilute solution of botulin toxin has been used to treat neurological and muscular disorders, in cosmetic treatment of facial wrinkles, and for chronic and migraine headaches. Think of what Paracelsus said 500 years ago.

The public's ignorance about the possible toxicity of tested drugs, environmental agents, and industrial chemicals has prompted the federal government to create regulatory agencies to ensure public safety:

The Food and Drug Administration (FDA) deals with pharmaceuticals, food additives, and medical devices.

The Environmental Protection Agency (EPA) works on agricultural and industrial chemicals released into the environment.

The Consumer Product Safety Commission is concerned with toxins in consumer products.

The Department of Transportation (DOT) watches over the shipment of toxic chemicals.

The Occupational Safety and Health Administration (OSHA) is concerned with exposure to chemicals in the workplace.

OSHA's hazard communication program includes training, labeling, and issuing Material Safety Data Sheets (MSDS). These sheets include facts on the physical and chemical properties of a material and potential health hazards, as well as other information.

Teacher Note

A typical MSDS for arsenic trioxide may be found in the appendix. See Blackline Master 8.1.

Let's review radioactivity in relation to the Litvinenko case study. Heavy elements, such as polonium, are unstable because they have too

8.1: International Espionage

CASE STUDY

In a case where truth is stranger than fiction, the poisoning of Aleksandr Litvinenko will long be remembered for the unusual and sophisticated method of killing. Litvinenko was a former lieutenant colonel in the Russian secret service (FSB, formerly the KGB) who defected and became a vocal critic of the Russian government. On November 1, 2006, he suddenly fell ill and was hospitalized. He died three weeks later in a London hospital. The diagnosis was acute radiation syndrome caused by ingestion of polonium-210, a rare and highly radioactive isotope.

Investigation revealed that Litvinenko had met with two former KGB operatives earlier in the day. It so happens that traces of polonium-210 can be detected with a Geiger counter, so the path of this isotope could be traced. The evidence pointed to a teacup in a London hotel where Litvinenko had met with his former associates, Andrei Lugovoi and Dmitry Kovtun. Traces of radiation were found in many places, significantly in several British Airways jets that had flown from Moscow to London just before November 1 and a few days after November 1. Andrei Lugovoi happened to have been on those flights.

Interestingly, others involved in this complex web of intrigue have been shot, have disappeared, or have suffered unexplained illness (including Dmitry Kovtun). No one has been arrested, and Russia will not allow extradition of Lugovoi to London to answer questions.

Theories, motives, and suspects abound, but Aleksandr Litvinenko is dead in a widely publicized, bizarre crime.

Photo released by the family of Aleksandr Litvinenko showing him in his hospital bed, at the University College Hospital in central London, Monday 20 November 2006.

many neutrons in their nucleus. They achieve stability by spontaneous decay, emitting any of three types of particles:

- Alpha (α) particle: a helium nucleus of 2 protons and 2 neutrons with a net positive charge of 2; heavy and slow, low penetrating power, stopped by a sheet of paper.
- Beta (β) particle: the same as an electron with a negative charge of 1, fast and light, more penetrating, stopped by a sheet of aluminum.
- Gamma (γ) ray: a packet of energy with no mass or charge, very fast and energetic, high penetrating power, stopped by a thick sheet of lead.

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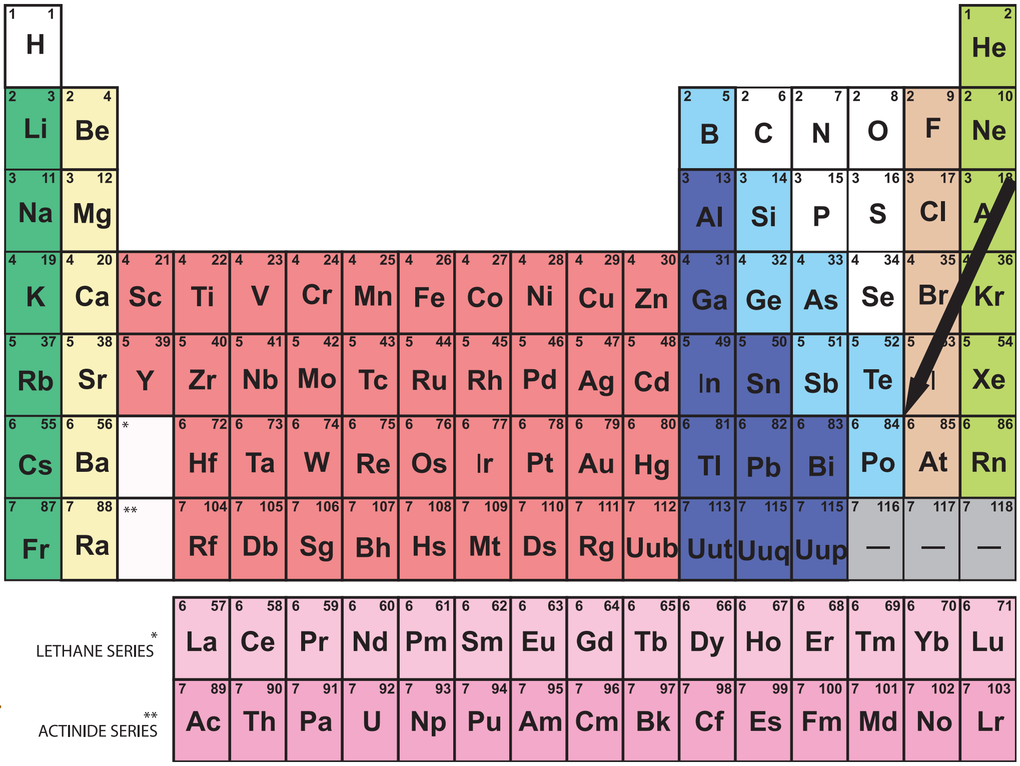
Polonium is very rare. One of its **isotopes**, polonium-210 (210 refers to its atomic mass), has a

isotopes: chemical elements that have the same number of protons, but different numbers of neutrons



Laboratory Activity 8.1, Advance Preparation

Obtain some paint flakes; they don't need to contain lead because you can "dope" them by immersing some in lead acetate solution for an hour or even overnight. Remove and pat dry. The standard will be the "undoped" paint flakes; the control, a dilute solution of lead acetate.

To make 0.1 M acetic acid, dilute the concentrated acid 1:170, or add about 0.6 ml concentrated acid to 100 ml water, or better, buy 0.1 M acetic acid.

To make 0.1 M sodium sulfide solution, add 2.4 g to 100 ml water, or buy the solution already made up.

Any soluble lead salt will work as a control and for "doping." Lead acetate works very well and is used in lab exercises in Chapter 6, "Fibers." Dissolve a little in water.

half-life: the time it takes for half a sample to decay

microgram: one-millionth of a gram, or one-thousandth of a milligram

Polonium was first discovered by the Curies in 1898; named after Marie Curie's native land, Poland.

half-life of 138 days; therefore, to make enough to kill a person, even at an estimated dosage of 1 **microgram**, requires a nuclear reactor. And even then, less than 3 percent would remain after two years because of its relatively short half-life.

Polonium-210 is strictly an α-emitter; thus, it could be carried around in the hand if one were foolish enough to do so. However, if taken internally, the α particles would cause massive cell damage. Indeed, the toxicity of polonium-210 is about the same as that of botulin.

Perhaps a polonium-210 salt such as a citrate or nitrate, dissolved in a small amount of water and carried in a glass vial (leaky?), was poured into Litvinenko's tea during that fateful meeting in the hotel.

Lead Poisoning

Lead compounds are not highly poisonous, but chronic exposure to lead poses a real health problem for many Americans, especially children, who are at far greater risk for lead poisoning than adults. The National Safety Council estimates that there are more than 400,000 children under the age of six who have higher-than-normal blood levels of lead, which can lead to subtle brain damage, affecting memory and thought processes as measured, for example, by IQ tests.

The most common method of exposure is contact with *lead-based paints*. Before these were banned in 1978, lead was a common ingredient in paint. One of the strange properties of lead compounds is that they taste sweet, so a child teething on a windowsill, for example, will want more mouth contact. It is estimated that there are still more than 38 million houses in the United States that contain some lead-based paint. In 1992, the federal government passed a law requiring anyone selling an older house to certify that no known lead-based paint is present.

How can you know whether there is lead in paint? Two chemical properties are commonly used as a qualitative spot test: (1) the reaction of dissolved lead with sulfide ion to form insoluble, brown-black lead sulfide and (2) a reaction with an organic complexing agent, sodium rhodizonate, to make a characteristic pink color. Neither of these tests is specific to lead compounds, but it is unlikely that interfering substances in the paint will give a false positive.

Lead-based paints are paints or other surface coatings that contain lead equal to or exceeding 1.0 milligram per square centimeter or 0.5 percent by weight or 5,000 parts per million (ppm) by weight.

Laboratory Activity 8.1, Advance Preparation, *continued*

For disposal: The amount of lead is small, and it is tied up in the insoluble sulfide, so it can be washed down the sink. Leftover lead solution should be precipitated with sulfide and the solid decanted or filtered, dried, enclosed in a plastic container, and thrown out.

The sulfides of lead, mercury, silver, bismuth, copper, cobalt, nickel, chromium, and iron are all dark brown or black.

Detecting Lead

Laboratory Activity 8.1

The following activity will give you practice in checking paint for the presence of lead.

Materials

For each investigative group of students:

- paint flakes
- tweezers
- test tubes
- 0.1 M acetic acid
- distilled water
- 0.1 M sodium sulfide
- sodium rhodizonate solution
- filter paper
- oven
- glass stirring rod

SAFETY ALERT! CHEMICALS USED
Always wear goggles and an apron when working in the labaratory

SAFETY NOTE *Also wear disposable laboratory gloves. Avoid inhalation, ingestion, and skin contact with chemicals.*

You may want to have a class discussion of exposure to leaded products.

You may want to purchase some lead test kits for house paint and have the students use them (your local hardware store may have them, or check the Web for suppliers). They use sodium rhodizonate test paper.

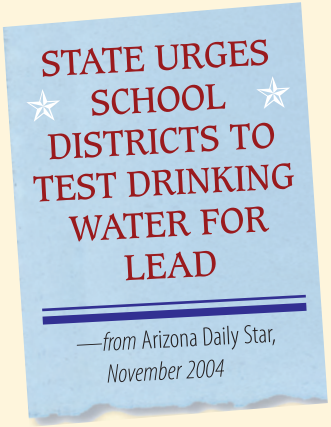
Buy sodium rhodizonate (contact your Kendall/Hunt representative; also available from Flinn Scientific at www.flinnsci.com). Dissolve only a little in 10 ml of distilled water to make an orange solution. Pour unused solution down the sink—it won't keep more than a day.

Laboratory Activity 8.1, *continued*

Procedure

Do not write in your textbook. Take notes in your science notebook.

1. Your teacher will give you several samples of paint flakes. Pick up a small piece (about 3 to 4 mm) with tweezers and put it in a small test tube.



2. Add 1–2 ml diluted acetic acid, and crush the mixture with a glass stirring rod to extract any leaded pigment.
3. Dilute 1:1 with distilled water, and add a drop or two of sodium sulfide solution. A brown-black precipitate shows the presence of lead. Run a standard (known to contain lead) and a control sample (contains no lead).

   What other substances could give a false positive? In Chapter 9 ("Trace Evidence"), you will use the formation of sulfides to make chromatographic separations of aluminum, cobalt, copper, nickel, and zinc visible.

Anyone living in an older home may want to test the paint. If you wish to do so, be sure to collect a sample down to the wood base, because the prime or older coats are the ones most likely to contain the lead. Besides the sulfide precipitation test that you have already performed, you can make your own sulfide and rhodizonate test papers.

Procedure

To make your own lead detection test strips:

1. Sodium sulfide strips: Cut Whatman #1 filter paper into strips and soak them in 0.1 M Na_2S for a few minutes. Dry in an oven set lower than 60°C or overnight. Pressing a standard paint chip onto the paper that has been wet with the acetic acid should leave a black impression. Test also with the control sample.
2. Rhodizonate test strips: Immerse filter paper strips and dry. The solution is unstable, so make a lot of strips and store them in a dry place. A positive result for the presence of lead is from pink to purple, depending on the concentration of lead. Wet the paper first with the acetic acid to dissolve any lead.

Laboratory Activity 8.2, Procedure Notes

Here is an activity in true scientific inquiry where an investigative group must use what information they have, what they can surmise, and what they can glean from the Internet and other sources to:

1. Determine what to look for.
2. Design or find an appropriate test they can carry out in your lab.
3. Adapt the test to the sample at hand.
4. Determine whether the test will give relevant and reliable results.
5. Interpret the results to decide what happened. Was the death accidental, deliberate, or natural?

You can tell the class that you were friends with Magnus. In fact, you witnessed the signing of a rather large life insurance policy and trust arrangement for your friend. Although Magnus was a bit eccentric and forgetful, he was a happy, bubbly person (to dispel the thought of suicide) despite the peptic ulcers that he kept under control with Pepto-Bismol (which contains bismuth subsalicylate). You remember seeing some chemicals in his garage, among them mercuric chloride and Paris green (which contains copper acetoarsenite).

You will want to guide your students toward using a particular test (the Reinsch test) for dissolved heavy metals (mercury, antimony, arsenic, and bismuth) with a conclusion that you can control by whatever you choose to put in the autopsy sample.

The obituary provides some clues: The students should find out what pulmonary edema is (basically pneumonia with fluid filling the lungs) and what n-semiconductors are made of (a few hits on the Web should give them phosphorus, antimony, and arsenic, among other elements); gaseous doping implies that such elements must be gases. A study of group **V**-A of the periodic table will show that all these elements form gaseous molecules with hydrogen. More searching should reveal that all these compounds are quite toxic and cause pulmonary edema. Now they know what to look for. Add mercuric chloride because it was found in Magnus's garage and is extremely poisonous.

How can your students find a test? Ask them right off what some methods of analysis might be, because they have experience in this matter, for example, chromatography and chemical analysis found in Chapters 6, "Fibers," and 7,

Other Sources of Lead in the Everyday Environment

The ban on leaded gasoline in 1995 reduced a source of environmental lead, but tons still remain in our soils. Indeed, lead has been found in soil and dirt along highways and even in school playgrounds. In 1986, a nationwide ban restricted the use of lead pipes in homes, yet some towns still have older lead pipes carrying drinking water in their systems. This is not normally a problem because metallic lead is so insoluble, but if the water is acidic, lead can be leached from the metal. Solder joints in older houses contain lead. Lead crystal and some ceramics should not be used to store acidic food and drink.

Laboratory Activity 8.2, Procedure Notes, *continued*

"Drugs." Searching the Web for those elements (with "test") will bring up lots of fancy analytical instrumentation and tests but should also show the Reinsch test, which is simple enough to carry out in a high school laboratory.

How should students physically carry out the test? Once they have figured out that they need standards, which they should realize by this point in their forensic careers, you can pull out the sets you have prepared. Steer them toward the use of small Erlenmeyer flasks or beakers, using 20 to 30 ml of each solution. What form of copper should be used? Wire is common, but foil or sheet works best. Should the solutions be heated? (Yes, boiling speeds up the process to just a few minutes.) How long should the copper be immersed? Let them work this out experimentally. Should the copper be cleaned first? (Probably, with alcohol, to remove oil and grease that would interfere with the electroplating.) Should it be washed off after plating? (Definitely, because it has acid on it.) You can hope that the students have also opted to run the standards, or even one standard, before the sample for selecting the best experimental conditions. There is only so much autopsy sample. See if anyone thinks of running a control, that is, copper in only acid.

Laboratory Activity 8.2

The Investigation of a Sudden Death

Advance Preparation

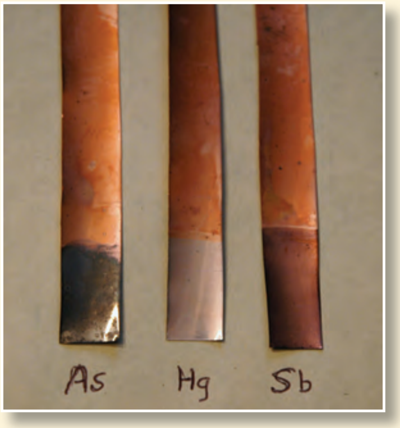
If you must purchase some, buy solid antimony potassium tartrate or a 0.1 M $SbCl_3$ solution (contact your Kendall/Hunt sales representative; also available from Flinn Scientific). Use only one heavy metal in the unknown; they mask each other.

For the demonstration: Prepare a 1 M solution of $CuSO_4 \cdot 5H_2O$, adding 25 g to 100 ml of water in a 250-ml beaker. Add a zinc strip and wait. Placing it on an overhead projector will allow the entire class to watch it.

For disposal: The copper plates can go in the trash. The acid solutions of the metals should be neutralized and the sulfides precipitated with Na_2S, dried, and placed in a plastic container (an empty film canister is handy for this) for the trash.

Here is a copy of the obituary of Dr. Albert Magnus. As is routine when the cause of death is not clear, and especially because he had seemed in such good health, an autopsy was performed.

Your lab has received a sample from Dr. Magnus's lungs with a request to look for a possible cause of death related to his work. What do you do?



Reinsch test

Albert Magnus

Albert Magnus, age 54, died unexpectedly on August 14 at University Hospital. He was admitted to the hospital the day before, complaining of a continual cough and extreme shortness of breath. The diagnosis was pulmonary edema, but his condition advanced so rapidly and pervasively that he could not be saved. Dr. Magnus had just recently pioneered a novel method of gaseous doping of n-semiconductors for Zener diodes. He is survived by his wife of three years and two children from a previous marriage.

Laboratory Activity 8.2, Procedure Notes, *continued*

The quickest and simplest verification of the method and results can be done by comparing data among the groups. Have each group take a picture of the plated copper, because its appearance will change.

If your students find arsenic, then the source could have been at Dr. Magnus's workplace, but an arsenic-containing compound was also seen in his garage, as was a very poisonous form of mercury. However, if these materials had been fed to him, perhaps by a greedy wife, they would not have been found in his lungs. If either antimony or bismuth were found, work practices are likely to have caused his death. If the test came up negative, Magnus's death was probably natural—or was there something in the autopsy sample that masked the poison? (Adding a portion of each standard to the sample and then testing it would answer that question.)

The Reinsch test leads beautifully into oxidation-reduction potentials. Demonstrate with a strip of metallic zinc immersed in a nice blue solution of copper sulfate; copper will plate onto the zinc as the blue color fades. Thus:

$Zn + Cu^{++} \longrightarrow Zn^{++} + Cu$

$Cu^{++} + 2e^- \longrightarrow Cu$ *reduction*

$Zn \longrightarrow Zn^{++} + 2e^-$ *oxidation*

Another example is the case of copper displacing mercury from solution: $Hg^{++} + Cu \longrightarrow Hg + Cu^{++}$

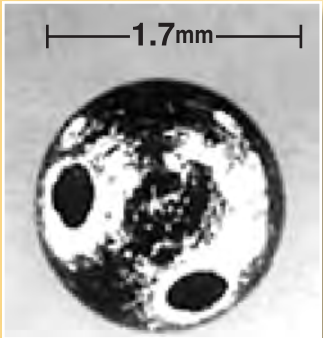
which accounts for the nice, shiny mercury mirror on the copper in the Reinsch test. You can carry this as far as you want using the table of reduction potentials in a chemistry text. Unfortunately, the heavy group V metals are not included in most tables.

8.2: The Case of Georgi Markov

CASE STUDY

Agents of the Bulgarian secret police assassinated Georgi Ivanov Markov in September 1978. Markov had defected to London from Bulgaria years before and was broadcasting programs critical of the Bulgarian regime.

On September 7, as Markov was waiting at a bus stop at Waterloo Bridge, he felt a sharp jab in his right thigh. He turned to see a man behind him with an umbrella, who apologized with a foreign accent. Markov thought nothing more of it, but the next morning he was admitted to the hospital with a high fever and vomiting. Despite being given massive amounts of antibiotics, Markov died three days later.



During an autopsy, examiners found in Markov's thigh a small platinum-iridium pellet, 1.7 mm in diameter, with two tiny holes precisely drilled at right angles to each other. The design of the pellet and the circumstances of Markov's death led investigators to believe that this was a poison pellet fired by some device in the umbrella. Markov was a healthy, husky, six-foot-tall man, but the pellet could not have contained much poison. No telltale metabolites were found in his body.

By a process of elimination, ricin became the suspected probable poison; the assassin used perhaps as little as 2 mg. Tests on a pig corroborated this assumption. Coincidentally, investigators learned that, in the previous year, another Bulgarian defector had been jabbed outside a Paris metro station. He had fallen ill but recovered. A surgeon extracted an identical pellet from his body. He had been jabbed in a muscle in his upper back, away from major blood vessels, which may be why he lived.

Consider how sophisticated poisoning has become since the days of Marie Lafarge, yet the evidence can still be discovered even if the culprit(s) cannot be apprehended. How many deaths from "natural causes" do you suppose are really the result of poisoning?

Laboratory Activity 8.2, Procedure Notes, *continued*

Materials

copper wire: 16- to 20-gauge (strip from house wiring); better is a copper sheet cut into strips, six strips per group

50-ml beakers or Erlenmeyer flasks

hot plate

2 M HCl; dilute concentrated hydrochloric acid 1:5, in a fume hood, wearing safety goggles and disposable laboratory gloves. Each investigative group will use 30 ml acid for each standard, the unknown, and a control, so make up 200 ml per group.

Standard solutions of $HgCl_2$, As_2O_3, $SbCl_3$, $BiCl_3$ in 2 M HCl. This is a very sensitive test; the amount of material you could fit on a pinhead would be adequate for a single sample of 30 ml. Weigh out about 0.01 g of each for 250 ml acid. The antimony chloride ($SbCl_3$) is hygroscopic and may have turned to a liquid; if so, just use a few drops.

Alcohol

GO TO www.scilinks.org
TOPIC alcohols
CODE forensics2E220

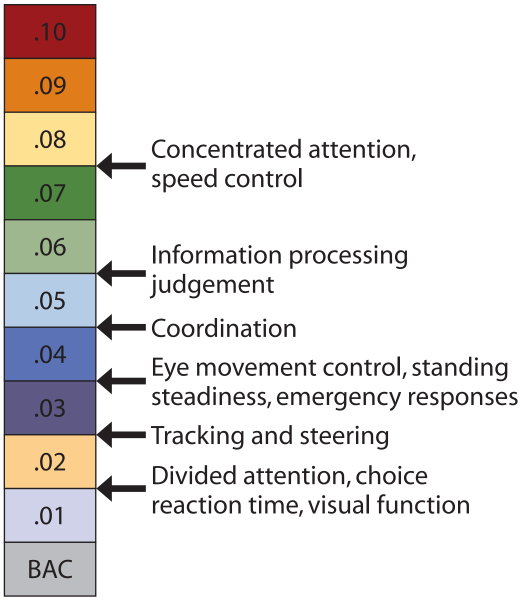
Alcohol (ethanol, ethyl alcohol) is the most abused drug in America. In the United States, about 40 percent of all traffic deaths are alcohol-related—16,885 in 2005 (and more than two million accidents)! This has been the justification for and focus of our **DUI** laws.

DUI: driving under the influence

DWI: driving while intoxicated
OUI: operating under the influence
OWI: operating while intoxicated
MIP: minor in possession

Ethanol, like all alcohols, is toxic. Its principal effect is on the central nervous system (CNS), especially the brain. Alcohol starts circulating in the bloodstream throughout the body almost immediately after consumption. The rate of absorption into the blood depends on the amount of alcohol drunk, the alcohol content of the beverage, how quickly it was drunk, and the quantity and type of food present in the stomach.

The law is concerned with the amount of ethyl alcohol in the blood (blood alcohol content, BAC), expressed as percent weight per volume. Many studies have related BAC to brain functions and behavioral symptoms, providing a basis for the legal limits of intoxication. At present, the limit is 0.08 percent; this means that there would be 0.08 grams of pure alcohol for every 100 ml of blood in your body. In July 2005 Minnesota became the last state in the United States to lower the BAC limit to 0.08 percent.



Levels of impairment at different BACs

The body starts to detoxify alcohol almost immediately on drinking (see Figure 8.1, sometimes referred to as the Widmark curve). The average rate of removal is 0.015 BAC per hour, but this can vary quite a bit.

About 90 percent of alcohol is chemically processed (metabolized) in the liver; it is

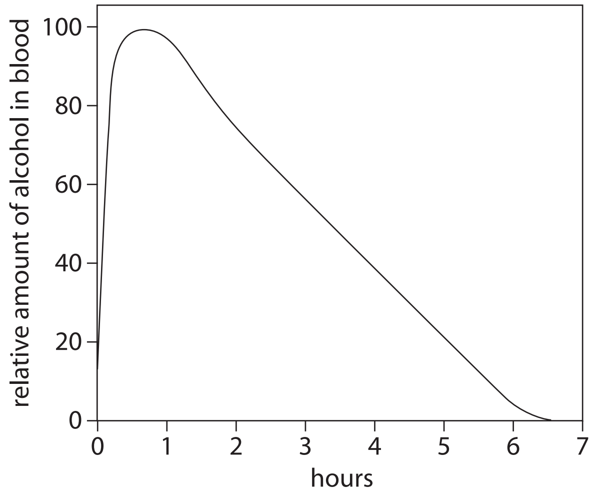


Figure 8.1 Metabolism of alcohol in the blood

changed first to acetaldehyde, a poison; then to acetic acid; and finally to carbon dioxide and water:

$$CH_3CH_2OH \xrightarrow{\text{enzymes}} CH_3\overset{\overset{\Large O}{\|}}{C}H$$

$$CH_3\overset{\overset{\Large O}{\|}}{C}H \xrightarrow{\text{enzymes}} CH_3\overset{\overset{\Large O}{\|}}{C}—OH$$

Here are three ways to draw the structure of ethanol Etoh (chemical shorthand):

CH_3CH_2OH

C_2H_5OH

```
    H   H
    |   |
H – C – C – O – H
    |   |
    H   H
```

Estimating BAC, even roughly, can be important in reconstructing responses in different situations. The most important

MANTEO, NC—A waitress with a history of drunk driving was convicted of second-degree murder in the deaths of four teenagers in a 1999 car collision. Melissa Marvin, 30, learned Saturday that she may spend the rest of her life in jail, as a North Carolina judge sentenced her to at least 60 years in prison.

A court-ordered blood test two hours after the accident indicated a blood alcohol content of .21, putting it at an estimated .28 at the time of the crash.

Jurors deliberated for slightly more than three hours Friday before returning their verdict. In addition to the second-degree murder conviction, Marvin was found guilty of assault with a deadly weapon.

—abstracted from an editorial at alcoholism.about.com/library/weekly/aa000116a.htm

considerations are body weight, alcohol content, and the number of drinks consumed, as well how much time has passed between drinking, the incident that prompted testing, and BAC measurement. A set of equations has been used to estimate BAC under different conditions (the differences in the constants between men and women come largely from differences in body water content):

$$BAC_{male} = \frac{0.071 \times [\text{vol consumed, oz}] \times [\%\ \text{alc}]}{\text{body weight}}$$

$$BAC_{female} = \frac{0.085 \times [\text{vol consumed, oz}] \times [\%\ \text{alc}]}{\text{body weight}}$$

For example, what would be the approximate BAC of a 185-pound man who has consumed three shots (1.5 oz each) of Jack Daniel's (80 proof = 40 percent alcohol) in an hour?

$$BAC_{male} = \frac{0.071 \times 4.5 \times 40}{185} = 0.07$$

Is it all right for him to drive home? No; although he is not legally drunk, his reactions and perceptions have been distorted so that he would be considered a hazard.

About 5 percent of the ethanol leaves the body unchanged in breath, perspiration, and urine. The concentration in breath is proportional to that in the blood, according to *Henry's law*. This law is the scientific basis of breath test instruments. The distribution of alcohol between blood and air expelled deeply from the lungs has been experimentally set at 1 to 2,100. Thus, 1 milliliter of blood will contain the same amount of alcohol as 2,100 milliliters of breath. Rather than having blood drawn as soon as possible after a driver is pulled over on suspicion of intoxication, the officer can quickly give a breath test. Blood, sampled under appropriate hygienic conditions, is preserved with an anticoagulant and sodium fluoride and kept cold until it can be analyzed by gas chromatography.

Henry's Law is the concentration of gas in solution, C_g, which is proportional to the partial pressure of the gas over the solution, P_g; k is the proportionality constant:

$$C_g = kP_g$$

Breath Tests

The following activity will give you practice in giving and evaluating breath tests to measure blood alcohol content.

Materials

- potassium dichromate
- silica gel
- beaker
- Pasteur pipette
- sulfuric acid
- cotton
- ethyl alcohol
- balloon
- straw

SAFETY ALERT! CHEMICALS USED
Always wear goggles and an apron when working in the labaratory

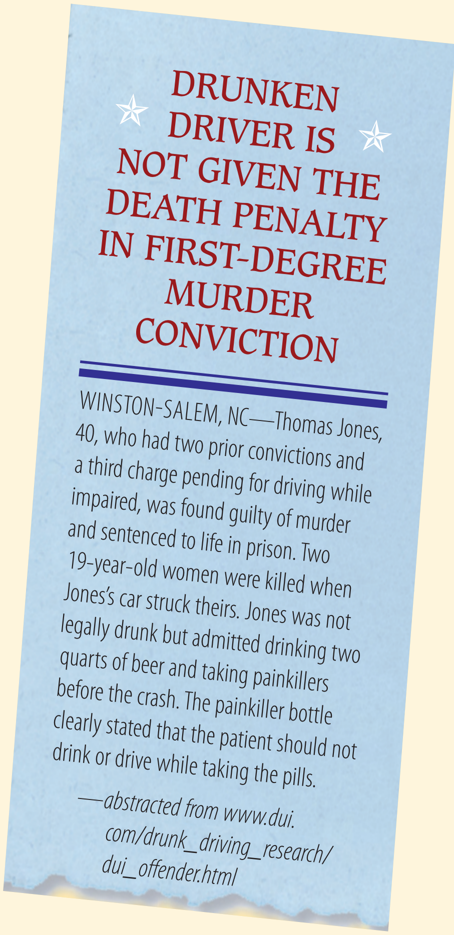
SAFETY NOTE ***Also wear disposable laboratory gloves. Avoid inhalation, ingestion, and skin contact with chemicals.***

Procedure

Do not write in your textbook. Take notes in your science notebook.

1. In a large test tube or small beaker, dissolve enough potassium dichromate in water to make a deep orange solution. Add about 2 cc of concentrated sulfuric acid or 6 cc of 6 M acid. (Remember: Always add acid to water!) Introduce two to three drops of ethyl alcohol into a balloon and blow it up. Slowly release the air into the solution through a straw. *Caution: Potassium dichromate is a strong oxidant, toxic, corrosive to the skin, and a known carcinogen. Wear gloves.*

   Disposal: The chromium salt can be precipitated as sulfide at a pH > 7, evaporated and landfilled (see the Flinn catalog safety section). *Caution: Concentrated sulfuric acid is extremely corrosive to the skin. Wear suitable eye and skin protection.*


DRUNKEN DRIVER IS NOT GIVEN THE DEATH PENALTY IN FIRST-DEGREE MURDER CONVICTION

WINSTON-SALEM, NC—Thomas Jones, 40, who had two prior convictions and a third charge pending for driving while impaired, was found guilty of murder and sentenced to life in prison. Two 19-year-old women were killed when Jones's car struck theirs. Jones was not legally drunk but admitted drinking two quarts of beer and taking painkillers before the crash. The painkiller bottle clearly stated that the patient should not drink or drive while taking the pills.

—abstracted from www.dui.com/drunk_driving_research/dui_offender.html

Teacher Note

A quantitative determination of "breath alcohol" can be carried out using a Spec 20-type spectrophotometer or a CBL and colorimeter. The students, however, are working with potentially nasty chemicals that have an even worse reputation. The basis of the analysis is given above; the concept of using spectroscopy is described in previous chapters; no new pedagogy is introduced. However, if you want the students to perform the experiment, directions can be obtained from the Web; for example, http://onsager.bd.psu.edu/~jircitano/chem2alcohol.pdf#search='experiment%20breath%20%20dichromate'.

Teacher Note

These activities are a nice example of an oxidation-reduction reaction with a practical aspect. Small, disposable breath-alcohol tubes are now being sold to the public. Breathing into one changes the color from orange to blue-green. Science, like life, is a great circle. These simple no-tech devices rely upon the dichromate-chromate(III) color change.

Laboratory Activity 8.3, *continued*

2. To make disposable indicator sticks, try this: Soak overnight about 5 g of silica gel (the kind used in thin-layer chromatography works well) in 20 ml of 0.1 M potassium dichromate (2 g/100 ml H_2O), 2 drops of 0.1 M silver nitrate catalyst (1.7 g/100 ml H_2O), and 10 ml of 6 M sulfuric acid. Filter and air-dry the yellow-colored crystals of silica gel. Cut the tip off a Pasteur pipette and push a small wad of cotton to the bottom. Pour the silica gel in and anchor it with another wad of cotton. Release the alcohol breath of the balloon into your detector. Brainstorm with the rest of your class how to estimate its sensitivity. What would be the effect of mouthwash?

The first test instrument, the Breathalyzer, was invented in 1954; it was based on the color change when an orange dichromate ion is reduced to a green chromium(III) ion by alcohol:

$$8H^+ + Cr_2O_7^{2-} + 3C_2H_5OH \rightarrow 2Cr^{3+} + 3C_2H_4O + 7H_2O$$

Field Sobriety Tests

Occasionally, a sobriety test may be administered by an officer at the scene of a traffic stop. This is equivalent to a presumptive or spot test. Standard actions involve walking a straight line, standing on one foot while counting, reciting the alphabet rapidly or counting from ten backwards, touching a finger to the nose, a nine-step heel-to-toe and turn, and observation of a horizontal gaze **nystagmus**.

nystagmus: rapid, involuntary jerking of the eyeball. There are many types of nystagmus which are not alcohol-related.

What is horizontal gaze nystagmus? Nystagmus refers to an involuntary twitching or jerking of the eyeball when attempting to follow an object with the eyes. It increases with the level of intoxication. An officer instructs the intoxicated suspect to hold his or her head steady and look straight ahead. He holds a pen about 12 inches from the person's face and moves it slowly to one side and then to the other on a 45-degree angle. An intoxicated person cannot follow the motion of the pen smoothly, and his or her eyeballs jerk as the pen is moved at an angle away from the face. The higher a person's blood alcohol, the sooner nystagmus occurs in the 45-degree arc and the more extreme it is at 45 degrees.

Vertical gaze nystagmus occurs when the eyes are turned upward, and is an indicator of whether the subject is under the influence of inhalants, depressants, or several widely used drugs.

Try observing nystagmus with your classmates.

Current Breath-Testing Technology

The newer breath-testing instruments are based on instrumental techniques, such as infrared (IR) spectrophotometry. A narrow band of IR light, chosen because of its absorption by ethanol, passes through a breath sample chamber. Comparing input and output energy, alcohol concentration is calculated using the Beer-Lambert law, which defines the relationship between concentration and light absorption. (See Chapter 7, "Drugs," for more about IR spectroscopy.)

Another device uses electrochemical fuel cell technology, which catalytically oxidizes ethanol to create a charge imbalance across a semiconductor. By calibrating the current to neutralize the charge, the tester can determine the amount of alcohol "fueling" the cell.

Fuel cell alcohol analyzer

Modern Breathalyzer

Answers

1. Examples include vitamins A and D, niacin, salt, water, zinc, iron, oxygen, possibly arsenic, sunlight, calories, and red wine.
2. As of this writing, Vioxx and Celebrex; also, the levels of ingestion of vitamin E have recently been under fire. There are also doubts about some natural product concoctions.
3. dose, form, mode of entry, physiology (age, sex, weight, and the like), duration of exposure, and coincident chemical effects
4. Arsenic reacts with sulfide linkages, which are especially prevalent in the cystine of keratin (see Chapter 5, "Hair," page 111).
5. NaCl, 218 g, about half a pound; $MgCl_2$, 108 g, about 4 ounces; $NiCl_2$, 7.6 g, about ¼ oz or one-half teaspoon. The differences mainly involve the target organ and rate of excretion.
6. A standard is a sample of known composition containing substances thought to be in the unknown to which it will be compared. A control is a sample of known composition without any material to be compared; it tests the method of analysis.
7. Possibilities include dust from leaded paint, soil and dust containing the remains of leaded fuels, leaded glass, ceramics, certain solders, old water pipes, bullets, metal ores, and X-ray shielding.
8. It will, even more easily than copper, because it has a greater reduction potential.
9. A Material Safety Data Sheet lists hazards, usage restrictions, and spill procedures that may save a life. The data can be used to evaluate whether certain chemicals should be used in high schools, for example.
10. the dose that kills 100 percent of the test animals
11. Uranium, thorium, radium, and radon all have no stable isotopes; potassium has one radioactive isotope.
12. Alpha (α), beta (β), gamma (γ). Alpha is stopped most easily because it has a charge, is relatively large, and is generally low-energy, but these characteristics also cause alpha particles to do the most damage to soft tissue.

Checkpoint Questions

Answer the following questions. Keep the answers in your notebook, to be turned in to your teacher at the end of the unit.

1. **List ten examples of substances that are beneficial in small quantities but poisonous in larger doses.**
2. **List at least two substances that were thought to be beneficial to humans but have recently been questioned.**
3. **What are some of the influences on the effect of poisons and toxins on the body?**
4. **Why does arsenic accumulate in hair and fingernails?**
5. **What is the estimated LD_{50} of table salt for a 160-pound man? What would it be for $MgCl_2$ (Epsom salt)? For $NiCl_2$? Why is there such a difference?**
6. **What is a standard? What is a control?**
7. **What sources of lead are there in our environment other than lead-based paint?**
8. **Predict from a table of reduction potentials whether zinc will displace dissolved mercury.**
9. **What is an MSDS? Why is it important?**
10. **What is LD_{100}?**
11. **Some elements are naturally radioactive; that is, they have either no stable isotopes or have one or more radioactive isotopes. List three common ones.**
12. **What are the three types of particles emitted by radioactive substances? Which one is stopped most easily? Why?**

13. Would Litvinenko have died if he had merely spilled tea laced with Po-210 on his shirt?

14. Would breath analyzers measure nonpotable alcohols or organic vapors, such as methanol or rubbing alcohol (isopropyl alcohol)? Explain.

15. It is not likely that a person gives off any nonalcoholic organic vapors—or is it? Do some research on medical conditions that might cause someone to emit organic vapors. How would this affect breath testing?

16. About how much total alcohol would you expect to find in the blood of a 110-pound woman with a BAC of 0.04?

17. Calculate how much blood the woman above has in her body. Show your work.

18. What would be the BAC of a 136-pound woman who has consumed three vodka tonics (2 oz of vodka each, with the vodka at 80 proof) during her lunch hour? If she forgets the time and talks for two more hours with her friend without having another drink, what will her BAC be when she gets back to work?

19. A 165-pound man was involved in a car accident at 10 PM. His BAC was measured at the time at 0.08, which he said was impossible because he had had only two beers (pint size, 5 percent alcohol) just after work at 6 PM. How many beers did he actually have?

20. After preliminary observations, a suspect is not required to do anything once pulled over under suspicion of intoxication. The observations consist of erratic driving, staggering, slurred speech, odors associated with alcohol, and the like. Evidentiary tests require the suspect to do something, such as blow into a test device, give blood, stand on one leg, or walk a straight line. Do these tests infringe on a person's constitutional rights?

Answers, *continued*

13. No; see answer to question 12.

14. Any organic reducing agent will react with dichromate. Organic compounds that absorb IR light in the same waveband as ethanol can be detected. An alcohol fuel cell will also run on similar organic substances.

15. Answers will vary.

16. about 0.05 oz or 1.5 ml or 1.2 g (d = 0.8 g/cc)

17. $\text{BAC} = \frac{\text{wt alcohol}}{\text{vol blood}} \times 100$

$\text{vol blood} = \frac{\text{wt alcohol}}{\text{BAC}} \times 100 = \frac{120}{0.04} = 3 \text{ L}$

3 L is low for a 110-pound woman (see p. 309 in Chapter 11, "Blood"), so we can see how uncertain the estimates are in calculating BAC.

18. a) 0.15
b) about 0.12 (loses 0.015 per hour; see p. 309)

19. He would have had a BAC of 0.07 on leaving the bar if he had drunk only two beers. Four hours elapsed, accounting for a reduction in BAC of 4 × 0.015, or 0.06, which when added to 0.08 equals a BAC of 0.14 when he left the bar. This is equivalent to consuming four beers.

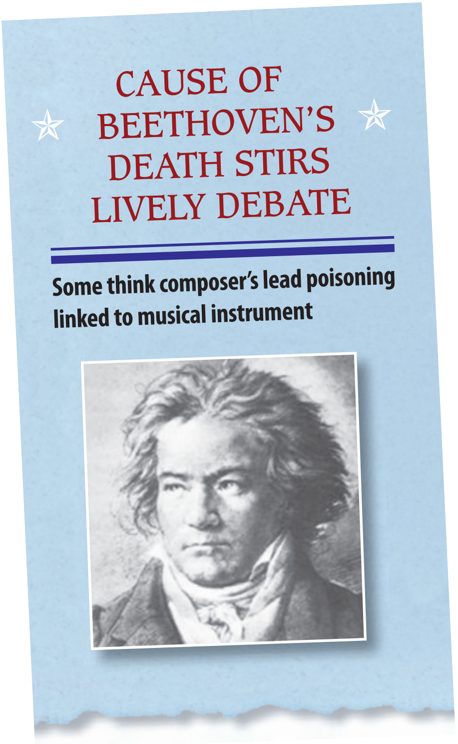
20. Answers will vary but must be supported.

Man Eats Underwear to Beat Breathalyzer

An 18-year-old man tried to eat his underwear while sitting in the back of a police car in the hope that it would absorb the alcohol before he took a Breathalyzer test.

—abstracted from *The Advocate*

Whatever works! This didn't. He had a BAC of 0.08.



CAUSE OF BEETHOVEN'S DEATH STIRS LIVELY DEBATE

Some think composer's lead poisoning linked to musical instrument

Additional Projects

1. Prepare a one-page report about a poison or toxin of your choice. Include as many of the following aspects as possible: a description of the substance and its source, toxicity, symptoms, detection, cure, lasting effects, history, examples, and social impact, if any. List resources and references.

2. Napoleon died in exile in 1821. After analysis of his hair, some investigators have suggested he was poisoned by the deliberate administration of arsenic; others suggest that it was vapors from the dyes in the wallpaper that did him in. Research the death of Napoleon and present your findings and conclusion to the class.

Did Napoleon die at the hands of a secret assassin?

3. Similarly, it has been suggested that lead may have contributed to Beethoven's death. What do you think? Justify your opinion.

4. There is conjecture that Lincoln suffered from the effects of mercury poisoning during the years he took "blue mass," a concoction once used for depression. Another famous man, Isaac Newton, was also said to suffer from mercury poisoning. Could either case be true?

Lincoln's blues

5. An epidemic of stillbirths and deaths of newborn foals in Kentucky's bluegrass region occurred in the spring of 2001. What caused it? Has such an incident occurred elsewhere or with other animals?

6. Why hasn't botulin toxin been used, or feared, as an agent in chemical warfare or terrorism? Check out "Operation Anthropoid" and "Operation Mongoose." Write a short report on your findings, being sure to reference your sources, or write it as a news article.

Teacher Note

Project 5 has a minor purpose in learning to pick key words for a search—that should be easy. The most important aspect of this project is to show how difficult it is sometimes to find an answer to a problem, and how much scientific research is involved.

Project 6 is interesting, yet should allay a fear of terrorist use.

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Meadows, R. "Buried in Ice," *Chem Matters*, April 1994, pp. 4–7.

Meadows, R. "The Toxic Patient," *Chem Matters*, October 1995, pp. 4–7.

Miller, H. Chapter 1 ("Carbon Monoxide Poisoning") and Chapter 3 ("A Deadly OTC Cocktail") in *What the Corpse Revealed*. New York: St. Martin's Press, Paperback, 2000.

Novels

Many novels have been written involving poisons. Some of the more famous are:

Azimov, I. *A Whiff of Death*. 1968.

Christie, A. *After the Funeral*. 1953.

Cornwell, P. *Cause of Death*. 1996.

Sayers, D. L. *Strong Poison*. 1930. This classic features the Marsh test.

Websites

www.atsdr.cdc.gov/toxpro2.html; toxicological profiles of common chemicals, with lots of information

http://en.wikipedia.org/wiki/Toxicity; good information on toxins, toxicology, poisons, and the like

www.courttv.com/trials/turner; the use of ethylene glycol as a poison

www.crimelibrary.com; search "poison" for many cases

http://sis.nlm.nih.gov/enviro/toxtutor.html; an excellent set of tutorials on toxicology

http://scifun.chem.wisc.edu/chemweek/ethanol/ethanol.html; an interesting essay on ethanol and its chemistry through the body

http://alcoholism.about.com/library/blnaa35.htm; alcohol metabolism and links