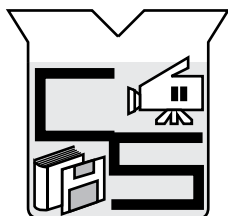


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*ChemSource Project Principal Investigator:
Mary Virginia Orna, OSU
Department of Chemistry
College of New Rochelle
New Rochelle, NY 10805
Phone: (914) 654-5302
FAX: (914) 654-5387*

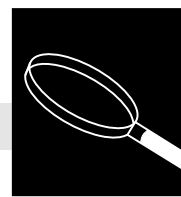


ChemSource

*Instructional Resources for Preservice and
Inservice Chemistry Teachers*

FORENSIC CHEMISTRY

Topic Overview



CONTENT IN A NUTSHELL

In running a routine route through a lighted park, a jogger was beaten and robbed by an attacker. There was a struggle and both people rolled on the ground. At the scene the investigating officer obtained a description of the attacker, discovered small pieces of glass, and noticed blood stains on the ground. The blood was determined to be of human origin and was *identified* as the victim's blood.

The victim picked out a suspect from a lineup, and the suspect's apartment was searched. The officers found a broken lens in the suspect's eyeglasses. The glass fragments found in the park *matched* the glass in the broken lens. A jacket was also examined. Soil particles were found embedded in the fabric. The soil found in the jacket was *compared* with the soil in the park area and was determined to be *identical*. Blood, glass, and soil are physical evidence. **Physical evidence** is anything that is found at the crime scene, including the victim and/or the suspect.

The forensic chemist's task is to assist the court in deciding whether physical evidence can be tied to a given individual. Evidence may also help exonerate an innocent person. This assistance allows the court to decide whether or not the particular individual has been involved in a crime.

The *examination* of physical evidence by a forensic chemist is usually undertaken for *identification* (Is it blood? Is it human blood?) or *comparison* (Does the crime specimen of blood match the suspect's blood specimen?). A variety of physical and chemical tests and sophisticated analytical instrumentation assist the forensic scientist in associating physical evidence with the suspect.

This module will provide teachers with an introduction to the kinds of physical evidence, physical and chemical tests, and analytical techniques that are routinely used by forensic chemists to associate or dissociate a suspect with a crime. Forensic science is an excellent example of the interdisciplinary nature of real science. It includes concepts from chemistry, physics, biology, and geology.

PLACE IN THE CURRICULUM

This module can be used toward the end of the second semester of the one-year course in chemistry. Because it concerns the application of chemistry to a topic of interest to many students, it serves as an example of a career opportunity utilizing science, in general, and chemistry, in particular.

CENTRAL CONCEPTS

1. Forensic science is the application of science to law.
2. The forensic scientist skillfully applies the principles and techniques of chemistry, biology, geology, and many other fields as well (physics, mathematics, *etc.*) to the analysis of the many types of evidence.
3. Evidence includes glass and soil samples, tire marks, blood, hair, drugs, fibers, firearms, bullets and cartridges, documents, indented writings, erasures, burned documents, body fluids, fingerprints, voice prints, and many other things.
4. The examination of physical evidence is undertaken for identification or comparison.

5. The process of identification determines a substance's physical or chemical identity with as much certainty as the employed analytical technique permits.
6. A comparative analysis subjects suspect and control specimens to the same tests and examinations for the purpose of determining whether they have a common origin.
7. Physical and chemical tests are used by forensic scientists. In chemistry, tests include density determination, elemental composition, chemical reactivity, and the determination of optical properties such as color. Biological tests include fingerprints, hair analysis, and blood identification. Tests involving physics include comparison of sound wave patterns, accident reconstruction, and index of refraction. In geology, soil analysis is studied. Instrumentation is an important aspect of the tests.
8. Modern analytical instruments available for identification and comparison include gas chromatography, thin layer chromatography, high performance liquid chromatography; infrared, ultraviolet, and mass spectroscopy; atomic absorption spectroscopy, and electrophoresis (see *Instrumentation* module).

1. Metric measurements
2. Density
3. Index of refraction
4. Chromatography
5. Chemical tests for anions and cations

RELATED CONCEPTS

1. Careful observation
2. Use of a microscope
3. Use of a balance and graduated laboratory glassware
4. Chemical separations

RELATED SKILLS

After completing their study of forensic chemistry, students should be able to:

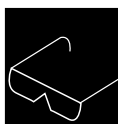
1. recognize the three primary activities of a forensic chemist: examination, identification, comparison.
2. see the interdisciplinary applications of forensic science to real life problems.
3. recognize the importance of modern instrumentation to solving problems.
4. list a number of careers that involve forensic science (firearms expert, medical examiner, museum curator, archaeologist, *etc.*).
5. identify and discuss a variety of separation techniques (see *Separations* module).
6. identify and discuss a variety of identification techniques.
7. use the above techniques to make reasonable comparisons.
8. provide possible physical and chemical explanations for these techniques used in forensic chemistry.

PERFORMANCE OBJECTIVES

Concept/Skills Development



LABORATORY ACTIVITY: STUDENT VERSION



Activity 1: Drug Identification

Introduction

In this activity, you will identify a drug. Drug identification is a routine procedure for a medical technician working in a hospital trying to identify the source of drug overdose, or the law enforcement investigator trying to identify a suspected controlled drug, or for the medicinal chemist employed by a pharmaceutical manufacturer trying to discover why a competitor's product is more effective.

Drugs can be identified in a variety of ways: characteristic colors when treated with special reagents, formation of crystalline solids with characteristic color and crystal structure when treated with appropriate reagents, or thin layer chromatography (TLC). In TLC, a drug is identified by its R_f value and by its color when treated with various reagents or when observed under ultraviolet light.

Purpose

To determine the composition of several over-the-counter (OTC) drug formulations using TLC. The drugs to be tested are aspirin, acetaminophen, caffeine, and salicylamide.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Ethyl acetate and iodine vapors can be irritating.
3. Do not look at the ultraviolet light.

Procedure

1. Obtain two precut (10 x 6.6 cm) TLC sheets. Do not touch the white surface and handle carefully only by the edges.
2. Using a lead pencil, draw a *light* line across the shorter dimension 1 cm from the bottom. Using a ruler as guide on the light line, mark off five equally spaced intervals on the line as shown in Figure 1.
3. Spot the sheet at each mark with the appropriate known solution: AC = Acetaminophen, AS = Aspirin, CF = Caffeine, SA = Salicylamide, and RF = Reference (Figure 2). These known solutions can be found in small reagent bottles. Use a melting point capillary tube or a wooden toothpick to spot the plate by dipping the tip of the tube (or toothpick) in the known solution and then touching the tip against the sheet at the appropriate mark. The applied spot should be no bigger than 1-2 mm. (Practice spotting on a piece of filter paper before spotting the TLC sheet.)

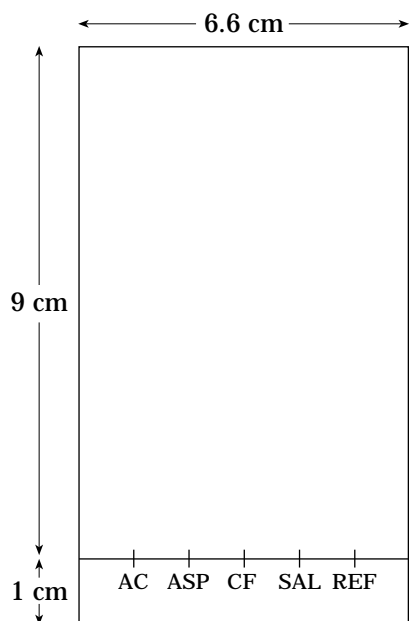


Figure 1. TLC plate.

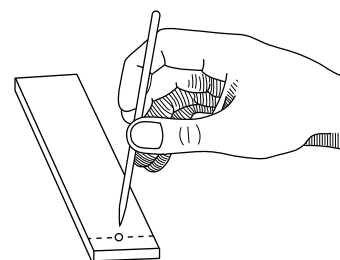


Figure 2. Spotting the TLC plate.

- Obtain a one-pint (16 oz) canning jar with a screw-cap lid for the development chamber. It should contain a filter paper liner as shown in Figure 3. Add ethyl acetate to the jar to a depth of about 0.5 cm and swirl to moisten the paper liner. (*REMEMBER:* The level of the solvent must be below the spots on the sheet—5 mL solvent is usually enough). Place the spotted sheet in the development chamber so that it rests in the solvent and against the jar wall. Replace the jar's lid and allow the sheet to develop (about 20 min).
- When the solvent has risen on the sheet to within 1 cm of the top, remove the sheet from the jar. Using a lead pencil, mark the position of the solvent front.
- Allow the sheet to air dry and then observe it under a short-wavelength ultraviolet lamp. Lightly mark any observable spots with a pencil and note the color of each spot.
- Obtain a one-pint canning jar and place a few iodine crystals in the jar. Cap the jar and place it on a hot plate (on low heat setting), preferably in a fume hood, until purple iodine vapor is quite visible. Place the TLC sheet in a jar of iodine vapor, cap the jar, and let stand about 30 sec. Observe and record which spots become visible (darken). Remove the sheet from the jar.
- Using a millimeter ruler, measure the distance that each spot (use center of spot for consistency) has traveled relative to the solvent front. Calculate its R_f value.

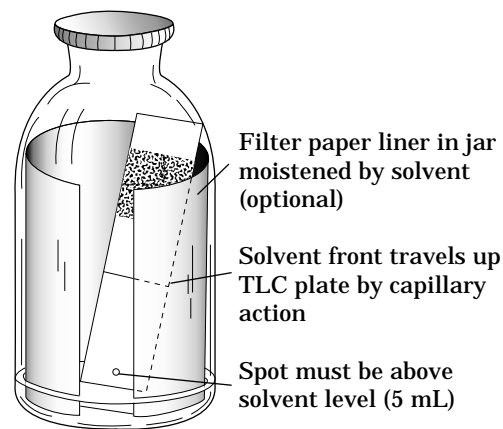


Figure 3. Development jar.

$$R_f = \frac{\text{Distance traveled by substance}}{\text{Distance traveled by solvent front}}$$

- Obtain one-half tablet of one of the following: Anacin™, Bufferin™, B.C. Powder™, Excedrin™, Tylenol™, generic aspirin, generic acetaminophen, or an OTC analgesic of your choice. Crush the tablet on a sheet of paper with a spatula. Transfer the crushed tablet to a small test-tube and add 3 mL each of absolute ethanol and methylene chloride [*CAUTION: Avoid breathing methylene chloride. It is toxic and can have a narcotic effect in high concentrations.*]. Using a stirring rod dissolve as much of the tablet as possible. It will not completely dissolve.
- Spot a TLC sheet with the reference solution and the unknown solution from Step 9.
- Develop the spotted sheet in the jar as before (Steps 4 and 5).
- Observe the sheet under ultraviolet light and mark visible spots (Step 6).
- Observe the sheet in the iodine jar and record visible spots (Step 7).
- Calculate R_f values for any spots (Step 8).
- Identify the components of your unknown analgesic.
- Thoroughly wash your hands before leaving the laboratory.

Data Analysis

- Can ultraviolet light be used to distinguish the substances from one another?
- Can iodine be used to distinguish the substances from one another?
- Can the R_f value be used to distinguish one substance from another?



4. Is it important that the sheets be examined under ultraviolet light before the iodine visualization?
5. Why do some substances move along the TLC plate at a rate different from other substances?

Implications and Applications

The analysis of an unknown analgesic drug can be performed by TLC. Specific components of a developed TLC sheet can be identified by the visualization method (under ultraviolet light or in iodine vapor) and from subsequent calculations of the R_f values. Crime laboratory technicians often use TLC to determine the presence of controlled substances (*e.g.*, cocaine) in an unknown sample.

The TLC technique is often used by forensic scientists to identify pen inks. For example, the need for differentiating inks arises when people prepare fraudulent documents. A person cheating the government may back-date a record to substantiate a false tax claim. The forensic scientist can determine how many inks or pens were used to prepare a document and the year of manufacture for the inks used.

Lipstick stains on clothing or cigarettes can also give valuable information about the identity of a likely suspect. The dyes that give lipstick its color can be identified by a TLC separation and compared with those used by the friends of the victim.

Activity 1: Drug Identification**Major Chemical Concept**

TLC is a separation technique. Specifically, substances in a mixture partition between a solid and liquid phase. A thin film of silica or alumina coated on a glass or plastic strip constitutes the solid phase. This thin film is called the stationary phase. The liquid phase is the solvent that ascends the solid layer by capillary action. The liquid phase is called the mobile phase. When a TLC sheet is spotted with a mixture of substances and placed in a solvent, the solvent (mobile phase) moves up the sheet and carries with it the various components of the spot. Because the molecules of each compound present have a different size, shape, and polarity, each compound will adhere to the stationary phase and dissolve in the solvent to a different degree. The stationary phase is typically polar and will hold polar compounds more tightly than nonpolar compounds (they will move more slowly). Less polar compounds will dissolve in the nonpolar mobile phase and move along the sheet faster. Once the flow of the mobile phase is stopped, the sheet is dried. The various spots, if not colored, can be made visible by either ultraviolet light or iodine vapor. The distance the compound moves relative to the distance the mobile phase moves is characteristic of that compound and is called the R_f value.

Level

This laboratory activity can be used in a general chemistry course.

Expected Student Background

Students should have an understanding of “like dissolves like.” A polar substance is more likely to dissolve in a polar solvent rather than a nonpolar solvent. However, it will not be obvious from the structural formulas of the substances used in this activity why one substance is more polar than another.

Time

The activity may take two or three 50-min periods. During the first period students should practice spotting filter paper and TLC sheets. The developing chambers should be set up and the solvent added. A discussion of TLC could be given. During the second period, students develop the sheets containing the knowns, perform the visualization tests, and calculate the R_f values. In the third period, they develop the sheets containing the reference mixture and one or two unknowns, perform visualization tests, calculate R_f values, and identify the compounds in their unknown. If only two days can be devoted to this activity, students should work in pairs, one student obtaining the chromatogram of the knowns and reference mixture of knowns, and the other obtaining the TLC of the reference mixture and the unknown(s).

Safety

Read the *Safety Considerations* in the *Student Version*. Caution students to avoid breathing methylene chloride. It is toxic and can have a narcotic effect in high concentrations. Ethyl acetate is flammable, and its vapors can be irritating but can be minimized by keeping the developing chamber closed unless a plate needs to be inserted or removed. Iodine vapors are irritating. Students should not look at the ultraviolet light.

**LABORATORY
ACTIVITY:
TEACHER
NOTES**



Materials (For 24 students working in pairs)

4 Small bottles (25-mL size) containing the “known” compounds in solvent (50:50 v/v methylene chloride and absolute ethanol).

4-Hydroxyacetanilide (acetaminophen) (1 g per 20 mL solvent)

Caffeine (1 g per 20 mL solvent)

Salicylamide (1 g per 20 mL solvent)

Acetylsalicylic acid (0.5 g per 20 mL solvent)

1 Small bottle, 20 mL of a combined standard reference mixture of the four compounds at the same concentration. (1 g of each of the above in 20 mL of solvent. Stir to dissolve.)

Methylene chloride, 100 mL

Ethanol, 95%, 100 mL

Ethyl acetate, 100 mL

Eastman Chromatogram Sheets with Fluorescent indicator (Eastman No. 13181, box of 20 sheets). Each sheet is cut into six 10 x 6.6 cm sheets. Thus four large sheets will suffice.



A hand-held ultraviolet lamp. Preferred: 4 watt long and short wavelength ultraviolet light. (Model Mineralight UVSL-25 available from Ultraviolet Products, Inc., 5100 Walnut Grove Avenue, San Gabriel, CA 91778 or Model UVGL-25 from Central Scientific Company, 11222 Melrose Avenue, Franklin Park, IL 60131-1364)

Thin-wall, open-end capillary tubing (1 mm) for micropipets; alternatively, use toothpicks

Filter paper, 12 squares for liners

24 Wide mouth, clear screw cap jars (Mason jars will work), 16 oz, or 600-mL beaker with aluminum foil cover also work well

Iodine, several crystals

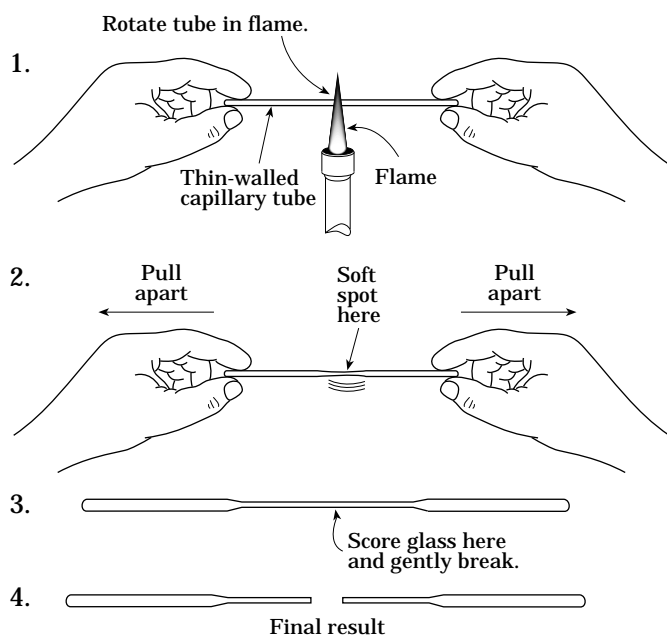


Figure 4. Preparation of micropipets.

Advance Preparation

Prepare the solutions of the knowns before the laboratory period. Spot the TLC in one area of the laboratory. Have students come to a table of knowns rather than taking the knowns to their individual desks. Keep development chambers at individual desks. Place the ultraviolet lamp in a darkened hood, darkened area of the laboratory room, or in a large upside-down cardboard box with appropriate holes cut for viewing.

Prepare about 10 micropipets as shown in Figure 4.

Pre-Laboratory Discussion

1. Give a brief introduction to the TLC techniques (see *Major Chemical Concept*).
2. Instruct students on importance of small spots. If spots are too large, tailing and poor separation will occur.
3. Explain why the spotted mixture should be above the solvent level. (If it is below, it will dissolve in the solvent and not separate.)

- Remind students not to move the jar during the development time to avoid splashing solvent on the plate.
- Explain to students how to calculate R_f values. Tell them to get their best estimate for the center of each developed spot.

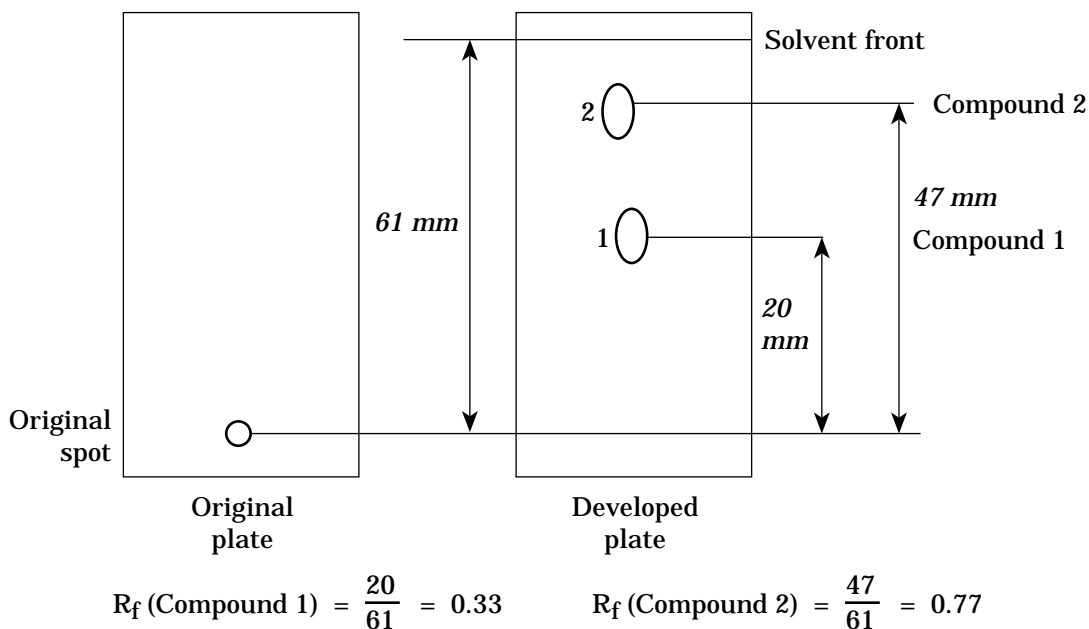


Figure 5. Calculation of R_f values from chromatograms.

Teacher-Student Interaction

Walk around laboratory and ask students if they understand what is happening. Discuss how to calculate R_f values. Caution students about inhaling solvent vapor.

Anticipated Student Results

Typical experimental results are:

$$R_f = \frac{\text{Distance traveled by substance}}{\text{Distance traveled by solvent front}}$$

Knowns

$$R_{f \text{ AC}} = \frac{3.2 \text{ cm}}{7.4 \text{ cm}} = 0.43$$

$$R_{f \text{ ASP}} = \frac{0.7 \text{ cm}}{7.4 \text{ cm}} = 0.09$$

$$R_{f \text{ CF}} = \frac{2.0 \text{ cm}}{7.4 \text{ cm}} = 0.27$$

$$R_{f \text{ SAL}} = \frac{5.4 \text{ cm}}{7.4 \text{ cm}} = 0.73$$

- Salicylamide and acetaminophen produce dark spots. Caffeine produces a light spot. Aspirin does not produce a spot.
- Yes. The approximate order of migration is salicylamide, followed by acetaminophen, caffeine, then aspirin.
- Yes. The iodine permanently darkens some of the spots.
- The differences in the rate of movement of substances depend upon solubility of the substance and adsorption properties of the backing on the plate. Because the solvent is typically nonpolar and the backing is strongly polar, the backing holds a polar substance more tightly than a nonpolar substance. These polar substances move considerably more slowly than nonpolar substances in the nonpolar solvent.

Assessing Laboratory Learning

- List the steps in the determination of the number of components in a mixture by TLC. *[Spot the plate, develop the chromatogram, visualize the spots, calculate R_f values, compare with suspected knowns.]*
- How is an R_f value determined? *[R_f is the distance the substance travels divided by the distance the solvent travels.]*
- Two substances have R_f values of 0.3 and 0.5, respectively. Which substance is carried farther by a polar solvent? Which substance is less polar? *[Substance with $R_f = 0.5$ is the polar substance and is carried better by the polar solvent. Substance with $R_f = 0.3$ is less polar.]*
- Name two ways of visualization of spots. *[Ultraviolet light and iodine vapor. Discuss with the students other possibilities for visualization. Lead them to think about color reactions, where the spots can be developed by spraying the TLC plate with reagents that react with the samples to give a color or a visible spot. For example, ninhydrin sprayed on hydrolyzed protein samples yields a purple color and conc. sulfuric acid dehydrates most organic compounds to yield yellow to brown (carbon) spots (see Demonstration 3).]*
- Identify the stationary and mobile phases in TLC. *[Solid adsorbent and solvent, respectively.]*
- Using the following chromatogram, decide which substances are identical? Which mixtures are identical? *[Identical substances: 1a, 2a, and 4a; 1b, 3b, and 4b; 1c and 4c. Identical mixtures: 1 and 4.]*

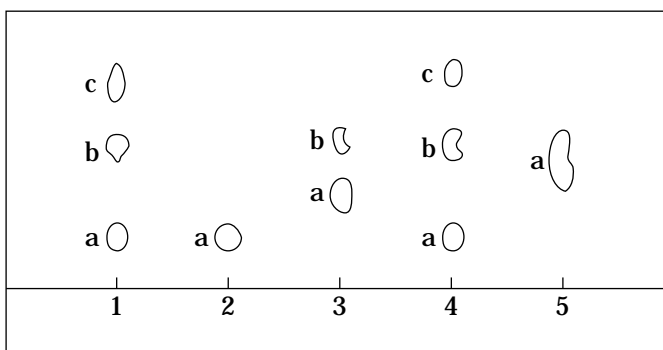


Figure 7. Chromatogram of unknowns.



DEMONSTRATIONS

CAUTION: Use appropriate safety guidelines in performing demonstrations. Only brief procedural steps are described here. Some of these demonstrations can be used as student activities.

Demonstration 1: Density of Glass

The analysis of shattered glass is very important in burglary and automobile accident cases. In addition to the glass particles left at the crime scene, some glass particles are also found on shoes or clothing of the suspect or on some parts of the car. If particles from the scene compare with those found on the suspect, the prosecution's evidence is strengthened.

Glass is a noncrystalline material of widely varied composition and properties. It contains silicon dioxide (sand), metallic oxides or carbonates, and other trace elements. The properties depend on the method of production, the annealing time and temperature, and the composition. The physical properties of glass vary sufficiently that they can be used to compare two samples of glass with each other. Glass gives a different appearance when viewed under ordinary light, ultraviolet light, and polarized light. Glasses also vary in density and index of refraction (see *Demonstration 2*). In this activity you will view two glass samples under the light described above and determine the density of a glass sample from its mass and volume (by water displacement).

Part A. Appearance of Glass Samples

Materials

- 2 Different glass bead samples
- Ultraviolet lamp
- Microscope
- Polarized film set
- Magnifying glass

Safety

Do not look directly at the ultraviolet lamp. Care must be taken when handling glass fragments because of sharp edges.

Procedure

1. Obtain a sample of each type of glass.
2. Observe the glass samples under a direct light using a magnifying glass.
3. Observe the glass samples under ultraviolet light using a magnifying glass.
4. Observe each glass sample under the microscope between two polarized films. One film should be positioned permanently while the other one is rotated 90°. As you rotate the film, more and more light is blocked out.
5. Compare the two glass samples under the three kinds of lighting. Are they distinguishable?

Part B. Density of Glass Samples

Materials

- 2 Different glass bead samples
- Balance
- Graduated cylinder, 10-mL
- Water, 100 mL

Procedure

1. Add 2-3 mL of water to the graduated cylinder. Read the volume to the nearest 0.01 mL. Determine the mass. Record both the volume and mass.
2. Add enough glass beads from one sample to the cylinder to increase the volume by about 5 mL. The additional glass beads should be submerged. Read the new volume to the nearest 0.01 mL and record. Determine the mass of this new combination and record.
3. Determine the density of this glass sample and record results.
4. In order to be sure your density is reliable, add a few more beads to this same cylinder. Record the final volume and determine the new mass.
5. Determine the density of this second trial by subtracting this final volume from the initial volume and by subtracting the final mass from the initial mass. Record results. Take an average of the two densities and record this average on the data sheet.
6. Repeat Steps 1-5 for the other glass sample.

Demonstration 2: Refractive Index of Glass

Refractive index is a measure of the bending of light as it passes from air into a solid or liquid. Determination of the refractive index of glass provides information about the common origin (or lack thereof) of two glass samples.

In the immersion method a glass sample is added to a pure liquid or liquid mixture of known refractive index. If the glass and liquid have different refractive indices, a colored boundary can be seen with the unaided eye. If they have the same index of refraction, the boundary will disappear and the specimen will be practically invisible.

Materials

- Several fragments of Pyrex™ glass
- Several fragments of common (flint) glass
- Baby oil or vegetable oil
- Test-tubes

Safety

Sharp glass may cause cuts and should be handled with care.

Procedure

1. Fill three test-tubes about half-full of oil.
2. Put some of the Pyrex™ fragments in one test-tube, some common glass fragments in another, and a mixture of Pyrex™ and common fragments in the third.
3. Stopper the three test-tubes. Observe.
4. The Pyrex™ glass will be nearly invisible when covered with the oil, while the flint glass will remain visible. The Pyrex™ glass has an index of refraction (1.47) that nearly matches the index of refraction of the oil, whereas flint glass has an index of refraction of 1.60.
5. Discussion. Many crime laboratories have a standard set of liquids of varying refractive index over a wide range and in small increments (typically 0.05). These so-called Cargille liquids allow the forensic specialist to determine the refractive index of transparent samples to an uncertainty of ± 0.05 by the immersion method.



Demonstration 3: Analysis of Fingerprints

Fingerprints are the most reliable means of identifying suspects. No two human fingerprints are exactly alike, and fingerprints do not change naturally. Fingerprints are classified into three main types: loop, arch, and whorl (see Figure 8). There is no set number of *points* of similarity used by experts when comparing fingerprints for identification. However, many latent print examiners often use seven *points* as a minimum.

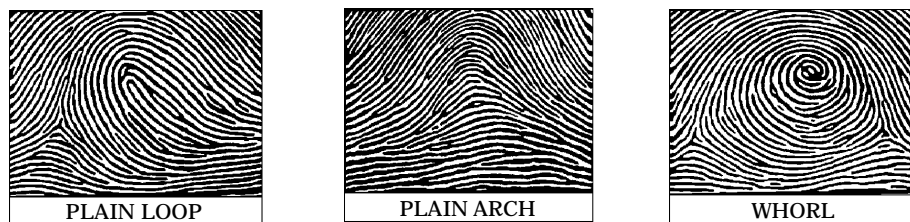


Figure 8. Types of fingerprints.

Part A. Obtaining a Fingerprint

Materials

Black ink stamp pad
Tissue paper
4 x 4 cm Card (cut from a 3 x 5 inch file card)
Tweezers

Safety

Wash hands thoroughly to remove the black ink.

Procedure

1. Handle the card only on the edges.
2. Place your right thumb on the black ink pad and then place your thumb print in the middle of the card.
3. Examine the print and identify it by main type.
4. Compare with other students in the class who have the same main type to determine if there are distinguishing features in the thumb prints.

Part B. Dusting for and Lifting Prints from a Smooth, Nonporous Surface

Materials

Dusting brush (one for each color of powder)
Dusting powders (aluminum and carbon black).
2 Beakers, 150-mL
Newspaper
2-inch wide Cellophane tape
Index card
Magnifying glass

Safety

Take care not to scatter dusting powders. Some people are sensitive to the airborne particulates.

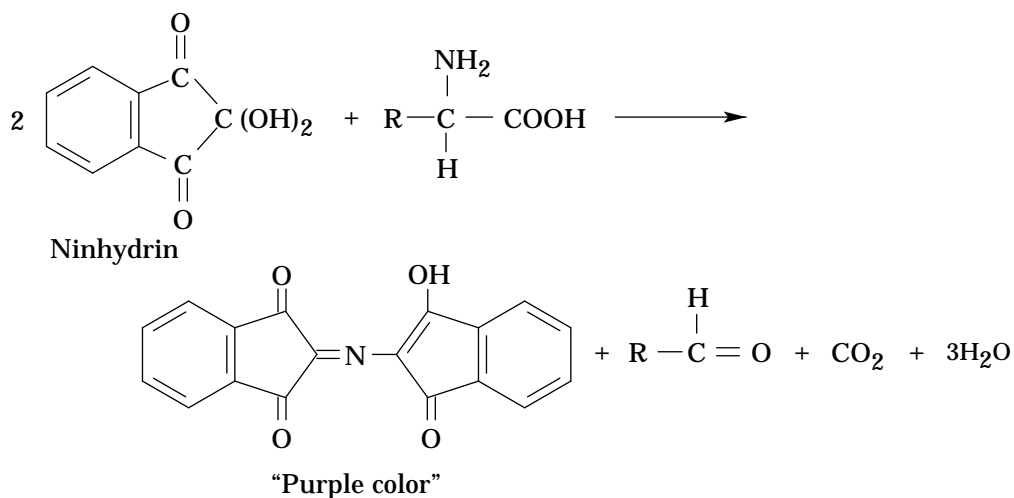
Procedure

1. Grab a 150-mL beaker so that your thumb print is left on the beaker.
2. Obtain a brush for dusting the print. Make sure it is clean and the bristles are separated from each other.

- Place a small amount of the dusting powder in a labeled beaker. Dip the brush in the powder and lightly dust the area containing the print. After the entire print is developed, remove the excess powder by gently brushing it away. Be careful not to destroy the print with too hard a brush stroke.
- To lift the print from the 150-mL beaker to the index card, unroll 9 cm of tape. Bend the tape strip in the form of a U so that the sticky side is facing the beaker. Place the point of the fold directly on the print. Gently place the rest of the stripe onto the beaker. The print can be removed by pulling up on the roll end of the tape and then placing it on the fingerprint card in the same manner as the tape was placed over the latent print. Make sure the tape is secure. Cut off the excess tape.
- Observe the print under the magnifying glass and compare it with your right thumb print from *Part A*.

Part C. Using Ninhydrin to Develop a Print on Paper

Ninhydrin reacts with amino acids in the perspiration on a fingerprint to form a purple compound. The reaction of ninhydrin with an amino acid may be represented as follows:



The purple-colored substance is formed by the reaction of some of the ninhydrin with its reduction product, hydrindantin, and ammonia, which is formed as a reaction intermediate.

Safety

Wear plastic gloves when handling ninhydrin since it will stain skin. Ethanol is volatile and flammable. Keep the solution away from open flames.

Materials

4" x 5" Sheet of white paper containing your right thumb print
 Ninhydrin solution (0.3 g ninhydrin in 100 mL ethanol)
 Forceps
 Plastic gloves
 Brush or cotton wads
 Magnifying glass
 Concentrated ammonia or steam iron



Procedure

1. Tape the top of the exhibit (white sheet of paper containing your right thumb print) to a paper towel. Do the following in a fume hood or in a well ventilated area. The ethanol used in preparing the ninhydrin solution is volatile and flammable. Keep this solution away from open flames. Wear plastic gloves when working with the ninhydrin solution as it will react with the amino acids in your hand and turn them blue to purple!
2. Dip the tip of the brush into the ninhydrin solution and carefully dab this liquid over the fingerprint area. Do not use too much pressure since that will destroy the print. Cotton wads held with tweezers can also be used to dab the liquid onto the fingerprint area.
3. Allow the paper to dry. It may take 24 hrs to develop. Observe the print under a magnifying glass and compare with the fingerprint obtained above.
4. If the print does not develop, expose the paper to the fumes from ammonia by opening a bottle of concentrated ammonia in the fume hood and holding the paper with the print over the opening of the bottle. Alternatively, a steam iron may be used.

Demonstration 4: Lipstick Fluorescence

Many substances contain molecules that absorb radiation in the ultraviolet portion of the spectrum and because of certain intramolecular phenomena, emit radiation in the visible region of the spectrum. This phenomenon is called fluorescence (see *Photochemistry* module). In this activity you will examine the fluorescence of lipstick. These observations suggest why makeup may appear different in a disco, or under a street light, as compared to inside a room.

Materials

- Lipstick samples
- Filter paper
- Ultraviolet lamp

Safety

Ultraviolet light can damage eyes. Do not look directly at the ultraviolet light.

Procedure

1. Obtain the several lipstick samples to be used in this demonstration. Record the color and manufacturer for each type, then describe the color.
2. Use a sheet of filter paper. Place a smear of each kind of lipstick onto the paper, using a mark about one-half inch long. Write the brand or other identification next to the smear for identification.
3. Expose the filter paper containing the lipstick stains to an ultraviolet lamp in a dark room. Observe which of the lipstick samples fluoresce under the light and circle those samples.

Demonstration 5: Examination of Hair

Hair is a common form of evidence in many homicide and sexual assault cases. Hair from any part of the body exhibits a range of characteristics such as color, length, and diameter. The parts of a hair that are easily seen by use of a microscope under magnification are the medulla and cortex. It is very difficult to see the hair cuticle. Figure 9 illustrates the parts of a hair and the various types of hair.

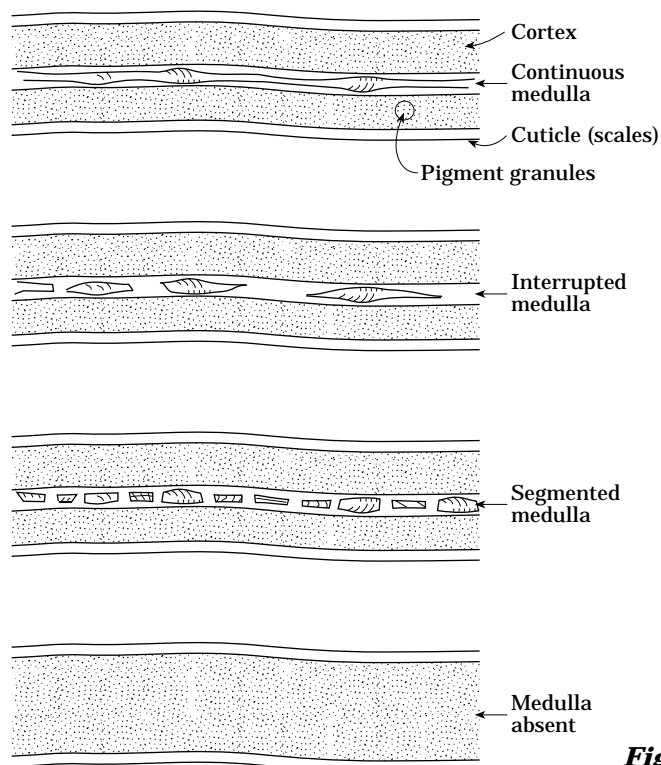


Figure 9. Types of hair.

Many animal hairs are easily distinguished from human hairs by the size and shape of their medullae and the patterns of their cuticle or scale structures (see Figure 10). Synthetic fibers have no medulla or scale pattern and are therefore readily distinguishable from animal hair.

Materials

- Microscope slides
- Compound microscope (100X is a good magnification)
- Tissue paper
- Tweezers
- Hair sample (yours, animal)
- Fiber sample
- Glycerol (glycerin)

Safety:

Glycerol (glycerin) should not be ingested.

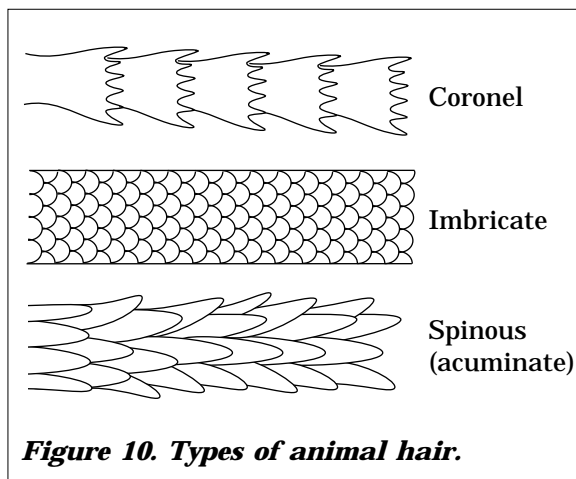


Figure 10. Types of animal hair.

Procedure

1. Obtain a strand of human hair and place it on a microscope slide.
2. Place a small drop of glycerol on the hair in order to hold it in place, and put a cover slip over it.
3. Place the slide on the stage of the compound microscope, clip in place, and adjust the magnification at 100X.
4. Locate the root end of the hair, if it has one. If the hair has been forcibly pulled out, you will see a bulb-shaped enlargement. This is the root.



5. Make a sketch of what you see.
6. Scan along the length of the hair body. Is the medulla (center) fragmented (present in isolated spots), interrupted (long columns with open spaces now and then), or continuous (unbroken column)? Make a sketch of the medulla you observe from the hair sample.
7. Note the color, diameter, and pigmentation of the hair.
8. Examine the tip of the hair. This can be done by observing a gradual tapering of the hair. If the hair has been recently cut, you will see a square tip where the hair ends abruptly. Normally, hair tapers to a fine point as it grows. If hair has split-ends, it is normally due to artificial waving or bleaching, although repeated brushing may also produce this effect.
9. Repeat Steps 1-8 for the sample of animal hair. Note any similarities and differences with the human hair.
10. Try to obtain various colors of hair from other persons in the class. Make comparisons about similarities and differences.
11. Obtain a fiber strand (cotton, nylon, silk, wool, Dacron, linen, rayon) and observe the color. If present, the color is due to a dye or stain. Prepare a microscope slide of the fiber and try to determine if the dye penetrates the fiber, or is found only on the surface.
12. Examine other fiber characteristics such as diameter, whether the surface is rough or smooth, whether the fiber is twisted or straight, whether it is continuous, or segmented, whether it is round, flat, oval, or has some other shape.
13. Compare and contrast human hair, animal hair, and fiber.

GROUP AND DISCUSSION ACTIVITIES

Key Questions

1. What are examples of physical evidence? [*Body fluids, hair, fingerprints, handwriting, tool marks, firearms, fibers, soil, inks, documents, etc.*]
2. Why is examination of physical evidence undertaken? [*For identification and comparison.*]
3. What is the purpose of identification? [*To determine a substance's physical or chemical identity with the certainty permitted by the analytical technique used.*]
4. What is the purpose of comparison? [*Comparison subjects the suspect and control specimens to the same tests and examinations to determine if a common origin exists.*]
5. Name some analytical techniques used by the forensic scientist. [*Electrophoresis, chromatography (gas, thin layer, high pressure liquid), spectroscopy (infrared, ultraviolet), neutron activation analysis, and atomic absorption spectroscopy.*]

Counterintuitive Examples and Discrepant Events

1. Appearances are deceiving.
2. Not all criminals look the part.
3. Things that look the same on the surface are different inside (*e.g.*, antiques versus reproductions).

Metaphors and Analogies

1. Forensic chemistry is like a zipper—everything must fit together.
2. Forensic chemistry is like the spokes on a wheel—to form a strong case, each spoke has to fit in the correct place.

Language of Chemistry

1. A full-service crime laboratory consists of specific units. These include (in addition to the unit's function):
 - a. **Physical Science Unit** Applies principles of chemistry, physics, and geology (*e.g.*, identification of glass, soil samples, or tire marks) to the identification and comparison of crime-scene evidence.
 - b. **Biology Unit** Examines blood, body fluids, hair, fibers, and botanical specimens.
 - c. **Firearms Unit** Examines firearms, bullets, cartridge cases, shotgun shells, tool marks, latent prints, and ammunition of all types.
 - d. **Document Examination Unit** Examines handwriting and typewriting on questioned documents; analyzes paper and ink, indented writings, obliterations, erasures, and burned or charred documents.
 - e. **Toxicology Unit** Examines body fluids and organs for drugs and poisons.
 - f. Other units include the **Identification Unit** (photography, fingerprint, polygraph, and voice-print analysis), and Evidence Collection Unit.
2. The **Evidence Collection Unit** dispatches trained personnel to the crime scene to retrieve evidence for laboratory examination. Physical evidence can be anything from massive objects to microscopic traces. The presence of many items of evidence is obvious, but some can only be detected by close laboratory scrutiny. Many examples of physical evidence were described above.
3. Forensic science is the application of science to criminal and civil laws.
4. Chemistry, biology, physics, and geology are useful for determining evidential value of crime scene and related evidence.
5. Forensic scientists may be called to testify in civil cases (*e.g.*, water quality or product liability).
6. The microscope is the most important tool in some crime laboratories. TLC is an important technique and GC is an important instrument.
7. Forensic scientists often deal with small amounts of the evidential sample, often necessitating, as the first choice, examination by a nondestructive laboratory test.
8. Samples examined by forensic chemists are usually impure. Tests will show the presence of “something” in a lot of “garbage.”
9. Forensic science laboratories are seldom on the forefront of technology in chemistry (or science). Attorneys and judges feel comfortable with what has already been accepted in the courts. On occasion, evidence will be accepted if it provides information that cannot be obtained otherwise (*e.g.*, DNA profiling).

TIPS FOR THE TEACHER



10. Confiscated street drugs may require extraction, isolation, and spectral analysis for identification. Extraction of a suspected compound from a mixture is often pH dependent (many of these compounds contain basic groups), dependent on the solubility of the suspected compound in the extraction solvent, and the resulting crystalline form depends on whether the substance is precipitated in neutral, acid, or base form. This may also be true of some pharmaceutical samples.

Common Student Misconceptions

1. **“Forensic chemistry can solve all crimes.”**

Forensic chemistry is only one of the sciences important in crime solving. The principles and techniques of biology, geology, and physics are applied to the many types of evidence. Mathematics and psychology are also important areas.

2. **“Crimes can be solved easily.”**

Despite the fact that many crimes as portrayed on television and in the movies are solved within 1-2 hrs, most crimes require a team effort involving deductive reasoning and sophisticated scientific techniques over a period of time. Some crimes are never solved.

3. **“Perfect fingerprints can be taken off anything.”**

Generally, smooth surfaces (glass, table tops, *etc.*) will yield good fingerprints; a rough surface (stone wall) will not. The quality of a fingerprint is also determined by the amount of skin oil.

4. **“Identical twins have the same fingerprints.”**

Fingerprints are individualized. In addition, other types of physical evidence that can be individualized include jigsaw matches, footwear and tire tread prints, striations present in tool marks, and ballistic evidence.

HISTORY: ON THE HUMAN SIDE

1. **Alphonse Bertillon**(1879) developed a systematic procedure of taking a series of body measurements as a means of distinguishing one individual from another.
2. **Sherlock Holmes**in Sir Arthur Conan Doyle's *A Study in Scarlet* (1877), described scientific methods of detection years before they were actually discovered and implemented. In the novel mentioned here, Holmes describes a chemical test for blood.
3. **Francis Galton**(1892) published a book describing the principles of the present system of fingerprint identification.
4. **Leone Lattes**(1915) devised a procedure for determining the blood group of a dried bloodstain. The procedure is still utilized today.
5. **Calvin Goddard**helped establish the comparison microscope as the indispensable tool of the modern firearms examiner.
6. **Albert Osborn**(1910) developed the principles of document examination.
7. **Edmond Locard**(1910) established the first workable crime laboratory in which the principles of chemistry, physics, mineralogy, and biology were utilized. He enunciated the creed of the forensic scientist when he said every criminal *carries something to and takes something from the crime scene* .
8. In 1932, the FBI organized a national laboratory that offered forensic services to law enforcement agencies throughout the country.

9. In 1948, the first school of criminology was formed at the University of California at Berkeley.
10. The Central Research Establishment in England was formed in 1966 and dedicated to performing basic research in forensic science (development of new forensic procedures, gathering statistical data, and collecting and disseminating vital information).

1. a. Silverstone, L. (1981, January). Queezy, *MAD*, 220, p. 43. E. C. Publications, Inc., 485 Madison Avenue, New York, NY 10022. A satire on a popular television show, "Quincy," about a medical examiner portrayed by Jack Klugman.
- b. *Murder in a Bookstore* (Treat, 1981). Used by permission of the publisher.

HUMOR: ON THE FUN SIDE

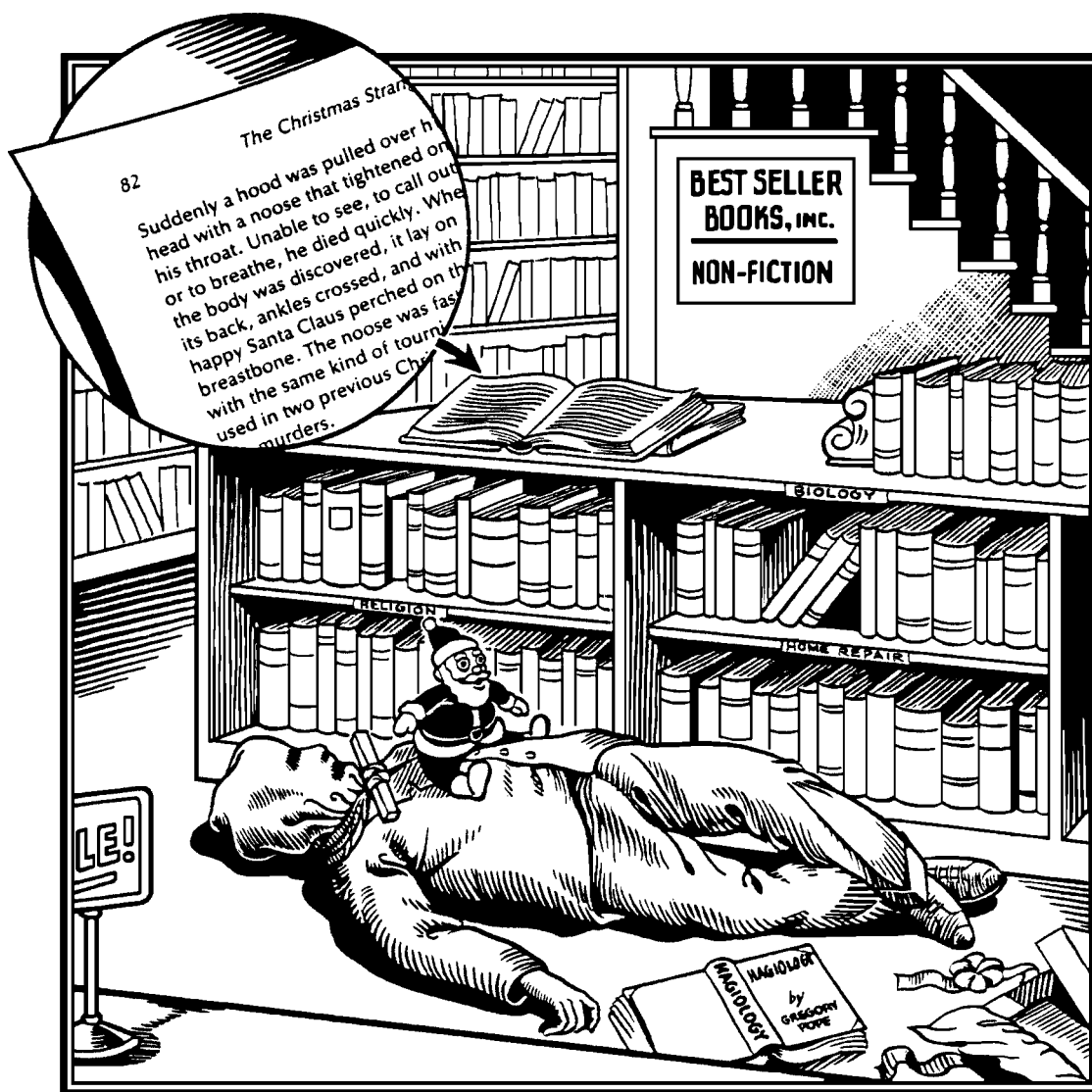


Figure 11. Murder in a bookstore.



On December 23rd the body of Quintus Tertius, a bibliophile, was found as shown in the basement of the Boswell Bookstore. Page 82 of *The Christmas Strangler*, by Elden Hack, lay open on a counter. Mr. Tertius, a regular customer, often rummaged in the stacks of books in the basement.

Eppis Pepys and his wife, Alice Pepys, were proprietors of the Boswell Bookstore. Each of them admitted having gone down to the basement within a half hour of the probable time of the murder.

E. Pepys said, "I went down to get a copy of Descartes' *Principles of Philosophy*. I saw no one in the basement."

A. Pepys said, "I went down to get a copy of Spinoza's *Ethics*. I saw no one in the basement."

From these facts and from an examination of the scene, can you tell who killed Quintus Tertius, and why?

Questions

1. Did Tertius commit suicide?
2. Is it likely that the murderer entered and left the bookstore without being noticed?
3. Do you think Tertius was reading *The Christmas Strangler* when he was accosted?
4. Did the murder method require preparation?
5. Do you think the killer brought his murder equipment with him?
6. Did Eppis Pepys have a motive for killing Tertius?
7. Did Alice Pepys have a motive for killing Tertius?
8. Do you think that the killer brought *The Christmas Strangler* with him?
9. Do you think that Tertius was engrossed in reading at the time of his murder?
10. Can you figure out a probable motive for this murder?
11. Who do you think killed Tertius?

Answers

1. No. You can't strangle yourself with a tourniquet. Don't try it!
2. Yes. December 23rd was at the height of the Christmas rush, when bookstores are crowded. Any bookseller can expand on the ordeal.
3. No. This was a nonfiction area frequented more by bibliophiles than mystery readers, and *Hagiology*, by Gregory Pope, lay open near the victim's hand, suggesting that he was reading this book when attacked by the murderer.
4. Yes. This is obvious from the presence of the tourniquet, the hood, and the gloating little Santa Claus, which are not objects ordinarily taken on a trip to a bookstore.
5. Yes. The opened package next to the body indicates how the murderer brought his equipment here.
6. No. You don't kill your customers. This is a rule that all booksellers follow faithfully.
7. No, for the reasons cited in (6).
8. Yes. This is a nonfiction area, where mystery novels would feel unwanted.

9. Yes. Otherwise it would have been difficult to throw a hood over him without leaving evidence of a fight.
10. Yes, publicity for the book.
11. Elden Hack, in order to get publicity for his book, which it got. And so did he.

c. CLUE™ Logic Problem

Logic problems are interesting and challenging forms of entertainment for many people. The challenge comes about because of the deductive reasoning processes that must be invoked. This example is developed around the game CLUE™, a copyrighted game produced by Parker Brothers. This version was developed and used by permission of Keith Berry.

Setting It was a very curious weekend when six victims (Kelly, Lynn, Robin, Leslie, Dana, and Chris) were invited by the owner of a great mansion (Colonel Mustard) and five of his friends (Miss Scarlet, Professor Plum, Mrs. Peacock, Mrs. White, and Mr. Green) to a grand party. Unfortunately, by the time the Inspector was called to the scene, all of the victims had died under strange circumstances, none before noon and none later than 10:00 P.M. on that Saturday.

Procedure Using the data statements below, you are to help the inspector determine who was killed in each murder, the weapon that was used by each, the room in which the crime occurred, the time at which each murder took place, the name of the victim for each of the murders, and the sex of each victim. All victims died in different rooms, at different times and from different weapons.

Data

1. Four victims were males, none of whom were killed before 2:00 P.M., shot, or found in the lounge, kitchen or conservatory.
2. Each murder occurred while the great grandfather clock was striking an even number. The clock sounded only on the hour.
3. Leslie and his twin sister arrived at 6:00 P.M., being greeted by their very good friend, Miss Scarlet, with whom they talked for 20 min.
4. The woman who used the candlestick killed a female in the conservatory.
5. Mrs. Peacock was in the library all afternoon, but was not strong enough to use a wrench.
6. Robin had once been married to Professor Plum and knew only him and her killer from among all those in the house when she got there early in the morning.
7. The person who fired the revolver in the lounge killed one of the twins after a person had already been stabbed to death.
8. The person who used the wrench used it at 4:00 P.M., just after the rope had been used and just before the knife was used.
9. All weapons were found in the room where they were used; none was found in the kitchen or dining room.
10. Kelly did not die before 5:00 P.M.
11. Professor Plum's victim was found in the study but had not been there when Colonel Mustard had gone in at 9:00 P.M.
12. The ballroom was being remodelled so no one could get into it.

Turn in your data table, noting what each type of mark represents.

Turn in your conclusions as to: murderer, room, time, weapon, victim, and victim's sex. See *Appendix* to make extra copies of data table.

Answers to Clue™ Logic Problem

	1	2	3	4	5	6
Murderer	Scarlet	Plum	Peacock	White	Green	Mustard
Room	Conserv.	Study	Library	Hall	Lounge	Billiard
Time	12:00	10:00	2:00	4:00	8:00	6:00
Weapon	Candle	Pipe	Rope	Wrench	Revolver	Knife
Victim	Robin	Leslie	Lynn	Chris	Dana	Kelly
Sex	Female	Male	Male	Male	Female	Male

2. Word Search (see *Appendix* for master copy)

B W Y Q P I K V E B C V T K J W T
 Y P H G X X W P T A N A L Y S I S
 P W W L Q C J X M U U D G C H L K
 O W G Z M L F E H J Q O S N E M M
 C T L C C H O P I Y L P P I D C Y
 S L M B S X A C S O P V G U N H D
 O X U N C R T M I F M N L Q A M E
 R X N J G M R B N X P C S I I R C
 T B E Y C A Z L A U Q S C K Z Z W
 C X L P E X T T O T S T D K A U F
 E O J R H C E I E L X A T Q M C U
 P E I J L D S J G Y L J P Y A Y O
 S F Z Y H P A R G O T A M O R H C

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Analysis technique used to separate mixtures into their component parts.
2. Another name for a lie detector.
3. Carrier of genetic information used by forensic chemists to match samples of body fluids to suspects (Abbrev.).
4. Separation technique using silica-coated glass or plastic plates (Abbrev.).
5. Technique used by forensic chemists to identify compounds by their interaction with radiation.
6. Forensic unit dealing with poisons or drugs.
7. Forensic unit dealing with blood, body fluids, hair, fibers, and botanical specimens.
8. Process of breaking down whole information available into its components.
9. Forensic unit that examines bullets, cartridge cases, and ammunition.
10. TV forensic chemist played by Jack Klugman.



Answers: 1. CHROMATOGRAPHY 2. POLYGRAPH 3. DNA 4. TLC
5. SPECTROSCOPY 6. TOXICOLOGY 7. BIOLOGY 8. ANALYSIS
9. FIREARMS 10. QUINCY

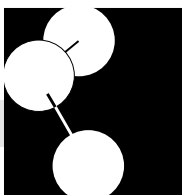
3. See cartoons at end of module.

MEDIA

1. Videotapes of "Demonstrations of Forensic Techniques," prepared by Everett Nienhouse, Vikas Productions, Department G, P.O. Box 6088, Bozeman, MT 59771-6088; (406) 587-9260.
Vol. 1 Basic Laboratory Measurements and an Introduction to Forensic Pathology.
Vol. 2 Forensic Microscopy: The Compound and Stereomicroscope
Vol. 3 Firearms Evidence Examination
Vol. 4 Analysis of Corrosive Materials; Acid/Base Concepts Encountered in Forensic Science
Vol. 5 Analysis and Identification of Drugs
Vol. 6 Gas Chromatography: The Analysis of Arson Debris
Vol. 7 Forensic Serology: The Analysis of Blood
2. Software published by *JCE: Software*, a publication of the *Journal of Chemical Education*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).
Spec20, by Ralph Gable and James McCormick. Vol. IV, No. 1, for IBM PS/2 PC-compatible computers.
3. Videodisc published by *JCE: Software*, a publication of the *Journal of Chemical Education*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).
"Mercury Determination Using a Spectrophotometer—Accuracy and Precision" and "A Generic Spectroscopic Instrument," two chapters on *The World of Chemistry: Selected Demonstrations and Animations*: Disc I (double sided, 60 min.), Special Issue 3.

INSTRUMENTA- TION

1. Spectronic 20
2. Simple gas chromatograph
3. Microscopes; polarized light microscopes
4. Electrophoresis (gel)



Links/Connections

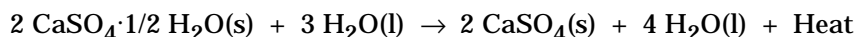
WITHIN CHEMISTRY

1. **Density.** A physical property. Because it is specific to the sample being measured (for example, glass), it can be used as a means of identification or comparison (see *Demonstration 1*).

Material	Density (g/mL)
Celluloid	1.4
Porcelain	2.3 - 2.5
Window glass	2.47 - 2.56
Headlight glass	2.47 - 2.63
Flint glass	2.9 - 5.9
Diamond	3.0 - 3.5

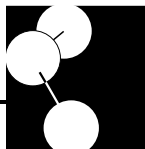
Figure 12. Density of common materials.

2. **Water of hydration** A compound in which water is an integral part of the crystal structure of a salt contains water of hydration. Plaster of Paris (calcium sulfate, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$) is used to make plaster casts. Prints from shoes and tires left in soil or sand can be preserved by making a plaster or plastic cast. When mixed with water, Plaster of Paris produces heat that drives off some of the excess water and leaves a solid product. When this mixture is poured into the depression left by a car tire or running shoes and allowed to harden, a cast can be obtained and compared to that of a suspected tire or running shoe.



3. **Elemental analysis**

- a. Heavy metal poisons (lead, arsenic) are determined by atomic absorption spectroscopy (see Item 8).
- b. Bullet lead contains a variety of trace elements whose concentrations vary with the bullet's source. A fired gun leaves invisible traces of antimony and barium on the firing hand from the cartridge primer (the exploding substance that propels the bullet). Cotton swabs moistened with dilute nitric acid are used to collect gunshot residues. The swabs are analyzed using flameless atomic absorption spectroscopy. Recently, the scanning electron microscope has been used to search for particles with features consistent with the gunpowder particles (intact or partially burned) combined with elemental analysis for lead, barium, and antimony using X-ray fluorescence.
- c. A variety of trace elements in paint pigments creates a difference in paint samples. The identity and quality of an element (Pb, Ti, Cr) present in a paint chip can help identify the source. Elemental analysis is performed by X-ray fluorescence or atomic absorption spectroscopy (see Item 8).
- d. The main elements in glass are sodium, silicon, and oxygen. Other elements are added to give glass color or a special property. Sometimes the element is present because of the mineral from which the glass is made. These elements can be detected and quantified using X-ray fluorescence.



4. **Qualitative chemical tests** Various routine chemical tests are used to identify gunshot residues, fabrics, drugs, blood, etc.
- Blood is usually detected by testing for heme (the porphyrin bonded to the protein portion of hemoglobin). Because heme acts as a catalyst, some tests for blood utilize hydrogen peroxide to oxidize compounds that result in a specific color change. For example, a stain can be identified as blood with a solution of phenolphthalein and hydrogen peroxide. This test depends on the fact that the hemoglobin present in the blood catalyzes the decomposition of hydrogen peroxide. The decomposition product oxidizes colorless, reduced phenolphthalein to pink-colored phenolphthalein.
 - When concentrated nitric acid is placed on wool or silk, a yellow color (which can be intensified with ammonia) due to the formation of xanthoproteic acid is formed. Only protein fibers, *e.g.*, wool and silk, give a positive test.
 - Smokeless powder contains nitrates. When a cartridge is fired and the powder burns, the nitrates are converted to nitrites. The presence of the latter on a fabric can help determine if a hole in the fabric was made by the passage of a bullet through the fabric. If the suspect weapon is available and the developed nitrite pattern is compared to patterns obtained from firing the weapon at known distances, the technique can be useful for determining a range of distance from the target to muzzle (homicide vs. suicide). To confirm nitrite, any particles remaining on the fabric surface are transferred to a chemically treated photographic paper that contains *p*-nitroaniline, 2-naphthol, and magnesium sulfate. Nitrite will form a red-colored complex with this mixture.
 - Qualitative tests for typically encountered drugs are summarized in the following table.

Substance	Reagent	Positive Test
Opium alkaloids: heroin, morphine, codeine	Formaldehyde/sulfuric acid	Violet color
Cocaine	Cobalt thiocyanate	Blue, flaky precipitate
Amphetamine	Cobalt thiocyanate	Orange color
LSD	<i>p</i> -Dimethylaminobenzaldehyde	Blue color
Tetrahydrocannabinol	Vanillin/acetaldehyde/ethanol/ chloroform	Purple color in chloroform layer
Barbiturates	Cobalt acetate/isopropylamine	Red-violet color

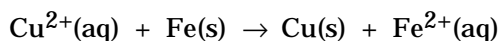
Figure 13. Tests for common drugs.

5. **Solubility** Many fibers can be identified by their solubility in selected solvents.

Figure 14. Fiber solubility.

Fiber	Solvent
Acetate	Boiling glacial acetic acid
Silk	Boiling 45% sodium hydroxide
Nylon	50% Hydrochloric acid
Wool	Boiling 5% sodium hydroxide
Cotton	70% Sulfuric acid
Dacron	55-60% Dimethylformamide (room temp.)

6. **Oxidation-reduction** Most commercial items are marked by the manufacturer as a means of identifying them. Usually marking is done by stamping a serial number (or other code) on the item. Even if the marking is sanded off, the surface can be treated so that the marking reappears to some identifiable degree. In the case of objects made of iron, etching solutions are used to restore obliterated markings. Etching solution contains acid and copper(II) ions. Iron, under stress from the marking stamp, will dissolve rapidly compared to the remainder of the metal according to the chemical equation:



This procedure requires patience, but the results are usually definitive for metal objects.

7. **Enzymes** Can be used to identify body fluids. Acid phosphatase is an enzyme secreted by the prostate gland into seminal fluid. Because its concentration in seminal fluid is much greater than in other body fluids, its presence can be used to characterize human seminal stains. If this enzyme is present in a specimen obtained from a rape victim, it causes certain dyes to give red-brown to violet-colored complexes.

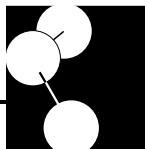
8. Instrumentation

- In X-ray fluorescence, the sample is subjected to an X-ray beam. The less energetic, fluorescent X-rays are emitted by the elements in the sample. The wavelengths of these X-rays are characteristic of the elements in the sample. The intensity of the X-ray at a particular wavelength is proportional to the concentration of the element in the sample. This technique leaves the sample intact.
- Bits of metal shavings or dust make good evidence. The metal is dissolved in acid and analyzed by atomic absorption spectroscopy. The intensity of light of a given wavelength that is absorbed by atoms of a given element that are heated in a flame is proportional to the amount of that element in the sample.
- Instrumental techniques are very useful for characterizing organic liquids—greases, oils, and gasoline. Gas chromatography (GC)-infrared spectrometry (IR) and GC-mass spectrometry (GC-MS) combinations are very useful for analyzing these organic materials.

Gas chromatography separates the individual organic compounds in the sample. These compounds are graphically recorded as individual peaks as each compound emerges from a chromatographic column. The peaks can be identified by infrared spectroscopy or mass spectrometry.

The infrared spectrometer gives a unique spectrum for each separated compound as the percentage of infrared radiation passing through a sample at different wavelengths.

The mass spectrometer breaks up each separated compound into a unique mass spectrum. In mass spectroscopy the molecules are converted to charged ions by electron bombardment. Each ion has a unique mass to charge (m/e) ratio. The various ions are separated by their m/e ratio using a magnetic field and then detected. Results are shown graphically.



The figures shown are the infrared and mass spectra of cocaine. The advantage of the combination lies in the fact that both infrared spectra and mass spectra are stored in data banks. Infrared and mass spectra can be matched with reference spectra by computer, thus providing a positive identification of the various organic compounds in the sample.

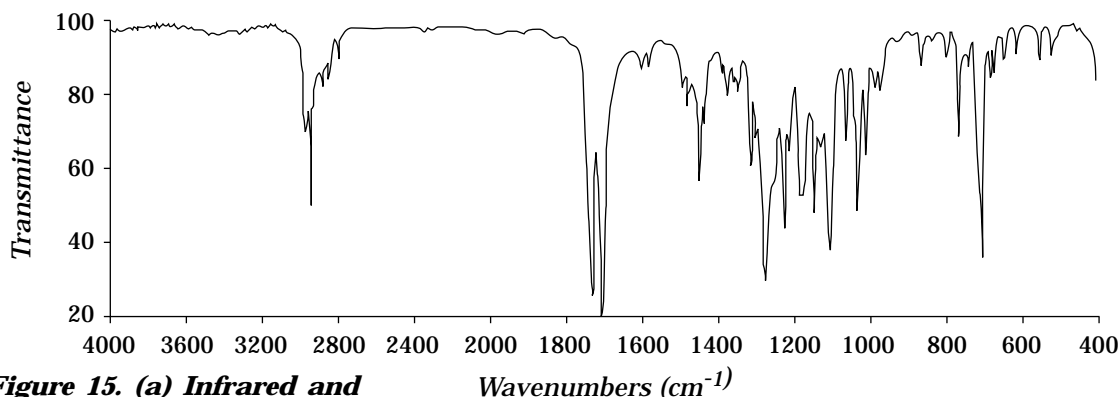
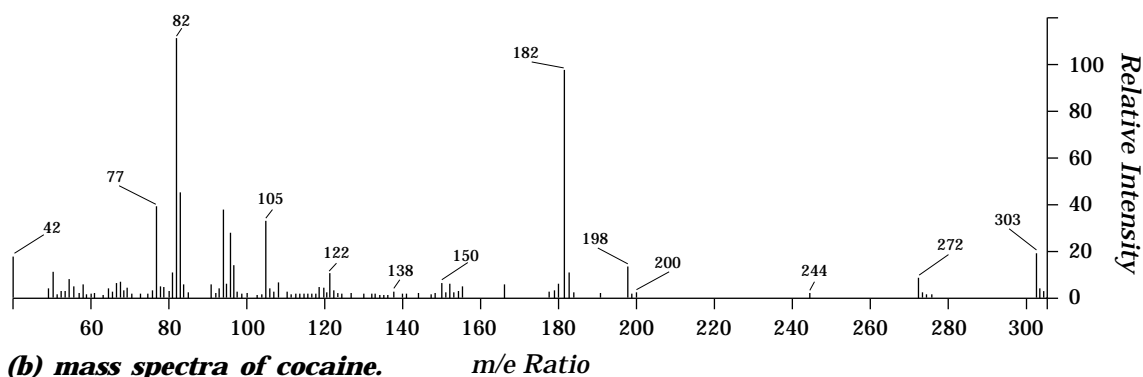


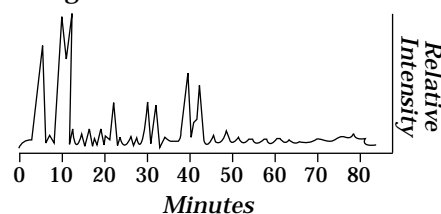
Figure 15. (a) Infrared and



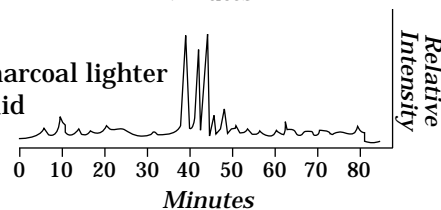
(b) mass spectra of cocaine.

d. Highly flammable hydrocarbons are often used to start a fire as well as spread it. If the container (plastic, metal) that held the hydrocarbons is left at the arson scene, the debris and residues that are left after the container and contents have burned can be analyzed. The debris sample is placed in a container (a new, unlined paint can), sealed, heated to 60-110 °C to separate the hydrocarbon vapors from the debris. A sample of the air above the debris is removed by a syringe and analyzed by gas chromatography. This technique can often distinguish hydrocarbons in Diesel fuel, gasoline, charcoal lighter fluid, and paint thinner.

Leaded gasoline



Charcoal lighter fluid



Diesel fuel

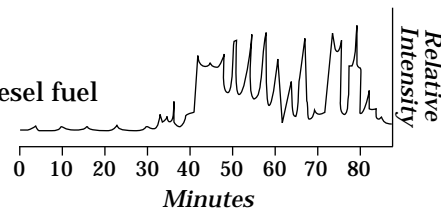


Figure 16. Gas chromatographic analysis of hydrocarbon mixtures.

- e. In addition to colored chemical tests, analysis of drugs can be carried out by ultraviolet spectrometry, high-performance liquid chromatography and thin-layer chromatography.

In ultraviolet spectrometry, ultraviolet (UV) light of different wavelengths is passed through a sample, and the amount of absorbed light is recorded at each wavelength. The resulting absorption spectrum is characteristic of a particular drug (see Figure 17). The identity of the drug is generally confirmed using the specific chemical test.

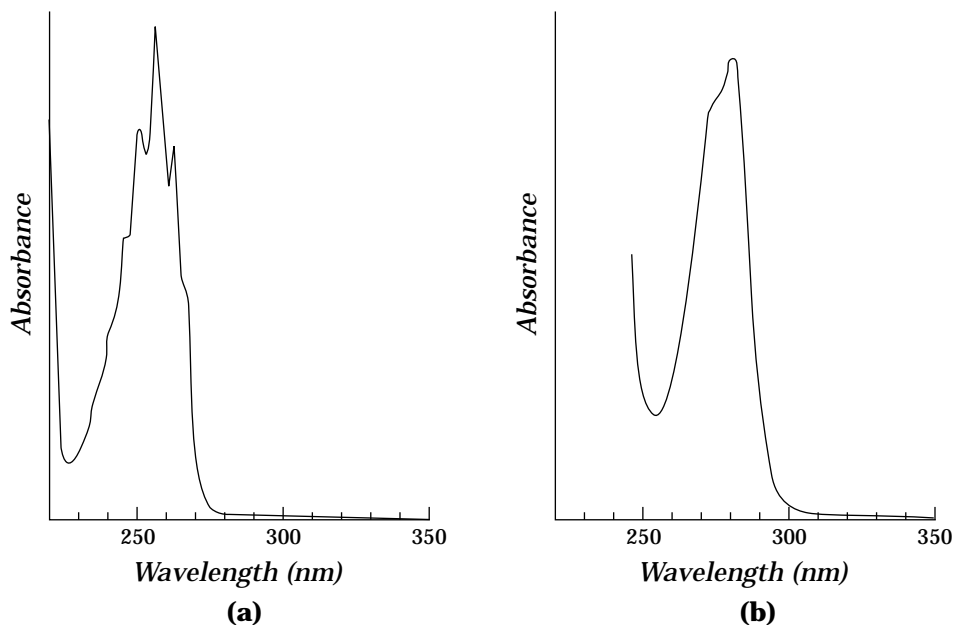
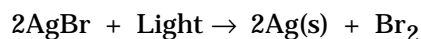


Figure 17. Ultraviolet spectra of (a) amphetamine and (b) heroin.

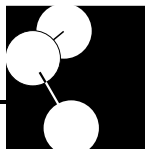
For drugs that do not vaporize without decomposition, high-performance liquid chromatography (HPLC) is used for identification. Instead of using gas to carry sample through the column (GC), solvent under high pressure is used.

Thin-layer chromatography (TLC) is a simpler analytical method. A separation is performed on a rectangular glass slide coated with a thin layer of adsorbent SiO_2 . The sample is spotted at one end of the slide, and this end dipped into a solvent that rises up the slide as it soaks the layer of adsorbent. Different materials in the sample are carried at different rates and are separated. The spot can be made visible by treatment with iodine and/or ultraviolet light (black light). Some spots will fluoresce (*i.e.*, glow under UV light). The retention times of each spot are compared with those of known compounds and identified. In addition to drugs (see *Activity 1*), TLC can be used to identify lipsticks and ink dyes.

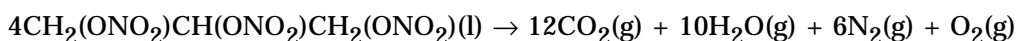
9. **Photography** Useful in criminal investigation. Photography uses silver bromide (AgBr) suspended in a gelatin emulsion mounted on a plastic (cellulose acetate) support film. Exposing the silver bromide to light (when the camera shutter is opened), produces metallic silver and bromine (which then reacts with other materials in the film).



The dark silver particles produce an image that can be developed by further chemical processing. Color photography is a more complicated process.



10. **Explosives** The criminal use of explosives is generally motivated by sabotage, mischief, revenge, or the desire to destroy property. Most bombing incidents involve the use of homemade explosives and incendiary devices. Forensic chemists are responsible for detecting and identifying both explosive chemicals and detonating mechanisms found at the crime scene. An explosion is a chemical reaction that proceeds at a rapid rate. There is a sudden buildup of large volumes of gas with enormously high pressures that cause a violent, physical disruption of the immediate environment. The decomposition of liquid nitroglycerin, produces four gaseous products, and is shown in the equation:



Examples of explosives are shown in Figure 18. Nitrogen and oxygen are the key elements in these explosives.

Name of explosive	Chemical composition
Black powder	Potassium nitrate, charcoal, sulfur
Single-base smokeless powder	Nitrocellulose
Double-base smokeless powder	Nitrocellulose and nitroglycerin
Dynamite	Nitroglycerin and ethylene glycol dinitrate (for stability)
TNT	2,4,6-Trinitrotoluene

Figure 18. Composition of explosives.

There are several simple color tests performed to screen for the presence of explosives. The tests are usually done on acetone-water extracts. Common explosives (black powder is an exception) are organic compounds that tend to be soluble in this solvent mixture. One reagent, Griess reagent, consists of sulfanilic acid, acetic acid, and 2-naphthylethylenediamine.

Explosive	Griess reagent	Diphenylamine
Nitrate	Pink to red	Blue
Nitrocellulose	Pink	Blue-black
Nitroglycerin	Pink to red	Blue
TNT	No color	No color

Figure 19. Color tests for explosives.

If sufficient amounts of explosives are recovered, confirmatory tests may be performed by infrared spectroscopy or X-ray diffraction.

Explosives are also used for commercial purposes: to remove barriers for construction of a tunnel through a mountain, to help excavate earth for building foundations, to destroy old buildings to make way for a modern structure, and as propellants for rocket engines (controlled “explosions”).

11. **Organic chemistry** An organic compound, 1,8-diazafluorenone (DFO), has been found useful for detecting latent fingerprints. Now available to forensic science laboratories, DFO reacts with α -amino acids producing a red, fluorescent substance. DFO is 2-3 times more sensitive than ninhydrin and is very useful for detecting latent fingerprints on paper.

BETWEEN CHEMISTRY AND OTHER DISCIPLINES

1. **Physics** In addition to color and density, refractive index is a useful way for identifying glass. Refractive index is the degree to which a beam of light bends as it passes from air into a solid or liquid.

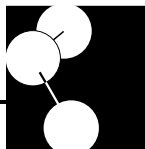
Glass	Index of refraction
Pyrex™ glass	1.47
Headlight glass	1.47 - 1.49
Television glass	1.49 - 1.51
Window glass, bottles	1.51 - 1.52
Ophthalmic lenses	1.52 - 1.53
Light flint glass	1.6

Figure 20. Refractive indices for glasses.

2. **Geology** Soil is a common form of physical evidence. Soil samples are analyzed to determine if they have a common origin. The methods include a density profile and settling rate curve. For example, a soil sample is dried and sieved. (Sieves containing 200 wires per in² = 200 mesh; 50 wires per in² = 50 mesh, *etc.* The higher the mesh size, the finer the particles.) A small amount of a desired mesh size (usually 30-45 g) is placed on the top of a column containing layers of immiscible liquids of different densities. Heavy particles will settle to their level in a few minutes. Light particles may take a few hours to stop moving. The soil profile at the scene is then compared to the soil profile from the suspect. (The same technique can be used to determine the density of small glass fragments.)
3. **Biological Science** Blood contains characteristic factors based on blood groups. A person's blood contains proteins called antibodies. Human blood can be grouped into types A, B, O, and AB, depending upon the antibodies present in the serum. If blood from people of other blood types are mixed, agglutination (clumping together) will occur. All four types can be identified by this method. Blood typing can be useful (but not conclusive) in establishing possible parents of children.

Blood proteins are controlled by genetics and are rather specific for an individual. The best tool for distinguishing blood proteins is electrophoresis. Proteins are electrically charged at a given pH. In the presence of an electric current and at the appropriate pH, the proteins migrate at different rates toward the positive electrode separating into different spots along the way. The spots are stained with ninhydrin, making them visible. Their relative positions are used to identify individual proteins (see *Enzymes* module).

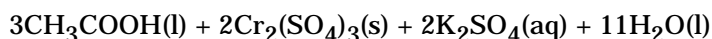
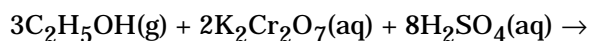
4. **Biological Science** DNA Profiling is a new technique that helps identify suspects from bodily traces (blood, semen, hair) often left at a crime scene. DNA consists of four bases attached to each other in pairs and connected like a zipper into a double helix pattern. The exact sequence of bases is unique to each person (except identical twins), somewhat like a fingerprint. To link a suspect to the crime, DNA is extracted from physical evidence found at the scene of a crime. Scientists split the DNA pairs into fragments and the fragments are separated into bands by electrophoresis. The fragments are mixed with radioactive bases that bind to the DNA as pairs as in the original sequence. When exposed to X-ray film, the DNA pattern appears in bands resembling a bar code on supermarket products. The DNA pattern from the evidence is compared to the DNA pattern in the suspect's blood sample.



TO THE CONTEMPORARY WORLD

1. **Court witness** The forensic chemist is often called to testify as an expert in civil and criminal cases. In criminal cases, forensic chemists may be asked to explain the identification (chemical test, analytical instrumentation, reliability of test, *etc.*) of a drug found in the body of a deceased person. In civil cases, he/she may testify in cases involving water quality, product liability, *etc.*

2. **Driving while intoxicated (DWI) and the Breathalyzer** The Breathalyzer has been shown to be a reliable, noninvasive instrument for forensic alcohol analysis. The chemistry of the Breathalyzer involves the reduction of orange potassium dichromate by ethanol contained in the breath of the test subject.



The reduction product, $\text{Cr}_2(\text{SO}_4)_3$, is a green solid. The Breathalyzer scale provides a percent blood-alcohol concentration. A value of 0.10% is the minimum amount for being legally intoxicated and subject to a DWI conviction (see *Demonstration 1* in *Chemistry in Medicine* module).

3. **Computers** In forensic laboratories computers can collect and store voluminous quantities of laboratory data. Minicomputers link local crime laboratories *via* telephone lines to large, perhaps national, computers. Such systems facilitate the collection of reference information on glass, paint, tire prints, shoe prints, and headlights. Computers can help with interpretation of data; instead of manually comparing and subjectively evaluating chromatograms of drugs, accelerants, paints, plastics, *etc.*, computers can be used to precisely scrutinize and compare samples to references by pattern recognition algorithms.

4. **Literature** As forensic science developed in police laboratories, fiction writers began to base some characters in their novels on forensic scientists. Sherlock Holmes is perhaps the most popular fictional detective. He is noted for solving crimes by the application of science. He recognized the odor of iodoform, the black mark of silver nitrate on a finger, and readily confirmed Watson's diagnosis concerning the "pleasant almondy odor" of a "small blue bottle" as prussic acid in Arthur Conan Doyle's *The Veiled Lodger*. The chemical discovery of which Holmes is most proud is described in *A Study in Scarlet*. "I've found it! I've found it!" he shouted, running toward us with a test-tube in his hand. 'I have found a reagent that is precipitated by hemoglobin and by nothing else.' In an instant, the contents assumed a dull mahogany color, and a brownish dust was precipitated to the bottom of the glass jar." [See Gillard, R. D. (1976). *Sherlock Homes: Chemist. Education in Chemistry*, p. 10.] However, Arthur Conan Doyle was surprisingly uninformed in science and Sherlock Holmes, as a scientific detective, perhaps was not really the scientist we thought. [See Asimov, I. (1983). *The roving mind, Part IV Science Opinion*, "Sherlock Holmes as a Chemist," Prometheus Books, Buffalo, NY.]

Ian Rae [Dustcoats in dust jackets. (1983). *Chemistry in Britain*, 19, 565.] discusses other authors who use chemistry in their novels, including Austin Freeman whose *Famous Cases of Dr. Thorndyke* (Hodder and Stoughton, London, 1929; reprinted 1965) contains much chemistry. In this book, Freeman describes the Marsh test for arsenic, including its distinction from antimony (using hypochlorite), and a description of an attempted poisoning by atropine that relied on secretion of this substance in eggs of pigeons that had been fed belladonna.

Dorothy Sayers apparently had learned some chemistry and used it in several of her novels. *Strong Poison* (Gollancz Publisher, London, 1930) deals with the ability of a practiced arsenic eater to withstand a dose that kills his victim. There is also an account of the Marsh test for arsenic. In *The Documents in the Case*, Sayers and Robert Eustace base the apprehension of a murderer on the stereoisomers in poisonous mushrooms. The poisoning occurred with the racemic mixture, indicating the death was not accidental.

Forensic chemistry is mentioned in other poisoning whodunits. Thallium poisoning was discussed in Agatha Christie's *The Pale Horse* (Fontana, London, 1972; first published 1961). Ngaio Marsh's *Final Curtain* (Middlesex Penguin, 1961; first published 1947) gives a sketchy description of the chemistry of embalming and the flame test for thallium.

Many of J. J. Connington's stories involve forensic chemistry. Connington was the pen name of A. W. Stewart, a professor of chemistry at Queen's University (Belfast, 1919-1944). *The Counsellor* (Hodder and Stoughton, London, 1939) discusses mescaline trances and *Jack in the Box* (Hodder and Stoughton, London, 1944) contains a poisoning with nickel tetracarbonyl.

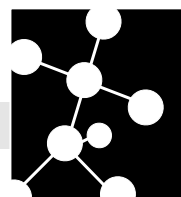
Forensic science techniques have been used in several recent fictional and nonfictional books. The following is a brief listing:

Ted Bundy: The Killer Next Door by Steven Winn
The Man Who Killed Boys by Clifford Linedecker
The French Connection by Robin Moore
Coma by Robin Cook
Fatal Vision by Joe McGinnis
The Third Deadly Sin by Lawrence Saunders
The Michigan Murders by Edward Keyes
The Boston Strangler by Gerald Frank
The Wood-Chipper Murder by Arthur Herzog

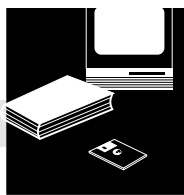
5. Community Resources

- a. Guest speaker from a local police department crime laboratory, the state crime laboratory, or the local medical examiner's office.
- b. Field trip to the local police department or crime laboratory.
- c. Guest speaker on uses of forensic chemistry in archaeology.
- d. Invite a race track tester or large-animal veterinarian for a classroom discussion on testing for drugs in horses.
- e. A museum curator is generally a good person to discuss art frauds.

Extensions



1. Examine the hairs of different people within a family, hairs of pets, *etc.*
2. Take broken glass samples from window pane, pop bottles, and headlight glass, and an unknown glass (from a roadway). Determine their densities using methods described in this module and try to identify the unknown glass.
3. Using a stereomicroscope, compare various paint chips (or flakes) obtained from cars in a junk yard. Mount the samples in putty or clay to hold on the scope and observe an edge to check for color layering.



References

Module drafted by Philip Ogata, James Schreck, and Courtney Willis, the Colorado (North) team.

Many ideas for laboratory activities in this module are from the personal collections of the following individuals. Their generosity in the use of their material is greatly appreciated and acknowledged.

Keith O. Berry*
Department of Chemistry
University of Puget Sound
Tacoma, WA 98416

Jan Harris
Cy-Fair High School
Rt. 12, Box 8B
Houston, TX 77040

Tom J. Griffin
Colorado Bureau of Investigation
690 Kipling
Denver, CO 80215

Everett Nienhouse
Physical Sciences Department
Ferris State University
Big Rapids, MI 49307

Barber, J. (1985). *Crime lab chemistry. Teacher's guide. Great explorations in math and science (GEMS)*. Berkeley, CA: Lawrence Hall of Science, University of California.

An activity (chromatography, separating mixtures, pigments, and solubility) in which students assume the role of a crime lab chemist and determine which black pen was used to write a ransom note.

Benfey, O. T. (Ed.). (1969). *Chemistry, 42(7)*. Washington, DC: American Chemical Society.

This entire issue is devoted to forensic science, including origins of modern criminology, scientific methods of crime investigation, and chromosomes and crime.

Robson, D. (Ed.). *ChemMatters*. Washington, DC: American Chemical Society.

Each issue contains a *Mystery Matters* feature that discusses an application of forensic science and chemistry to the real world.

Gerber, S. (Ed.). (1983). *Chemistry and crime: From Sherlock Holmes to today's courtroom*. Washington, DC: American Chemical Society.

Techniques used in crime novels both influence and reflect the scientific basis of crime detection.

James, R., Meloan, C., and Saferstein, R. (1980). *Laboratory manual for criminalistics*. Englewood Cliffs, NJ: Prentice Hall.

A set of laboratory experiments for the novice student that demonstrates what happens to physical evidence when sent to a forensic laboratory.

Labianca, D. (1990). The chemical basis of the breathalyzer: A critical analysis. *Journal of Chemical Education, 67*, 259-261.

Lewis, R. (1988). DNA fingerprints: Witness for the prosecution. *Discover, 9(6)*, 44-52.

A new courtroom drama unfolds as the basic material of life itself is called to the stand.

* deceased, March 30, 1993



Manahan, S. (1982). *General applied chemistry* (2nd Ed.). Boston, MA: Willard Grant.

Chapter 21, "Chemistry and Crime," is an introduction to forensic chemistry.

Outlaw, H. E., and Berry, K. (Eds.). (1985). Forensic chemistry—A symposium collection. *Journal of Chemical Education*, 62, 1043-1060.

Pavia, D., Lampman, G., and Krutz, G. (1988). *Introduction to organic laboratory techniques* (3rd Ed.). New York, NY: Saunders.

Laboratory Activity 1 was adapted from this text.

Saferstein, R. (1990). *Criminalistics: An introduction to forensic science* (4th Ed.). Englewood Cliffs, NJ: Prentice Hall.

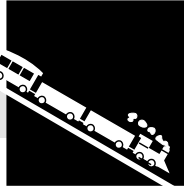
A presentation of the techniques, skills and limitations of the modern crime laboratory for the reader with no background in the forensic sciences.

Treat, L. (1981). *Crime and punishment*. Boston, MA: David R. Godine Publisher.

Twenty-four solve-them-yourself picture mysteries.

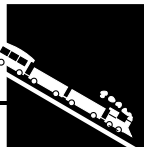
Zonderman, J. (1990). *Beyond the crime lab: The new science of investigation*. New York, NY: John Wiley & Sons.

This book bridges the gap between the basic and advanced treatments of physical evidence in forensic sciences. It describes how computerized databases can help draw conclusions about victims and suspects, as well as how high-technology surveillance equipment can help keep a close watch on individuals under investigation.

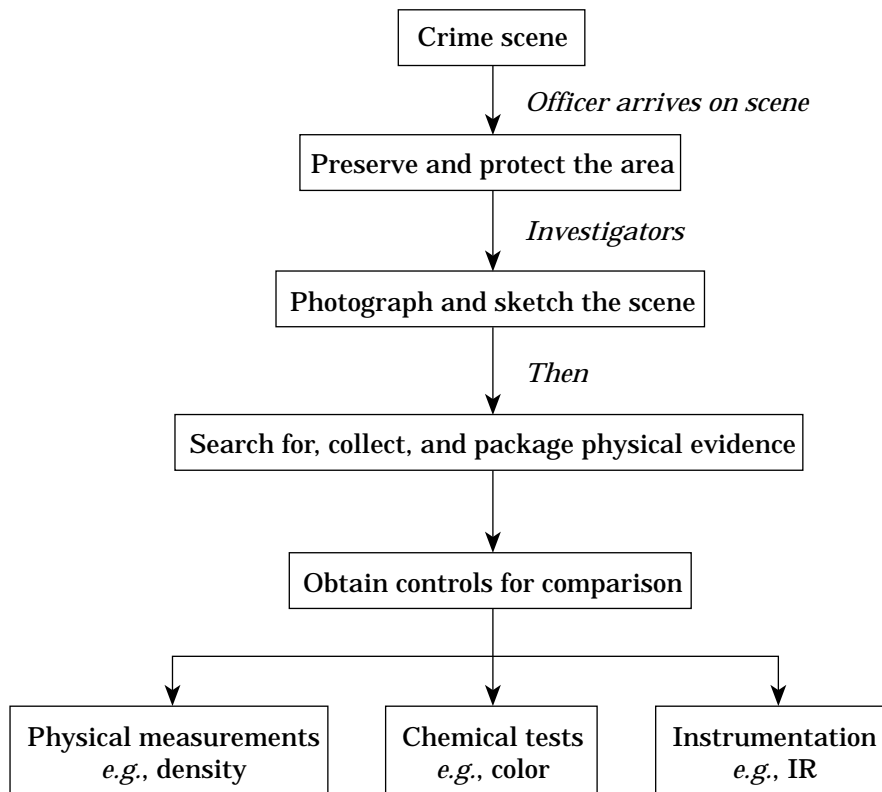


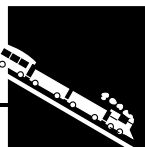
Appendix

- **Transparency Masters**
 1. Flow Chart for a Criminal Investigation
 2. CLUE™ Logic Problem Data Table
 3. Word Search
- **Humor**



Flow Chart for a Criminal Investigation





Word Search

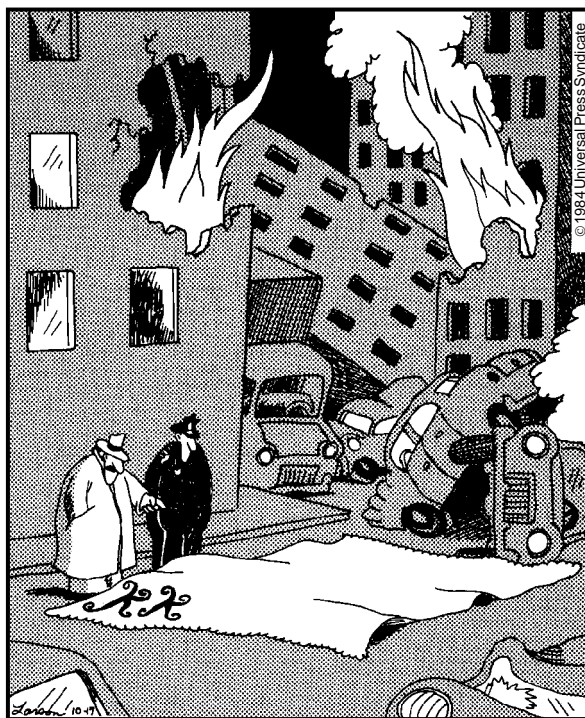
B W Y Q P I K V E B C V T K J W T
Y P H G X X W P T A N A L Y S I S
P W W L O C J X M U U D G C H L K
O W G Z M L F E H J Q O S N E M M
C T L C C H O P I Y L P P I D C Y
S L M B S X A C S O P V G U N H D
O X U N C R T M I F M N L Q A M E
R X N J G M R B N X P C S I I R C
T B E Y C A Z L A U O S C K Z Z W
C X L P E X T T O T S T D K A U F
E O J R H C E I E L X A T Q M C U
P E I J L D S J G Y L J P Y A Y O
S F Z Y H P A R G O T A M O R H C

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Analysis technique used to separate mixtures into their component parts.
2. Another name for a lie detector.
3. Carrier of genetic information used by forensic chemists to match samples of body fluids to suspects (Abbrev.).
4. Separation technique using silica-coated glass or plastic plates (Abbrev.).
5. Technique used by forensic chemists to identify compounds by their interaction with radiation.
6. Forensic unit dealing with poisons or drugs.
7. Forensic unit dealing with blood, body fluids, hair, fibers, and botanical specimens.
8. Process of breaking down whole information available into its components.
9. Forensic unit that examines bullets, cartridge cases, and ammunition.
10. TV forensic chemist played by Jack Klugman.

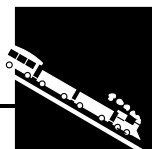
THE FAR SIDE

By GARY LARSON



“Take this handkerchief back to the lab, Stevens. I want some answers on which monster did this—Godzilla? Gargantua? Who?”

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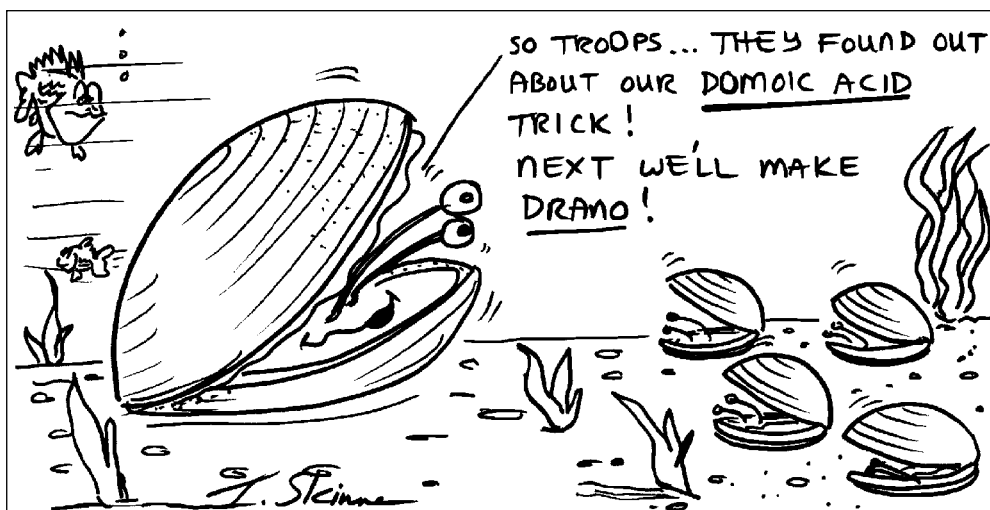
Calvin and Hobbes

by Bill Watterson



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DOMOIC ACID POISONS CLAM EATERS



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