GENERAL INFORMATION ON FORENSIC 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, $CaSO_4 \cdot 1/2\ H_2O$) 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.

$$2\ CaSO_4 \cdot 1/2\ H_2O(s) + 3\ H_2O(l) \rightarrow 2\ CaSO_4(s) + 4\ H_2O(l) + \text{Heat}$$

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.*

   a. 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.

   b. 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.

   c. 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.

   d. 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	*p* -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.

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.)

Figure 14. Fiber solubility.

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:

$$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$$

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 prostrate 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**

   a. 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.

   b. 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.

c. 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.

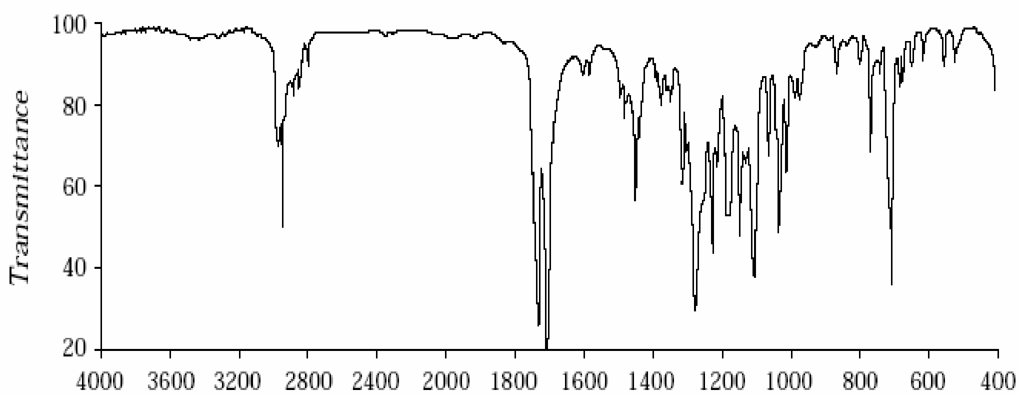
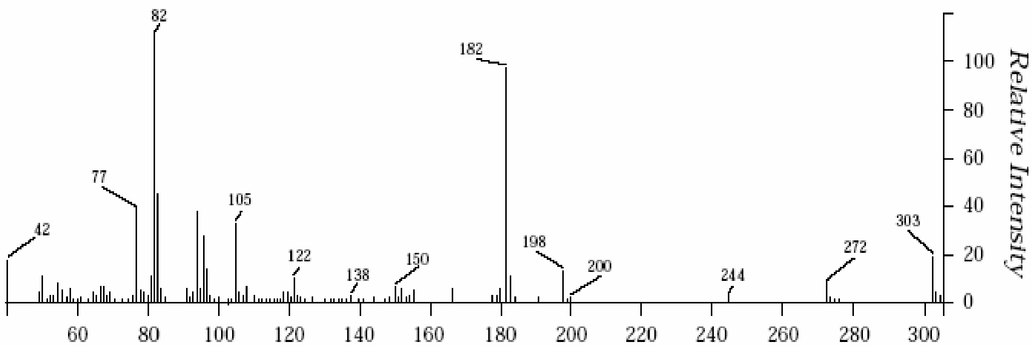


Figure 15. (a) Infrared and



(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.

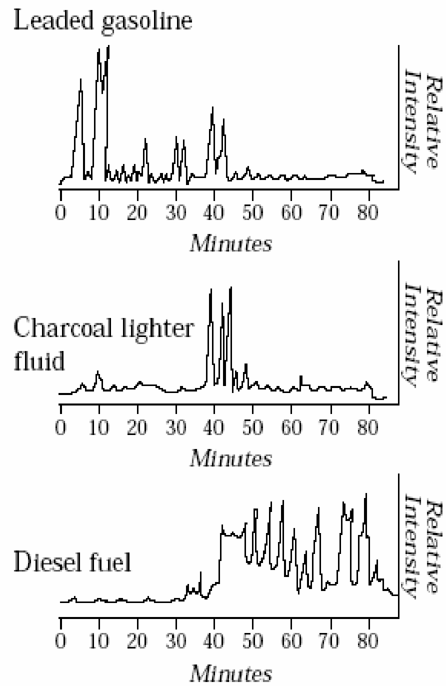


Figure 16. Gas chromatographic analysis of hydrocarbon mixtures.

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.

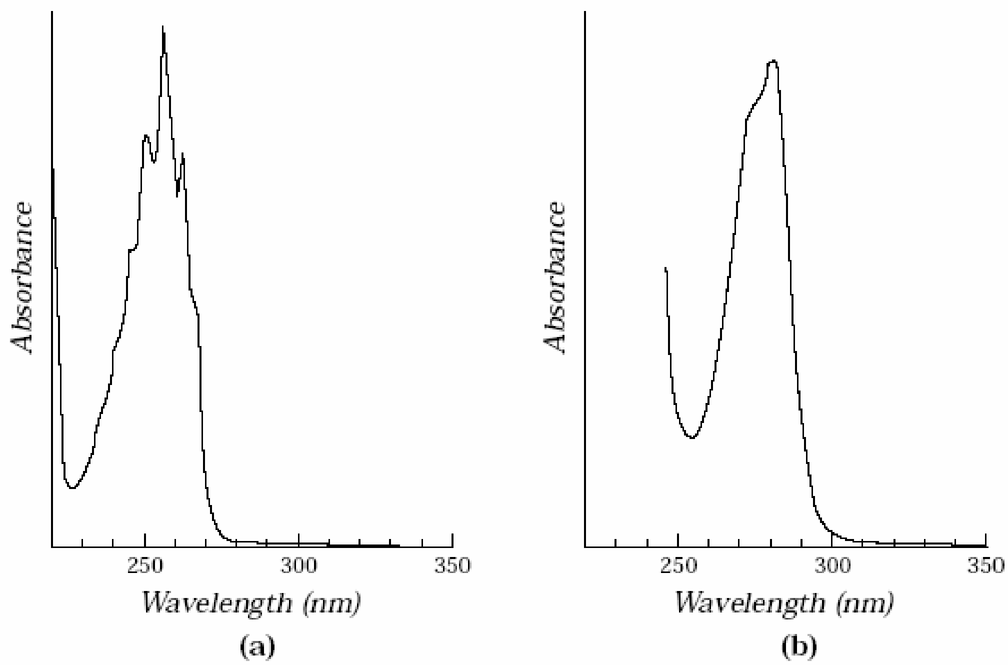


Figure 17. Ultraviolet spectra of (a) amphetamine and (b) heroin.

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).

$$2AgBr + \text{Light} \rightarrow 2Ag(s) + Br_2$$

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:

$$4CH_2(ONO_2)CH(ONO_2)CH_2(ONO_2)(l) \rightarrow 12CO_2(g) + 10H_2O(g) + 6N_2(g) + O_2(g)$$

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 areanalyzed 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 in^2 = 200 mesh; 50 wires per in^2 = 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.

$$3C_2H_5OH(g) + 2K_2Cr_2O_7(aq) + 8H_2SO_4(aq) \rightarrow$$
$$3CH_3COOH(l) + 2Cr_2(SO_4)_3(s) + 2K_2SO_4(aq) + 11H_2O(l)$$

The reduction product, $Cr_2(SO_4)_3$, 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.