Chapter 9 Trace Evidence

Objectives

After reading this chapter, you will understand:

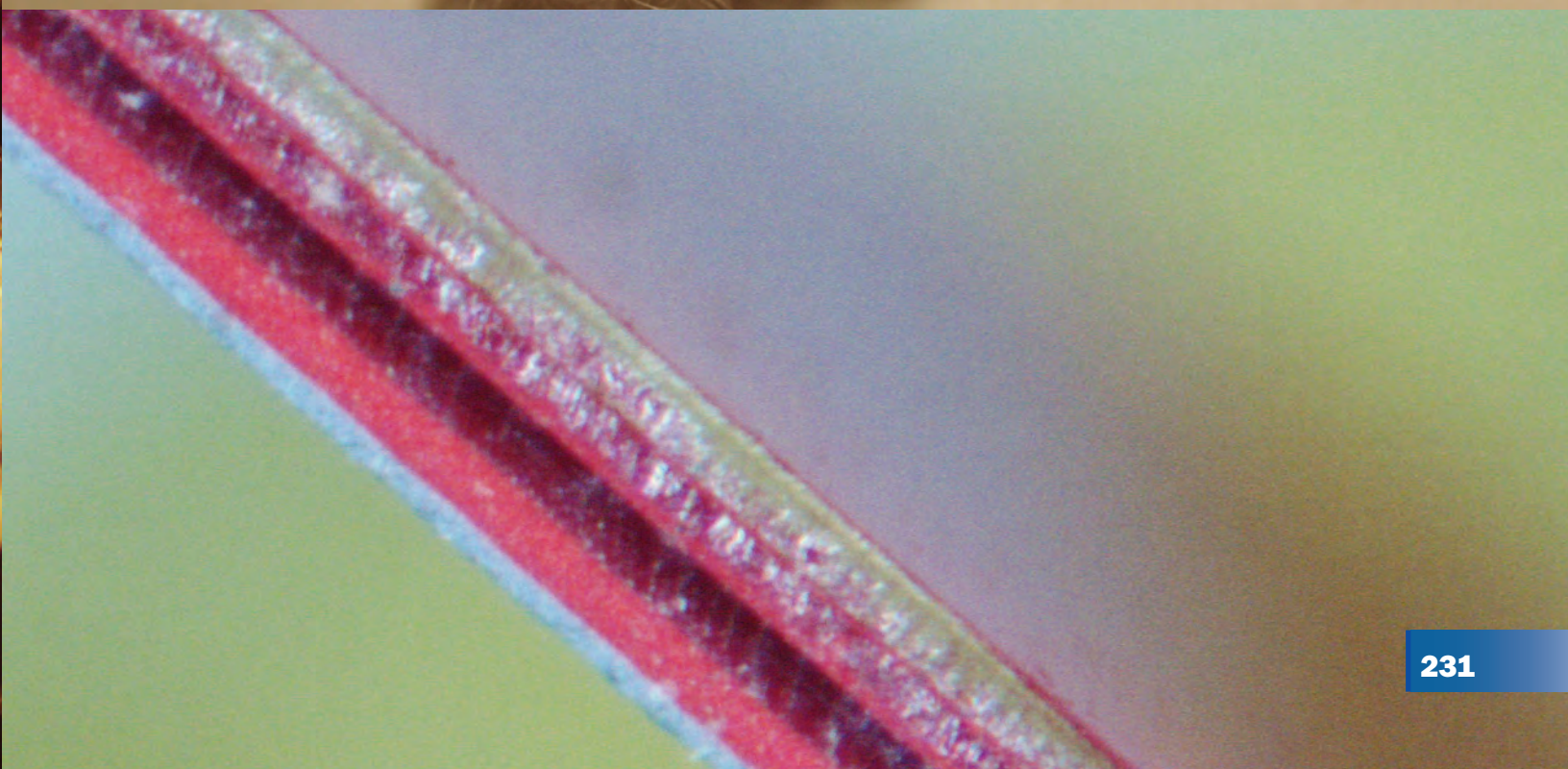
- How to apply deductive reasoning to analytical data.
- How to follow qualitative analytical schemes.
- How to gather and use information to solve problems.

You will be able to:

- Identify traces of white powder.
- Identify metals.
- Classify lip prints.
- Compare paint chips from hit-and-run cases.
- Use chromatography to compare lipsticks.
- Design and conduct scientific investigations.
- Identify questions and concepts that guide scientific investigations.
- Communicate and defend a scientific argument.

"Breadth of view is one of the essentials of our profession. The interplay of ideas and the oblique use of knowledge are often of extraordinary interest."

—*Arthur Conan Doyle's Sherlock Holmes, in* The Valley of Fear



Trace Evidence at the Crime Scene

Teacher Note

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

Trace evidence is physical evidence found in small amounts at a crime scene—items too small to make a physical match, yet large enough to be analyzed. Common examples would be hair, fiber, paint chips, body fluids, stains, powders, explosive and gunshot residues, glass particles, vegetative matter, metal particles, soil, and even odors. Occasionally, even large objects will wind up in the trace evidence lab. (In one case, a hockey puck was left at the scene of an attempted rape!) .

Activity 9.1 How Well Can You Identify Trace Evidence?

"You know my method. It is founded upon the observation of trifles."
—Sherlock Holmes in *The Boscombe Valley Mystery*

In your notebook, write what you think each object or material is, how you would go about learning more about it, and what probative value it might have. For example, item #1 is a key. A locksmith might be able to tell what type of lock it fits. This happens to be a mailbox key which could lead to a name.

Teacher Note

Answers and suggestions/ideas:

2. Cement. Look for recent construction or masonry at the site; ask local contractors.
3. A black twist tie. Usually black twist ties tie electronic cables; check local computer, video service providers.
4. Chewing gum. Looks like a breath-freshener type. Smell it. Who chews gum?
5. Broken lead from a red pencil. Look for a teacher!
6. Thin copper wires. Twisted strands of copper wire can be used to connect electronic components. See #3. Where is the insulation?
7. A fingernail. Who chews their fingernails? Look at suspect's hands. This looks large—large fingers? Thumb?
8. Fishing line—a clear plastic leader. Look for a fisherman.
9. Part of a banana peel. Where is the rest of it? If in the garbage, check for fingerprints. Or head for the zoo.
10. A burnt match. Pipe smokers may use a wooden match.

Trace evidence may corroborate other evidence and provide links connecting objects, individuals, and locations.

This chapter covers several examples of trace evidence analysis not covered in the rest of the text:

Metals: You will look at a way of detecting metals from a product liability case and an environmental contamination problem solved with paper chromatography and some detective work.

Powders: We will use a qualitative chemical scheme to identify a set of white powders.

Lipstick: A comparison of lip prints leads to a robbery suspect, and thin-layer chromatography of lipstick components solves a murder.

Paint: Microscopic examination can sometimes solve a hit and run.

Teacher Note, *continued*

11. A red seed. Appears rather exotic; take it to a nursery or botanist.

12. Red pigment. Perhaps used for making pottery or by an artist.

13. Wood shaving, from a plane. Look for a carpenter.

14. Short-grain rice. A recent wedding?

15. A pearlescent button. From a shirt, blouse? Too bad no thread was attached.

Metals: Product Liability?

Often investigators must identify small bits of metal that have been found in the soil, swept up from the carpet or floor of a crime scene, or found contaminating a consumer product.

For example, a lawyer calls you with a problem. He has a client who baked a loaf of whole-wheat bread. As the family was eating it for supper, they complained of hard bits and pieces in it; the client even broke her tooth biting down on one of the pieces.

Examining the bread and flour, they found a number of what appeared to be metallic particles. Family members had already swallowed some of these particles, and now they were worried more about poisoning than about the broken tooth.

The client called the lawyer, intending to sue Happy Miller, the company that made and sold what seemed to be contaminated flour. The lawyer wants you to analyze these particles. If indeed they are metallic, could they have come from the machinery used to produce the flour? If so, shouldn't Happy Miller recall all its whole-wheat flour packages? Or did the client purposely add some contaminant to the flour to extort money from Happy Miller?

The bread in question

A few quick phone calls reveal that the grinding, separating, mixing, and filling equipment at the flour mill is made of high-chrome stainless steel and brass.

The family seems ordinary enough. The client has had problems with her teeth—lots of

fillings, with not all costs covered by dental insurance. Her husband is a welder at a local construction plant and is partially blind in his left eye.

Your task is to analyze the contaminating particles, determine what they are, and give an opinion as to where they came from and how they got into the flour. Construct a table in your notebook for your observations or use the handout from your teacher.

Laboratory Activity 9.1

Identification of Metals

Caution: The chemical reagents that you will be using are strong acids and bases that can burn your skin and ruin your clothing, so wear your safety glasses, apron, and gloves; follow instructions; don't make a mess; and wash up afterward. In addition, some of the reagents smell bad or can form noxious vapors and gases. Be careful!

Advance Preparation

Refer to Blackline Masters 9.1 and 9.2 for use with this activity. Check with your Kendall/Hunt representative for supplies. Bromoform is also available from chemical supply houses such as Aldrich (www.sigmaaldrich.com/catalog/search/AdvancedSearchPage) or Flinn Scientific. It is also used in Chapter 10, "Soil and Glass Analysis." Note: Bromoform is toxic. Use it in a well-ventilated place. Minimize students' handling of it. Dispose of it by evaporation. Bromoform darkens with age, even stored in a brown bottle, making it useless for density measurements. It can be cleaned up, however, by mixing it with a fine activated charcoal and then filtering.

6 M sodium hydroxide (NaOH): 24 g/100 ml water

6 M nitric acid (HNO_3): dilute concentrated 1:2 (1 part acid to 2 parts water). *Always add acid to water and wear your safety goggles.*

Materials

For each group:

- metal standard samples: copper, magnesium, aluminum, lead, zinc, iron,nickel, chromium
- test tubes
- hand magnifier or stereoscope
- 10-ml beaker with 5-ml bromoform (keep under hood)
- magnet
- forceps
- 6 M sodium hydroxide (NaOH)
- 6 M nitric acid (HNO_3)
- 6 M hydrochloric acid (HCl)
- 6 M ammonium hydroxide (NH_4OH)
- 6 M acetic acid
- 0.1 M sodium sulfide (Na_2S)
- 0.1 M potassium chromate (K_2CrO_4)
- 0.1 M potassium thiocyanate (KSCN)
- 3 percent hydrogen peroxide
- S & O reagent
- aluminon reagent
- dimethyl glyoxime solution
- unknown sample(s) of contaminating particles
- test tube rack
- safety goggles
- lab apron
- disposable gloves
- small beaker of alcohol

SAFETY ALERT! CHEMICALS USED

Always wear goggles and an apron when working in the labaratory

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

Procedure

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

Physical Tests

You must first determine the **physical properties** of these eight metals: copper (brass contains copper), magnesium, aluminum, lead, zinc (galvanized iron contains zinc), iron, nickel, and chromium (stainless steel contains iron and chromium). These tests are the easiest and are nondestructive.

1. Observe a sample of each metal under magnification. Note their size, shape, color, and any other characteristics that may aid in identification. Record your observations.
2. Test the metals to identify which are magnetic. Record your observations.

Of these eight metals, aluminum and magnesium are very light; their densities are 2.70 and 1.74 g/cc, respectively. All the other metals are heavier, with densities greater than 7.0 g/cc. The density of liquid bromoform is 2.89 g/cc. Will aluminum and magnesium float in it? What is the density of water?

3. Test the density of your samples, using the bromoform under the hood. Use your forceps to retrieve the samples; then swish them around in the beaker of alcohol next to the bromoform to clean them off so that you can use them for further tests. *Caution: Bromoform is toxic. Use it in a well-ventilated place.* Record your observations.
4. Lead is soft and **malleable**. Can you scratch it? Bend it?
5. Observe the physical properties of the unknown(s). Can you predict what it (they) might be?

Chemical Tests

Now you can test the **chemical properties** of your samples.

6. Set up 16 test tubes in two rows in a test tube rack. Place one test tube in the third row. Add *one* piece of each of the known metals to the eight test tubes in the first row and one piece to each of the test tubes in the second row. These will be your standards.
7. Add 1 ml of HNO_3 to one of each of the test tubes in the first row; note any reaction. Be patient; sometimes it takes longer for certain reactions to occur.
8. Add 1 ml of NaOH to the set of test tubes in row 2. Observe and record what happens.
9. Add a sample of chromium and 1 ml HCl to the test tube in the third row.
10. If there appear to be different metal particles in your unknown sample, separate them and drop each into a clean test tube.

physical properties: characteristics that do not involve a change in the identity of a substance, such as odor, color, boiling point, density, and refractive index

malleable: capable of being shaped, bent, or drawn out; flexible

chemical properties: characteristics that determine how a substance will change to another substance with different physical properties

Advance Preparation, *continued*

6 M hydrochloric acid (HCl): dilute concentrated 1:1 (1 part acid to 1 part water)

6 M ammonium hydroxide (NH_4OH): dilute concentrated 1:2

6 M acetic acid: dilute concentrated 1:2

0.1 M sodium sulfide solution: 2.4 g $Na_2S \cdot 9H_2O$/100 ml water

0.1 M potassium chromate solution: 1.94 g K_2CrO_4/100 ml water

0.1 M potassium thiocyanate solution: 0.97 g KSCN/100 ml water

All of the above are available from science supply houses as made-up solutions. They cost a little more but are definitely worth the savings in time and trouble if you don't have this kind of material in your lab or school.

11. Repeat the tests you performed on the standards on your unknowns.

You may be pretty sure of what your samples are by now, but it is important, especially in forensic science, to be as sure as you can possibly be. After all, someone's life may depend upon it. The confirmatory tests listed in steps 12 through 19 are used to verify, or disprove, results. Do you have to run *all* these confirmatory tests on your unknown flour contaminants? After you have narrowed the possibilities, pick the appropriate tests to identify the contaminating particles. Run a known standard if you are unsure of any outcome.

12. If you think you have aluminum, confirm it by adding two drops of aluminon reagent to the test tube containing your unknown sample in the NaOH. Mix and let it set for a while. A pink, gel-like layer at the bottom of the test tube confirms the presence of aluminum.
13. If you think you have copper, confirm it by adding NH_4OH to the HNO_3 solution until you get a deep blue solution.
14. If you think you have magnesium, confirm it by adding one to two drops of S & O reagent to the sample in the HNO_3; then slowly add NaOH until you see a fluffy, blue precipitate or gel.
15. If you think you have zinc, confirm it by adding a few drops of sodium sulfide solution (Na_2S) to the metal in the HNO_3 and look for a yellowish or white precipitate.
16. If you think you have iron, confirm it by diluting your acid solution 10 or more times with water until it is almost clear. Add a drop of potassium thiocyanate solution (KSCN) and note a brown-red or red color.
17. If you think you have lead, confirm it by adding an equal amount of acetic acid (HAc) to the HNO_3 solution. Do it in the hood, because HAc smells pretty bad—like very strong vinegar. Mix, and add a few drops of bright yellow potassium chromate solution (K_2CrO_4) to get an orange precipitate.
18. If you think you have nickel, confirm it by adding twice the amount of NH_4OH to the acid solution, mix, and add a few drops of dimethyl glyoxime reagent to form a red-violet precipitate.
19. If you think you have chromium, confirm it by noting what happened when you added the HCl to the chromium. Look for the same reaction and add several drops of H_2O_2. A momentary yellow color should appear.

Conclusions

Based on the results of your analyses, what are the contaminating particles in the flour? Write an opinion paper as to where they came from and explain why you think so. It is not enough in a court of law to say, "It looks like copper to me"; you must back up your opinions with physical and chemical testing.

Advance Preparation, *continued*

3 percent hydrogen peroxide

S & O reagent: Dissolve 1 g NaOH in 100 ml water, then add 0.5 g p-nitrophenyl-azoresorcinol. Dilute 5 to 10 times. This produces a sky-blue precipitate with Mg. Co and Ni interfere. The solution is available from Flinn, as is solid p-nitrophenyl-azoresorcinol (Flinn Scientific; www.flinnsci.com).

Aluminon reagent: Dissolve 1 g aluminon (ammonium salt of aurin tricarboxylic acid) in 1 L water. For best results, add ammonium acetate to make a pH of 4.5 to 5.5, then add ammonium hydroxide and ammonium carbonate to adjust the pH of the solution to 7.1 to 7.3. Under these conditions, only Fe interferes. Aluminon is available from Flinn also.

Dimethyl glyoxime: Make a 1 percent solution in ethanol: 1 g dimethyl glyoxime in 100 ml ethanol. This is available from Flinn (don't use their 0.1 percent solution; it's too weak).

Metals (Al, Cr, Cu, Fe, Mg, Ni, Pb, Zn): You can purchase these from supply houses, but most are easy to obtain. It is good to have two different forms of them, with one to use strictly as an unknown just to throw off any student preconceptions.

You can opt for contamination from the factory by using chromium and iron and nickel (stainless steel) or copper and zinc (brass). Or you can use aluminum and magnesium, which could come from a welding shop. Clean the Al and Cu with steel wool prior to cutting it up.

Flush all solutions and precipitates down the drain with lots of water. Save the metal pieces, dry, and discard in the wastebasket or use again.

Some analytical schemes are described in the flow chart shown in Figure 9.1.

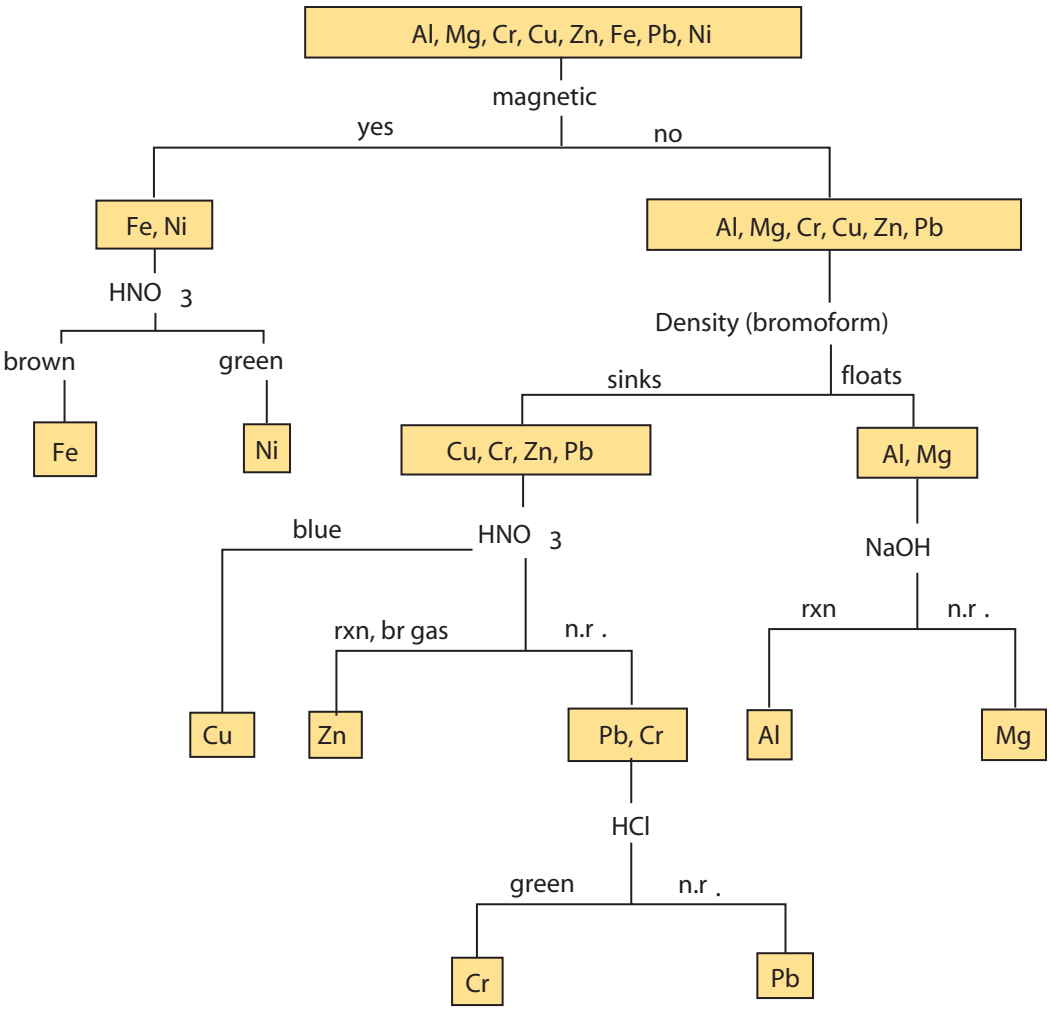


Figure 9.1 Metals analytical scheme for Laboratory Activity 9.1

Teacher Note

Figure 9.1 is also included as Blackline Master 9.2 on the TRCD for use with Laboratory Activity 9.1.

Table T9.1: Table of Observations

Metal	HNO_3	NaOH	Confirmatory Tests	Magnetic	Density
Al	n.r	bubbles	pink gel	no	floats
Mg	violent rxn, br gas	n.r.	blue ppt	no	floats
Cr	n.r.	n.r.	gr in HCl yel in H_2O_2	no	sinks
Cu	blue	n.r.	deep bl	no	sinks
Zn	voilent rxn, br gas	n.r.	yel/wh ppt	no	sinks
Fe	bubbles, turns br	n.r.	red	yes	sinks
Pb	n.r.	n.r.	or ppt	no	sinks
Ni	slow bubbles	n.r.	violet ppt	yes	sinks

Metals: Environmental Contamination

Mr. Calamine's farmland

Mr. Calamine owns a farm on the lowlands of the Marggraf River. Traditionally, early spring rains flood the sections of the farm that support his annual peanut crop. Last year, his peanut harvest was a disaster—the plants hardly grew, even though they had enough water. Later that summer, sheep that had been grazing the pastures near the river became sick. Mr. Calamine began to wonder if something out of the ordinary was going on.

A neighbor pointed out to Mr. Calamine that he should look to the river for answers because several new industries had started production upriver:

- a plant that manufactured rechargeable batteries
- a company making brass hardware

Mr. Calamine's peanut harvest during a regular year

Mr. Calamine's sheep prior to getting sick

Industrial effluent into the Marggraf River

- an operation producing specialty Alnico magnets for the recycling industry

Mr. Calamine has sent samples from the water's edge of his farm to your environmental forensic lab, asking for a qualitative analysis of the following dissolved metals: Al, Co, Cu, Ni, Zn.

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TOPIC environmental forensic science
CODE forensics2E239

Testing for Environmental Contamination

Laboratory Activity 9.2

In the previous problem, solid metal samples were individually analyzed using their physical and chemical properties. In this analysis, you will use paper chromatography to separate the dissolved components, visualization techniques to observe them, and controls to identify them.

Paper chromatography is based on the partitioning or separation of substances between a solid absorbent medium and a liquid solvent. The affinity of the unknown substance for each phase determines the degree of separation; this affinity might be related to the sample's solubility, polarity, or even its size. In this activity, the absorbent is filter paper, also referred to as the **stationary phase**, and the solvent is acetone/HCl, also called the **mobile phase**.

stationary phase: the fixed adsorbing medium of analytes in chromatographic separations

mobile phase: the carrier of analytes in chromatographic separations; also called the developing solvent

Materials

For each investigative group:

- 800- to 1,000-ml beaker with cover
- open capillary tubes
- safety goggles
- ruler
- strips of filter or chromatography paper
- developing solvent (mobile phase): HCl, acetone
- metal ion standards: Al^{+3}, Co^{+2}, Cu^{+2}, Ni^{+2}, Zn^{+2}
- oxine (8-hydroxyquinoline)
- Beral pipettes
- ammonium hydroxide
- sodium sulfide solution
- UV light
- river water sample

SAFETY ALERT! CHEMICALS USED

Always wear goggles and an apron when working in the labaratory

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

Procedure

Record your observations in your notebook and use the data table provided by your teacher.

1. **Draw a line, in pencil, 1 cm from the bottom of each piece of chromatography paper and put a tick mark in the center of the line.**
2. **Label the top of each paper with the name of the material to be analyzed.**
3. **Using an open-ended capillary for each of the metal ion standards, gently touch the tick mark to transfer a drop onto the paper. Try to keep the spot smaller than 3 mm. Let it dry. Repeat several times, drying in between.**
4. **Find a way to hang the chromatography strips in the developing tank so that they do not touch each other and are 1 or 2 mm off the bottom (see Figure 9.2).**
5. **Add sufficient mobile phase so that the bottom of each strip is immersed, but keep the level well below the spot. *This is important!***

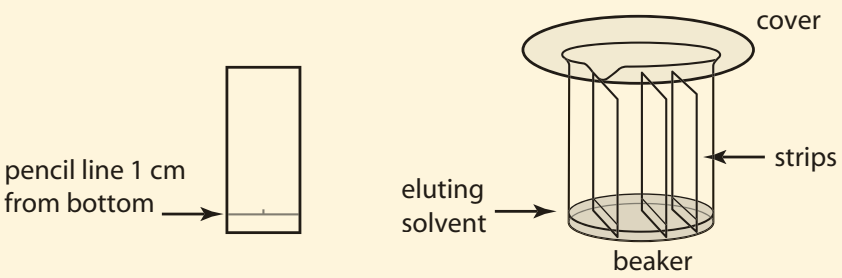

Figure 9.2 Preparation for paper chromatography

Advance Preparation

Hand out copies of Blackline Master 9.3, found on the Teacher Resource CD, to be used with this lab.

Metal ions: Prepare a set of standards by dissolving each of the following in 100 ml of distilled water:

Al^{+3}: 0.9 g $AlCl_3 \cdot 6H_2O$

Co^{+2}: 0.4 g $CoCl_2 \cdot 6H_2O$

Cu^{+2}: 0.3 g $CuCl_2 \cdot 2H_2O$

Ni^{+2}: 0.4 g $NiCl_2 \cdot 6H_2O$

Zn^{+2}: 0.2 g $ZnCl_2$

The weighing need not be precise, because you need only approximate 1 percent solutions of the metal ion. Dilute a portion of each solution about tenfold to make a 0.1 percent standard solution, bottle it up for each student's or group's experiment, and label it. Mix the 1 percent copper and zinc solutions about equally, dilute 1 to 4 with muddy water, bottle the mixture, and label it. This will be the unknown.

Use Whatman No. 1 filter paper or chromatography paper cut into strips about 12 cm long and 2 cm wide. Separate strips are better than having several different spots on a larger paper because of cross-contamination of eluted spots at the final solvent front.

For the developing solvent (mobile phase), add 10 parts 6 M HCl to 35 parts acetone (hardware purity is fine). *Caution: The mobile phase is strongly acidic; wear safety goggles.* A chromatography developing tank can be an 800–ml to 1000-ml beaker. Cover only the bottom 2 to 3 mm with the solvent.

The students should have found copper and zinc. You may have gotten a few "eeeww" reactions when they saw the muddy

6. Add the chromatography strips and cover the top of the developing tank with a glass plate or plastic film. *Note: The mobile phase is strongly acidic. Wear safety goggles and follow good laboratory practices!*
7. Watch as the solvent front creeps up the strips, and remove them when the front approaches within 1 cm of the top. Mark the solvent front with a pencil.
8. Note the location and color of any spots. Air-dry the strips overnight or in an oven at less than 50°C. Again, observe each strip.

When substances being separated are colorless, various techniques may make them more visible. In this lab, you will use several methods, going from the least destructive to the most.

9. Examine the chromatograms under long-wave ultraviolet light in a darkened room and outline any spots lightly with a pencil.
10. Develop the strips with ammonia, either by spraying them with a fine aerosol of ammonium hydroxide or by suspending them above concentrated ammonium hydroxide; use a hood in either case.
11. Dry the strips and note any color development.
12. Spray the strips with an organic compound (oxine). Oxine forms a fluorescent complex molecule with certain metal ions. Allow the strips to dry, noting any fluorescence at long-wavelength UV light.
13. Finally, if you are still not sure about the location or behavior of a metal, spray the strip with a sodium sulfide solution, preferably in a hood. What sort of chemical reaction does this cause, and why is it useful for many metals?
14. Compare your control chromatograms—the knowns—to the unknown sample from Mr. Calamine's farm. Can you offer an opinion about its constituents?
15. The retention factor, R_f, is used to characterize and compare components of samples (see Figure 9.3). Calculate the R_f value for each of the spots on the chromatogram:

$$R_f = \frac{\text{distance from origin to spot}}{\text{distance from origin to solvent front}}$$

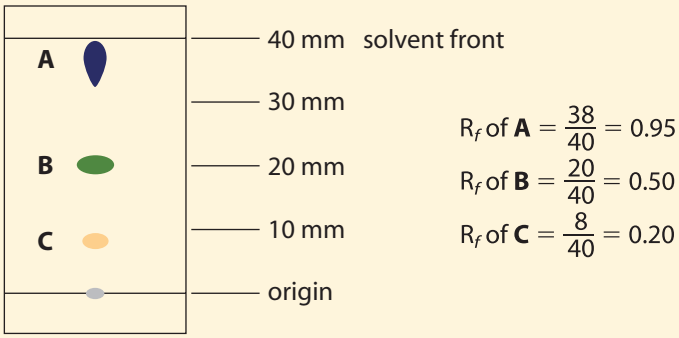

Figure 9.3 Chromatogram with retention factors

Make a table in your notebook or use the one handed out in class to record your observations.

Advance Preparation, *continued*

sample. Why didn't it cause a problem? The separation was strictly physical in this case. Centrifugation or filtration also would have taken care of it.

Advance Preparation

The next step for the students is to find out what metal(s) each new industry uses in their production. This can be done on the Web with judicious choice of search words, such as "rechargeable battery composition." Alnico magnets are named for the elements they contain. Students should come to the conclusion that the manufacturer of brass hardware is the culprit. The really good student will tie everything together with floodwaters depositing dissolved copper and zinc in the soil. Peanuts are very sensitive to zinc, as are sheep to copper; but will the grass take up enough copper to cause the sickness?

Your visualizing agents, in the order used, will be:

Long-wavelength ultraviolet lamp: A black light (ultraviolet light) is available from any scientific supply house or rock shop. One with just the long wavelength is adequate for this activity and considerably cheaper. *Caution: Ultraviolet light can severely damage eyesight. Do not allow anyone to look at it directly.*

Ammonia: Use in a fume hood or well-ventilated spot.

Oxine: This is 8-hydroxyquinoline or 8-quinolinol. It is used as an analytical reagent and a fungicide. It is a bit expensive, so check your local college chemistry department. Otherwise, it can be purchased

Advance Preparation, *continued*

from Fisher Scientific (https://www1.fishersci.com). Dissolve 0.25 g in a mixture of 20 ml ethanol and 40 ml distilled water.

The oxine solution should be stored in a dark, plastic bottle until pronounced discoloration occurs.

Sodium sulfide: Prepare 100 ml of fresh 0.1 M solution by dissolving 2.4 g $Na_2S \cdot 9H_2O$ in 100 ml of distilled water. Use the solution from the previous lab activity.

In the quantities used, all reagents and solutions can be flushed down the drain.

Laboratory Activity 9.2, *continued*

16. **What materials did you find in Mr. Calamine's water sample?**
17. **Now the question arises: Where did these pollutants come from? Is there a source upriver that can be identified? Here is where the detective work comes in; use your knowledge and research, using the Web to support any conclusions. Write a report defining the problem and describing your lab procedure and results, analytical conclusions, method of determining the polluting source, and any other pertinent observations and data to reconstruct what happened. Be aware that you may be called as an expert witness in a civil suit.**

Qualitative Analysis of Powders

When investigators find substances at the scene of a crime and send them to the laboratory for identification, the forensic chemist uses several techniques or lab tests to identify them. In the following laboratory activity, you will examine some basic physical and chemical properties, such as solubility, reaction with an acid, and reaction with a base. You will be able to easily identify and distinguish between substances that seem to be alike in a preliminary examination.

Some products that consist of white powders

Teacher Note

Table T9.2 goes with Laboratory Activity 9.2.

Table T9.2: Chromatography Visualization

Solution	UV	NH_3	Oxine-UV	Na_2S	R_f*
Al	neg	neg	fluoresces	light gray	0.3
Co	neg	red	neg	black	0.4
Cu	neg	blue	neg	brown	0.75
Ni	neg	light blue	neg	black	0.2
Zn	neg	neg	fluoresces	neg	1.00
Unknown	neg	blue	fluoresces	brown	0.75, 1.00

*May differ slightly from these values depending upon HCl/acetone ratio, type of paper, and the like.

In 1912 Emile Gourbin, a bank clerk in Lyon, France, was suspected of strangling his girlfriend, Marie Latelle. Gourbin was arrested but had what appeared to be an air-tight alibi. Edmond Locard went to Gourbin's cell and removed scrapings from under his fingernails. The scrapings contained tissue that was possibly from Marie's neck, but this could not be proved. Locard noticed that the tissue was coated with a pink dust, which he identified as rice starch. On the particles he found bismuth, magnesium stearate, zinc oxide, and a reddish iron oxide pigment called Venetian red. Examination revealed that a face powder prepared for Marie by a Lyon druggist was similar in composition. In these days of mass-produced cosmetics, this would have far less significance; but in 1912, because of the special preparation, this evidence led to Gourbin's confession.

Analysis of White Powders

Laboratory Activity 9.3

Advance Preparation

Refer to Blackline Master 9.4 for use with Laboratory Activity 9.3.

You have ten numbered samples of unidentified white powders, listed on the next page. You will observe their chemical and physical properties to identify them. Record your observations in your notebook. Your goal is to identify each of the numbered samples by its chemical name.

White powders

Materials

For each investigative group:

- unknown white powders numbered 1 through 10
- test tube rack
- test tubes
- stereomicroscope
- iodine solution
- distilled water
- phenolphthalein
- spatula
- spot plate or weighing tray
- isopropyl alcohol
- acetic acid
- 0.3 M NaOH
- glass stirring rod

continued

Materials, *continued*

Your task is to identify the numbered powders from the following list:

- sodium chloride (NaCl), salt
- sodium carbonate (Na_2CO_3), baking powder
- sodium bicarbonate ($NaHCO_3$), baking soda
- sodium hydroxide (NaOH), lye
- boric acid (H_3BO_3)
- calcium sulfate ($CaSO_4$), gypsum
- calcium carbonate ($CaCO_3$), chalk
- starch (cornstarch)
- sucrose (sugar)
- magnesium sulfate ($MgSO_4$), Epsom salts

SAFETY ALERT! CHEMICALS USED

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

Advance Preparation

0.3 M NaOH: Dilute 6 M 1:19 (one part 6 M NaOH, 19 parts water)

vinegar (which is 5 percent acetic acid), or dilute concentrated acid 1:20, or dilute the 6 M acid used in the first activity about 1:10

iodine solution (tincture of iodine): 4 g iodine crystals, 6 g KI in 100 ml water or alcohol

phenolphthalein solution: 1 g in 50 ml ethyl alcohol and 50 ml water

isopropyl alcohol (rubbing alcohol)

Procedure

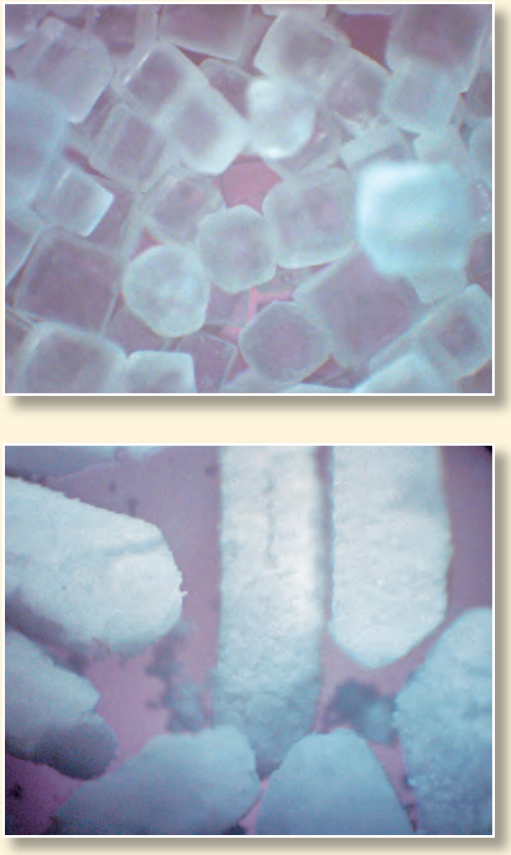
Do not write in your textbook. Take notes in your science notebook.

1. Using a stereomicroscope or magnifying glass, examine each of the samples to be tested and note any differences. Do not touch them. Use a spatula to place a very small amount in a weighing tray; then discard the powder into the sink. All reagents and samples are environmentally benign. Record your observations.
2. Test for solubility by placing a small amount of each sample (about the size of a pea) in a test tube. Add half a test tube of water. Mix by flicking the test tube or use a stirrer. If you use a stirrer, be sure to wash it before using it in another test tube; otherwise you may contaminate one substance with another. (Imagine if this were to occur in a crime laboratory; you might produce a false positive that could send an innocent person to jail!) Indicate next to each number in your data table whether the powder is soluble or insoluble.
3. Three of the samples will not dissolve readily and will appear to be the most cloudy: starch, $CaSO_4$, and $CaCO_3$. If starch is present, a drop of iodine solution added to the test tube will form a deep blue starch–iodine complex. (This reaction was used in Chapter 4, "Fingerprints.") You now have one of your samples identified.
4. If the iodine test is negative, carefully **decant** by pouring the liquid out of the test tube, leaving the solid at the bottom. Add 1 cm of acetic acid. The appearance of carbon dioxide gas bubbles (CO_2) indicates that the sample is $CaCO_3$. If there is no gas, the sample must be $CaSO_4$. You have now identified

decant: to pour off the top layer of liquid after the bottom material has settled

two more of the ten powders; label them and set them aside.

5. The remaining solids are water-soluble. Two of them, NaOH and Na_2CO_3, produce strongly alkaline solutions (basic, the opposite of acidic) that will turn bright pink with the addition of the phenolphthalein indicator. Choose the two that have the most vibrant pink color. One is NaOH, and the other is Na_2CO_3.
6. Add 1 cm acetic acid to each sample that turned bright pink. The vigorous evolution of CO_2 indicates the presence of Na_2CO_3. If there is no gas, or only a small amount, the sample must be NaOH. Identify and label these samples.
7. Add 1 ml of 0.3 M NaOH to each of the remaining five unknowns. They will turn violet if phenolphthalein has already been added. Identify the sample that becomes cloudy; this means that a precipitate is being formed. The sample is $MgSO_4$.
8. Prepare new samples of the four remaining solids. Adding acetic acid will produce CO_2 gas that will identify the $NaHCO_3$.
9. Of the three solids left, only H_3BO_3 is soluble in alcohol. Add half a test tube of isopropyl alcohol to fresh samples of the three remaining powders. Identify the H_3BO_3.
10. Sucrose and NaCl are the only remaining solids. Sucrose is more soluble in water than NaCl. Add a small amount of each solid to a clean test tube. Fill halfway with water. Stir or hold the test tubes under hot tap water or in a water bath. Identify the more soluble sample.

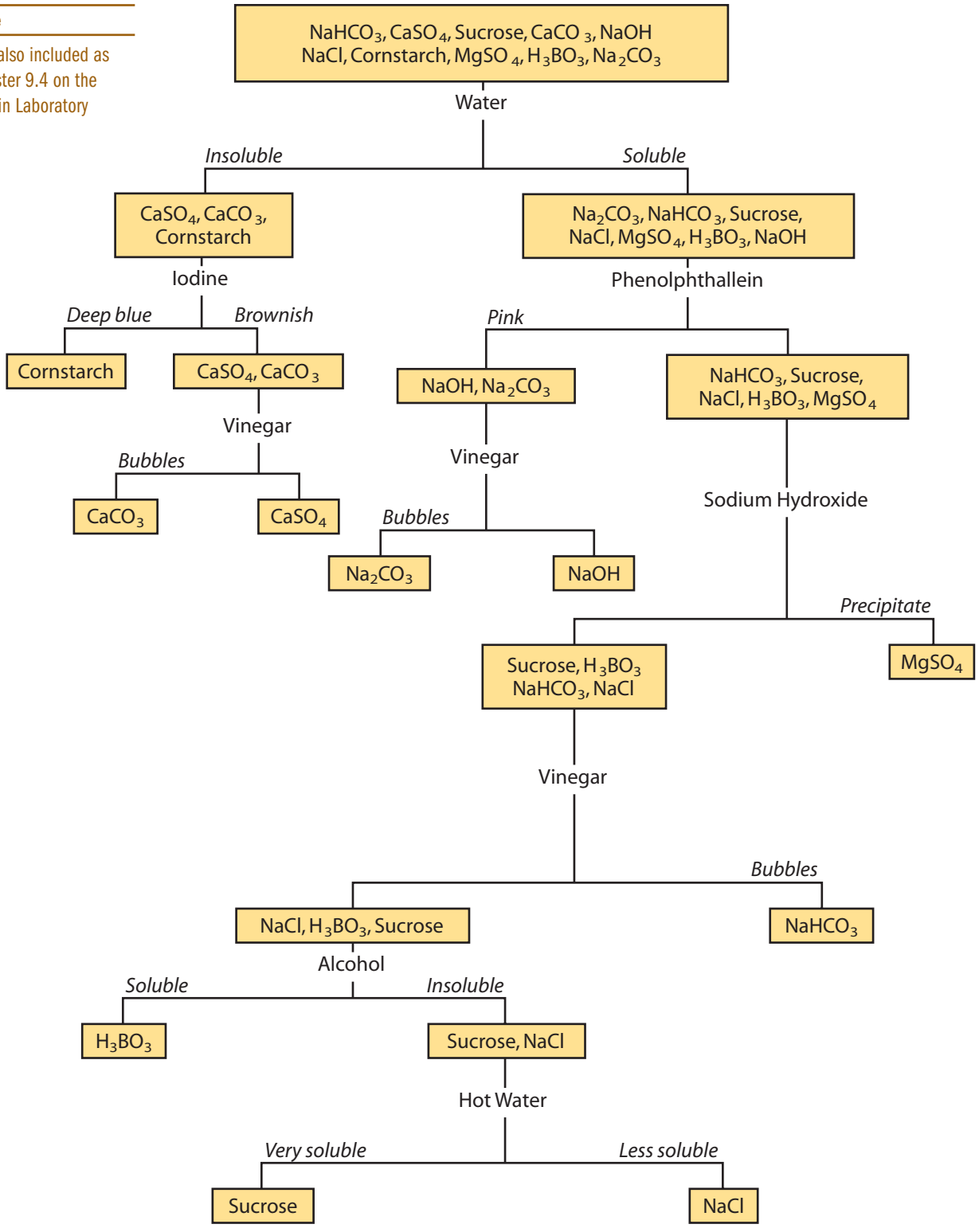


Photomicrographs of two different white powders

Check your data to make sure it is complete. In the next exercise, you will analyze an unknown sample of a powder or powders using a flow chart of the analysis scheme (Figure 9.4).

Teacher Note

Figure 9.4 is also included as Blackline Master 9.4 on the TRCD for use in Laboratory Activity 9.3.



Modified from Solomon et. al., *Qualitative Analysis of Eleven Household Chemicals*

Figure 9.4 Qualitative analysis scheme for Laboratory Activity 9.3

The Case of the Purloined Pennies

Laboratory Activity 9.4

A tan, leather, felt-lined briefcase containing a valuable coin collection was stolen from the backseat of a car. Aston Albright was terribly distraught. He was going to sell his collection and retire from teaching. Investigators found no clues at the scene of the theft. Police alerted pawnshops and coin dealers throughout the region.

Boscoe's coins

A week later, a short, swarthy man named Boscoe Balmer visited a coin dealer saying that a friend of his was going to pay off an outstanding debt by giving him some rare coins. He wanted to know their value. The coins were in a cloth sack; when Balmer dumped them on the counter, some white powder also fell out.

The coin dealer immediately recognized several pieces that were on the list of stolen coins. He discreetly called the police, who nabbed the man as he was leaving the store. When arrested on suspicion of grand larceny, Balmer claimed that the coins were not his. He promptly named Durston Dalrymple, a car salesman, as the owner of the coins. Dalrymple denied everything.

The police investigator collected the white powder from the counter and sack and sent it to your crime lab for analysis. The police report says that Balmer is a construction worker who, because of a sprained wrist and stomach problems, has recently been doing residential drywalling. Dalrymple fancies himself to be a gourmet cook, but his favorite foods are scrapple and scones.

Who is the culprit? What is the basis of your opinion?

Materials

- unknown powder
- known or standard powders from previous activity
- reagents from previous activity
- material and apparatus from previous activity

SAFETY ALERT! CHEMICALS USED

Always wear goggles and an apron when working in the labaratory

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

Teacher Note

Balmer is likely to have been in contact with calcium sulfate (gypsum, a component of drywall) and magnesium sulfate (Epsom salts) for soaking his sprained wrist. Dalrymple is a cook, so he would be in contact with any white powder that might be found in the kitchen. Use whichever unknowns you choose.

Laboratory Activity 9.4, *continued*

Procedure

Follow the flow chart in Figure 9.4 and your identification procedure from the earlier laboratory activity to identify the unknown powder and the thief.

The following case study shows how a broad background of knowledge and experience can aid in an investigation; however, preconceived ideas should never interfere with an open mind and objective analysis. Forensic science is largely based on comparative analysis, which can either eliminate a source or link or provide a possible, maybe even a probable, relationship between unknown and known. In this particular case, examination eliminated arsenic as the problem and provided a possible source of the powder. It also demonstrated that preconceived notions are hard to dispel, even in the face of scientific and logical evidence. Or was there a motive in this woman's insistence that she was being poisoned?

9.1: White Powder

CASE STUDY

From the files of coauthor John Funkhouser

Several years ago I was asked by a forensic science agency to investigate a case involving white powder. A woman had complained that she was being poisoned by powder being introduced into her high-rise condo, coating her clothing, furniture, kitchenware, and just about everything. She insisted it was arsenic.

I requested samples of various items that were coated with the material. In talking to her, I asked about previous health issues and her present symptoms, which were a rash and respiratory problems. These symptoms did not match those associated with either ingestion or breathing of arsenic oxide. She also could not opine as to how or why this was happening or who might be responsible.

Almost as an aside, she mentioned that the apartment directly above hers was being renovated. Ding! Most construction in the United States uses sheetrock (also called drywall or wallboard), which is gypsum (a natural mineral of calcium sulfate) sandwiched between two paper layers. Pieces of sheetrock are cut to the desired dimensions and nailed to studs, joists, and rafters. Seams are taped, and spackle, which also may contain gypsum, is applied

and sanded smooth when dry. Additionally, holes are cut into the sheetrock for receptacles, light fixtures, etc. Consequently, lots of white powdered gypsum is released. I had a possible lead as to what this contaminant might logically be.

CASE STUDY CONTINUED

Once samples of clothing, a purse, a belt, a shoe, and a soap dish arrived, I was surprised to find so little powder adhering to the articles or in the plastic bags in which they were packed, contrary to the woman's description.

I used arsenic trioxide, arsenic pentoxide, and crumbled sheetrock as controls (knowns in this instance) to compare to the unknown white powder. Microscopic examination of a number of individual particles (all 1 mm or smaller) in reflected, transmitted, and polarized light (see Chapter 10, "Soil and Glass Analysis") revealed a match of the unknowns with the gypsum particles only. Comparative solubility studies of individual particles of the unknown substance again ruled out the arsenic oxides, but showed the substance to be consistent with the sheetrock control.

Rather than spend more time and money on confirmatory and sophisticated analyses such as X-ray microprobe and SEM, I surmised that the white powder was not arsenic but gypsum, and originated from the renovation site upstairs, probably dispersed in the woman's apartment through a faulty ventilation system.

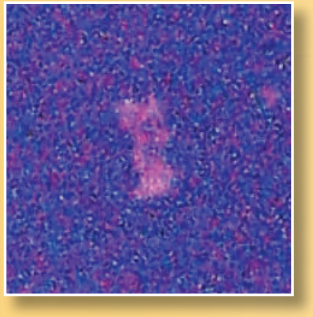
When I reported my opinion and my reasoning, she still wanted to believe that she was being poisoned. Oh, well.

Typical particles at 60×, low-resolution magnification

Unknown particle:

Reflected light

Transmitted light

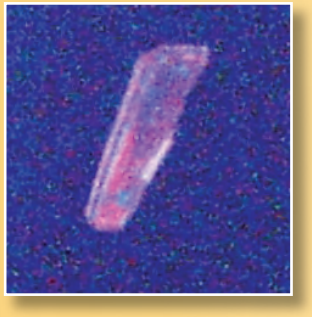


Polarized light

Gypsum control:

Reflected light

Transmitted light



Polarized light

Flame Tests

You have learned how to detect some metals using their physical and chemical properties, by chromatography, with color spot tests (Chapter 8, p. 215), and electroanalytically (Chapter 8, p. 218, Reinsch test). Under certain circumstances, a simple flame test can be used to check for the presence of a metal **salt**. For example, a white powder is found on a table at a restaurant where a customer became violently ill. Is it sugar, salt, or something that shouldn't be there?

SCILINKS NSTA
GO TO www.scilinks.org
TOPIC fireworks
CODE forensics2E250

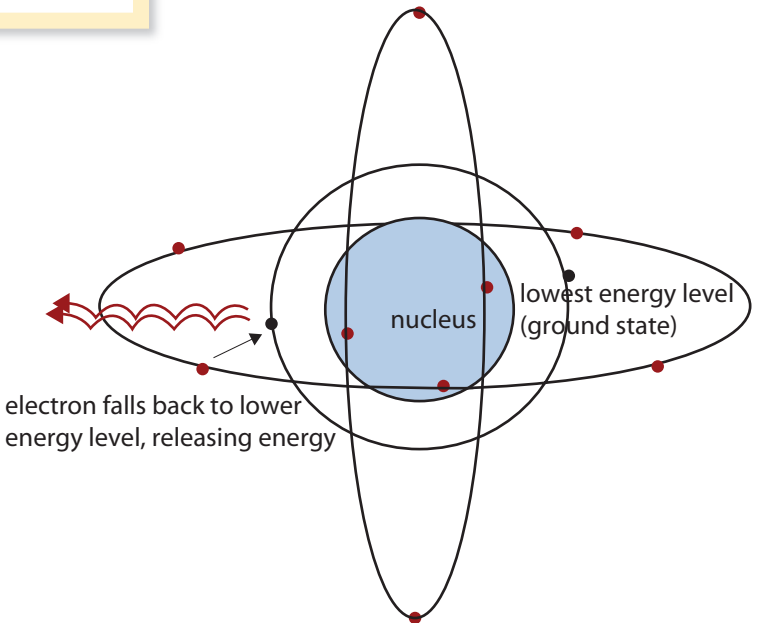
Many metal salts show a distinct color when heated. In fact, all elements when heated emit energy at characteristic wavelengths as electrons drop back to ground state levels. This is the basis of emission spectroscopy (see Chapter 7, p. 193). Colors of a few metal salts are given in Table 9.1.

Table 9.1: Flame Colors

Metal	Flame Colors
arsenic	blue
barium	light green
boron	green
calcium	red
copper	blue-green
iron	gold
magnesium	white
potassium	violet
sodium	orange
strontium	crimson
zinc	blue-green

salt: in chemistry, the product of an acid with a base: for example, magnesium hydroxide and sulfuric acid combine to make magnesium sulfate

The distinctive colors of fireworks are produced by metal salts.



Laboratory Activity 9.5, Advance Preparation

Use at least a 4-inch wire. If you do not have platinum wire, use Nichrome, a resistance wire for making heating elements. Rather than a Bunsen burner, the

Flame Tests

Laboratory Activity 9.5

Materials

- platinum or Nichrome wire
- Bunsen burner
- 1M HCl
- sugar
- table salt
- calcium chloride
- potassium chloride
- boric acid
- zinc chloride
- cobalt glass filter (optional)

SAFETY ALERT! CHEMICALS USED

Always wear goggles and an apron when working in the labaratory

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

Procedure

1. Clean the metal wire provided by dipping it in 1 M HCl and holding it in the blue flame of a Bunsen burner until there is no color. Dip it into a labeled sample and note the color of the flame. Wash the wire with distilled water, dip it again into the acid, and test for contamination with the burner. Repeat this procedure with all the samples and record the results in your notebook. Compare your results with those in the table. Note and explain any discrepancies. This test only works for a pure substance; mixtures will give false results.
2. Now test the unknown from the restaurant. What is it? Could it have caused the customer's illness? Was it logical to find it in a restaurant? Should more testing be considered?

Sodium flame

Advance Preparation, *continued*

blue flame of an alcohol lamp can suffice. Prepare saturated solutions or pastes of each material using distilled water. (Check your water in the flame to ensure no color–sodium is the major problem. Blue cobalt glass will filter out the intense orange of sodium.) If your water is not pure, hammer out the end of the wire or squeeze it in a vise to make a microspatula and use just the dry powder.

For the unknown, you can use sugar, salt, or any of the other white powders tested. If any of the latter, then students could research what the product could be, how it could have gotten on the restaurant table, and its health consequences. For example, boric acid is used to kill cockroaches, but it is not toxic to humans (though you probably would not want to eat at an establishment with boric acid on the tables). Potassium chloride is often substituted for table salt to reduce the amount of sodium in the diet, so maybe the customer brought it with him/her. Likewise, calcium is a dietary supplement. So is zinc, which, overdosed, can cause nausea, vomiting, and diarrhea.

Colorful demonstrations of flame colors are described at www.chem.ox.ac.uk/vrchemistry/FilmStudio/flamecolours/HTML/page01.htm and http://sciencekit.com/product.asp?pn=IG0024771&bhcd2=1199501862.

The concept of flame colors is a logical lead-in to atomic energy levels and spectroscopy, even to the construction and use of a simple spectroscope using a diffraction grating or a CD/DVD. See Additional Projects, #4.

Cheiloscopy: The Study of Lip Prints

cheiloscopy: the study of lip prints, from the Greek word *cheilos*, meaning "lip"

Classification of many similar items makes identification easier and quicker. Consider the classification schemes in science: biology uses kingdom, phylum, class, order, family, genus, and species to sort out the 1.5 million organisms discovered so far. Chemists use the periodic table; astronomers, the Hertzsprung–Russell diagram.

Classifying things in an orderly way that indicates natural relationships is called *taxonomy*.

You know that fingerprints are unique characteristics of an individual and, as such, can be used for identification. Well, so can lip prints, through **cheiloscopy**.

For example, suppose a bank robber was startled by an alarm just as the teller handed her the money. She grabbed the money and, in her haste to get away, ran smack-dab into a glass door. She managed to recover and get away. Subsequent examination of the door revealed a red lipstick imprint of the robber's mouth. Later, police picked up a suspect but needed evidence to link her to the robbery.

How can this problem be solved?

Laboratory Activity 9.6

Lip Prints—A Bank Robbery with Impact

Materials

- lipstick or lip balm
- index cards
- fingerprint powder and brushes
- clear tape
- piece of glass with the robber's lip print

Procedure

1. Make a lip print on an index card (see Figure 9.5). Develop with black powder if necessary. Label with your name.
2. Examine the lip prints of your classmates.
3. Do the lip prints have similar patterns? Can the patterns be grouped and given descriptive labels? Develop a classification scheme identifying different types of lip patterns created by the lines or creases in lips.
4. Does the crime scene lip print fit into the classification scheme your class developed? Determine which type of print the bank robber made.
5. Identify the culprit.

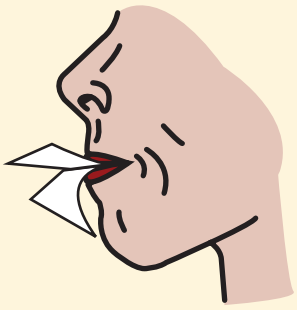


Figure 9.5 Making a lip print

Teacher Note

This activity could have been done in Chapter 4, "Fingerprints," but it has been inserted here to break the tedium of fingerprinting, and it is a fun activity. Identification of lipsticks follows in the next activity.

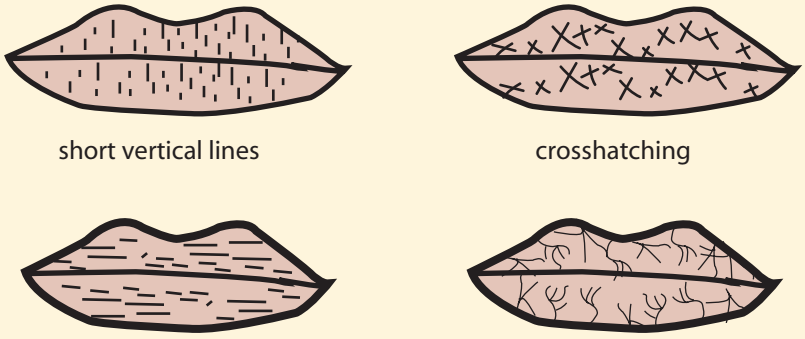
Simulate the evidence by having a student wearing lipstick secretly press his or her lips against a clean glass object, such as a pane of glass or any sort of drinking glass. Make sure the print is clear and readable. Set the glass with the lip print in the front of the class for students to examine. Characteristics such as color, gloss, and odor should be noted and recorded. The lip print may be enhanced by dusting it gently with fingerprint powder. Lift the print, just as you did in Chapter 4, by pressing a piece of 2-inch clear tape gently over it, smoothing the tape out to prevent folds and bubbles. Pull the tape off slowly and

Students can collect lip prints from classmates. The simplest way to collect a good lip print is to press the lips against a folded piece of paper (see Figure 9.5). Lipstick or lip balm will show enough detail when dusted with fingerprint powder—so even the guys can participate. Indeed, maybe the bank robber was a guy! The idea here is to develop a classification system.

Lips

Can you match the suspect's and robber's lip prints?

There are said to be at least four common lip print patterns (see Figure 9.6). How do the classification categories you developed in class compare to those in Figure 9.6? What is the probability, based on the class sampling, that two people might have the same lip print? How would a lawyer argue this case for the defense? Gather some statistics in class regarding how common each type of lip print is.



short vertical lines

crosshatching

short horizontal lines

branching grooves

Figure 9.6 Common lip patterns

Teacher Note, *continued*

evenly, and smooth it out on a piece of white paper.

Be sure that the student who made the unknown lip print is included in the collection.

Enough Lipstick

The junior high school principal had a problem with some girls who were starting to use lipstick. When applying it in the bathroom, they would blot their lips on the mirrors, leaving lip prints.

So he spoke to the teachers and asked them for their help. They promised they would speak to the girls, but after two weeks, the situation didn't improve at all.

He even called a few of the girls' parents who were his friends for their advice, but to no avail. The mirrors were constantly a mess.

Finally he thought of a way to stop it. One day he gathered together all the girls who wore lipstick. He then took them, along with the custodian, into the bathroom and lectured the girls about how hard it was to clean the lipstick off the mirrors.

You could see the young girls all nodding, but privately smirking to one another.

The principal then asked the custodian to demonstrate how difficult it was to clean the mirrors.

The custodian took a long-handled brush, dipped it into the toilet, and vigorously rubbed the lipstick off the mirror.

From that day forward, the mirrors stayed lipstick-free.

Lipstick: The Telltale Smudge

A prosecutor's witness was having a drink alone in a booth at a busy restaurant. A waiter noted that he was soon joined by a woman with dark hair, wearing sunglasses. The waiter brought her a drink and was surprised to see her leaving very shortly after that. He glanced over at the table and noticed that the man seemed to be asleep. However, he was not asleep; he was dead, apparently poisoned. A key piece of evidence was a red lipstick smudge on a paper napkin found on the seat by the body.

Seven women were picked up shortly afterward near the restaurant, based on the waiter's rather vague description of the mystery woman. All denied ever having set foot in the restaurant. Two of the women were wearing red lipstick, one had on purple lipstick, and the other four wore none, although two of those four had tubes of red lipstick in their purses. Three were wearing dark glasses. Samples of red lipstick were collected by smearing each one on a paper napkin.

Can the lipstick of each suspect be matched to the sample left at the scene of the crime? Let's find out in the next activity.

Laboratory Activity 9.7

Analyzing Lipstick with Thin-Layer Chromatography

The analytical method of choice here is thin-layer chromatography (TLC).

Lipstick is composed of fats, oils, waxes, pigments, dyes, perfumes, and flavoring. After you extract the dyes from the lipstick, you can separate the color components to form a characteristic pattern or chromatogram, which can then be compared to other samples.

Materials

- TLC plate
- test tubes
- glass stirring rods
- open-ended capillary tubes
- beaker with cover
- filter paper
- UV light
- extracting solvent—ethanol, 2 M HCl
- eluting solvent—isoamyl alcohol, acetone, water, NH_4OH
- four samples of known lipstick smudges on napkins
- the telltale smudge (unknown)

SAFETY ALERT! CHEMICALS USED

Always wear goggles and an apron when working in the labaratory

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

Procedure

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

1. Cut a small (approx. 3 × 3 mm) lipstick smudge from the crime scene napkin and from each sample.
2. Place each sample in a labeled 10-cm test tube. Add just enough extracting solvent so that there are a few drops of unabsorbed liquid.
3. Mix with a glass stirring rod for about 10 minutes. Note the color of the solution.
4. For five samples, you will need a TLC plate of about 5 × 10 cm. Draw a pencil line 1 cm up from the short end of the plate and spot the dye solutions on the line about 1 cm apart. To do this, take up the solution with an open-end boiling point capillary and *gently* touch the silica gel plate.
5. Repeat ten times for each sample, drying the spots between applications to prevent the spot from spreading. A hair dryer is handy for this, or just place the TLC plate on a hot plate at the lowest temperature setting.
6. The developing tank can be a 400-ml to 600-ml beaker. Pour enough eluting solvent to cover the bottom to about 3 mm deep. Place filter paper, cut to size, inside the beaker to saturate the air space in the beaker with solvent vapor. Check the level of the eluting solvent in the developing tank to be sure that it will be several millimeters below the pencil line on the TLC plate.
7. Carefully place the plate into the beaker, leaning it against the wall. Up to three plates can be placed in a 500-ml beaker, but they should not touch

The word *chromatography* comes from the Greek *chroma*, "color," and *graphe*, "writing." It is a method of separating components of mixtures based upon preferential adsorption or partitioning of components in a gas, liquid, or solution. In paper chromatography, the cellulose of the paper acts as the adsorbing medium. In thin-layer chromatography (TLC), the silica gel or alumina selectively adsorbs the components of the mixture. A chromatogram is the record of the separation.

Advance Preparation

You will need four different red lipsticks of the same shade and smell, if possible, each smudged on a paper napkin and identified.

The TLC sheets (silica gel on plastic or aluminum backing) can be obtained from many scientific supply houses such as Carolina Biological Supply Co. (www.carolina.com). Flinn sells single 20 × 20-cm sheets. Each sheet can be cut with scissors to make the 5 × 10-cm plates. Unfortunately, paper chromatography will not work for this experiment.

For an extracting solvent, use a mixture of 10 parts of ethanol to one part of 2 M HCl (dilute

Advance Preparation, *continued*

the 6 M acid used earlier 1:2), although methanol will work almost as well.

For an eluting or developing solvent, use 10 parts of isoamyl alcohol, 10 parts of acetone, 5 parts of water, and 10 to 12 drops of 6 M NH_4OH (the same reagent you already used in the metals product liability case).

Teacher Note

A lawyer could argue that many of the same lipsticks were in use and perhaps the perpetrator was not included in the sweep of suspects. Quite true, but one must look at probabilities: Two out of seven women wore red lipstick and one of two matched the napkin; thus there was a one out of 14 chance that she was the culprit.

Laboratory Activity 9.7, *continued*

each other. Cover the beaker (see Figure 9.7).

8. Remove the TLC plate before the solvent front reaches the top or before the end of class. This will generally take about an hour. Mark the solvent front with a pencil. Dry the plate overnight.
9. Now you are ready to analyze the experimental results. Compare the chromatograms visually and under ultraviolet light (at both short and long wavelengths, if possible). Does the unknown match any of the samples?

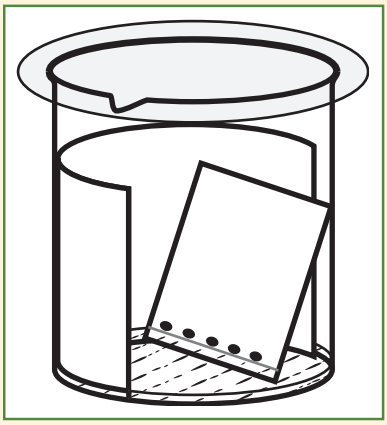


Figure 9.7 TLC chamber

10. Draw the chromatogram, describing each color band. Calculate the R_f for each sample. (See the section on environmental metal contamination earlier in this chapter).
11. What is the probability that the suspect was at the crime scene, based on the TLC results? What arguments would the suspect's lawyer make to weaken the TLC evidence?

Paint

Paint can be used as evidence in particular areas of investigation:

A. In a vehicular hit and run, paint chips are often left at the scene of impact and can be compared to the parent vehicle, if found. New cars commonly come off the assembly line with four coats of paint:

paint: a coating consisting of pigments, a polymeric film-former ("binder"), a suspending medium or a solvent, and various additives. Three classes of paints are oil-based ("alkyd"), water-based ("latex"), and solvent-based (like varnishes and lacquers).

1. an electrocoat primer added for corrosion protection
2. one or more primers, usually light or dark, depending on the next coat
3. a base coat of the final color
4. a clear coat for protection, appearance, and gloss

Reminder

probative: tending to prove something related to a crime

Examining the cross section of a paint chip at a magnification of 10–40× reveals these layers. This in itself may not allow differentiation of different paints of the same color. However, if a car is repainted, then the added layer greatly adds to its *probative* value.

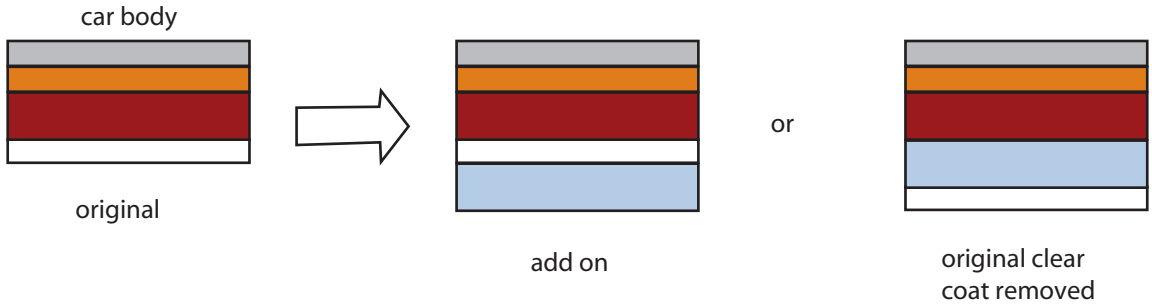
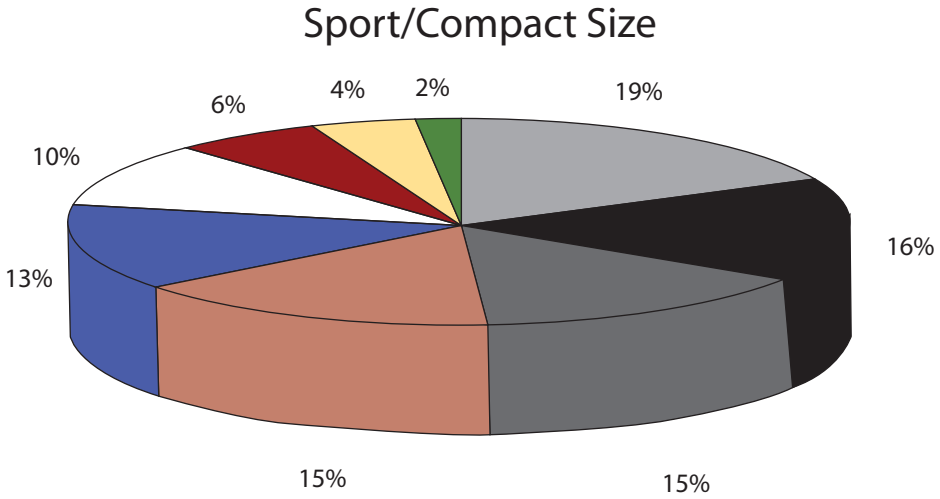
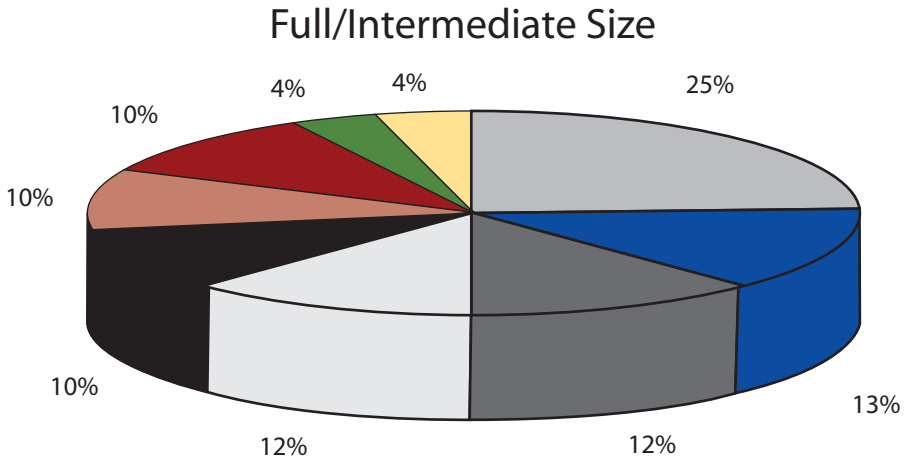


Figure 9.8 Automotive paint layers

In a sideswipe, a smear of the top layer of the car's paint may be transferred to the struck object. Analysis is far more complex in this case.

B. Often, the make, model, and year of an automobile can be discovered from sophisticated analysis of a paint chip. Instrumentation would involve PGC-MS (Chapter 6, p. 157), FTIR (Chapter 7, p. 195), SEM (Chapter 5, p. 112), fluorescence and polarized light microscopy, and





Most popular car colors, 2006

X-ray diffraction. Information is fed into a database maintained by the Royal Canadian Mounted Police (RCMP) called Paint Data Query (PDQ). The database contains the chemical composition of paint from most vehicles sold in North America after 1973. Additionally, the FBI has a similar database of more than 40,000 paint samples.

C. Sometimes, traces of house paint are left on a **jimmy** or other type of tool used in a forced entry for the purpose of burglary or assault/rape. By comparing the properties of the disturbed paint at the crime scene with that recovered from the suspect's tool, a very strong association can be made. Rather sophisticated analytical tools are required to make a good comparison, but just the color is often enough with other circumstantial evidence.

jimmy: a short crowbar with curved ends

D. Art forgery: Analysis of paint from a painting can often verify or refute authenticity. Pigment analysis usually provides the key. For example, the inorganic pigments available to forgers may be of different composition and particle size. If any pigments contain lead, mass spectrometry can determine the concentration of lead-210, a radioactive *isotope* of lead with a *half-life* of 22 years. If there is a significant concentration, then the alleged "old master" is a fake.

Reminder

isotope: a chemical element with the same number of protons, but different numbers of neutrons

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

Laboratory Activity 9.8

Paint Chip Analysis

Automotive paint chips are brittle, so the mounting can be tedious; otherwise, observe and record.

Advance Preparation

On your annual trip to the junkyard for broken glass, seat fabric, flaked chrome, and other car parts that can be used to simulate a hit and run or other crime scenes, collect paint samples. Get as many of the same color as you can. Take a putty knife to dislodge chips and a hand lens to check out the cross section. Record the make, model, and year. (The VIN, or serial number, can be used to obtain such information, but that process can be tedious. See http://en.wikipedia.org/wiki/Vehicle_identification_number for an explanation of the number

☆ PAINT CHIPS CATCH KILLER ☆

A man was killed by an automobile while riding his bike late one night. The defendant was charged with failure to stop at the scene of a serious personal injury accident. A smudge on the bumper of the defendant's automobile matched the color of paint on the bike. Scientific analysis of paint chips revealed that the layering of the paint samples was sufficiently unique to suggest that they all came from the same source. Additionally, microscopic analysis of various pieces of amber plastic revealed that many of the pieces found at the scene of the accident conclusively matched a piece of plastic found in the defendant's garage. Case closed.

—adapted from www.law.depaul.edu/criminalscienc/crimescene/

Materials

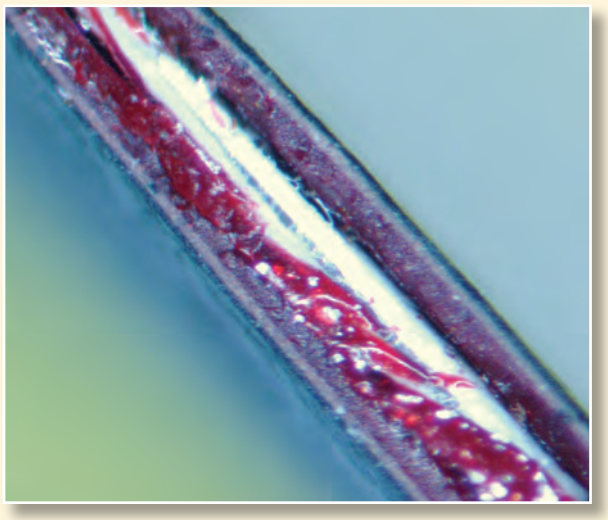
- assorted paint chips of the same color
- modeling clay or Sculpey
- stereoscope
- single-edge razor blade
- vernier caliper

Procedure

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

1. Describe and draw each of the known paint chips.
2. Measure the thickness with a vernier caliper.
3. If there is a good, straight edge on a chip, just stick it in modeling clay, straight edge up. If there is not a good edge, embed the sample in Sculpey, bake it according to the directions, and cut off the outer edge to make a clean cut for observation.
4. Count the layers, note colors, and designate the outer layer. Make a drawing.
5. From the thickness of the chip, estimate the thickness of each layer.
6. Examine the unknown provided by your teacher and identify it.

The type of binder can sometimes be ascertained and compared using solubility tests in the same manner as with fiber analysis (Chapter 6, p. 146). Solvents generally used are acetone, xylene, concentrated nitric acid, and chloroform. This test is optional, as several of the solvents are potentially harmful and must be used in a fume hood.



Multilayered paint chip

Advance Preparation, *continued*

and www.mitchellsupport.com/ondemand5/VIN/VIN.pdf for codes for all makes and years.)

Assign each investigative group five chips of the same color. Consider having two that are the same. You may wish to place each in a glassine envelope, such as those used for stamps, labeled with the car information.

Description should include a drawing; color; dimensions, including thickness; number of layers; and the color and estimated thickness of the layers.

Give each group an unknown from the known samples. Have them identify it, or sneak in a new one.

CASE STUDY

On the night of June 18, 1999, arsonists destroyed the library and damaged the sanctuary at the B'Nai Israel Synagogue in Sacramento, California. Within the next 45 minutes, fires were set at two other synagogues. Items of physical evidence included three black 1-gallon Mobil oil jugs. A torn piece of fabric was tied around the handle of each of the jugs. Tufts of trace debris could be seen adhering to the oily mouth of these jugs. A wooden crate with a newspaper at the bottom was recovered from the exterior of the synagogue. The newspaper was the *Record Searchlight* from Redding, California, 150 miles north of Sacramento. Anti-Jewish propaganda flyers were strewn about the other two synagogues.

The following items of trace evidence were removed from the oil jugs:

- Paint chips with a light blue top coat over a red layer
- Red plastic chip
- White cotton strips of fabric
- White and brown dog hairs
- Numerous feathers, primarily white and brown in color
- Numerous miscellaneous fibers of various types and colors

On the evening of July 1, 1999, Gary Matson and Winfred Mauder were murdered in bed while they were asleep. They died in the town of Happy Valley, a small community located in the Redding area of California. Gary and Winfred were an openly gay couple. Their vehicle and some credit cards were also stolen. On the evening of July 2, 1999, an office building in Sacramento housing a medical clinic that performed abortions was burned by arsonists. This arson was not linked to the synagogue arsons until later in the investigation. On July 3, the vehicle belonging to Matson and Mauder was found abandoned in the Oroville area. Oroville is located between Redding and Sacramento. When the investigators opened the door to search inside, they noticed a strong odor of gasoline.

The break in these cases came when the credit card of Gary Matson was used to order ammunition from Arizona. The ammunition had been shipped

to a United Parcel Service depot in Yuba City, California. Yuba City is just south of Oroville. On July 7, as the police arrived at the depot in Yuba City to investigate this lead, they observed brothers Benjamin Matthew Williams and James Tyler Williams picking up the ammunition. Both were arrested for possession of a stolen credit card. Numerous weapons and thousands of rounds of ammunition were recovered in subsequent searches of their vehicle and residence. One of the recovered weapons was identified as the murder weapon that killed Gary Matson and Winfred Mauder. The Williams brothers were arrested for murder.

CASE STUDY CONTINUED

A black pry bar and a black wrecking bar were collected from the Williamses' vehicle. Receipts showed that the bars had been purchased just prior to the synagogue arsons. Both bars had powdered glass fragments embedded in indentations on the surface. In addition, a large green paint spot on an aluminum metal shaving was present on the blade of the pry bar. None of the paint samples collected from any of the synagogues had green paint. After a discussion among investigators as to possible sources of this paint, the arson scene at the medical building in Sacramento was revisited on July 28. This was a white stucco building with green trim. The glass in the upper portion of the door had been struck by a linear-shaped object. The frame of the door was aluminum that had been painted green. A black paint transfer was present on the broken edges of the glass. A comparison of the green paint chip on the pry bar and the black paint on the glass established that this pry bar most likely broke this window. Some of the glass on the pry bar was similar in refractive index to the broken window of the clinic.

In a prior search of the brothers' parents' residence, Mobil oil bottles similar to those found at B'Nai Israel Synagogue had been recovered. This suggested that the parents' residence was the place at which the arson devices were constructed. New search warrants authorized collection of reference materials such as paint, animal hairs, feathers, and fabrics for comparison to the trace evidence already isolated from the arson devices used in setting the fires. A blue jumpsuit from a bedroom in the house and additional Mobil oil bottles from a shed outside the house were collected. Reference materials and additional trace evidence were collected from the Williamses' vehicle and the Matson vehicle in order to link the Williamses' vehicle to the synagogue fires and Matson's vehicle to the medical clinic fire in Sacramento.

Examination of the physical evidence established many associations, including:

CASE STUDY CONTINUED

Medical Clinic Evidence

- Green paint on the blade of the black pry bar in the Williamses' vehicle was similar to that from the door of the medical clinic.
- Black paint on the broken glass of the door of the medical clinic was similar to the pry bar paint.
- Glass on the pry bar was similar in refractive index and semiquantitative elemental analysis to the glass from the window in the door of the medical clinic.

- Glass on the floor of the Matson vehicle was similar in refractive index and semiquantitative elemental analysis to the glass from the door of the medical clinic.
- Glass on the jumpsuit recovered from the parents' residence was similar in refractive index and semiqualitative elemental analysis to glass from the door of the medical clinic.
- Fibers on the jumpsuit recovered from the parents' residence were similar to fibers from the upholstery of the Matson vehicle.
- Fibers on the front seats of the Matson vehicle were similar to fibers from the fabric of the jumpsuit.
- DNA on the jumpsuit matched that of James Williams, indicating that the younger Williams brother wore this jumpsuit.

B'Nai Israel Synagogue Evidence

- Glass on the black wrecking bar recovered from the Williamses' vehicle was similar in refractive index to the glass from a broken window at B'Nai Israel Synagogue.
- Paint on the broken glass of the window at B'Nai Israel Synagogue was similar to the wrecking bar paint.
- Oil jugs found at B'Nai Israel Synagogue were similar to the Mobil oil jug from the Williamses' parents' residence.

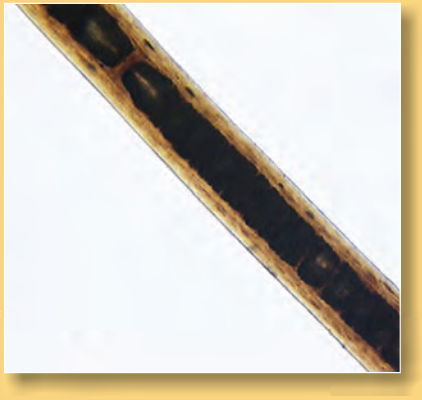
- Dog hairs and feathers on the mouths of the oil jugs and the rags tied to the oil jugs were similar to those from animals at the parents' residence.
- Blue-over-red paint chips on the mouths of the oil jugs were similar to the paint from the shed at the parents' residence.
- Newspaper in the bottom of a crate left at the synagogue arson site was from the Redding area.
- A palm print on one anti-Jewish flyer left at the synagogues was identified as being from Benjamin Williams.

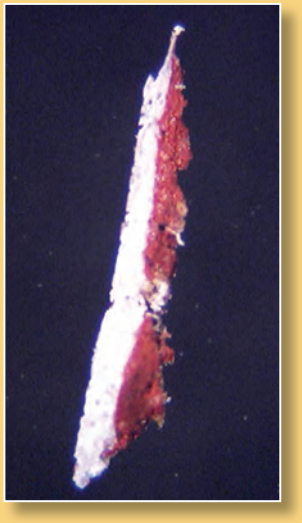
CASE STUDY CONTINUED

Both brothers were charged with several counts of arson, hate crimes, and murder. The attorneys for the defendants made a motion for a *Daubert* hearing in forensic hair analysis, forensic paint analysis, forensic glass analysis, and forensic fiber analysis. They claimed that present technology had changed significantly over the years and was not universally accepted by the scientific community. The federal court judge denied this request for a hearing upon receiving declarations attesting to the validity and admissibility of the trace evidence analyses.

Benjamin Williams committed suicide and James Williams pled guilty to murder, with a penalty of life in prison without parole.

—condensed from *Summer of Terror: Trace Evidence in a Series of Hate Crimes*, with permission of Faye A. Springer and the Sacramento County District Attorney's Office





This is a classic case of using many kinds of trace evidence that we have studied, or are about to study, to associate knowns to unknowns, victims to perpetrators, and perpetrators to the crimes committed. It also reminds us of the impact the *Daubert* ruling has in the legal system.

Answers

1. The metal would float. It must be aluminum or magnesium. Density is a physical property.
2. Iron and nickel. An alloy of aluminum, nickel, and cobalt is also a common magnet.
3. It is flexible and can be bent or shaped. It can be scratched.
4. An investigator performs a confirmatory test after a preliminary examination. It confirms or gives a positive identification of an unknown substance. Aluminon reagent gives a pink gel in the presence of aluminum ions.
5. The metals were copper and zinc, or brass. They probably came from the company upriver making brass hardware.

   At least 12 percent chromium with iron resists rust in stainless steel. Bronze is made of copper, tin, and some zinc. Pewter used to be made of lead and tin; now it is mostly tin, with some copper and antimony.
6. The mobile phase is the eluting solvent. The stationary phase is the filter or chromatography paper.
7. Chromatography uses the concept of separation of mixtures based on solubility, size, and shape. Yes, it could have been used in the contamination case if the samples were dissolved.
8. Ingredients in the ink would separate and interfere with the analysis.
9. First, it may not be necessary if the next spring flood washes out residual copper and zinc, assuming the polluter has cleaned up its operation. Otherwise, have students search the Internet for possibilities.

Checkpoint Questions

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

1. **A piece of metal is placed in a beaker of bromoform (density 2.89 g/cc). If the density of the metal is less than that of the bromoform, what will the metal do? Of the metals you tested, identify the possibilities. Is density a physical or chemical property of aluminum?**
2. **Which of the common metals are magnetic?**
3. **What are some physical properties of a malleable metal?**
4. **What is meant by a confirmatory test? What is the confirmatory test for the detection of Al^{+3}?**
5. **What metal contaminants were found in Mr. Calamine's water sample? Where did they come from? What are the major components of stainless steel? Of bronze? Of pewter?**
6. **When you use paper chromatography for the metal analysis, what is the mobile phase? What is the stationary phase?**
7. **What is chromatography? Could you use the same method in the Calamine case that you used in the metal contamination case?**
8. **Why is pencil and not pen used to mark the chromatography strips?**
9. **How could Mr. Calamine clear his farmland of the current pollution?**

10. In the qualitative analysis of white powders, what is meant by solubility? What factors may affect the apparent solubility of the first ten samples? Is solubility a physical or chemical property?

11. In the analysis in question 10, what indicates that a chemical reaction has taken place?

12. What is R_f, and how is it calculated?

13. Use the Internet to determine whether lip prints have been used as evidence in a trial. Is the admissibility of lip prints related to the *Daubert* ruling? Discuss.

14. What causes metal salts to show colors in a flame?

15. What single instrument is the forensic scientist's best friend?

16. Why do more layers of paint in a chip increase its value as evidence?

17. Why can't a copper wire, rather than expensive platinum, be used for flame tests?

18. What is a VIN and why is it important in forensic science?

19. In Case Study 9.2, what provided a break in the case leading to identification of the suspects?

20. What trace evidence in Case Study 9.2 linked the synagogue fires to the medical building fire?

Answers, *continued*

10. Solubility is the ability to dissolve. Stirring, heating, or adding more water could affect it. Substances that are insoluble do not dissolve regardless of the above. Solubility is a physical property.
11. Indicators include color changes, production of gas bubbles, and the formation of a precipitate.
12. R_f is retention factor, which characterizes how a given substance travels along a chromatography strip or column. It is calculated by measuring the distance the substance travels divided by the distance the eluting solution travels.
13. Answers will vary.
14. Heat from the flame excites electrons in the atoms to higher energy levels. The electrons in the atoms in the cooler parts of the flame fall back to lower energy levels, emitting energy at visible wavelengths.
15. the microscope
16. Each layer puts the sample into successively smaller classes until it is in a class of one, which is individual evidence. It's like a new shoe; the more it is worn and scuffed, the more unique it becomes.
17. Copper imparts a blue-green color to the flame.
18. The vehicle identification number, which is like a person's Social Security number. It allows abandoned and stolen vehicles to be identified.
19. the use of a credit card from the murder victim
20. green paint associated with a pry bar

Additional Projects

1. How does the HCl/acetone ratio influence the R_f values of the metal ions you have studied? What would happen if you used ethanol or isopropanol instead of acetone?
2. Investigate whether this method with similar reagents can be used to separate and visualize other metal ions, such as iron, manganese, chromium, and the like.
3. An interesting application of the complexing (chelating) nature of the quinolinol (oxine) used in this experiment was proposed in 1970. When you grip a metal object in your hand, especially under stress, trace metal ions are left behind (remember Locard's Principle?). If you spray your hand with a 0.2 percent solution of quinolinol in ethanol or isopropanol and then let it dry, the imprint of the metal object may become visible under UV light. Different metals can produce different fluorescent colors. Try this with various objects—aluminum, iron, brass—with different shapes, like a rod, a wrench, scissors, a knife, and the like. You must grip the object hard, even dampening the palm of your hand, to mimic actual use of a weapon. The oxine solution is perfectly safe under the conditions of use, but you can always wear a glove.
4. The emission of light energy by metal atoms is the basis of emission spectroscopy. The flame colors seen in Activity 9.6 are a combination of many wavelengths corresponding to the release of energy from excited atomic energy levels. Specific wavelengths can be resolved using a simple spectroscope which can be constructed from cardboard, tape, and a diffraction grating, or even a CD or DVD. See, for example, http://ioannis.virtualcomposer2000.com/spectroscope/toyspectroscope.html or *J. Chem. Ed.* Vol. 75 (1998), p. 1568A. Construct such a spectroscope (or use one from the physics department) to look at the colored flames. Does the red flame of strontium appear different from the red flame of calcium and lithium through a spectroscope?

Holding a copper pipe

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Books and Articles

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Solomon, S., A. Fulep-Poszmik, and A. Lee. "Qualitative Analysis of Eleven Household Chemicals," *J. Chem. Ed.* Vol. 68 (1991), pp. 328–329.

Dornberg, John. "Artists Who Fake Fine Art Have Met Their Match—in the Laboratory," *Smithsonian Magazine* (September 1985), pp. 60–69.

Videos and Films

HBO's *Autopsy 6* showed a bank robber running into a glass door and leaving a lip print that was used as evidence. This segment is a natural lead-in for the first exercise. It is out of stock, but it would be worthwhile to try to find it: "The Telltale Imprint," www.hbo.com/autopsy/episode/episode_6_the_telltale_imprint.html.

Websites

www.fbi.gov/hq/lab/fsc/backissu/july1999/painta.htm; forensic paint analysis and comparison guidelines

www.nrcan.gc.ca/mms/scho-ecol/tour/home_e.htm; interactive program showing the composition of common materials in the home