

What Killed Napoleon?

Napoleon I, emperor of France, was sent into exile on the remote island of St. Helena by the British after his defeat at the Battle of Waterloo in 1815. St. Helena was hot, unsanitary, and rampant with disease. There, Napoleon was confined to a large reconstructed agricultural building known as Longwood House. Boredom and unhealthy living conditions gradually took their toll on Napoleon's mental and physical state. He began suffering from severe abdominal pains and experienced swelling of the ankles and general weakness of his limbs. From the fall of 1820, Napoleon's health began to deteriorate rapidly until death arrived on May 5, 1821. An autopsy concluded the cause of death to be stomach cancer.

It was inevitable that dying under British control, as Napoleon did, would bring with it numerous conspiratorial theories to account for his death. One of

the more fascinating inquiries was conducted by a Swedish dentist, Sven Forshufvud, who systematically correlated the clinical symptoms of Napoleon's last days to those of arsenic poisoning. For Forshufvud, the key to unlocking the cause of Napoleon's death rested with Napoleon's hair. Forshufvud arranged to have Napoleon's hair measured for arsenic content by neutron activation analysis and found it consistent with arsenic poisoning over a lengthy period of time.

Nevertheless, the cause of Napoleon's demise is still a matter for debate and speculation. Other Napoleon hairs have been examined and found to be low in arsenic content. Some question whether Napoleon even had clinical symptoms associated with arsenic poisoning. In truth, forensic science may never be able to answer the question—what killed Napoleon?

Trace Evidence II Metals, Paint, and Soil



Key Terms

alpha ray
atomic mass
atomic number
beta ray
continuous spectrum
density-gradient tube
electron
electron orbital
emission spectrum
excited state
gamma ray
isotope
line spectrum
mineral
neutron
nucleus
proton
pyrolysis
radioactivity

Learning Objectives

After studying this chapter you should be able to:

- Describe the usefulness of trace elements for forensic comparison of various types of physical evidence
- Define and distinguish protons, neutrons, and electrons
- Define and distinguish atomic number and atomic mass number
- Explain the concept of an isotope
- Understand how elements can be made radioactive
- List the most useful examinations for performing a forensic comparison of paint
- Distinguish continuous and line emission spectra
- Understand the parts of a simple emission spectrograph
- Appreciate the phenomenon of how an atom absorbs and releases energy in the form of light
- Describe proper collection and preservation of forensic paint evidence
- List the important forensic properties of soil
- Describe proper collection of soil evidence

Considering that most materials originate from the earth's crust, it is not surprising that they are rarely obtained in pure form; instead, they include numerous elemental impurities that usually must be eliminated through industrial processing. However, it is usually not economically feasible to completely exclude all such minor impurities, especially if their presence has no effect on the appearance or performance of the final product. For this reason, many manufactured products, and even most natural materials, contain small quantities of elements present in concentrations of less than 1 percent, which are known as *trace elements*.

Forensic Analysis of Metals

For the criminalist, the presence of trace elements is particularly useful because they provide “invisible” markers that may establish the source of a material or at least provide additional points for comparison. For example, comparison of trace elements present in two metallic specimens may provide data on their source or origin. Table 11–1 illustrates how two types of brass alloys can readily be distinguished by their elemental composition.

Forensic investigators have examined the evidential value of trace elements present in metallic objects as well as paint, soil, glass, and fibers. One example is the examination of the bullet and bullet fragments recovered after the assassination of President John F. Kennedy.

Evidence in the Assassination of President Kennedy

Ever since President Kennedy was killed in 1963, questions have lingered about whether Lee Harvey Oswald was part of a conspiracy to assassinate the president, or a lone assassin. The Warren Commission, the official government body appointed to investigate the shooting, concluded that Oswald acted alone. This conclusion was criticized widely at the time it was reported, and has been a source of controversy since that day.

Reconstructing the Assassination In arriving at its conclusions, the Warren Commission reconstructed the crime as follows: From a hidden position on the sixth floor of the Texas School Book Depository building, Oswald fired three shots from behind the president. The president was struck by two bullets, with one bullet totally missing the president's limousine. One

Table 11–1 Elemental Analysis of Brass Alloys

	High-Tensile Brass (percentage)	Manganese Brass Element (percentage)
Copper	57.0	58.6
Aluminum	2.8	1.7
Zinc	35.0	33.8
Manganese	2.13	1.06
Iron	1.32	0.90
Nickel	0.48	1.02
Tin	0.64	1.70
Lead	0.17	0.72
Silicon	0.08	Nil

Source: R. L. Williams, "An Evaluation of the SEM with X-Ray Microanalyzer Accessory for Forensic Work," in *Scanning Electron Microscopy/1971*, O. Johari and I. Corvin, eds. (Chicago: IIT Research Institute, 1971), p. 541.



FIGURE 11–1 President John F. Kennedy, Governor John Connally of Texas, and Mrs. Jacqueline Kennedy ride through Dallas moments before the assassination. *Courtesy Corbis/Bettmann*

bullet hit the president in the back, exited his throat, and went on to strike Texas Governor John Connally, who was sitting in a jump seat in front of the president. The bullet hit Connally in his back, exited his chest, struck his right wrist, and temporarily lodged in his left thigh. This bullet was later found on the governor's stretcher at the hospital. A second bullet in the skull fatally wounded the president.

In a room at the Texas School Book Depository, a 6.5-millimeter Mannlicher-Carcano military rifle was found with Oswald's palm print on it. Also found were three spent 6.5-millimeter Western Cartridge Co./Mannlicher-Carcano (WCC/MC) cartridge cases. Oswald, an employee of the depository, had been seen there that morning and also a few minutes after the assassination, disappearing soon thereafter. He was apprehended a few miles from the depository nearly two hours after the shooting.

Questions and Criticisms Critics of the Warren Commission have long argued that evidence proves that Oswald did not act alone. Eyewitness accounts and acoustical data interpreted by some experts have been used to contend that a second shooter fired at the president from a region in front of the limousine (the so-called grassy knoll). Furthermore, critics argue that the Warren Commission's reconstruction of the crime assumed that only one bullet caused both the president's throat wound and Governor Connally's back wound. Critics contend that such damage would have deformed and mutilated a bullet. Instead, the recovered bullet showed some flattening, no deformity, and only about 1 percent weight loss.

In 1977 the U.S. House of Representatives Select Committee on Assassinations requested that the bullet taken from Connally's stretcher—along with bullet fragments recovered from the car and various wound areas—be examined for trace element levels. Because lead alloys used to manufacture bullets contain an assortment of trace elements, analysis of those trace elements provides a possible means for characterizing lead bullets. For example, antimony is often added to lead as a hardening agent; copper, bismuth, and silver are other trace elements commonly found in bullet lead.

Investigators compared the antimony and silver content of the bullet and bullet fragments recovered after the assassination. Previous studies had amply demonstrated that the levels of these two elements are particularly important for characterizing WCC/MC bullets. Bullet lead from this type of ammunition ranges in antimony concentration from 20 to 1,200 parts per million (ppm) and 5 to 15 ppm in silver content.

As can be seen in Table 11-2, the samples designated Q1 (the Connally stretcher bullet) and Q9 (bullet fragments from Connally's wrist) are indistinguishable from one another in antimony and silver content. The samples

Table 11-2 Antimony and Silver Concentrations in the Kennedy Assassination Bullets

Sample	Silver (parts per million) ^a	Antimony (parts per million)	Sample Description
Q1	8.8 ± 0.5	833 ± 9	Connally stretcher bullet
Q9	9.8 ± 0.5	797 ± 7	Fragments from Connally's wrist
Q2	8.1 ± 0.6	602 ± 4	Large fragment from car
Q4, 5	7.9 ± 0.3	621 ± 4	Fragments from Kennedy's brain
Q14	8.2 ± 0.4	642 ± 6	Small fragments found in car

^aOne part per million equals 0.0001 percent.

Source: Reprinted with permission from V. P. Guinn, "JFK Assassination: Bullet Analyses," *Analytical Chemistry* 51 (1979): 484 A. Copyright 1979, American Chemical Society.

designated Q4 and Q5 (fragments from Kennedy's brain) are indistinguishable in antimony and silver content from samples Q2 and Q14 (fragments recovered from two different areas in the car). However, all four of those samples are different from Q1 and Q9.

Conclusions From studying these results we can derive the following conclusions:

1. There is evidence of only two bullets—one composed of 815 ppm antimony and 9.3 ppm silver, the other composed of 622 ppm antimony and 8.1 ppm silver.
2. Both bullets have a composition highly consistent with WCC/MC bullet lead, although other sources cannot be ruled out entirely.
3. The bullet found on the Connally stretcher also damaged Connally's wrist. The absence of bullet fragments from the back wounds of Kennedy and Connally prevented any effort at linking these wounds to the stretcher bullet.

None of these conclusions can verify absolutely the Warren Commission's reconstruction of the assassination, but the results are at least consistent with the commission's findings. The analyses on the Kennedy assassination bullets used a method known as *neutron activation analysis*, one of several forensic techniques we will examine in this chapter.

Atomic Structure

To understand the principle behind neutron activation analysis, one must first understand the fundamental structure of the atom. Each atom is composed of elementary particles that are collectively known as *subatomic particles*. The most important subatomic particles are the **proton**, **electron**, and **neutron**.

The properties of the proton, neutron, and electron are summarized in the following table:

Particle	Symbol	Relative Mass	Electrical Charge
Proton	P	1	+
Neutron	n	1	0
Electron	e	1/1837	-

As you can see, the masses of the proton and neutron are each about 1,837 times the mass of an electron. The proton has a positive electrical charge; the electron has a negative charge equal in magnitude to that of the proton; and the neutron is a neutral particle with neither a positive nor a negative charge.

A popular descriptive model of the atom, and the one that will be adopted for the purpose of this discussion, pictures an atom as consisting of electrons orbiting a central **nucleus** composed of protons and neutrons—an image that is analogous to our solar system, in which the planets revolve around the sun.¹ To maintain a zero net electrical charge, the number of protons in the nucleus must always equal the number of electrons in orbit around the nucleus.

With this knowledge, we can describe the atomic structure of the elements. For example, hydrogen has a nucleus consisting of one proton and no neutrons, and it has one orbiting electron. Helium has a nucleus comprising two protons and two neutrons, with two electrons in orbit around the nucleus (see Figure 11-2).

proton

A positively charged particle that is one of the basic structures in the nucleus of an atom.

electron

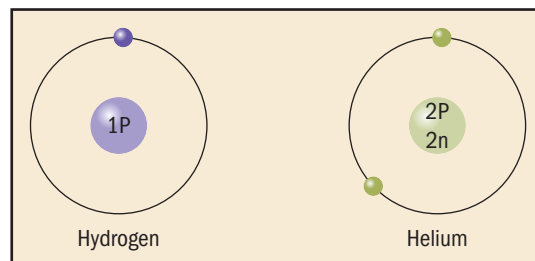
A negatively charged particle that is one of the fundamental structural units of the atom.

neutron

A particle with no electrical charge that is one of the basic structures in the nucleus of an atom.

nucleus

The core of an atom, consisting of protons and neutrons.

FIGURE 11-2 The atomic structures of hydrogen and helium.**atomic number**

The number of protons in the nucleus of an atom.

The behavior and properties that distinguish one element from another must be related to the differences in the atomic structure of each element. One such distinction is that each element possesses a different number of protons. This number is called the **atomic number** of the element. As we look back at the periodic table on p. 119, we see that the elements are numbered consecutively. Those numbers represent the atomic number or number of protons associated with each element. An element is therefore a collection of atoms that all have the same number of protons. Thus, each atom of hydrogen has one and only one proton, each atom of helium has 2 protons, each atom of silver has 47 protons, and each atom of lead has 82 protons in its nucleus.

Isotopes and Radioactivity

Although the atoms of a single element must have the same number of protons, nothing prevents them from having different numbers of neutrons. The total number of protons and neutrons in a nucleus is known as the **atomic mass** number. Atoms with the same number of protons but differing solely in the number of neutrons are called **isotopes**.

atomic mass

The sum of the number of protons and neutrons in the nucleus of an atom.

For example, hydrogen consists of three isotopes: ordinary hydrogen, which has one proton and no neutrons in its nucleus, and two other isotopes called deuterium and tritium. Deuterium (or heavy hydrogen) also has one proton, but contains one neutron as well. Tritium has one proton and two neutrons in its nucleus.

isotope

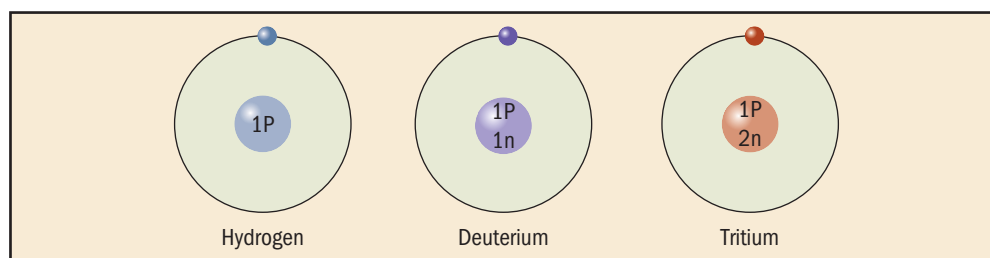
An atom differing from another atom of the same element in the number of neutrons it has in its nucleus.

Therefore, all the isotopes of hydrogen have an atomic number of 1 but differ in their atomic mass numbers. Hydrogen has an atomic mass of 1, deuterium a mass of 2, and tritium a mass of 3. Ordinary hydrogen makes up 99.98 percent of all the hydrogen atoms found in nature. The atomic structures of these isotopes are shown in Figure 11-3.

radioactivity

The emission of high-energy subatomic particles that accompanies the spontaneous disintegration of unstable nuclei.

Like hydrogen, most elements have two or more isotopes. Tin, for example, has ten isotopes. Many of these isotopes are quite stable, and the isotopes of any one element have indistinguishable properties. Others, however, are not as stable and decompose over time by a process known as *radioactive decay*. **Radioactivity** is the emission of high-energy

**FIGURE 11-3** Isotopes of hydrogen.

subatomic particles that accompanies the spontaneous disintegration of unstable nuclei.

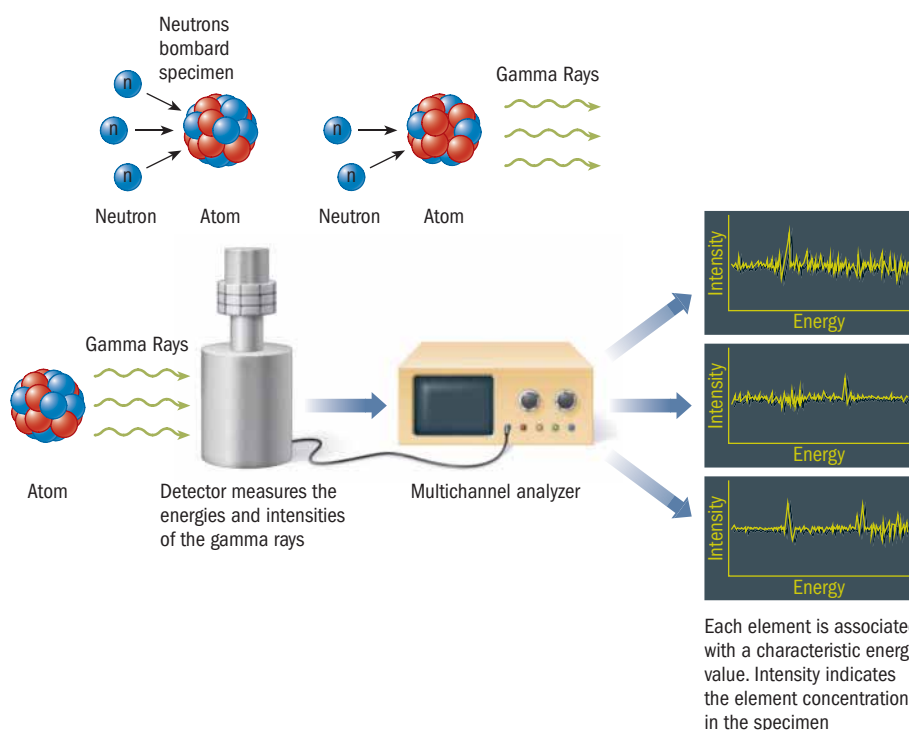
Radioactivity is composed of three types of radiation: **alpha rays**, **beta rays**, and **gamma rays**. Alpha rays are helium atoms stripped of their orbiting electrons; thus, they are positively charged particles. Each alpha ray particle has a mass approximately four times that of a hydrogen atom. Beta rays are electrons, and gamma rays are a form of electromagnetic radiation similar to X-rays (discussed in Chapter 4), but of a higher frequency and energy. Fortunately, most naturally occurring isotopes are not radioactive, and those that are—radium, uranium, and thorium—are found in such small quantities in the earth's crust that their radioactivity presents no hazard to human survival.

When an atom is bombarded with neutrons, some neutrons are captured to form new isotopes. This is what happens in a nuclear reactor. A nuclear reactor is simply a source of neutrons that bombard the atoms of a specimen, thereby creating radioactive isotopes. The nucleus of an atom that has captured one or more neutrons is said to be activated, and it often begins to decompose immediately, emitting radioactivity.

Neutron Activation Analysis

Forensic chemists can characterize the trace elements in a specimen by bombarding it with neutrons and measuring the energy of the gamma rays emitted by the activated isotopes. The gamma rays of each element are associated with characteristic energy values, and thus exhibit unique levels of energy. This technique, known as neutron activation analysis, is depicted in Figure 11–4. Once an element has been identified, its concentration can be measured by the intensity of its gamma-ray radiation; the intensity of the radiation is directly proportional to the concentration of the element in a specimen.

The major advantage of neutron activation analysis is that it provides a nondestructive method for identifying and quantitating trace elements. A median detection sensitivity of one-billionth of a gram (1 nanogram) makes



alpha ray

Radiation composed of helium atoms minus their orbiting electrons.

beta ray

Radiation composed of electrons.

gamma ray

A high-energy form of electromagnetic radiation.

FIGURE 11–4 The neutron activation process requires the capture of a neutron by the nucleus of an atom. The new atom is now radioactive and emits gamma rays. A detector permits identification of the radioactive atoms present by measuring the energies and intensities of the gamma rays emitted.

Table 11–3 Concentration of Trace Elements in Copper Wire

	Selenium	Gold	Antimony	Silver
Control Wire				
A ₁	2.4	0.047	0.16	12.7
A ₂	3.5	0.064	0.27	17.2
A ₃	2.6	0.050	0.20	13.3
A ₄	1.9	0.034	0.21	12.6
Suspect Wire				
B	2.3	0.042	0.15	13.0

Note: Average concentration measured in parts per million.

Source: R. K. H. Chan, "Identification of Single-Stranded Copper Wires by Nondestructive Neutron Activation Analysis." *Journal of Forensic Sciences* 17 (1972): 93. Reprinted by permission of the American Society for Testing and Materials, copyright 1972.

neutron activation analysis one of the most sensitive methods available for quantitative detection of many elements. Further, neutron activation can simultaneously analyze twenty to thirty elements. A major drawback to the technique is its expense. Only a handful of crime laboratories have access to a nuclear reactor; in addition, sophisticated analyzers are needed to detect and discriminate gamma-ray emissions.

Neutron activation has been used to characterize trace elements in metals, drugs, paint, soil, gunpowder residues, and hair. A typical illustration of its application occurred during the investigation of a theft of copper telegraphic wires in Canada. Four lengths of copper wire (A₁, A₂, A₃, A₄) found at the scene of the theft were compared by neutron activation with a length of copper wire (B) seized at a scrap yard and suspected of being stolen. All were bare, single-strand wire with the same general physical appearance and a diameter of 0.28 centimeter.

Prior experiments had revealed that significant variations could be expected in the concentration levels of the trace elements selenium, gold, antimony, and silver for wires originating from different sources. Analysts compared these elements present in the wire involved in the theft. After exposing the wires to neutrons in a nuclear reactor, neutron activation analysis revealed a match between A₁ and B that was well within experimental error (see Table 11–3). The findings suggested a common origin of the control and suspect wires.

Key Points

- Trace elements are small quantities of elements present in concentrations of less than 1 percent. They provide "invisible" markers that may establish the source of a material or provide additional points for comparison.
- The three most important subatomic particles are the proton, neutron, and electron. The proton has a positive electrical charge, the neutron has no electrical charge, and the electron has a negative electrical charge.
- Atomic number indicates the number of protons in the nucleus of an atom. Atomic mass refers to the total number of protons and neutrons in a nucleus.

- An isotope is an atom differing from other atoms of the same element in the number of neutrons in its nucleus.
- Radioactivity is the emission of high-energy subatomic particles that accompanies the spontaneous disintegration of the nuclei of unstable isotopes. The three types of radiation are alpha rays, beta rays, and gamma rays.
- In neutron activation analysis, a sample is bombarded with neutrons and the energy of the gamma rays emitted by the activated isotopes is measured. The gamma rays of each element are associated with characteristic energy values that helps identify the specific element that produces them.

Forensic Examination of Paint

Our environment contains millions of objects whose surfaces are painted. Thus paint, in one form or another, is one of the most prevalent types of physical evidence received by the crime laboratory.

Paint as physical evidence is perhaps most frequently encountered in hit-and-run and burglary cases. For example, a chip of dried paint or a paint smear may be transferred to the clothing of a hit-and-run victim on impact with an automobile, or paint smears could be transferred onto a tool during a burglary. Obviously, in many situations a transfer of paint from one surface to another could impart an object with an identifiable forensic characteristic.

In most circumstances, the criminalist must compare two or more paints to establish their common origin. For example, such a comparison may associate an individual or a vehicle with the crime site. However, the criminalist need not be confined to comparisons alone. Crime laboratories often help identify the color, make, and model of an automobile by examining small quantities of paint recovered at an accident scene. Such requests, normally made in hit-and-run cases, can lead to the apprehension of the responsible vehicle.

Composition of Paint

Paint is composed of a binder and pigments, as well as other additives, all dissolved or dispersed in a suitable solvent. Pigments impart color and hiding (or opacity) to paint and are usually mixtures of different inorganic and organic compounds added to the paint by the manufacturer to produce specific colors and properties. The binder is a polymeric substance that provides the support medium for the pigments and additives. After paint has been applied to a surface, the solvent evaporates, leaving behind a hard polymeric binder and any pigments that are suspended in it.

One of the most common types of paint examined in the crime laboratory is finishes from automobiles. Manufacturers apply a variety of coatings to the body of an automobile; this adds significant diversity to automobile paint and contributes to the forensic significance of automobile paint comparisons. The automotive finishing system for steel usually consists of at least four organic coatings:

Electrocoat Primer The first layer applied to the steel body of a car is the electrocoat primer. The primer, consisting of epoxy-based resins, is

electroplated onto the steel body of the automobile to provide corrosion resistance. The resulting coating is uniform in appearance and thickness. The color of these primers ranges from black to gray.

Primer Surfacer Originally responsible for corrosion control, the surfacer usually follows the electrocoat layer and is applied before the basecoat. Primer surfacers are epoxy-modified polyesters or urethanes. The function of this layer is to completely smooth out and hide any seams or imperfections, because the basecoat will be applied on this surface. This layer is highly pigmented. Color pigments are used to minimize color contrast between primer and topcoats. For example, a light gray primer may be used under pastel shades of a colored topcoat; a red oxide may be used under a dark-colored topcoat.

Basecoat The next layer of paint on a car is the basecoat or colorcoat. This layer provides the color and aesthetics of the finish and represents the “eye appeal” of the finished automobile. The integrity of this layer depends on its ability to resist weather, UV radiation, and acid rain. Most commonly, an acrylic-based polymer comprises the binder system of basecoats. Interestingly, the choice of automotive pigments is dictated by toxic and environmental concerns. Thus, the use of lead, chrome, and other heavy-metal pigments has been abandoned in favor of organic-based pigments. There is also a growing trend toward pearl luster or mica pigments. Mica pigments are coated with layers of metal oxide to generate interference colors. Also, the addition of aluminum flakes to automotive paint imparts a metallic look to the paint’s finish.

Clearcoat An unpigmented clearcoat is applied to improve gloss, durability, and appearance. Most clearcoats are acrylic based, but polyurethane clearcoats are increasing in popularity. These topcoats provide outstanding etch resistance and appearance.

Microscopic Examination of Paint

The microscope has traditionally been and remains the most important instrument for locating and comparing paint specimens. Considering the thousands of paint colors and shades, it is quite understandable why color, more than any other property, imparts paint with its most distinctive forensic characteristics. Questioned and known specimens are best compared side by side under a stereoscopic microscope for color, surface texture, and color layer sequence (see Figure 11–5).

The importance of layer structure for evaluating the evidential significance of paint evidence cannot be overemphasized. When paint specimens possess colored layers that match in number and sequence of colors, the examiner can begin to relate the paints to a common origin. How many layers must be matched before the criminalist can conclude that the paints come from the same source? There is no one accepted criterion. Much depends on the uniqueness of each layer’s color and texture, as well as the frequency with which the particular combination of colors under investigation is observed. Because no books or journals have compiled this type of information, the criminalist is left to his or her own experience and knowledge when making this decision.

Unfortunately, most paint specimens do not have a layer structure of sufficient complexity to allow them to be individualized to a single source, nor is it common to have paint chips that can be physically fitted together to prove common origin, as shown in Figure 11–6. However, the diverse chemical composition of modern paints provides additional points of comparison

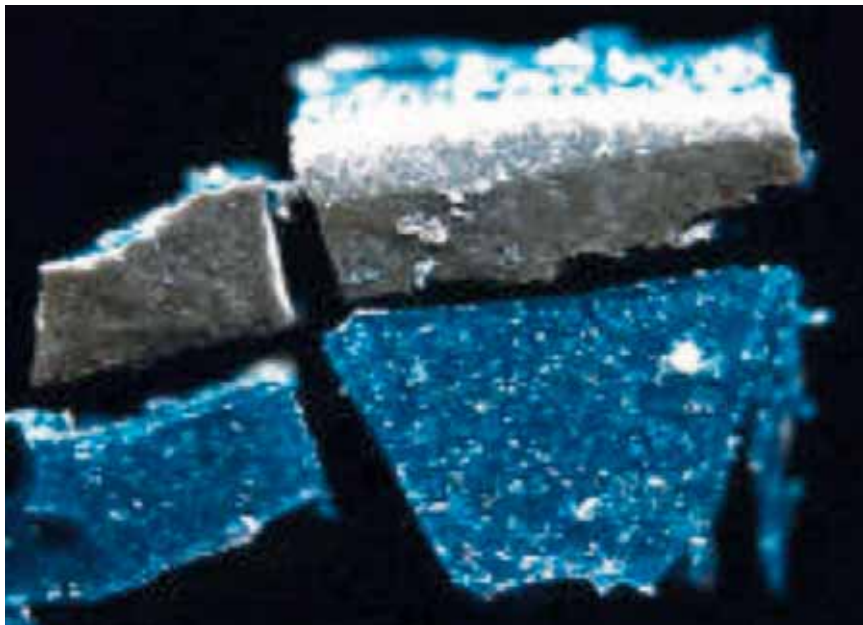


FIGURE 11-5 A stereoscopic microscope comparison of two automotive paints. The questioned paint on the left has a layer structure consistent with the control paint on the right. *Courtesy Leica Microsystems, Inc., Buffalo, N.Y., www.leica-microsystems.com*

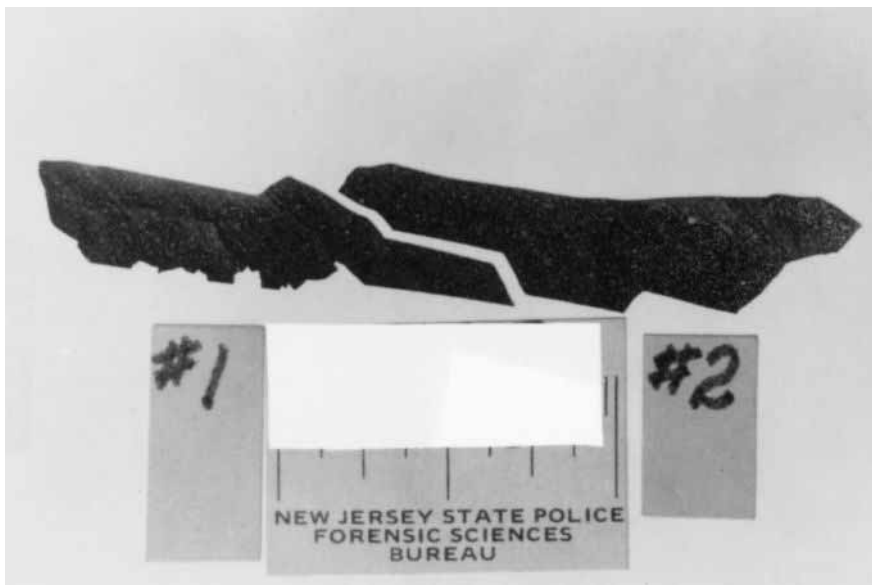


FIGURE 11-6 Paint chip 1 was recovered from the scene of a hit-and-run. Paint chip 2 was obtained from the suspect vehicle. *Courtesy New Jersey State Police*

between specimens. Specifically, a thorough comparison of paint must include a chemical analysis of the paint's pigments, its binder composition, or both.

Analytical Techniques Used in Paint Comparison

The wide variation in binder formulations in automobile finishes provides significant information. More important, paint manufacturers make automobile finishes in hundreds of varieties; this knowledge is most helpful to

the criminalist who is trying to associate a paint chip with one car as distinguished from the thousands of similar models that have been produced in any one year. For instance, there are more than a hundred automobile production plants in the United States and Canada. Each can use one paint supplier for a particular color or vary suppliers during a model year. Although a paint supplier must maintain strict quality control over a paint's color, the batch formulation of any paint binder can vary, depending on the availability and cost of basic ingredients.

pyrolysis

The decomposition of organic matter by heat.

Characterization of Paint Binders An important extension of the application of gas chromatography to forensic science is the technique of **pyrolysis gas chromatography**. Many solid materials commonly encountered as physical evidence—for example, paint chips, fibers, and plastics—cannot be readily dissolved in a solvent for injection into the gas chromatograph. Thus, under normal conditions these substances cannot be subjected to gas chromatographic analysis. However, materials such as these can be heated, or *pyrolyzed*, to high temperatures (500–1000°C) so that they will decompose into numerous gaseous products. Pyrolyzers permit these gaseous products to enter the carrier gas stream, where they flow into and through the GC column. The pyrolyzed material can then be characterized by the pattern produced by its chromatogram, or *pyrogram*.

Pyrolysis gas chromatography is particularly invaluable for distinguishing most paint formulations. In this process, paint chips as small as 20 micrograms are decomposed by heat into numerous gaseous products and are sent through a gas chromatograph.

As shown in Figure 11–7, the polymer chain is decomposed by a heated filament, and the resultant products are swept into and through a gas chromatograph column. The separated decomposition products of the polymer emerge and are recorded. The pattern of this chromatogram or “pyrogram” distinguishes one polymer from another. The result is a pyrogram that is

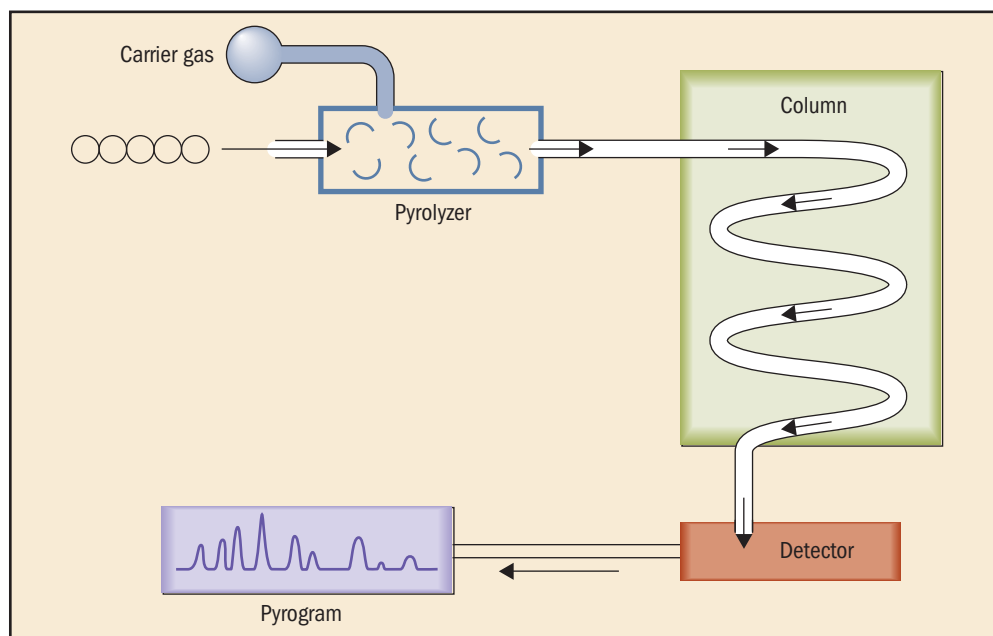


FIGURE 11–7 Schematic diagram of pyrolysis gas chromatography.

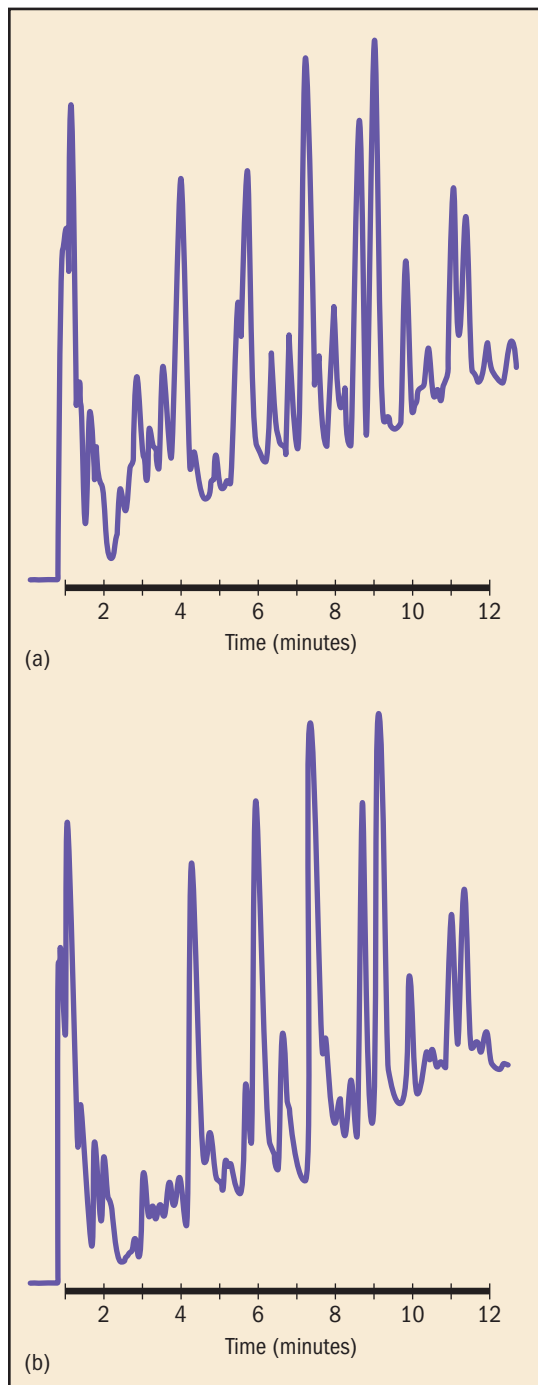


FIGURE 11-8 Paint pyrograms of acrylic enamel paints. (a) Paint from a Ford model and (b) paint from a Chrysler model. Courtesy Varian Inc., Palo Alto, Calif.

sufficiently detailed to reflect the chemical makeup of the binder. Figure 11-8 illustrates how the patterns produced by paint pyrograms can differentiate acrylic enamel paints removed from two different automobiles.

Infrared spectrophotometry is still another analytical technique that provides information about the binder composition of paint.² Binders selectively absorb infrared radiation to yield a spectrum that is highly characteristic of a paint specimen.

Characterization of Paint Pigments The elements that constitute the inorganic pigments of paints can be identified by a variety of techniques:

emission spectroscopy, neutron activation analysis, and X-ray spectroscopy (pp. 252–253). The emission spectrograph for example, can simultaneously detect fifteen to twenty elements in most automobile paints. Some of these elements are relatively common to all paints and have little forensic value; others are less frequently encountered and provide excellent points of comparison between paint specimens.

We saw in Chapter 5 that organic compounds can be characterized by selective absorption of ultraviolet, visible, or infrared radiation. Equally significant to the forensic chemist is the knowledge that elements also selectively emit and absorb light. These observations form the basis of emission spectroscopy.

When sunlight or the light from an incandescent bulb is passed through a prism, a range of rainbow colors is produced. The resulting display of colors is called an **emission spectrum**. This type of emission spectrum is called a **continuous spectrum** because all the colors merge or blend into one another to form a continuous band.

Not all light sources, however, produce a continuous spectrum. For example, if the light from a sodium lamp, a mercury arc lamp, or a neon light is passed through a prism, the resultant spectrum consists not of a continuous band, but of several individual colored lines separated by dark spaces. Here, each line represents a definite wavelength or frequency of light that is separate and distinct from all others in the spectrum. This type of spectrum is called a **line spectrum**. Figure 11–9 shows the line spectra of three elements. If a solid or liquid is vaporized and “excited” by exposure to high temperature, each element that is present emits light composed of select frequencies that are characteristic of the element. This spectrum is in essence a “fingerprint” of an element and offers a practical method of identification for liquid media such as paint. Sodium vapor, for example, always shows the same line spectrum, which differs from the spectrum of all other elements.

emission spectrum

Light emitted from a source and separated into its component colors or frequencies.

continuous spectrum

A type of emission spectrum showing a continuous band of colors all blending into one another.

line spectrum

A type of emission spectrum showing a series of lines separated by black areas. Each line represents a definite wavelength or frequency.

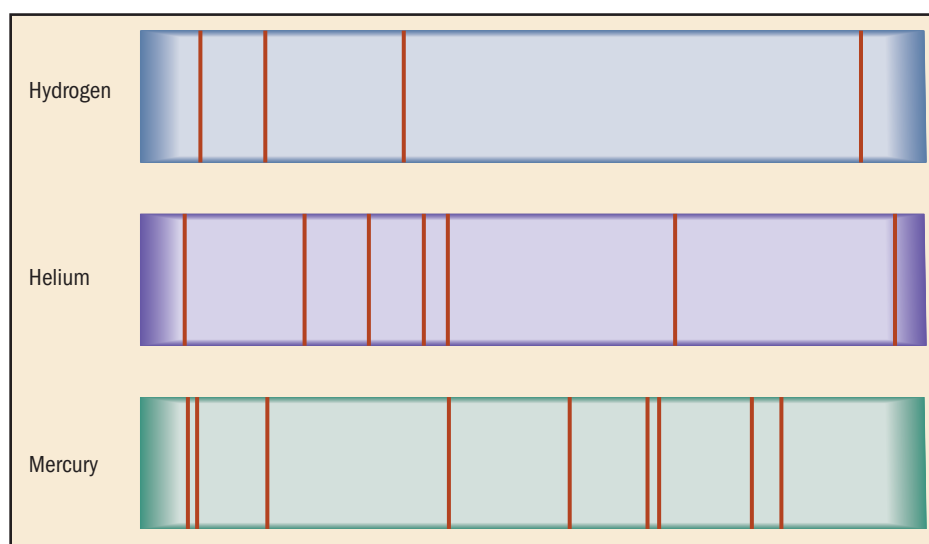


FIGURE 11–9 Some characteristic emission spectra.

Closer Analysis

The Carbon Arc Emission Spectrograph

An *emission spectrograph* is an instrument used to obtain and record the line spectra of elements. This instrument requires a means for vaporizing and exciting the atoms of elements so that they emit light, a means for separating this light into its component frequencies, and a means of recording the resultant spectrum. A simple emission spectrograph is depicted in Figure 1.

The specimen under investigation is inserted between two carbon electrodes through which a direct current arc is passed. The arc produces enough heat to vaporize and excite the specimen's atoms. A lens collects the light emitted by the excited atoms and focuses it onto a prism that disperses it into component frequencies.

The separated frequencies of light are then directed toward a photographic plate, where they are recorded as line images. Normally, a specimen consists of numerous elements; hence, the typical emission spectrum contains many lines.

Each element in the spectrum can be identified when it is compared to a standard chart that shows the position of the principal spectral lines of all the elements. However, forensic analysis usually requires a rapid comparison of the elemental composition of two or more specimens. This is easily accomplished by comparing the emission spectra line for line, as illustrated in Figure 2, in which the emission spectra of two paint chips are shown to be comparable.

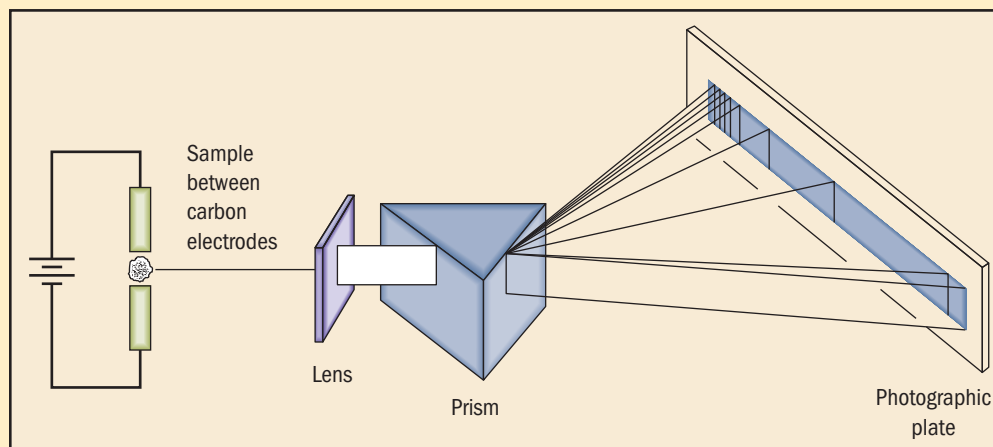


FIGURE 1 Parts of a simple emission spectrograph.



FIGURE 2 A comparison of paint chips 1 and 2 by emission spectrographic analysis. A line-for-line comparison shows that the paints have the same elemental composition.

Closer Analysis

The Origin of Emission Spectra

electron orbital

The path of electrons as they move around the nuclei of atoms; each orbital is associated with a particular electronic energy level.

excited state

The state in which an atom absorbs energy and an electron moves from a lower to a higher energy level.

To explain the origin of atomic spectra, we must focus on the *electron orbitals* of the atom. As electrons move around the nucleus, they are confined to a path from which they cannot stray. This orbital path is associated with a definite amount of energy and is therefore called an *energy level*. Each element has its own set of characteristic energy levels at varying distances from the nucleus. Some levels are occupied by electrons; others are empty.

An atom is in its most stable state when all of its electrons are positioned in their lowest possible energy orbitals. When an atom absorbs energy, such as heat or light, its electrons are pushed into higher-energy orbitals. In this condition, the atom is in an *excited state*. However, because energy levels have fixed values, only a definite amount of energy can be absorbed in moving an electron from one level to another. This is an important observation; atoms absorb only a definite value of energy, and all other energy values are excluded, as shown in the figure.

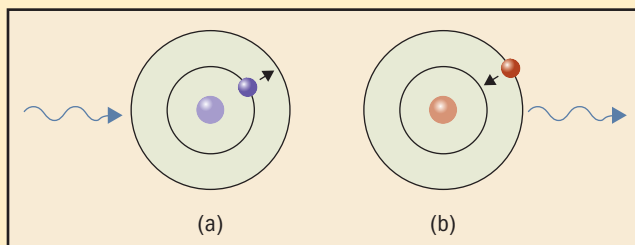
A specific frequency of light is required to cause this transition, and its energy must correspond to the exact energy difference between the two orbitals involved. This energy difference is expressed by the relationship $E = hf$, where E represents the energy difference between the two orbitals, f is the frequency of absorbed light, and h is a universal constant called Planck's constant. Any energy value that is more or less than

this difference will not produce the transition. Hence, an element is selective in the frequency of light it will absorb, and this selectivity is determined by the electron energy levels each element possesses.

In the same manner, if atoms are exposed to intense heat, enough energy will be generated to push electrons into unoccupied higher-energy orbitals. Normally the electron does not remain in this excited state for long, and it quickly falls back to its original energy level. As the electron falls back, it releases energy. An emission spectrum shows that this energy loss comes about in the form of light emission (see figure). The frequency of light emitted is again determined by the relationship $E = hf$, where E is the energy difference between the upper and lower energy levels and f is the frequency of emitted light. Because each element has its own characteristic set of energy levels, each emits a unique set of frequency values. The emission spectrum thus provides a "picture" of the energy levels that surround the nucleus of each element.

Thus, we see that as far as atoms are concerned, energy is a two-way street. Energy can be put into the atom at the same time that energy is given off; what goes in must come out. The chemist can study the atom using either approach.

(a) The absorption of light by an atom, causing an electron to jump into a higher orbital.
(b) The emission of light by an atom, caused by an electron falling back to a lower orbital.



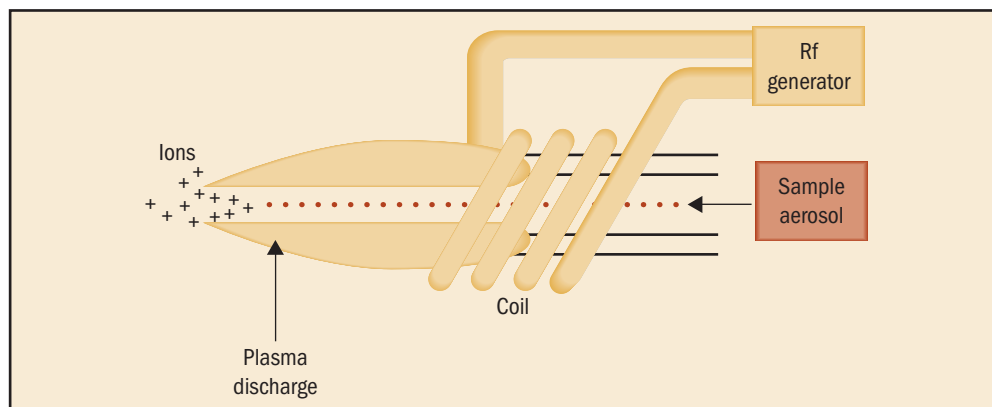


FIGURE 11-10 The creation of charged particles in the torch of an ICP discharge.

Inductively Coupled Plasma Emission Spectrometry (ICP) Recently, inductively coupled plasma (ICP) emission spectrometry has supplanted carbon arc emission spectroscopy for most applications. Like emission spectroscopy, ICP identifies and measures elements through light energy emitted by excited atoms. However, instead of using an electrical arc, the atoms are excited by placing the sample in a hot plasma torch. The torch is designed as three concentric quartz tubes through which argon gas flows (see Figure 11-10). A radio-frequency (RF) coil that carries a current is wrapped around the tubes. The RF current creates an intense magnetic field.

The process begins when a high-voltage spark is applied to the argon gas flowing through the torch. This strips some electrons from their argon atoms. These electrons are then caught and accelerated in the magnetic field such that they collide with other argon atoms, stripping off still more electrons. The collision of electrons and argon atoms continues in a chain reaction, breaking down the gas into argon atoms, argon ions, and electrons, forming an *inductively coupled plasma discharge*. The discharge is sustained by RF energy that is continuously transferred to it from the coil.

The plasma discharge acts like a very intense continuous flame generating temperatures in the range of 7,000–10,000°C. The sample, in aerosol form, is then introduced into the hot plasma, where it collides with the energetic argon electrons and generates charged particles (ions). The ions emit light of characteristic wavelengths that correspond to the identity of the elements in the sample.

The Significance of Paint Evidence

Once a paint comparison is completed, the task of assessing the significance of the finding begins. How certain can one be that two similar paints came from the same surface? For instance, a casual observer sees countless identically colored automobiles on our roads and streets. If this is the case, what value is a comparison of a paint chip from a hit-and-run scene to paint removed from a suspect car?

From previous discussions it should be apparent that far more is involved in paint comparison than matching surface paint colors. Paint layers beneath a surface layer offer valuable points of comparison. Furthermore, forensic analysts can detect subtle differences in paint binder

Closer Analysis

ICP Analysis of Bullets

Mutilated bullets often are not suitable for traditional microscopic comparisons against an exemplar test-fired bullet. In such situations, ICP has been used to obtain an elemental profile of the questioned bullet fragment for comparison against an unfired bullet generally found in the possession of the suspect.

For a number of years forensic scientists have been aware of significant compositional differences among lead sources for the manufacture of lead-based bullets. Knowledge of these differences can be valuable when comparing bullets that are too mutilated to analyze with a microscope. Compositional differences in trace elements are typically reflected in the copper, arsenic, silver, antimony, bismuth, cadmium, and tin profiles of lead bullets.

When two or more bullets have comparable elemental compositions, evidence of their similarity may be offered in a court of law. In this respect, the comparison of lead bullets

faces the same quandary as most common types of class physical evidence. The forensic analyst must convince a jury that the test results are meaningful to a criminal inquiry in the absence of any supporting statistical or probability data. Furthermore, creating meaningful databases to define the statistical significance of bullets compared by elemental profiles is currently an unrealistic undertaking.

Nevertheless, the significant diversity of bullet lead compositions in our population, like other class evidence such as fibers, hairs, paint, plastics, and glass, makes their chance occurrence at a crime scene and subsequent link to a defendant highly unlikely. However, care must be taken to avoid giving the impression that elemental profiles constitute a definitive match.

Given the millions of bullets produced each year, one cannot conclusively rule out the possibility of a coincidental match with a non-case-related bullet.

formulations, as well as major or minor differences in the elemental composition of paint. Obviously, these properties cannot be discerned by the naked eye.

The significance of a paint comparison was convincingly demonstrated from data gathered at the Centre of Forensic Science, Toronto, Canada.³ Paint chips randomly taken from 260 vehicles located in a local wreck yard were compared by color, layer structure, and, when required, by infrared spectroscopy. All were distinguishable except for one pair. In statistical terms, these results signify that if a crime-scene paint sample and a paint standard/reference sample removed from a suspect car compare by the previously discussed tests, the odds against the crime-scene paint originating from another randomly chosen vehicle are approximately 33,000 to one. Obviously, this type of evidence is bound to forge a strong link between the suspect car and the crime scene.

Crime laboratories are often asked to identify the make and model of a car from a very small amount of paint left behind at a crime scene. Such information is frequently of use in a search for an unknown car involved in a hit-and-run incident. Often the questioned paint can be identified when its color is compared to color chips representing the various makes and models of manufactured cars. However, in many cases it is not possible to state the exact make or model of the car in question, because any one paint color can be found on more than one car model. For

instance, General Motors may have used the same paint color for several production years on cars in its Cadillac, Buick, Pontiac, and Chevrolet lines.

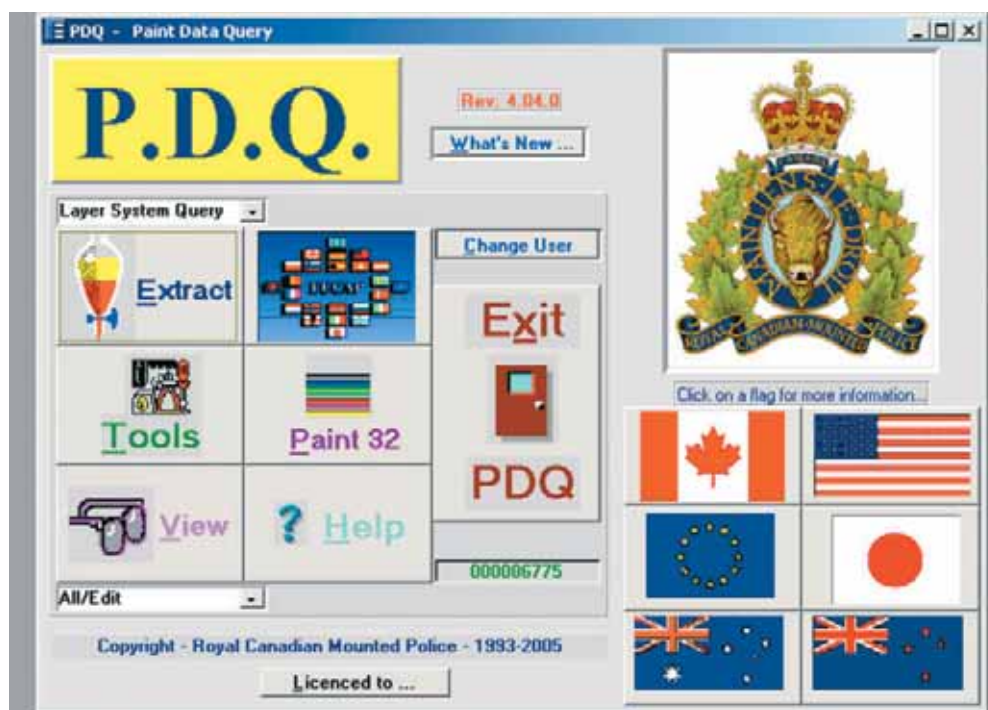
Color charts for automobile finishes are available from various paint manufacturers and refinishers (see Figure 11–11). Since 1975, the Royal Canadian Mounted Police Forensic Laboratories have been systematically gathering color and chemical information on automotive paints. This computerized database, known as PDQ (Paint Data Query), allows an analyst to obtain information on paints related to automobile make, model, and year. The database contains such parameters as automotive paint layer colors, primer colors, and binder composition (see Figure 11–12). A number of U.S. laboratories have access to PDQ.⁴ Also, some crime laboratories maintain an in-house collection of automotive paints associated with various makes and models, as shown in Figure 11–13.

Collection and Preservation of Paint Evidence

As has already been noted, paint chips are most likely to be found on or near people or objects involved in hit-and-run incidents. The recovery of loose paint chips from a garment or from the road surface must be done with the utmost care to keep the paint chip intact. Paint chips may be



FIGURE 11–11 Automotive color chart of various car models. *Courtesy Damian Dovanganes, AP Wide World Photos*



(a)

PDQ #	Layers	Sample	Make	Line	Model	Specs	Comments
UAZP00178	C	0	CAR	CHR	STH	2000	2003-Sep-09
UAZP00179	C	0	CAR	CHR	BEL	2000	2001-Jul-11
UAZP00180	C	0	TRK	CHR	DOD	2000	2000-May-12
UAZP00181	C	0	TRK	CHR	STL	2000	2003-Sep-04
UAZP00182	C	0	CAR	FOR	HER	2000	2000-Apr-13
UAZP00183	C	0	CAR	FOR	WIX	2000	2000-Apr-13
UAZP00184	C	0	CAR	GEN	OSH	2000	2000-Apr-14
UAZP00185	C	0	TRK	CHR	SAL	2000	2003-Jun-05
UAZP00186	C	0	CAR	CHR	BRA	2000	2000-Apr-13
UAZP00187	C	0	CAR	FOR	STT	2000	2000-May-05
UAZP00188	C	0	CAR	NIS	SMY	2000	2001-Apr-09
UAZP00189	C	0	TRK	CHR	STL	2000	2003-Sep-04
UAZP00190	C	0	TRK	CHR	STL	2000	2003-Sep-02
UAZP00191	C	0	CAR	HYU	ULS	1999	2000-Apr-14

(b)

FIGURE 11-12 (a) Home screen for PDQ database. (b) Partial list of autopaids contained in the PDQ database. Courtesy Royal Canadian Mounted Police

picked up with a tweezers or scooped up with a piece of paper. Paper drug-gist folds and glass or plastic vials make excellent containers for paint. If the paint is smeared on or embedded in garments or objects, the investigator should not attempt to remove it; instead, it is best to package the whole item carefully and send it to the laboratory for examination.

When a transfer of paint occurs in hit-and-run situations (such as to the clothing of a pedestrian victim), uncontaminated standard/reference



FIGURE 11-13 A crime laboratory's automotive paint library. Paints were collected at an automobile impound yard and then cataloged for rapid retrieval and examination. *Courtesy Gavin Edmonstone, Centre for Forensic Sciences, Toronto, Canada*

paint must always be collected from an undamaged area of the vehicle for comparison in the laboratory. The collected paint must be close to the area of the car that is suspected of being in contact with the victim. This is necessary because other portions of the car may have faded or been repainted.

Standard/reference samples are always removed so as to include all the paint layers down to the bare metal. This is best accomplished by removing a painted section with a clean scalpel or knife blade. Samples 1/4 inch square are sufficient for laboratory examination. Each paint sample should be separately packaged and marked with the exact location of its recovery.

When a cross-transfer of paint occurs between two vehicles, again all of the layers, including the foreign as well as the underlying original paints, must be removed from each vehicle. A standard/reference sample from an adjacent undamaged area of each vehicle must also be taken in such cases. Carefully wipe the blade of any knife or scraping tool used before collecting each sample, to avoid cross-contamination of paints.

Case Study

The Predator

September in Arizona is hot and dry, much like the rest of the year—but September 1984 was a little different. Unusually heavy rains fell for two days, which must have seemed fitting for the friends and family of 8-year-old Vicki Lynn Hoskinson. Vicki went

missing on September 17 of that year, and her disappearance was investigated as a kidnapping. A school-teacher who knew Vicki remembered a suspicious vehicle loitering near the school that day, and he happened to jot down the license plate number. This
(continued)

Case Study

The Predator (*continued*)

crucial tip led police to 28-year-old Frank Atwood, recently paroled from a California prison. Police soon learned that Atwood had been convicted for committing sex offenses and for kidnapping a boy. This galvanized the investigators, who realized Vicki could be at the mercy of a dangerous and perverse man.

The only evidence the police had to work with was Vicki's bike, which was found abandoned in the middle of the street a few blocks from her home. Police found scrapes from her bike pedal on the underside of the gravel pan on Atwood's car, as well as pink paint apparently transferred from Vicki's bike to Atwood's front bumper. The police believed that Atwood deliberately struck Vicki while she was riding her bicycle, knocking her to the ground.

The pink paint on Atwood's bumper was first looked at microscopically and then examined by pyrolysis gas chromatography, which entails heating the paint sample to extremely high temperature to vaporize and fragment the components of the paint. The pyrolyzed sample, in the form of a gas, is then pushed through a gas chromatographic column. By the time the paint components have reached the end of the column, they have separated and each chemical constituent is recorded. This technique provides investigators with a "fingerprint" pattern of the paint sample, enabling them to compare this paint to any other paint evidence. In this case, the pink paint on Atwood's bumper matched the paint from Vicki's bicycle.

Further evidence proving Atwood's involvement in the crime came when a

gouge on the surface of Vicki's bicycle was checked for its elemental composition with the aid of a scanning electron microscope (SEM) in combination with an X-ray analyzer. Traces of nickel were found on the gouge's surface. The bumper of Atwood's car was coated with a thin film of nickel, providing solid evidence of the cross-transfer of paint and metal between the bumper of Frank Atwood's car and Vicki Lynn's bicycle.

Vicki's skeletal remains were discovered in the desert, several miles away from her home, in the spring of 1985. Positive identification was made using dental records, but investigators wanted to see if the remains could help them determine how long she had been dead. Atwood was jailed on an unrelated charge three days after Vicki disappeared, so the approximate date of death was very important to proving his guilt.

Investigators found adipocere, a white, fatty residue produced during decomposition, inside Vicki's skull. This provided evidence that moisture was present around Vicki's body after her death, which does not make sense considering she was found in the Arizona desert! A check of the weather revealed that there had been an unusual amount of rainfall at only one time since Vicki was last seen alive: a mere forty-eight hours after her disappearance. This put Vicki's death squarely within Frank Atwood's three-day window of opportunity between her disappearance and his arrest. Frank Atwood was sentenced to death in 1987 for the murder of Vicki Lynn Hoskinson. He remains on death row awaiting execution.

Key Points

- Paint spread onto a surface dries into a hard film that is best described as consisting of pigments and additives suspended in the binder.
- Questioned and known paint specimens are best compared side by side under a stereoscopic microscope for color, surface texture, and color layer sequence.

- Pyrolysis gas chromatography and infrared spectrophotometry are used to distinguish most paint binder formulations.
- Emission spectroscopy and inductively coupled plasma are techniques available for determining the elemental composition of paint pigments.
- PDQ (Paint Data Query) is a computerized database that allows an analyst to obtain information on paints related to automobile make, model, and year.

Forensic Analysis of Soil

There are many definitions for the term *soil*; however, for forensic purposes, soil may be thought of as any disintegrated surface material, natural or and artificial, that lies on or near the earth's surface. Therefore, forensic examination of soil not only is concerned with analysis of naturally occurring rocks, minerals, vegetation, and animal matter; it also encompasses detection of such manufactured objects as glass, paint chips, asphalt, brick fragments, and cinders, whose presence may impart soil with characteristics that make it unique to a particular location. When this material is collected accidentally or deliberately in a manner that associates it with a crime under investigation, it becomes valuable physical evidence.⁵

The Significance of Soil Evidence

The value of soil as evidence rests with its prevalence at crime scenes and its transferability between the scene and the criminal. Thus, soil or dried mud found adhering to a suspect's clothing or shoes or to an automobile, when compared to soil samples collected at the crime site, may link a suspect or object to the crime scene. As with most types of physical evidence, forensic soil analysis is comparative in nature; soil found in the possession of the suspect must be carefully collected to be compared to soil samplings from the crime scene and its vicinity.

However, one should not rule out the value of soil even if the site of the crime has not been ascertained. For instance, small amounts of soil may be found on a person or object far from the actual site of a crime. A geologist who knows the local geology may be able to use geological maps to direct police to the general vicinity where the soil was originally picked up and the crime committed.

Forensic Examination of Soil

Most soils can be differentiated by their gross appearance. A side-by-side visual comparison of the color and texture of soil specimens is easy to perform and provides a sensitive property for distinguishing soils that originate from different locations. Soil is darker when it is wet; therefore, color comparisons must always be made when all the samples are dried under identical laboratory conditions. It is estimated that there are nearly 1,100 distinguishable soil colors; hence, color offers a logical first step in a forensic soil comparison.

Microscopic Examination of Soil Low-power microscopic examination of soil reveals the presence of plant and animal materials as well as of artificial debris. Further high-power microscopic examination helps characterize minerals and rocks in earth materials. Although this approach to

mineral

A naturally occurring crystalline solid.

forensic soil identification requires the expertise of an investigator trained in geology, it can provide the most varied and significant points of comparison between soil samples. Only by carefully examining and comparing the minerals and rocks naturally present in soil can one take advantage of the large number of variations between soils and thus add to the evidential value of a positive comparison.⁶

A **mineral** is a naturally occurring crystal, and like any other crystal, its physical properties—for example, color, geometric shape, density, and refractive index or birefringence—are useful for identification. More than 2,200 minerals exist; however, most are so rare that forensic geologists usually encounter only about twenty of the more common ones. Rocks are composed of a combination of minerals and therefore exist in thousands of varieties on the earth's surface. They are usually identified by characterizing their mineral content and grain size (see Figure 11–14).

Considering the vast variety of minerals and rocks and the possible presence of artificial debris in soil, the forensic geologist is presented with many points of comparison between two or more specimens. The number of comparative points and their frequency of occurrence must be considered before concluding similarity between specimens and judging the probability of common origin.

Rocks and minerals not only are present in earth materials but are also used to manufacture a wide variety of industrial and commercial products. For example, the tools and garments of an individual suspected of breaking into a safe often contain traces of safe insulation. Safe insulation may be made from a wide combination of mineral mixtures that provide significant points of identification. Similarly, building materials such as brick, plaster, and concrete blocks are combinations of minerals and rocks that can easily be recognized and compared microscopically to similar minerals found on the breaking-and-entering suspect.

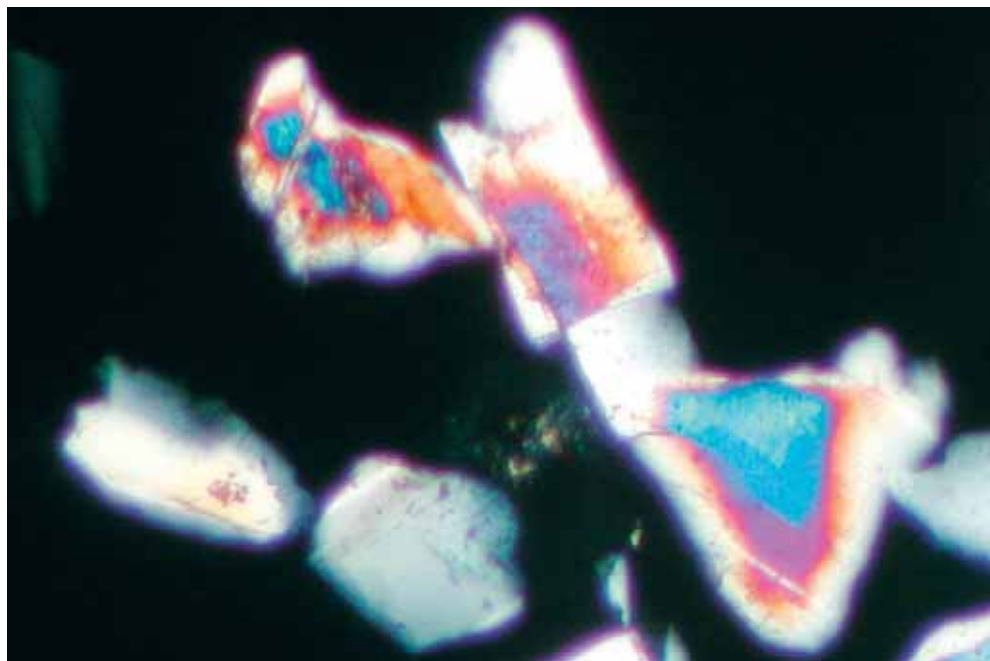


FIGURE 11–14 A mineral viewed under a microscope. Courtesy Chris Palenik, Ph. D., Microtrace, Elgin, IL., www.microtracescientific.com

Density-Gradient Tube Some forensic laboratories utilize the **density-gradient tube** technique to compare soil specimens. Typically, glass tubes 6–10 millimeters in diameter and 25–40 centimeters long are filled with layers of two liquids mixed in varying proportions so that each layer has a different density value. For example, tetrabromoethane (density 2.96 g/mL) and ethanol (density 0.789 g/mL) may be mixed so that each successive layer has a lower density than the preceding one, from the bottom to the top of the tube. The simplest gradient tube may have from six to ten layers, in which the bottom layer is pure tetrabromoethane and the top layer is pure ethanol, with corresponding variations of concentration in the layers between these two extremes.

When soil is added to the density-gradient tube, its particles sink to the portion of the tube that has a density of equal value; the particles remain suspended in the liquid at this point. In this way, a density distribution pattern of soil particles can be obtained and compared to other specimens treated in a similar manner (see Figure 11–15).

Only a few crime laboratories use this procedure to compare soil evidence. There is evidence that the test is far from definitive, because many soils collected from different locations yield similar density distribution patterns.⁷ At best, the density-gradient test is useful for comparing soils when it is used in combination with other tests.

Variations in Soil

The ultimate forensic value of soil evidence depends on its variation at the crime scene. If, for example, soil is indistinguishable for miles surrounding the location of a crime, it will have limited value in associating soil found on the suspect with that particular site. Significant conclusions relating a suspect to a particular location through a soil comparison may be made when variations in soil composition occur every 10–100 yards from the crime site. However, even when such variations do exist, the forensic geologist usually cannot individualize soil to any one location unless an unusual combination of rare minerals, rocks, or artificial debris can be located.

density-gradient tube

A glass tube filled from bottom to top with liquids of successively lighter densities; used to determine the density distribution of soil.

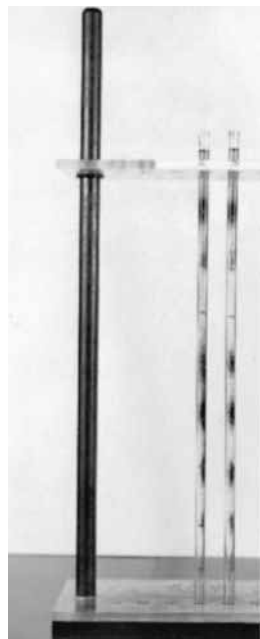


FIGURE 11–15 A soil comparison by density gradient tubes.

Courtesy Philadelphia Police Department Laboratory

No statistically valid forensic studies have examined the variability of soil evidence. A study conducted in southern Ontario, Canada, seems to indicate that soil in that part of Canada shows extensive diversity. It estimated a probability of less than 1 in 50 of finding two soils that are indistinguishable in both color and mineral properties but originate in two different locations separated by a distance of 1,000 feet. Based on these preliminary results, similar diversity may be expected in the northern United States, Canada, northern Europe, and eastern Europe. However, such probability values can only generally indicate the variation of soil within these geographical areas. Each crime scene must be evaluated separately to establish its own soil variation probabilities.

Collection and Preservation of Soil Evidence

When gathering soil specimens, the evidence collector must give primary consideration to establishing the variation of soil at the crime-scene area. For this reason, standard/reference soils should be collected at various intervals within a 100-yard radius of the crime scene, as well as at the site of the crime, for comparison to the questioned soil. Soil specimens also should be collected at all possible alibi locations that the suspect may claim.

All specimens gathered should be representative of the soil that was removed by the suspect. In most cases, only the top layer of soil is picked up during the commission of a crime. Thus, standard/reference specimens must be removed from the surface without digging too deeply into the unrepresentative subsurface layers. Approximately a tablespoon or two of soil is all the laboratory needs for a thorough comparative analysis. All specimens collected should be packaged in individual containers, such as plastic vials. Each vial should be marked to indicate the location at which the sampling was made.

Soil found on a suspect must be carefully preserved for analysis. If it is found adhering to an object, as in the case of soil on a shoe, the investigator must not remove it. Instead, each object should be individually wrapped in paper, with the soil intact, and transmitted to the laboratory. Similarly, loose soil adhering to garments should not be removed; these items should be carefully and individually wrapped in paper bags and sent to the laboratory for analysis. Care must be taken that particles that may accidentally fall off the garment during transportation will remain in the paper bag.

When a lump of soil is found, it should be collected and preserved intact. For example, an automobile tends to collect and build up layers of soil under the fenders, body, and so on. The impact of an automobile with another object may jar some of this soil loose. Once the suspect car has been apprehended, a comparison of the soil left at the scene with soil remaining on the automobile may help establish that the car was present at the accident scene. In these situations, separate samples are collected from under all the fender and frame areas of the vehicle; care is taken to remove the soil in lump form in order to preserve the order in which the soil adhered to the car. Undoubtedly, during the normal use of an automobile, soil will be picked up from numerous locations over a period of months and years. This layering effect may impart soil with greater variation, and hence greater evidential value, than that normally associated with loose soil.

Key Points

- A side-by-side visual comparison of the color and texture of soil specimens provides a way to distinguish soils that originate from different locations.

- Minerals are naturally occurring crystalline solids found in soil. Their physical properties—for example, color, geometric shape, density, and refractive index or birefringence—are useful for characterizing soils.
- Some crime laboratories compare soils by using density-gradient tubes filled with layers of liquids with different density values.

Forensic Brief

Soil: The Silent Witness

Alice Redmond was reported missing by her husband on a Monday night in 1983. Police learned that she had been seen with a co-worker, Mark Miller, after work that evening. When police questioned Miller, he stated that the two just “drove around” after work and then she dropped him off at home. Despite his statement, Miller was the prime suspect because he had a criminal record for burglary and theft.

Alice’s car was recovered in town the following morning. The wheel wells were thickly coated in mud, which investigators hoped might provide a good lead. These hopes were dampened when police learned that Alice and her husband had attended a motorcycle race on Sunday, where her car was driven through deep mud.

After careful scrutiny, analysts found two colors of soil on the undercarriage of Alice’s car. The thickest soil was brown; on top of the brown layer was a reddish soil that looked unlike anything in the county. Investigators hoped the reddish soil, which had to have been deposited sometime after the Sunday night motorcycle event and before the vehicle was discovered on Tuesday morning, could link the vehicle to the location of Alice Redmond.

An interview with Mark Miller’s sister provided a break in the case. She told police that Mark had visited her on Monday

evening. During that visit, he confessed that he had driven Alice in her car across the Alabama state line into Georgia, killed her, and buried her in a remote location. Now that investigators had a better idea where to look for Alice, forensic analysts took soil samples that would prove or disprove Miller’s sister’s story.

Each field sample was dried and compared for color and texture by eye and stereomicroscopy to the reddish-colored soil gathered from the car. Next, soils that compared to the car were passed through a series of mesh filters, each of a finer gauge than the last. In this way, the components of the soil samples were physically separated by size. Finally, each fraction was analyzed and compared for mineral composition with the aid of a polarizing light microscope.

Only samples collected from areas across the Alabama state line near the suspected dump site were consistent with the topmost reddish soil recovered from Alice’s car. This finding supported Miller’s sister’s story and was instrumental in Mark Miller’s being charged with murder and kidnapping. After pleading guilty, the defendant led the authorities to where he had buried the body. The burial site was within a half mile of the location where forensic analysts had collected a soil sample consistent with the soil removed from Alice’s vehicle.

Source: T. J. Hopen, “The Value of Soil Evidence,” in *Trace Evidence Analysis: More Cases in Mute Witnesses*, M. M. Houck, ed. (Elsevier Academic Press, Burlington, Mass., 2004), pp. 105–122.

Chapter Summary

For the criminalist, the presence of trace elements is particularly useful, because they provide “invisible” markers that may establish the source of a material or at least provide additional points for comparison.

A popular descriptive model of the atom pictures an atom as consisting of electrons orbiting a central nucleus. The nucleus is composed of positively charged protons and neutrons that have no charge. Because the atom has no net electrical charge, the number of protons must always equal the number of electrons in orbit around the nucleus.

One method used to identify trace elements in metals is neutron activation analysis, which measures the gamma-ray frequencies of specimens that have been bombarded with neutrons. The nucleus of an atom captures one or more neutrons and forms an isotope and often decomposes, emitting radioactivity in the form of gamma-ray frequencies. This method provides a highly sensitive and nondestructive analysis for simultaneously identifying and quantitating twenty to thirty trace elements. Because this technique requires access to a nuclear reactor, however, it has limited value to forensic analysis.

Paint spread onto a surface dries into a hard film consisting of pigments and additives suspended in the binder. One of the most common types of paint examined in the crime laboratory is finishes from automobiles. Manufacturers apply a variety of coatings to the body of an automobile. Hence, the wide diversity of automotive paint contributes to the forensic significance of an automobile paint comparison.

Questioned and known paint specimens are best compared side by side under a stereoscopic microscope for color, surface texture, and color layer sequence. Pyrolysis gas chromatography and infrared spectrophotometry are invaluable for distinguishing most paint formulations, adding further significance to a forensic paint comparison.

Emission spectroscopy and inductively coupled plasma are two techniques available to forensic scientists for determining the elemental composition of paint and other substances. An emission spectrograph vaporizes and heats samples to a high temperature so that the atoms in the material achieve an “excited” state. Under these circumstances, the excited atoms emit light. If the light is separated into its components, one observes a line spectrum. Each element in the spectrum can be identified by its characteristic line frequencies. In inductively coupled plasma, the sample, in the form of an aerosol, is introduced into a hot plasma, creating charged particles that emit light of characteristic wavelengths corresponding to the identity of the elements present.

The value of soil as evidence rests with its prevalence at crime scenes and its transferability between the scene and the criminal. Most soils can be differentiated by their gross appearance. A side-by-side visual comparison of the color and texture of soil specimens is easy to perform and provides a sensitive property for distinguishing soils that originate from different locations. In many forensic laboratories, forensic geologists characterize and compare the mineral content of soils. Some crime laboratories use density-gradient tubes to compare soils. These tubes are typically filled with layers of liquids that have different density values.

Review Questions

Facts and Concepts

1. What are trace elements and how are they useful to forensic scientists?
2. Forensic analysis of the bullets recovered after the assassination of President John F. Kennedy focused on the concentration of what two trace elements?
3. Which of the following conclusions can be drawn from the forensic analysis of the bullets recovered after the assassination of President John F. Kennedy?
 - a. The analysis absolutely verified the findings of the Warren Commission.
 - b. The analysis cast doubt on the findings of the Warren Commission.
 - c. The analysis generally supported the findings of the Warren Commission.
 - d. The analysis absolutely disproved the findings of the Warren Commission.
4. Name the three most important subatomic particles and their electrical charges, and indicate where each is located in the atom.
5. How does atomic number differ from atomic mass?
6. What is an isotope?
7. What is radioactivity? What are the three types of radiation?
8. Briefly describe the process of neutron activation analysis.
9. Name two advantages and two drawbacks of neutron activation analysis.
10. In what types of criminal cases is paint evidence most frequently encountered?
11. Describe the basic composition of paint. What component of paint evaporates after paint is applied to a surface?
12. What aspect of the automotive painting process is helpful in forensic characterization of automobile paint? How is it helpful?
13. What is the best way to make a microscopic comparison of paint chips?
14. What characteristics does a criminalist look for when comparing paint chips under a microscope? Which of these characteristics is most important in evaluating the significance of paint evidence?
15. A thorough comparison of paint must include a chemical analysis of what two properties?
16. What chromatographic process has proven to be particularly invaluable for distinguishing most paint formulations? Why is it so useful in the comparison of paint?
17. Briefly describe the process of emission spectroscopy.
18. What technique has largely supplanted carbon arc emission spectroscopy for most applications? What is the main difference between the two techniques?
19. What is PDQ and how is it helpful to forensic scientists?
20. Why must paint collected from a vehicle involved in a hit-and-run accident be taken from the area of the car suspected of being in contact with the victim?
21. How should the investigator handle the collection of trace paint evidence left on a tool?

22. What is the first step in a forensic soil comparison?
23. What is a mineral? How are minerals useful in forensic soil analysis?
24. Briefly describe how soil is separated in a density-gradient tube.
25. From what areas should standard/reference soils be collected when gathering soil evidence?
26. How should soil evidence adhering to shoes and clothing be collected and packaged?
27. How should lumps of soil be collected and preserved? Why?

Application and Critical Thinking

1. Using the periodic table shown in Chapter 4, determine the atomic numbers for antimony, tin, barium, and lead. Which do you think has the largest atomic mass? Which do you think has the smallest atomic mass? Explain your answers.
2. You are investigating a hit-and-run accident and have identified a suspect vehicle. Describe how you would collect paint to determine whether the suspect vehicle was involved in the accident. Be sure to indicate the tools you would use and the steps you would take to prevent cross contamination.
3. Criminalist Jared Heath responds to the scene of an assault on an unpaved lane in a rural neighborhood. Rain had fallen steadily the night before, making the area quite muddy. A suspect with very muddy shoes was apprehended nearby, but claimed to have picked up the mud either from his garden or from the unpaved parking lot of a local restaurant. Jared uses a spade to remove several samples of soil, each about 2 inches deep, from the immediate crime scene, and places each in a separate plastic vial. He collects the muddy shoes and wraps them in plastic as well. At the laboratory, he unpackages the soil samples and examines them carefully, one at a time. He then analyzes the soil on the shoes to see if it matches the soil from the crime scene. What mistakes, if any, did Jared make in his investigation?

Case Analysis

In the case of the CBS Murders, police suspected that the female victim had been moved from the location where she was murdered. Although an eyewitness placed a woman at the scene of the shooting, trace evidence ultimately was the key to solving the case.

1. What was the primary challenge facing the investigators in this case?
2. What items of evidence directly linked the victim to the suspect? Which items indirectly linked the two?
3. How was paint evidence used to show that the female victim was shot at the garage?

Web Resources

Forensic Paint Analysis and Comparison Guidelines (Article from the July 1999 issue of the online FBI journal *Forensic Science Communications*)

www.fbi.gov/hq/lab/fsc/backissu/july1999/painta.htm

Collecting Crime Evidence from Earth (Online article by forensic geologist Raymond C. Murray that includes a discussion of soil analysis)

www.forensicgeology.net/science.htm

Forensic Examination of Soil Evidence (Online report from Interpol about methods/advances in soil examination)

www.interpol.int/Public/Forensic/IFSS/meeting13/Reviews/Soil.pdf

The Atom Builder (Interactive exercise that explains fundamentals of atomic structure and allows users to try to construct stable atoms from subatomic particles)

www.pbs.org/wgbh/aso/tryit/atom/#

The Atom and Electromagnetic Radiation (Discussion of nuclear structure and electromagnetic radiation with practice problems)

chemed.chem.purdue.edu/genchem/topicreview/bp/ch6/atom_emrframe.html

Intro to Quantum Mechanics (Layperson's explanation of basic concepts of quantum theory)

www.hi.is/~hj/QuantumMechanics/quantum.html

Endnotes

1. Actually, the electrons are moving so rapidly around the nucleus that they are best visualized as an electron cloud spread out over the surface of the atom.
2. P. G. Rodgers et al., "The Classification of Automobile Paint by Diamond Window Infrared Spectrophotometry, Part I: Binders and Pigments," *Canadian Society of Forensic Science Journal* 9 (1976): 1; T. J. Allen, "Paint Sample Presentation for Fourier Transform Infrared Microscopy," *Vibration Spectroscopy* 3 (1992): 217.
3. G. Edmondstone, J. Hellman, K. Legate, G. L. Vardy, and E. Lindsay, "An Assessment of the Evidential Value of Automotive Paint Comparisons," *Canadian Society of Forensic Science Journal* 37 (2004): 147.
4. J. L. Buckle et al., "PDQ—Paint Data Queries: The History and Technology behind the Development of the Royal Canadian Mounted Police Laboratory Services Automotive Paint Database," *Canadian Society of Forensic Science Journal* 30 (1997): 199. An excellent discussion of the PDQ database is also available in A. Beveridge, T. Fung, and D. MacDougall, "Use of Infrared Spectroscopy for the Characterisation of Paint Fragments," in B. Caddy, ed., *Forensic Examination of Glass and Paint* (New York: Taylor & Francis, 2001), pp. 222–233.
5. E. P. Junger, "Assessing the Unique Characteristics of Close-Proximity Soil Samples: Just How Useful Is Soil Evidence?" *Journal of Forensic Sciences* 41 (1996), 27.
6. W. J. Graves, "A Mineralogical Soil Classification Technique for the Forensic Scientist," *Journal of Forensic Sciences* 24 (1979): 323; M. J. McVicar and W. J. Graves, "The Forensic Comparison of Soil by Automated Scanning Electron Microscopy," *Canadian Society of Forensic Science Journal* 30 (1997): 241.
7. K. Chaperlin and P. S. Howarth, "Soil Comparison by the Density Gradient Method—A Review and Evaluation," *Forensic Science International* 23 (1983): 161–177.

Case Reading

The CBS Murders*

In the early morning hours . . . atop a lonely roof garage on the west side of Manhattan, three men [all employed by CBS-TV] were found murdered. Each man had been shot once in the back of the head. A light-colored van was seen speeding away from the scene. Hours later, in a secluded alley street on the lower east side of Manhattan, the body of a fully clothed woman was found lying face down by two dog walkers. The woman had been killed in the same manner as the men on the roof garage. The condition of the woman's body, and other evidence, made it apparent that she had been shot at the garage, and then transported to the alley.

An eyewitness to the incident stated that he saw a man shoot a woman and place her in a light-colored van. The gunman then chased down the three men who were coming to the woman's aid, and shot each one of them. Days later, the prime suspect to the killings was arrested in Kentucky, in a black-colored van.

Numerous items of evidence (over 100) were collected from the van, and forwarded to the New York City police laboratory for examination. Among the items of evidence forwarded were three sets of vacuum sweepings from the van's interior.

An autopsy of the woman produced several items of trace evidence that were removed from the victim and forwarded to the author for microscopic examination. The woman's clothing was also received by the author for trace analysis.

A prime question that arose during the investigation was: could the woman's

body, which had been placed in a light-colored van at the garage, and later left in an alley on the lower east side, be associated with the black van recovered over 1000 km (600 miles) away from the scene? Microscopic analysis and comparison of the trace evidential materials found on the victim and inside the van made this association possible.

Listed in Table 1 are all the items of similar trace materials that both the victim and the van had in common.

Microscopic comparisons of the questioned human head hair present on the victim's clothing were made with known samples. Ten of the brown-colored and gray-colored Caucasian head hairs from the victim's blazer were consistent in microscopic characteristics to the defendant's known head hair sample. One chemically treated head hair found on the victim was consistent in microscopic characteristics to the known head hair sample obtained from the defendant's wife. One forcibly removed, brown-colored, Caucasian head hair that was found on the rear door of the van's interior by the Kentucky state police was found to be consistent in all characteristics with the decedent's known head hair sample.

Microscopic comparisons of the white- and brown/white-colored dog hair from the victim's clothing, and the van's interior, were made with known samples of dog hair obtained from a dog owned by the defendant's nephew, the van's previous owner. The questioned dog hairs were found to be consistent with the hair from the nephew's dog.

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* This case takes its title from the fact that the three victims were employees of CBS-TV.

Table 1 Items of Similar Trace Evidence That Were Recovered from Both the Victim and the Van's Interior

Trace Evidence	Source	
	Victim	Van
White seed	mouth	sweepings
Paint chips gray/metallic/ black	hair and wool blazer	sweepings and floor
Sawdust	hair, blazer, and sheet	sweepings and misc. items
Glass fragments clear amber green	wool blazer and sheet	sweepings and misc. items
Cellophane	wool blazer	floor
Urethane foam foam mattress	wool blazer	sweepings, misc. items, and foam mattress
Blue olefin plastic	skirt	floor
Dog hair brown/white white	wool blazer	sweepings and misc. items
Human hair brown gray	wool blazer	hairbrush, sweepings, and misc. items

The white seed that was recovered from the victim's mouth by the medical examiner, and the white seed that was found in the van's sweepings by the author, were forwarded to an internationally known botanist for identification and comparison. During the trial, the botanist testified that the two seeds were identical in all respects, and that although he could not identify the seed, both were either from the same species of plant, if not the same plant, probably a rare wild flower.

Sixteen gray metallic/black-colored paint chips from the victim and her clothing were

compared to the gray metallic/black-colored paint removed from the van. Samples from the questioned and known sources were examined and compared by microscopic, chemical, and instrumental means. All of the paint specimens from the van and from the victim were found to be similar in all respects.

The remaining items of trace evidence from the victim and the van were examined and compared microscopically, and where necessary, by chemical and instrumental methods. Each of the remaining types of trace evidence from the victim was found to be similar to its counterpart from the van.

Blue- and black-colored flakes of acrylic paint were found in the van's sweepings, and on the suspect's sneakers. No blue- or black-colored paint flakes were found on the victim and her clothing. During a crime scene search of the defendant's residence in New Jersey, a large quantity of blue- and black-colored acrylic paint was found in the garage. It was apparent from the evidence present in the defendant's garage that a large rectangular shaped object had recently been painted with blue- and black-colored paint. The blue and black paint flakes from all the sources and the known blue (undercoat) and black (topcoat) paint from the van were compared by microscopic, chemical, and instrumental

means. All the samples of paint were found to be consistent in every respect.

At the trial, extensive testimony concerning the collection, examination, identification, and comparison of the trace evidence from the victim and the van was given by the author, over a two-day period. When questioned about the source of the trace evidence found on the victim and her clothing, the author stated unequivocally that the trace evidence on the victim was from the defendant's van. On the basis of this evidence and other circumstantial evidence, the defendant was found guilty of all charges and sentenced to 100 years in prison.