

## chapter 6

# Inorganic Analysis

### Key Terms

alpha ray

atomic mass

atomic number

beta ray

continuous spectrum

electron

electron orbital

emission spectrum

excited state

gamma ray

isotope

line spectrum

neutron

nucleus

proton

radioactivity

X-ray diffraction

## **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
- Distinguish continuous and line emission spectra
- Understand the parts of a simple emission spectrograph
- List the parts of a simple atomic absorption spectrophotometer
- Define and distinguish protons, neutrons, and electrons
- Define and distinguish atomic number and atomic mass number
- Appreciate the phenomenon of how an atom absorbs and releases energy in the form of light
- Explain the concept of an isotope
- Understand how elements can be made radioactive
- Describe why an X-ray diffraction pattern is useful for chemical identification

## **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. St. Helena was hot, unsanitary, and rampant with disease. There, in 1815, Napoleon was confined to a large reconstructed agricul-**

tural 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 at a rapid rate 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?

In the previous chapter, analytical techniques were described for characterizing a class of matter known as organics. Generally, these materials contain carbon. Although organic substances constitute a substantial portion of the physical evidence submitted to crime laboratories, carbon does not appear among the earth's most abundant elements. Surprisingly about three-quarters of the weight of the earth's crust is composed of only two elements—oxygen and silicon. In fact, only

ten elements make up approximately 99 percent of the earth's crust (see Table 6–1). The remaining elements may almost be considered impurities, although exceedingly important ones. Carbon, the element that is a constituent of most chemical compounds, constitutes less than 0.1 percent of the earth's crust.

Considering these facts, it is certainly reasonable that non-carbon-containing substances—that is, inorganics—are encountered as physical evidence at crime scenes. One only has to consider the prevalence of metallic materials, such as iron, steel, copper, and aluminum, in our society to understand the possibilities of finding tools, coins, weapons, and metal scrapings at crime scenes.

**Table 6–1 Elemental Abundances as Percentages in the Earth's Crust**

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<b>Element</b>	<b>Percentage by Weight</b>
Oxygen	47.3
Silicon	27.7
Aluminum	7.9
Iron	4.5
Calcium	3.5
Sodium	2.5
Potassium	2.5
Magnesium	2.2
Titanium	0.5

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Hydrogen	0.2
Other elements	1.2

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Less well known, but perhaps almost as significant to the criminalist, is the use of inorganic chemicals as pigments in paints and dyes, the incorporation of inorganics into explosive formulations, and the prevalence of inorganic poisons such as mercury, lead, and arsenic.

To appreciate fully the role of inorganic analysis in forensic science, we must first examine its application to the basic objectives of the crime laboratory—identification and comparison of physical evidence. Identification of inorganic evidence is exemplified by a typical request to examine an explosive formulation suspected of containing potassium chlorate, or perhaps to examine a poisonous powder thought to be arsenic. In each case, the forensic scientist must perform tests that will ultimately determine the specific chemical identity of the suspect materials to the exclusion of all others. Only after completing the tests and finding their results identical to previously recorded tests for a known potassium chlorate or a known arsenic can the forensic scientist draw a valid conclusion about the chemical identity of the evidence.

However, comparing two or more objects in order to ascertain their common origin presents a different problem. For example, a criminalist may be asked to determine whether a piece of brass pipe found in the possession of a suspect compares to a broken pipe found at the crime scene. The condition of the two pipes might not allow for comparison by physically fitting together any broken edges. Under these circumstances, the only alternative will be to attempt a comparison through chemical analysis. It is not enough for the analyst to conclude that the pipes are alike because they are brass (an alloy of copper and zinc). After all, hundreds of thousands of brass pipes exist, a situation that is hardly conducive to proving that these two particular pipes

were at one time a single unit. The examiner must go a step further to try to distinguish these pipes from all others. Although this may not be possible, a comparison of the pipes' trace elements—that is, elements present in small quantities—will provide a meaningful criterion for at least increasing the probability that the two pipes originated from the same source.

Considering that most of our raw 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 have to be eliminated through industrial processing. However, in most cases it is not economically feasible to completely exclude all such minor impurities, especially when their presence will have 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. 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. Table 6–2 illustrates how two types of brass alloys can readily be distinguished by their elemental composition. Similarly, the comparison of trace elements present in paint or other types of metallic specimens may provide particularly meaningful data with respect to source or origin. Forensic investigators have examined the evidential value of trace elements present in soil, fibers, and glass, as well as in all types of metallic objects. One example of this application occurred with the examination of the bullet and bullet fragments recovered after the assassination of President Kennedy.

**Table 6–2 Elemental Analysis of Brass Alloys**

	<b>High-Tensile Brass</b>	<b>Manganese Brass</b>
<b>Element</b>	<b>(percentage)</b>	<b>(percentage)</b>

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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

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

## **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, as the Warren Commission concluded, a lone assassin. In arriving at their conclusions, the Warren Commission reconstructed the crime as follows: Oswald fired three shots from behind the president while positioned in the Texas School Book Depository building. The president was struck by two bullets, with one bullet totally missing the president's limousine. One bullet hit the president in the back,

exited his throat, and then went on to strike Governor Connally, who was sitting in a jump seat in front of the president. The bullet hit Connally first in his back, then exited his chest, struck his right wrist, and temporarily lodged in his left thigh. This bullet was later found in 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-mm Mannlicher-Carcano military rifle was found with Oswald's palm print on it. Also found were three spent 6.5-mm 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.

Critics of the Warren Commission have long argued that evidence exists that would prove Oswald did not act alone. Eyewitness accounts and acoustical data interpreted by some experts have been used to advocate the contention that someone else fired at the president from a region in front of the limousine (the so-called grassy knoll). Furthermore, it is argued that the Warren Commission's reconstruction of the crime relied on the assumption that only one bullet caused both the president's throat wound and 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, at the request of the U.S. House of Representatives Select Committee on Assassinations, the bullet taken from Connally's stretcher along with bullet fragments recovered from the car and various wound areas were examined for trace element levels.

Lead alloys used for the manufacture of bullets contain an assortment of trace elements. 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. In this case, the bullet and bullet fragments were compared for their antimony and silver content. 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 6–3, the samples designated Q1 and Q9 (the Connally stretcher bullet and fragments from Connally’s wrist, respectively) are indistinguishable from one another in antimony and silver content. The samples Q2; Q4, 5; and Q14 (Q4, 5 being fragments from Kennedy’s brain, and Q2 and Q14 being fragments recovered from two different areas in the car) also are indistinguishable in antimony and silver content but are different from Q1 and Q9.

The conclusions derived from studying these results are as follows:

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 entirely be ruled out.
3. The bullet found in 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.

**Table 6–3 Antimony and Silver Concentrations in the Kennedy Assassination Bullets**

Silver (parts	Antimony	Sample Sample Description
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	per million) <sup>a</sup>	(parts per million)	
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

<sup>a</sup>One 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.**

None of these conclusions can totally verify 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 were performed by neutron activation analysis. The remainder of this chapter describes this and other techniques currently used to examine inorganic physical evidence.

## THE EMISSION SPECTRUM OF ELEMENTS

We have already observed that organic molecules can readily be characterized by their selective absorption of ultraviolet, visible, or infrared radiation. Equally significant to the analytical chemist is the knowledge that elements also selectively absorb and emit light. These observations form the basis of two important analytical techniques designed to determine the elemental com-

position of materials—*emission spectroscopy* and *atomic absorption spectrophotometry*.

The statement that elements emit light should not come as a total surprise, for one need only observe the common tungsten incandescent lightbulb or the glow of a neon light to confirm this observation. When the light emitted from a bulb or from any other light source is passed through a prism, it is separated into its component colors or frequencies. The resulting display of colors is called an **emission spectrum**.

When sunlight or the light from an incandescent bulb is passed through a prism, we have already observed that a range of rainbow colors is produced. This emission spectrum is called a **continuous spectrum** because all the colors merge or blend into one another to form a continuous band. However, not all light sources produce such a spectrum. For example, if the light from a sodium lamp, a mercury arc lamp, or a neon light were passed through a prism, the resultant spectrum would consist 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 present in the spectrum. This type of spectrum is called a **line spectrum**. Figure 6–1 shows the line spectra of three elements.

Heated matter in a solid or liquid state produces a continuous spectrum that is not very indicative of its composition. However, if this same matter is vaporized and “excited” by exposure to high temperature, each element 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. Sodium vapor, for example, always shows the same line spectrum, which differs from the spectrum of all other elements.

An *emission spectrograph* is an instrument used to obtain and record the line spectra of ele-

ments. Essentially, 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 6–2.

The specimen under investigation is excited when it 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. The resultant emitted light is collected by a lens and focused onto a prism that disperses it into component frequencies. The separated frequencies 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 present 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 more commonly requires simply a rapid comparison of the elemental composition of two or more specimens. This can readily be accomplished when the emission spectra are matched line for line, an approach illustrated in Figure 6–3, in which the emission spectra of two paint chips are shown to be comparable.

Carbon arc emission spectrometry has been supplanted by *inductively coupled plasma (ICP) emission spectrometry*. Like the former, 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. 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 and 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 extremely high temperatures in the range of 7,000–10,000°C. The sample, in the form of an aerosol, is then introduced into the hot plasma, where it collides with the energetic argon electrons generating charged particles (ions) that emit light of characteristic wavelengths corresponding to the identity of the elements present (see Figure 6–4).

Two areas of forensic casework in which ICP has been applied are the identification and characterization of mutilated bullets<sup>1</sup> and glass fragments.<sup>2</sup> 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 taken advantage of significant compositional differences among lead sources for the manufacture of lead-based bullets. Compositional differences in the trace elements that constitute lead bullets 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—how can a forensic analyst explain to a jury that such a finding has meaningful consequences to a criminal inquiry without being able to provide statistical or

probability data to support such a contention? Furthermore, the creation of meaningful databases to statistically define the significance of bullets compared by their 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 a highly unlikely event. However, care must be taken to avoid giving the trier of fact 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.

## **ATOMIC ABSORPTION SPECTROPHOTOMETER**

When an atom is vaporized, it absorbs many of the same frequencies of light that it emits in an excited state. The selective absorption of light by atoms is the basis for a technique known as *atomic absorption spectrophotometry*. A simple atomic absorption spectrophotometer is illustrated in Figure 6-5.

In atomic absorption spectrophotometry, the specimen is heated to a temperature that is hot enough to vaporize its atoms while leaving a substantial number of atoms in an unexcited state. Normally, the specimen is inserted into an air-acetylene flame to achieve this temperature. The vaporized atoms are then exposed to radiation emitted from a light source. The technique achieves great specificity by using as its radiation source a discharge tube made of the same element being analyzed in the specimen. When the discharge lamp is turned on, it emits only the frequencies of light that are present in the emission spectrum of the element. Likewise, the sample absorbs these frequencies only when it contains the same element. Therefore, to determine the presence of antimony in a specimen, the atomic absorption spectrophotometer must be fitted

with a discharge lamp that is constructed of antimony. Under these conditions, the sample will absorb light only when it contains antimony.

Once the radiation has passed through the sample, a monochromator, consisting of a prism or a diffraction grating and a slit, isolates the desired radiation frequency and transmits it to a detector. The detector converts the light into an electrical signal, the intensity of which is recorded on a strip-chart recorder.

The absorption of light by the element of interest is the phenomenon that is being measured in atomic absorption spectrophotometry. The concentration of the absorbing element is directly proportional to the quantity of the light absorbed. The higher the concentration of the element, the more light is absorbed. For this reason, atomic absorption spectroscopy is most useful for accurately determining an element's concentration in a sample. Furthermore, the technique is sufficiently sensitive to find wide application in detecting and quantitating elements that are present at trace levels. However, the technique does have one drawback in that the analyst can determine only one element at a time, each time having to select the proper lamp to match the element under investigation.

Although atomic absorption spectrophotometry has been used for chemical analysis since 1955, it has not yet found wide application for solving forensic problems. However, a modification in the design of the instrument promises to change this situation. By substituting a heated graphite furnace or a heated strip of metal (tantalum) for the flame, analysts have achieved a more efficient means of atomic volatilization and as a result have substantially increased the sensitivity of the technique. Many elements can now be detected at levels that approach one-trillionth of a gram.

The high sensitivity of “flameless” atomic absorption now equals or surpasses that of most known analytical procedures. Considering the relative simplicity and low cost of the technique, atomic absorption spectrophotometry has become an attractive method for detecting and measuring the smallest levels of trace elements present in physical evidence.

## THE ORIGIN OF EMISSION AND ABSORPTION SPECTRA

Any proposed theory that attempts to explain the origin of emission and absorption spectra must relate to the fundamental structure of the element—the atom. Scientists now know that the atom is composed of even more elementary particles that are collectively known as *subatomic particles*. The most important subatomic particles are the **proton**, **electron**, and **neutron**. 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 having neither a positive nor a negative charge. The properties of the proton, neutron, and electron are summarized in the following table:

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

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 around a central nucleus—an image that is analogous to our solar system, in which the planets revolve around the sun.<sup>3</sup> The **nucleus** of the atom 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 be equal to the number of negatively charged electrons in orbit around the nucleus.

With this knowledge, we can now begin to 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 6–6).

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 illustrated in Figure 5–1, 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.

To explain the origin of atomic spectra, our attention must now 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 in the atom. When an atom absorbs energy, such as heat or light, its elec-

trons 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 a most important observation, for it means that atoms absorb only a definite value of energy, and all other energy values will be excluded. In atomic absorption spectrophotometry, a photon of light interacts with an electron, causing it to jump into a higher orbital, as shown in Figure 6–7(a). 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 in the transition. 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 is 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 testifies to the fact that this energy loss comes about in the form of light emission [see Figure 6–7(b)]. 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. Atomic absorption spectrophotometry carefully measures the value and amount of light energy going into the atom; emission spectroscopy collects and measures the various light energies given off. The result is the same: atoms are identified by the existence of characteristic energy levels.

## NEUTRON ACTIVATION ANALYSIS

Once scientists realized that it was possible to change the number of subatomic particles in the atom's nucleus, the unleashing of a new source of energy—nuclear energy—was inevitable. This energy has proven so awesome in its power that the survival of civilization will depend on our ability to refrain from using its destructive forces. Of course, this threat does not obscure the fact that controlled nuclear energy promises to be a source of power capable of relieving our dependency on the earth's dwindling reserves of fossil fuels. For the chemist, nuclear chemistry provides a new tool for identifying and quantitating the elements.

Until now, our discussion of subatomic particles has been limited to the proton and electron. However, to understand the principles of nuclear chemistry, we must look at the other important subatomic particle, the neutron. 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**. For example, hydrogen consists of three isotopes; besides ordinary hydrogen, which has one proton and no neutrons, two other isotopes exist, deuterium and tritium. Deuterium (or heavy hy-

drogen) also has one proton but contains one neutron as well. Tritium has one proton and two neutrons in its nucleus. The atomic structures of these isotopes are shown in Figure 6–8. Therefore, all the isotopes of hydrogen have an atomic number of 1 but differ in their atomic mass numbers. Hydrogen has an atomic mass number 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.

Like hydrogen, most elements are known to have two or more isotopes. Tin, for example, has ten isotopes. Many of these isotopes are quite stable, and for all intents and purposes, the isotopes of any one element have indistinguishable properties. Others, however, are not as stable and decompose with time by a process known as *radioactive decay*. **Radioactivity** is the emission of radiation that accompanies the spontaneous disintegration of unstable nuclei. Radioactivity is actually composed of three types of radiation: **alpha rays**, **beta rays**, and **gamma rays**.

Alpha rays are positively charged particles, each with a mass approximately four times that of a hydrogen atom. These particles are helium atoms stripped of their orbiting electrons. Beta rays are actually electrons, and gamma rays are electromagnetic radiations similar to X-rays but of a higher frequency and energy (refer to the electromagnetic spectrum in Figure 5–15). 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.

The existence of isotopes would be of little importance to the forensic chemist were it not for the fact that scientists have mastered the techniques for synthesizing radioactive isotopes. If the only distinction between isotopes of an element is the number of neutrons each possesses, is it not reasonable to assume that when atoms are bombarded with neutrons, some neutrons will be captured to make new isotopes? This is exactly what happens in a nuclear reactor. A nuclear re-

actor is simply a source of neutrons that can be used to bombard the atoms of a specimen, thereby creating radioactive isotopes. When the nucleus of an atom captures a neutron, a new isotope with one additional neutron is formed. In this state, the nuclei are said to be activated, and many immediately begin to decompose by emitting radioactivity.

To identify the activated isotope, it is necessary to measure the energy of the gamma rays emitted as radioactivity. The gamma rays of each element can be associated with a characteristic energy value. Furthermore, once the element has been identified, its concentration can be measured by the intensity of its gamma-ray radiation; intensity is directly proportional to the concentration of the element in a specimen. The technique of bombarding specimens with neutrons and measuring the resultant gamma-ray radioactivity is known as *neutron activation analysis*. The process is depicted in Figure 6–9.

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

**Table 6–4 Concentration of Trace Elements in Copper Wire**

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Selenium	Gold	Antimony	Silver
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Control Wire				
A <sub>1</sub>	2.4	0.047	0.16	12.7
A <sub>2</sub>	3.5	0.064	0.27	17.2
A <sub>3</sub>	2.6	0.050	0.20	13.3
A <sub>4</sub>	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.**

As far as forensic analysis is concerned, neutron activation has been used to characterize trace elements present 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 (A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, A<sub>4</sub>) 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. A comparison of these elements present in the wire involved in the theft was undertaken. After exposing the wires to neutrons in a nuclear reac-

tor, neutron activation analysis revealed a match between A<sub>1</sub> and B that was well within experimental error (see Table 6–4). The findings suggested a common origin of the control and suspect wires.

## X-RAY DIFFRACTION

Until now, we have discussed methods for detecting and identifying the elements. Emission spectroscopy, atomic absorption, and neutron activation analysis tell us what elements are present in a particular substance, but they do not provide any information as to how the elements are combined into compounds. One way to elicit this information is to aim a beam of X-rays at a crystal and study how the X-rays interact with the atoms that compose the substance under investigation. This technique is known as **X-ray diffraction**.

X-ray diffraction can be applied only to the study of solid, crystalline materials—that is, solids with a definite and orderly arrangement of atoms. For example, sodium chloride (common table salt), pictured in Figure 4–8, is crystalline. Fortunately, many substances, including 95 percent of all inorganic compounds, are crystalline and thus identifiable by X-ray diffraction analysis. The atoms in a crystal can be thought of as being composed of a series of parallel planes. As the X-rays penetrate the crystal, a portion of the beam is reflected by each of the atomic planes. As the reflected beams leave the crystal's planes, they combine with one another to form a series of light and dark bands known as a *diffraction pattern*. Every compound produces a unique diffraction pattern, thus giving analysts a means for “fingerprinting” compounds.

A diagram depicting the X-ray diffraction process is illustrated in Figure 6–10. Diffraction patterns for potassium nitrate and potassium chlorate, two common constituents of homemade explosives, are shown in Figure 6–11. Comparing a questioned specimen with a known X-ray

pattern is a rapid and specific way to prove chemical identity.

One drawback to X-ray diffraction is its lack of sensitivity. The technique is suitable for identifying the major constituents of a mixture, but it often fails to detect the presence of substances constituting less than 5 percent of a mixture. For this reason, the forensic chemist must use more sensitive techniques—emission spectroscopy, atomic absorption, and neutron activation analysis—to identify trace elements that may be present.

## **Chapter Summary**

Inorganic substances are encountered by forensic scientists as tools, explosives, poisons, and metal scrapings as well as trace components in paints and dyes. Many manufactured products and even most natural materials contain small quantities of elements in concentrations of less than 1 percent. For the criminalist, the presence of these 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.

Emission spectroscopy, inductively coupled plasma, and atomic absorption spectrophotometry are three techniques available to forensic scientists for determining the elemental composition of materials. An emission spectrograph vaporizes and heats samples to a high temperature so that the atoms present 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 present 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.

In atomic absorption spectrophotometry, the specimen is heated to a temperature that is hot enough to vaporize its atoms while leaving a substantial number of atoms in an unexcited state. The vaporized atoms are then exposed to radiation emitted from a light source specific for a particular element. If the element is present in the material under investigation, a portion of the light is absorbed by the substance. In this manner, many elements can be detected at levels that approach one-trillionth of a gram. Neutron activation analysis measures the gamma-ray frequencies of specimens that have been bombarded with neutrons. 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.

X-ray diffraction is used to study solid, crystalline materials. As the X-rays penetrate the crystal, a portion of the beam is reflected by each atomic plane. As the reflected beams leave the crystal's planes, they combine with one another to form a series of light and dark bands known as a diffraction pattern. Every compound produces a unique diffraction pattern, thus giving analysts a means for "fingerprinting" inorganic compounds.

## Review Questions

1. The elements \_\_\_\_\_ and \_\_\_\_\_ make up 75 percent of the weight of the earth's crust.
2. Only \_\_\_\_\_ elements make up about 99 percent of the weight of the earth's crust.
3. The presence of \_\_\_\_\_ elements in materials provides useful "invisible" markers when comparing physical evidence.
4. The knowledge that elements selectively \_\_\_\_\_ and \_\_\_\_\_ light provides the

basis for important analytical techniques designed to detect the presence of elements in materials.

5. A(n) \_\_\_\_\_ is a display of colors or frequencies emitted from a light source.
6. True or False: A continuous spectrum consists of a blending of colors. \_\_\_\_\_
7. A(n) \_\_\_\_\_ spectrum shows distinct frequencies or wavelengths of light.
8. A line spectrum of an element (is, is not) characteristic of the element.
9. True or False: Matter in a solid or liquid state produces an emission spectrum that is characteristic of its composition. \_\_\_\_\_
10. The \_\_\_\_\_ is an instrument used to obtain and record the line spectrum of elements.
11. Excitation of a specimen can be accomplished when it is inserted between two \_\_\_\_\_ electrodes.
12. The selective absorption of light by atoms is the basis for a technique known as \_\_\_\_\_.
13. The composition of the discharge lamp (does, does not) have to be taken into consideration when performing an analysis by atomic absorption for a particular element.
14. True or False: One advantage of atomic absorption analysis is that it can simultaneously detect twenty to thirty elements. \_\_\_\_\_
15. Three important subatomic particles of the atom are the \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_.
16. The proton and electron (are, are not) of approximately equal mass.

17. A proton imparts the nucleus of an atom with a \_\_\_\_\_ charge.
18. The number of protons (is, is not) always equal to the number of electrons in orbit around the nucleus of an atom.
19. Each atom of the same element always has the same number of \_\_\_\_\_ in its nucleus.
20. The number of protons in the nucleus of an atom is called the \_\_\_\_\_.
21. True or False: Each element has its own characteristic set of energy levels. \_\_\_\_\_
22. True or False: To move an electron from one energy level to the next requires a definite amount of energy. \_\_\_\_\_
23. As an electron falls from a higher to a lower energy level, it emits \_\_\_\_\_.
24. The total number of protons and neutrons present in a nucleus is known as the \_\_\_\_\_.
25. Atoms differing only in the number of neutrons present in their nuclei are called \_\_\_\_\_.
26. True or False: Deuterium has the greatest number of protons of all the isotopes of hydrogen. \_\_\_\_\_
27. Radioactivity is composed of the following emissions: \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_.
28. Beta rays are identical to \_\_\_\_\_.
29. Electromagnetic waves similar to X-rays but of a higher energy are \_\_\_\_\_.
30. A nuclear reactor is a source of \_\_\_\_\_.
31. The technique of bombarding specimens with neutrons and measuring the resultant gamma

ray emissions is known as \_\_\_\_\_.

32. As X-rays are reflected off a material's surface, they form a series of light and dark bands known as a(n) \_\_\_\_\_.

33. X-ray diffraction patterns are obtained from (crystalline, amorphous) substances.

## Further References

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## 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.

### **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 containing the protons and neutrons.

### **Atomic Number**

The number of protons in the nucleus of an atom. Each element has its own unique atomic number.

### **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.

### **Atomic Mass Number**

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

### **Isotope**

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

### **Radioactivity**

The particle and/or gamma-ray radiation emitted by the unstable nucleus of some isotopes.

### **Alpha Ray**

A type of radiation emitted by a radioactive element. The radiation is composed of helium atoms minus their orbiting electrons.

### **Beta Ray**

A type of radiation emitted by a radioactive element. The radiation consists of electrons.

### **Gamma Ray**

A high-energy form of electromagnetic radiation emitted by a radioactive element.

### **X-ray diffraction**

An analytical technique for identifying crystalline materials.

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

**Figure 6–1** Some characteristic emission spectra.

**Figure 6–2** Parts of a simple emission spectrograph.

**Figure 6–3** 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.**

**Figure 6–4 The creation of charged particles in the torch of an ICP discharge.**

**Figure 6–5 Parts of a simple flame atomic absorption spectrophotometer.**

**Figure 6–6 The atomic structures of hydrogen and helium.**

**Figure 6–7 (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 6–8 Isotopes of hydrogen.**

**Figure 6–9 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.**

**Figure 6–10 A beam of X-rays being reflected off the atomic planes of a crystal. The diffraction patterns that form are recorded on photographic film. These patterns are unique for each crystalline substance.**

(a)

(b)

**Figure 6–11 X-ray diffraction patterns for (a) potassium nitrate and (b) potassium chlorate.**

<sup>1</sup> R. D. Koons and J. Buscaglia, “Forensic Significance of Bullet Lead Compositions.” *Journal of Forensic Sciences* 50 (2005): 341; C. A. Peters. “The Basis for Compositional Bullet Lead Com-

parisons,” *Forensic Science Communications* 4 (2002),

<http://www.fbi.gov/hg/lab/fsc/backissu/july2002/peters.htm>.

<sup>2</sup> S. Montero, A. L. Hobbs, T. A. French, and J. Almirall, “Elemental Analysis of Glass Fragments by ICP-MS as Evidence of Association: Analysis of a Case,” *Journal of Forensic Sciences* 48 (2003): 1101.

<sup>3</sup> Actually, the electrons are moving so rapidly around the nucleus as to best be visualized as being in the form of an electron cloud spread out over the surface of the atom.