FORENSIC CHEMISTRY

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Forensic scientists play a key role in criminal investigations. Fingerprints collected from a suspect will be compared to fingerprints collected at the crime scene after being developed in the lab by a forensic scientist.

Prime-time television is chock-full of drama centered on the criminal justice system. Programs such as *CSI: Crime Scene Investigation*, *Law & Order*, *Criminal Minds*, and *Cold Case* carry the viewer through stimulating, yet nearly impossible-to-solve, investigations that culminate with the evidence revealing the entire untold story behind a crime in one hour or less. In real life the collection and analysis of evidence involves painstaking care and rigorous application of scientific principles.

Have you ever wondered how evidence in an actual case tells the story, what information each item of evidence holds, and how this information can be elucidated in a crime laboratory? In this chapter we will explore the world of forensic chemistry, focusing on the theory and processes of forensic analysis and showing the role that chemistry plays in criminal investigations.

By the end of this chapter, you should be able to answer some basic questions about forensic chemistry:

- What is forensic science?
- How is chemistry used in forensic science?
- What determines the value of each item of evidence?
- Is the analysis process for each item of evidence the same?
- What type of information allows for an *exclusive* link?

1 INTRODUCTION TO FORENSIC SCIENCE

Forensic science applies science principles, techniques, and methods to the investigation of crime. A lesser known definition of the adjective *forensic* is anything argumentative or debatable. At first, this definition of *forensic* may seem to have no connection with the more popular crime-solving definition—but it does. Legal truth is sought through the use of the adversarial system (rather than the scientific method), and decisions are made only after each side has been given an equal opportunity to argue all the issues at hand. When one of the issues being argued is a scientific analysis (using the scientific method) of an item of evidence, the debate that ensues over the science involved could be called *forensic* science.

Other related definitions of *forensic* may include (1) the use of science to aid in the resolution of legal matters and (2) a scientific analysis for the purpose of judicial resolve. For example, saying that something was *forensically* determined suggests the information was *scientifically* determined with the intent to be presented (and debated) in a court of law.

Recently the term *forensic* has also been used to describe many scientific investigations—even if no crime is suspected. Often these investigations are of historical significance and may or may not have legal consequences. For example, a forensic scientist may work on the discovery of the composition of ancient pottery, the detection of Renaissance art techniques, or the identification of ancient human remains. **Forensic history** is the use of science to answer historical questions.

Role of a Forensic Scientist

Most forensic scientists analyze evidence in a crime laboratory and spend little time at the crime scene. The duties of forensic scientists are not exactly as they are portrayed on many popular television shows, where the crime scene investigator plays the role of Sherlock Holmes and does everything from collecting the evidence to solving the crime.

In real life a team of experts does the job of television's crime scene investigators. The forensic scientists do not directly solve crimes; they simply analyze the **physical evidence**. Physical evidence includes all objects collected and packaged at a crime scene that will be subsequently analyzed in a crime laboratory. This evidence is typically collected by police officers or specially trained crime scene investigators; however, the evidence of a crime is not limited to those items sent to the crime laboratory. Other evidence may include interrogations, eye witness stories, police reports, crime scene notes and sketches, and anything else determined to aid in the investigation. Subsequently, the detective assigned to the case pieces together all the evidence in an attempt to solve the crime. Interpretation of all the evidence and the accompanying scientific results is also practiced by many attorneys, but typically the forensic

Forensic science The application of science principles, techniques, and methods to the investigation of crime; the use of science to aid in the resolution of legal matters; scientific analysis for the purpose of judicial resolve.

Forensic history The use of science to answer historical questions.

Physical evidence Evidence of a physical nature that can be collected and subsequently analyzed in a crime laboratory.

scientist does not get involved in this aspect of the investigation. Figure 1 illustrates the role that each of these individuals plays in an investigation.

Although the service provided by the forensic scientist is central to the solving of many crimes, it is not usually required for crimes like speeding or shoplifting. In fact, most crimes do not require a forensic analysis of physical evidence. Physical evidence present at a crime scene may not even be collected; and if it is collected, it may not be analyzed. The decision to collect and subsequently analyze physical evidence depends on the seriousness of the crime, police department protocol, the state of the investigation, laboratory capabilities, and crime scene resources.

A large number of forensic scientists are chemists. Forensic chemists employ their knowledge of chemistry to analyze evidence such as fibers, paint, explosives, charred debris, drugs, glass, soil, documents, tool marks, and firearms. To a lesser extent, forensic chemists also use their knowledge for toxicology (the study of poisons and their effects), fingerprints, footwear impressions, tire impressions, and hair analyses. Although many forensic analyses require the expertise of a chemist, chemistry is not the only discipline that contributes to the extremely vast and truly interdisciplinary field of forensic science. Other disciplines and professions contributing to the field include engineering, computer science, entomology, anthropology, pathology, physics, nursing, and psychology, among many others. Virtually any discipline, profession, or trade that has an expertise that can aid in the solving of crimes will fall under the umbrella of forensic science. This chapter will focus on some of the many applications of chemistry in forensic science.

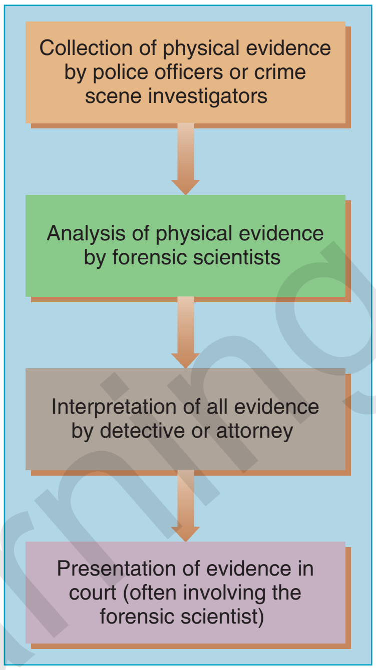

FIGURE 1 Involvement of various individuals in an investigation.

The Forensic Generalist and Specialist

Despite the wide variety of evidence that forensic scientists can analyze, most present-day forensic scientists are not generalists. Historically, **forensic generalists** would analyze all types of physical evidence. Their familiarity with many forensic analysis techniques was extremely diverse, and their ability to carry out any given analysis was limited only by their knowledge and resources. The forensic generalist served the role of a family doctor in the field of forensic science—whatever was needed to be analyzed, the generalist could help. Today, however, forensic generalists are slowly being replaced by forensic specialists due to the ever-increasing complexity of the field of forensic science.

Charles D. Winters

Chemistry is used in the analysis of explosives like dynamite.

Forensic specialists dedicate the majority of their efforts to becoming experts in only one or a few branches of forensic science. Forensic chemistry, for example, is now a specialized field of forensic science. The forensic chemist does not typically analyze biological evidence or carry out DNA analyses. These analyses are typically performed by a forensic biologist. Many argue that forensic specialization is appropriate and necessary due to the vast scope of forensic science and the diversity in analysis techniques. As is true with all other sciences, forensic science continues to evolve and develop. With such a vast body of knowledge, it is inconceivable that a single person could become an expert in all areas of science, and it is equally inconceivable that a person could become an expert in all areas of forensic science.

Specialization is not unique to forensic science and has become commonplace in the medical profession. When children are sick, we take them to a pediatrician; when we have an ear infection, we see an ear, nose, and throat doctor; and when we need a heart operation, we see a heart surgeon. With the wide variety of evidence that may be analyzed by the forensic chemist, subspecialization is also quite common. It is not unusual for a forensic chemist to be given a subtitle such as firearms analyst, trace evidence analyst, fingerprint

Forensic generalist A forensic scientist familiar with most areas of forensic science and capable of analyzing most items of physical evidence, but not necessarily considered an expert in any area of forensic science.

Forensic specialist A forensic scientist that has become an expert in one or a few branches of forensic science.

MEET A FORENSIC SCIENTIST

AN INTERVIEW WITH MELISSA VALADEZ

Q: What activities do you perform regularly at in the crime lab?

A: I work in the trace evidence section of a crime laboratory and analyze evidence such as hairs, fibers, paints, shoe and tire impressions, physical matches, and vehicle lamp filaments. Most of my work is done in the lab using microscopes and other instrumentation, but sometimes I am asked to collect evidence from crime scenes as well. I also travel across the state in order to testify in the court of law to explain my procedures and conclusions to juries.

Q: What is your educational background?

A: I have a Bachelor of Science in Chemistry from Texas A&M University and a Master of Science in Forensic Science (MSFS). Once I was hired as a forensic scientist, I went through an extensive in-house training program prior to working on any cases. Since then I have attended numerous conferences and training classes in order to further my knowledge.

Q: What do you like best about your job?

A: There is so much variety in what I do on a daily basis. Each case that


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comes in has its own story, and each item of evidence has to be handled in its own unique way. I get to do something different every day, and my knowledge base is constantly expanding. One day I might be working on a homicide case with bloody shoe impression evidence and the next day it may be a criminal mischief case involving paint. You just never know where each case will take you.

Q: How does what you do compare to what is portrayed on crime shows like *CSI*?

A: The most obvious difference is that we can't solve cases in an hour.

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We may work on one case for months and still only be able to provide investigators with minimal information. In other cases, it might take only a single day to provide all the information that investigators need to wrap up the investigation.

Another big difference is that most of our work is done in the lab. Occasionally we will process a scene and collect our own evidence, but most forensic scientists stay in the lab. The investigation side and the forensics side are usually kept separate and are dealt with by separate entities. The law enforcement agencies, the attorneys, and the laboratory staff all keep in contact and work closely together in order to see a case through to the end.

analyst, or drug chemist. Because more than 70% of all evidence is drug related, drug chemists are quite common in crime laboratories. Although subspecialization is becoming widespread, many forensic chemists may still become proficient in many areas of forensic chemistry.

Forensic chemists may also be given the title of **criminalist**. This title, although less descriptive, is quite common and originates from *criminalistics*, the branch of forensic science heavily enriched in chemistry and biology applications for the analysis of physical evidence. Criminalistics encompasses a broader area of forensic science than just forensic chemistry and includes most of the areas of forensic science practiced in a traditional crime laboratory, for example, drugs, fingerprints, DNA, serology (biological fluid testing), firearms, and questioned documents.

Criminalist A forensic scientist utilizing chemistry and biology for the analysis of physical evidence.

2 FORENSIC CHEMISTRY

To analyze physical evidence, forensic chemistry draws on chemistry principles and concepts. Investigating the physical and chemical properties of a substance is central to forensic chemistry. Without an appreciation for these properties and the scientific method, forensic chemistry would not be possible.

Physical and Chemical Properties

Recall that **physical properties** are properties of a substance that can be described or displayed without requiring a chemical change. For example, sulfur is yellow (see Figure 2), iron is malleable (able to be hammered into sheets), cocaine is a white solid, and the density of a glass fragment broken from a windowpane at a crime scene is approximately 2.5 g/mL.

Chemical properties are properties of a substance that can be described through a chemical change only. Chemical changes require a chemical reaction to occur between reactants, generating new products. The chemical properties of a substance are described by the reaction that occurs and the products that are formed. For example, a chemical property of baking soda (sodium bicarbonate) is its reactivity with vinegar (acetic acid) to produce carbon dioxide bubbles, as shown in Figure 3. This reaction also describes a chemical property of vinegar—its reactivity with baking soda. A chemical property of cocaine is its reactivity with cobalt thiocyanate, which produces a blue-colored product. This chemical property of cocaine, in conjunction with its physical properties (a white, fluffy powder), help investigators identify cocaine.

Scientific Method

Although the exact manner in which the physical and chemical properties are analyzed for each substance differs, the analyses are all based on the principles of the **scientific method**. The scientific method begins with *observations*. Scientists attempt to organize observations and look for trends or patterns. When the scientists find what appears to be a relationship among the observations, they suggest a *hypothesis* (an educated guess) that tentatively explains what is being observed. A plan is devised to test the hypothesis. Ultimately, the plan is carried out and further observations are made. If the new observations contradict the original hypothesis, a new hypothesis is suggested and tested. However, if the new observations validate the original hypothesis, the scientists often choose to devise a subsequent plan to further validate the hypothesis. This cycle, as illustrated in Figure 4, continues until the hypothesis has been sufficiently validated.

For example, when an unknown substance is submitted to a crime laboratory, the forensic chemist will first *observe* the properties of the substance. She may notice that the substance is a crushed and dried green-leafy material. Next, she will suggest a *hypothesis* as to the identity of the substance: The unknown substance is marijuana. This is an extremely crucial step because the analysis to be performed (the plan for testing the hypothesis) is different for each unknown substance. The chemist will then devise a plan to test the hypothesis: to view the substance under the microscope looking for properties of crushed marijuana leaves. If the microscopic observations validate the hypothesis, she will develop a subsequent plan to further validate the hypothesis: to react the marijuana leaves with Duquenois-Levine reagent to observe chemical properties. If the microscopic features do not validate the hypothesis, she will suggest and test an alternative hypothesis: The unknown substance is oregano.

Charles D. Winters

FIGURE 2 One physical property of this sulfur powder is its bright yellow color.

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FIGURE 3 The reactivity of baking soda with vinegar is a chemical property.

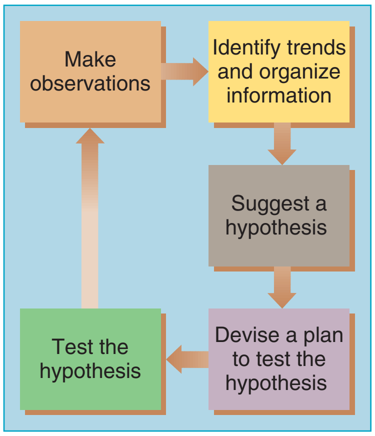


FIGURE 4 The scientific method.

Physical properties Properties of a substance that can be described or displayed without a chemical reaction.

Chemical properties Properties of a substance that can *only* be described or displayed through a chemical reaction.

Scientific method The process of investigation involving observation and hypothesis testing.

PhotoDisc

Dried oregano leaves may be visually mistaken for marijuana, shown in this photo.

Questioned sample The sample being analyzed having an unknown identity and/or origin.

Known sample The sample having a known identity and origin.

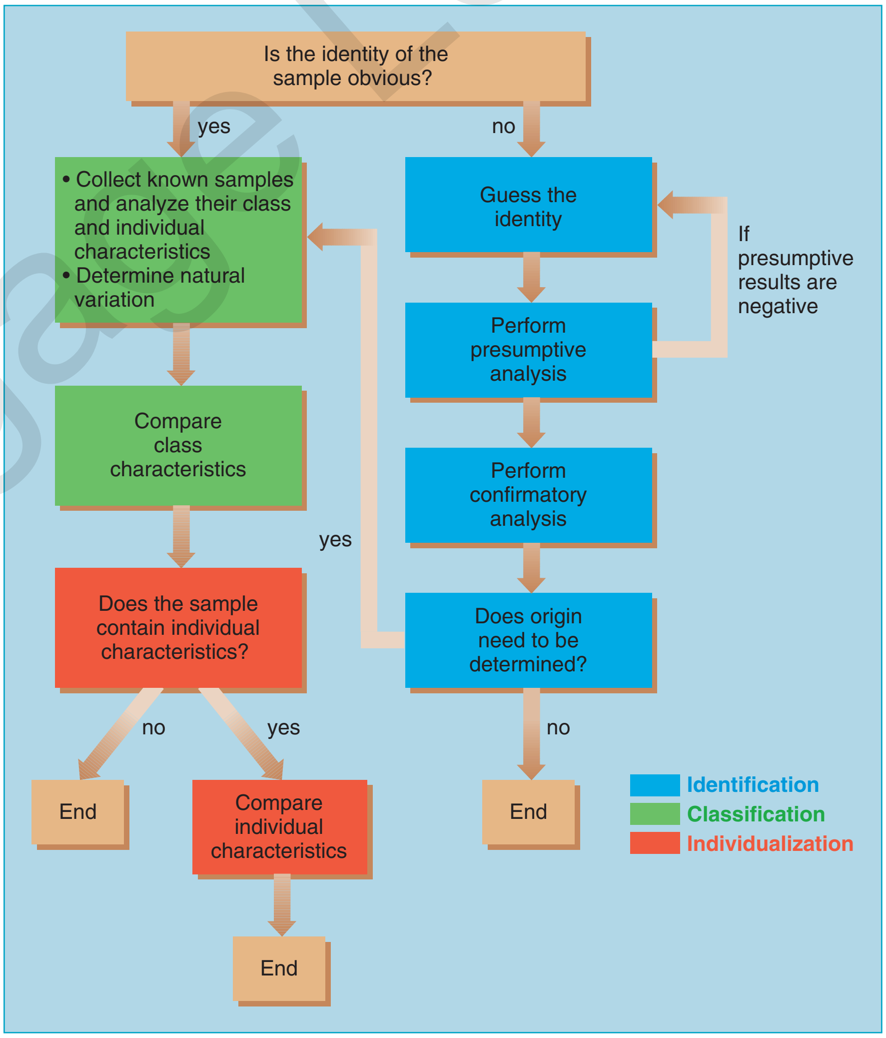
In chemistry, physical and chemical properties are used to characterize and distinguish one compound or element from another. In forensic chemistry, these properties aid in the identification, classification, and individualization of physical evidence.

3 THEORY OF FORENSIC ANALYSIS

After a police officer or investigator has collected evidence at a crime scene, some evidence may be brought to the crime lab for a forensic chemist to analyze. The chemist follows a specific process, based on the scientific method, for analyzing evidence. Samples collected from a crime scene and brought to the lab for analysis are called **questioned samples** because the identities and origins of those samples are unknown. In order to draw conclusions about the identity or origins of questioned samples, the forensic chemist will need **known samples** as a reference. A known sample might be collected as part of the evidence—for instance a hair sample collected from a suspect.

Forensic analyses may be performed to (1) *identify* a questioned sample or (2) *compare* a questioned sample to a known sample for the purpose of determining the source or origin of the sample (where it came from). The results of such comparisons can link a questioned sample and several known samples either to a class of samples with several possible origins (classification) or to a single origin (individualization). Thus, a forensic chemist will analyze much

FIGURE 5 The stages of analysis.

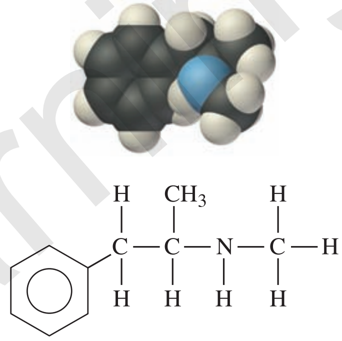


more than the questioned sample. A comparative analysis may require the examination of several known samples for each questioned sample.

A forensic analysis follows the order of identification, classification, and individualization, as illustrated in Figure 5. The challenges found during each phase of analysis are different for each item of evidence. Often, identification is straightforward and obvious to the untrained eye (for instance, hair); other times expertise and sophisticated instrumentation are required (for instance, drug analysis). We will discuss each of these phases of analysis in more detail in the sections that follow.

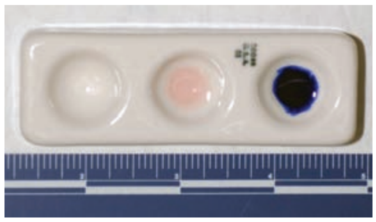
Identification

When a questioned sample is submitted to a crime laboratory for analysis, the first task is **identification**. For example, if a white powder is submitted for analysis, the primary objective will be to determine its identity. If the powder is suspected of being a controlled substance, the forensic scientist will carry out a series of analyses to identify the powder. However, because each drug has a different set of physical and chemical properties, a different series of analyses is required to identify each drug. As mentioned during our discussion of the scientific method, the forensic scientist must first make an educated guess as to the identity of the substance. Using known drug standards for each type of drug to be analyzed, she must develop and validate a series of analyses prior to analyzing the questioned samples. Consequently, the identification of an uncommon drug can be challenging.



Methamphetamine

Two types of analysis can be used to identify the substance: presumptive and confirmatory. **Presumptive analyses** look at chemical and physical properties that are not unique enough by themselves for identification but that provide enough information to narrow the search. For example, the forensic scientist may guess that the questioned sample is methamphetamine. A known chemical property of methamphetamine is that it will react with sodium nitroprusside in the presence of sodium bicarbonate and produce a very deep blue-colored product, so the scientist will carry out this test. If the reaction produces a blue product, as shown in Figure 6, she can conclude that the unknown substance might be methamphetamine. However, a number of similar compounds (all containing a nitrogen atom with one hydrogen atom and two attached carbon atoms) will also produce a deep blue-colored product. This analysis does not confirm that the substance is methamphetamine, but it does reduce the number of possibilities. Now the forensic scientist can proceed to more time-consuming or expensive tests knowing that she is on the right track. Presumptive analyses are usually quick and inexpensive to perform. When presumptive analyses are negative, they exclude potential drug candidates; when they are positive, they direct the forensic scientist toward viable confirmatory analyses.



Courtesy of Texas DPS Crime Laboratory Services

FIGURE 6 The presumptive color test for methamphetamine shows a deep blue-colored product.

Whereas presumptive analyses only narrow the possible identities of a substance, **confirmatory analyses** identify a questioned sample absolutely. They are required for court and must be performed to convict someone for possession of an illegal substance. These analyses use the unique chemical or physical properties of a substance for the purpose of identification. Typically, confirmatory analyses require more time and expense than presumptive analyses. These analyses often require the use of sophisticated chemical instrumentation to measure the unique properties that lead to identification.

One instrument used by the forensic chemist is the **Fourier transform infrared spectrophotometer (FTIR)**, as shown in Figure 7. With the FTIR, the forensic chemist can begin to identify the questioned sample by measuring its unique interactions with infrared light. This pattern of interaction, which is a function of wavelength, is sometimes called a *chemical fingerprint*. It is unique to a pure substance and allows for its identification. However, because

Identification Analysis performed to determine the identity of a questioned sample.

Presumptive analysis A relatively quick and inexpensive type of forensic analysis, exploiting both chemical and physical properties of an item of evidence, performed with the intent of reducing the number possibilities for identification.

Confirmatory analysis A type of forensic analysis, exploiting *unique* chemical and physical properties of an item of evidence, performed with the intent of identification at the exclusion of all other substances.

Fourier transform infrared spectrophotometer An instrument used to measure the unique interactions (absorbencies) of infrared light with matter.

Courtesy of the Perkin-Elmer Corporation

FIGURE 7 The infrared spectrophotometer shown here produces a chemical fingerprint of a substance.

questioned samples are typically mixtures, rather than pure substances, an additional step is often needed in the analysis.

The compounds in a mixture can be separated, and each compound can subsequently be identified by an instrument called a **gas chromatograph-mass spectrometer** (GC-MS). After the compounds are separated in the gas chromatograph, the mass spectrometer breaks the separated compounds into fragments and measures the mass of each fragment (see Figure 8). The profile of fragment masses that is generated is exclusive to the compound and allows for identification. To understand why this works, suppose the only information you have about two people is their weight (mass). You might find it difficult to distinguish a tall and thin person from a short and stout person. However, if you could take separate weight measurements of the arms, legs, torso, head, fingers, and feet of each person, you would more likely be able to identify each individual. A system of identification like this was actually used in early investigations. A Frenchman named Alphonse Bertillon developed a technique called anthropometry around the year 1880; it used eleven length (rather than weight) measurements of the human body for identification. Anthropometry was replaced 20 years later by fingerprinting, which was more accurate for identification.

Comparative Analysis: Classification and Individualization

Many forensic analyses end with identification (for example, identifying an unknown substance as a drug, explosive, or accelerant used in arson), but some proceed on to comparison. The purpose of a **comparative analysis** is to link a questioned sample and a known sample to a common origin. The origin may be broad, resulting in a **classification**, or exclusive, resulting in **individualization**. In the case of a hair sample, its identification is often obvious, or may be easily established in the laboratory. In fact, the forensic value of the hair sample as evidence is not found in its identification as a piece of hair. What is more important to the investigation is the source or origin of the sample in a particular species or individual. This can be determined through comparative analysis with several samples of a known origin.

Class characteristics are properties of a substance that are shared by a group of substances, but are not unique to all substances of a single origin.

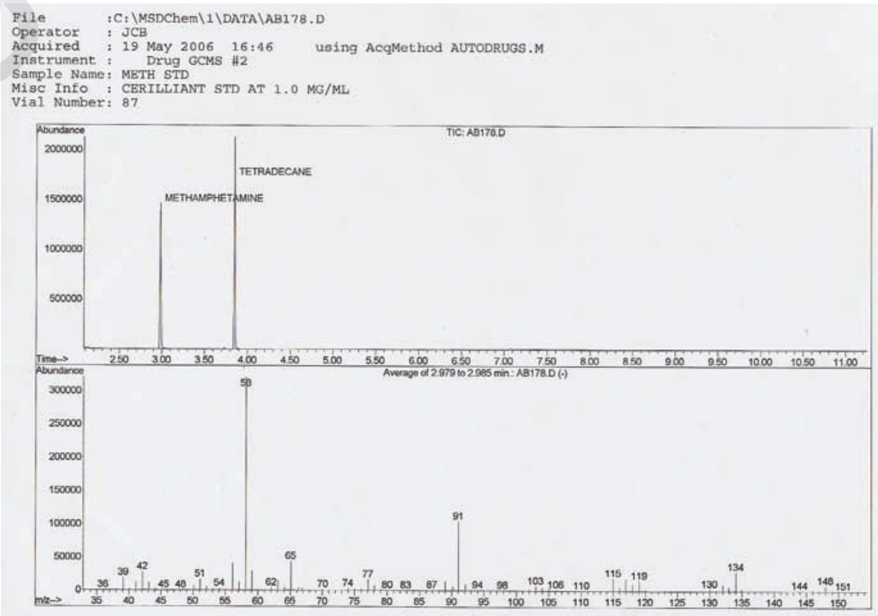
Gas chromatograph–mass spectrometer An instrument used to first separate a mixture of compounds (in the gas chromatograph) and subsequently measure the mass of each fragment of the separated compounds (in the mass spectrometer) for the purpose of their identification.

Comparative analysis A type of forensic analysis performed to determine the origin of a questioned sample.

Classification The linkage of a questioned sample and several known samples to a class with several possible origins.

Individualization The linkage of a questioned sample and several known samples to a single origin.

Class characteristics Chemical and physical properties of a substance representative of a substance's origin, but not unique to an exclusive origin. These characteristics are far more common than individual characteristics.



Courtesy of Texas DPS Crime Laboratory Services

FIGURE 8 The chromatogram (top) and mass spectrum (bottom) show unique properties of methamphetamine.

They allow for the placing of a questioned sample into a class or group of several possible origins. For example, a class characteristic of hair is its color. If a questioned hair sample is brown, it could be determined that the hair originated from a person with brown hair. These properties are analogous to those used when conducting a presumptive test for the purpose of identification.

Not only are class characteristics common to other substances, but they may also vary within a substance. A class characteristic that varies within a substance is called **natural variation**. When attempting to determine the origin of a questioned sample, the forensic chemist must know all the possible variations of the class characteristics from a known sample. Consequently, he must have available several samples of the same known origin. For example, when a questioned hair sample is being compared to the scalp hairs of a suspect, often more than fifty scalp hairs are collected to determine natural variation. The forensic chemist then will compare length, color, pigment distribution, coarseness, and other properties of the known samples. It is likely that there will be a range in values of all these characteristics among a representative collection of a suspect's scalp hair. If the suspect has a mullet haircut (short on top, long in back), there will be a broad range (natural variation) of scalp hair lengths. If the suspect has dark hair with light blonde highlights, there will be a broad natural variation in the individual's scalp hair color. Figure 9 shows the natural variation of hair seen under a microscope. It is imperative that the forensic chemist identify the natural variation within all the known samples of a single origin prior to comparing these class characteristics to a questioned sample.

Courtesy of Texas DPS Crime Laboratory Services

FIGURE 9 Natural variation seen in hairs under a microscope.

In the preceding example, the forensic chemist can make a connection between a sample of a questioned origin and several samples of a known origin if the values of the class characteristics of the questioned sample fall within the range of natural variation. In such a scenario, he can conclude that the questioned hair is found to be "consistent with" or "similar to" the known hairs *based on the comparative analyses performed*. However, the hairs may not share a common origin—for two reasons. First, the properties being compared (class characteristics) are not exclusive to a single origin, and, second, the natural variation of a class characteristic increases the range of possible origins. It is extremely important not to interpret more into an analysis than what is being suggested. This is a common mistake.

Virtually all physical evidence has class characteristics. These characteristics are more common than individual characteristics. Many items of evidence, like hair, fiber, glass, soil, and paint, routinely *only* have class characteristics. In other words, classifications are more common than individualizations. This does not, however, suggest that comparative analyses of items only containing class characteristics are unimportant. The ability to *exclude* is a very powerful aspect of class characteristics. If, for example, a comparative analysis excludes a questioned hair from originating from the suspect's head, this information is just as important as individualization—the suspect may be exonerated (set free of guilt). Also, if the class characteristics of many questioned items of evidence are similar to those of many samples of known origins, each additional link (even if tentative) further incriminates the suspect. For example, if a pubic hair, a scalp hair, a glass fragment, a cat hair, and two fibers found on a suspect were all consistent with those found at the crime scene, although no single item offers an exclusive link, the composite becomes highly significant. Fibers were the key to solving a series of child murders in Atlanta, Georgia, when between 1979 and 1981 over twenty African-American children were killed. This infamous child murder case was ultimately solved by linking 19 sources of fibers found in the personal environment of the suspect Wayne Williams to several of his victims. Wayne Williams was only tried and found guilty for two murders, although many attribute all the murders to him.

Individual characteristics are properties of a substance that are unique and can be used to establish origin. For example, if the brown hair sample

Natural variation The range of variation of class-characteristic values within a substance of a known origin.

Individual characteristics Chemical and physical properties of a substance unique to the substance's origin that can be used to determine origin at the exclusion of all other origins.

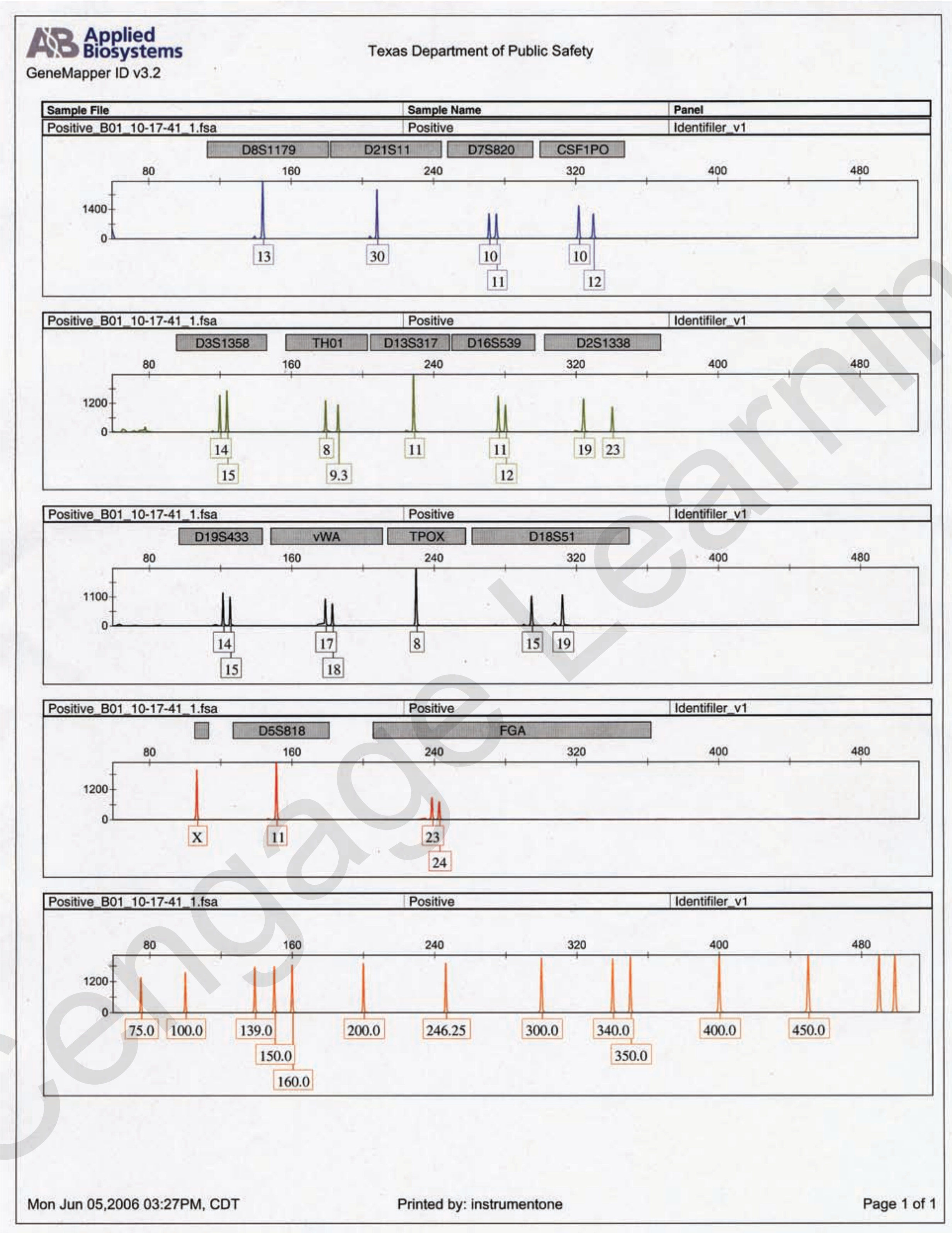


FIGURE 10 An electropherogram showing the results for a DNA analysis.

contained enough DNA in its root for a DNA analysis, the DNA would be considered an individual characteristic that would exclusively link the hair sample to a single origin (person). DNA found in semen on Ms. Monica Lewinsky's dress was used to exclusively link President Bill Clinton to her dress. Figure 10 shows the results of a DNA analysis. These properties are analogous to those exploited when conducting a confirmatory test for the purpose of identification; however, during a comparative analysis these properties are used to determine the *origin* of a substance rather than simply to identify it.

A **physical match** is the classic example of an individual characteristic. A physical match, or jigsaw fit, is what occurs when a questioned and a known sample fit together like puzzle pieces. For example, a diamond might be chipped as it is being forcibly removed from a ring during the commission of a crime. If the chipped piece is located at the crime scene with the ring, and the diamond is recovered from the suspect, all that may be needed to link the diamond to the same origin as the chipped piece (the victim's ring) is a physical match seen under a microscope.

Other common items of evidence having individual characteristics include fingerprints, footwear impressions, tool marks, and bullets. Comparative analyses of all these items of evidence often result in a linkage to a single origin when the questioned sample is compared to several known samples. In the case of a DNA or fingerprint analysis, a link can be made exclusively to a single person. In the case of a footwear or tool mark impression, if individual characteristics are present (which is not always the case), a link can be made to a single shoe or tool, respectively. Figure 11 shows a court display that compares the footwear impression found at a crime scene to one from a known source. In addition to class characteristics like tread pattern and size, the impression displays individual characteristics (marked in yellow in the figure) that link it to a specific origin. However, as mentioned earlier, many items of evidence do not have individual characteristics that can be used for individualization so investigators must rely solely on class characteristics. Table 1 gives examples of class and individual characteristics for common physical evidence.

Physical match An individual characteristic of a questioned sample represented by its physical features matching those of a sample with a known origin in a manner similar to matching two puzzle pieces; may occur from a cut, rip, break, or tear.

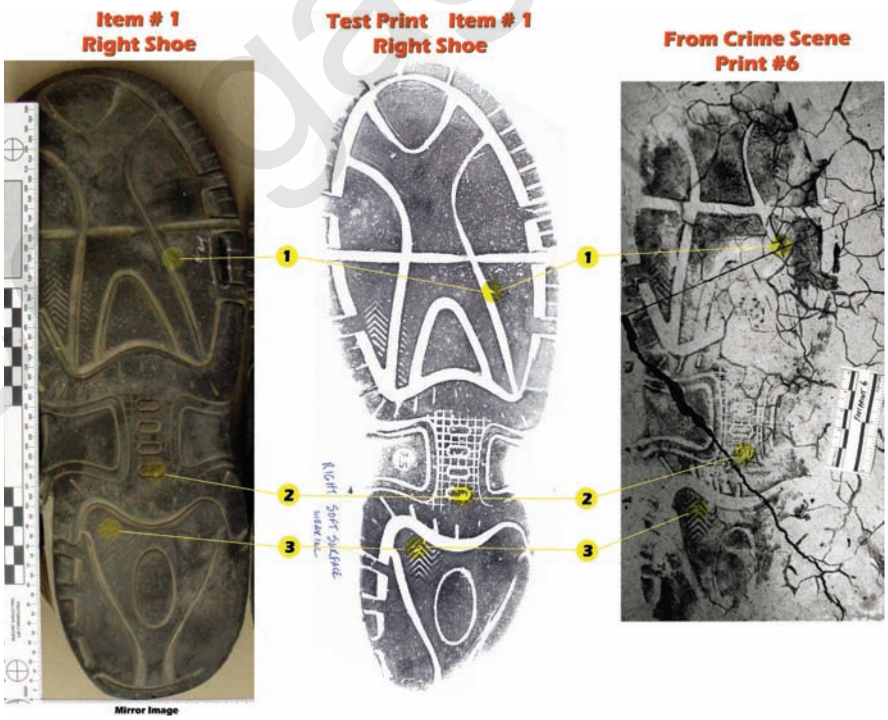


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FIGURE 11 This footwear impression shows individual characteristics used to link it to a single origin (shoe).

TABLE 1 Examples of Class and Individual Characteristics for Common Evidence

Evidence	Class Characteristics	Individual Characteristics
Fingerprints	General pattern type (arch, loop, whorl)	Relative location of fine detail (bifurcations and ridge endings)
Bullets	Diameter, # of land and groove impressions, mass, and direction of twist	Individual striations (scratches) imparted from the barrel
Hair	Color, length, and diameter	DNA only found in the root or attached skin cells
Glass	Color, thickness, density, refractive index, and curvature	Physical match
Soil	Color, pH, particle size distribution, and density distribution	Uncommon
Fibers	Color, cross section, chemical composition, microscopic features, refractive index, and solubility	Uncommon

THE WORLD OF CHEMISTRY

Son of Sam

During the summer of 1976, New York City was terrorized by a serial killer known as the "Son of Sam." The first murders occurred July 29 just outside an apartment complex in Bronx, New York. Two teenagers sitting in a parked car (Jody Valenti and Donna Lauria) were shot from a distance in cold blood. Jody lived, but Donna's injuries resulted in death. The case was considered a random shooting and went virtually unnoticed for three months. On October 23, two other teenagers (Carl Denaro and Rosemary Keenan) were shot while sitting in a car. Carl was shot in the head but survived. Rosemary died. Then, in November Donna DeMasi and Joanne Lomino were shot while walking home from the movie theater. Both survived, but Joanne was paralyzed for life.

After three shooting incidences, the New York City Forensic Firearms Analysts began to recognize a trend. All the shootings involved a not-so-common .44 caliber firearm. This was determined by examining the *class characteristics* of several bullets recovered from the crime scenes. The analysts discovered that all the bullets had been fired from a .44-caliber Charter Arms Company firearm with the model name "Bulldog."

Shootings continued into the summer of 1977 with several more deaths. The killer began to taunt police with letters signed "Son of Sam." Further analysis of the *individual characteristics* of all the recovered bullets suggested that not only was a Bulldog .44 caliber Charter Arms Company firearm being used in all the crimes, but the *exact same* Bulldog firearm was being used. In an attempt to find the firearm used to commit the crimes, many .44 caliber firearms in the city were confiscated and sent to the crime laboratory for analysis. It was hoped that if they could find the firearm, they would find the killer. No matches were found.

In desperation, investigators began to review parking ticket records for vehicles ticketed near the location of a shooting and during the same time period of a shooting. While investigating the vehicle of David Berkowitz, they observed through the car window what appeared to be a Bulldog .44 caliber firearm. The officers called for backup and quickly applied for a vehicle search warrant. When Berkowitz left his apartment and approached his car, he was detained and questioned. Surprisingly, Berkowitz freely admitted he was the "Son of Sam" and sarcastically stated, "What took you so long?"

The firearm found in Berkowitz's car was sent to the crime lab for analysis. Bullets were fired through the weapon, and both *class* and *individual characteristics* were compared to those obtained from the crime scenes—they matched perfectly. Berkowitz was sentenced to 365 years in prison.

CONCEPT CHECK A

1. The term *forensic* suggests detective work only. (a) True, (b) False.
2. Most crimes do not require the analysis of physical evidence. (a) True, (b) False.
3. A forensic __________ dedicates the majority of his/her efforts to becoming an expert in only one or a few branches of forensic science.
4. __________ is the branch of forensic science that draws heavily on chemistry and biology applications for the analysis of physical evidence.
5. A chemical property can be determined (with/without) a chemical reaction.
6. A linkage of a questioned sample and several known samples to several possible origins is called a(n) __________.
7. A(n) __________ and a(n) __________ are instruments commonly used by a forensic scientist to perform a confirmatory analysis.
8. A range in class characteristic values is best described as __________.
9. A physical match is an example of a (class/individual) characteristic and can be used for (identification/comparison).
10. Several class characteristics can be used to link a questioned sample to an exclusive origin. (a) True, (b) False.
11. Class characteristics are more common than individual characteristics. (a) True, (b) False.

4 FINGERPRINT DEVELOPMENT

Suppose a burglar enters your home while you are away and steals your plasma television. Examining your home, you see the burglar has left nothing behind but cut wires, a broken window, and a few holes in your wall. Is there anything the police can do to catch the thief? Could hidden clues have been left behind that you missed? If so, how can these hidden clues be discovered?

Among the most common items of evidence collected at a crime scene are fingerprints. The ridged-skin patterns at the end of our fingers contain individual characteristics that make them highly unique. When perspiration on the hands and fingers combines with oils, dirt, or other substances, these fingertip ridges can leave an impression on surfaces that are touched. Fingerprints are useful in investigations because an individual's fingerprints are consistent over time, and no two fingerprints have ever been found that are exactly alike. Even identical twins have unique fingerprints. Fingerprints collected at a crime scene can be compared to fingerprints collected from suspects and from individuals who had legitimate reasons to be at the crime scene. They can be checked against databases of prints collected by law enforcement agencies. Figure 12 shows a court display comparing a print found at a crime scene to a print from a known source, with individual characteristics marked. The ability to compare fingerprints is an art that requires skill and training; fingerprint analysts spend years perfecting these skills.

Fingerprint development is the process by which hidden fingerprints can be found, visualized, and examined. There are three different types of fingerprints: latent, plastic, and negative. **Latent** (hidden) **fingerprints** are those most common to a crime scene. These prints are produced by touching a surface and leaving behind *fingerprint residue* (oils, dirt, perspiration) in the pattern of the ridges. Because the prints are invisible to the naked eye, investigators must use development techniques to find them. Development techniques use the chemical and physical properties of the fingerprint residue to produce

Fingerprint development The process by which hidden fingerprints can be seen.

Latent fingerprints Hidden fingerprints; created by the transfer of a minute amount of fingerprint residue to a surface.

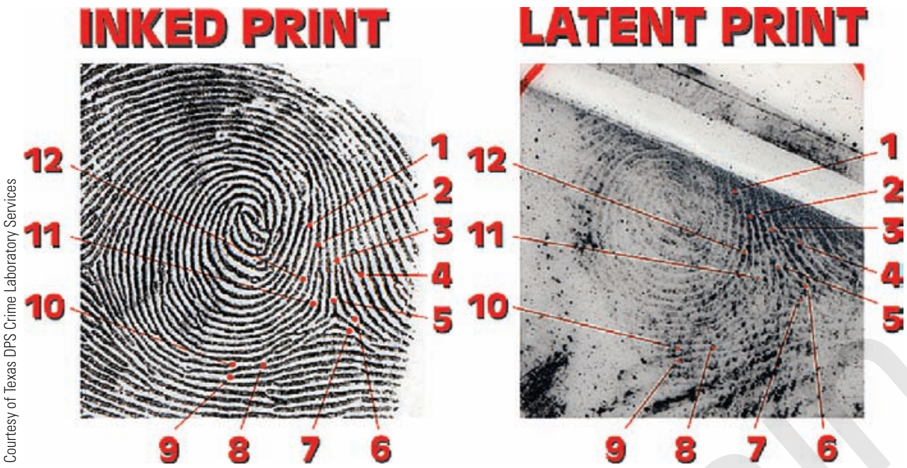


FIGURE 12 Individual characteristics link this fingerprint found at a crime scene to a known origin (person).

contrast so the hidden prints can be observed. To develop a latent fingerprint, investigators must understand the potential composition of the residue. Fingerprints typically not requiring development include **plastic fingerprints** made into soft surfaces such as silly putty, butter, or clay and **negative fingerprints** created as the skin ridges of a finger remove transferable material from a surface leaving behind a pattern of the ridges (e.g., a person touches a dusty chalkboard or a greasy wrench).

Virtually all fingerprint residues of latent fingerprints contain perspiration because our hands and fingers contain sweat glands. The composition of perspiration is slightly different for each individual and changes as a function of diet and throughout the day. Perspiration comprises water and any water-soluble salts (sodium chloride and potassium chloride), acids (lactic acid and acetic acid), and proteins composed of amino acids. Skin cells are continually being shed from the fingers and may also be present in fingerprint residue.

In addition, our hands are very active during the day and come in contact with many items. Without thinking about it, we may scratch our backs or necks, rub our noses, touch our ears, or massage our foreheads. All these activities put our fingers in locations that contain sebaceous glands, which are found at the base of hair follicles and exude fats and oils. Contact with these locations will transfer **sebum**, a mixture composed of fatty acids, triglycerides, squalene, and wax esters. Cosmetic products may also be transferred to our fingers. In addition, we put lotion on our hands, touch dirty surfaces, use household cleaners, pick up food, and even occasionally forget to wash our hands after using the restroom. All these activities potentially add to the composition of our fingerprint residue. Because the composition of one person's fingerprint residue may be considerably different from that of another, many development techniques have been established. A technique that works well for one fingerprint residue may not work well for another. In addition, some development techniques work better on fingerprints found on certain surfaces. Several fingerprint development techniques will be discussed in the following sections. The properties of the components allowing for development and the surfaces on which the techniques work best will be identified.

Plastic fingerprints Fingerprints molded into a soft surface.

Negative fingerprints Fingerprints created by the removal of residue from a surface.

Sebum A fat- and dead cell–containing secretion of sebaceous glands produced to protect and waterproof skin, keeping it soft and free of dryness and cracks.

Powder dusting The use of fine powders to visualize latent fingerprints.

Dusting for fingerprints at a crime scene.

Powder Dusting

Powder dusting involves the use of fine powders to visualize latent fingerprints. It works well on smooth nonporous surfaces such as glass, certain plastics, and ceramics but is less effective on porous surfaces such as paper or cardboard (the residue tends to absorb into the fibers over time) or on wet or sticky surfaces. Among the many components of fingerprint residue, sebum and perspiration tend to adhere to powder particles. This physical property of fingerprint residue, in conjunction with the fact that many smooth, nonporous surfaces do not adhere well to powder particles, allows for fingerprint development. The contrast developed between the adhered powder and the surface allows for visualization. The same concept is illustrated when spilled flour sticks to residue on the counter or when beard and mustache shavings stick to the toothpaste stains in the sink.

Investigators use many different types of powders. Most black powders are made from fine carbon or iron. Light-colored gray or white powders can be made of any number of substances, such as finely divided aluminum. There are also fluorescent powders in red, green, yellow, or orange, some of which may also contain iron particles. Any powder containing iron may be applied with a magnetic applicator. The magnetic applicator, a small cylinder the size of a marker or pencil, contains a sliding magnet that can be moved up or down the inside of the cylinder. When the magnet is positioned at the tip of the applicator inside the cylinder, powder containing iron will adhere to the tip and provide a collection of powder for application. Sliding the magnet away from the tip will release any excess powder. Other powders are typically applied with a variety of fine brushes made of animal hair or synthetic fibers.

Whether magnetic or nonmagnetic powder or black or fluorescent powder is used depends on personal preference and the contrast needed. Some forensic scientists prefer magnetic powders because they believe brush bristles damage the fingerprint; others think magnetic powders are too messy.

Once the powder has been applied and contrast can be seen, the fingerprint can be lifted and preserved using fingerprint tape, a high-quality transparent tape typically at least an inch wide. The lifted fingerprint can then be placed onto a fingerprint lift card that offers the greatest contrast (black for white-powder lifts and white for black-powder lifts). Identifying information such as the name of the investigator, date and time of collection, location of fingerprint, and case number all should be recorded on the card. Figure 13 shows a fingerprint lift of a black powder impression.

Ninhydrin Reaction

For years, biochemists have used the ninhydrin reaction for both qualitative and quantitative determination of **α-amino acids**. There are approximately 20 α-amino acids that comprise proteins. **Proteins** are natural **polymers** (molecules composed of repeating **monomer** units) containing α-amino acid monomers. Ninhydrin is known to react with α-amino acids and produce a

α-amino acids A group of small biological molecules containing both an amino and carboxylic acid group; the monomers of a protein polymer.

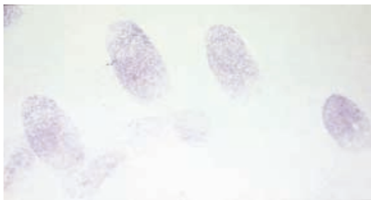
Proteins Natural polymers composed of α-amino acids performing a wide variety of biological functions.

Polymers Large and very long molecules composed of smaller repeating units.

Monomers Small molecules of a moderate molecular weight that when combined in a repeating fashion (through a process of polymerization) produce polymers.

Courtesy of Texas DPS Crime Laboratory Services

FIGURE 13 A fingerprint lift of a black powder impression.



Courtesy of Texas DPS Crime Laboratory Services

FIGURE 14 Fingerprints developed with ninhydrin.

purple-colored product called Rhuemann's purple, named after Siegfried Ruhemann who discovered the reaction in 1910. The reaction is sensitive enough to be used on the development of the small amounts of α-amino acids found in fingerprint residue. It became popular with forensic scientists in the 1950s and is still used frequently by most fingerprint examiners. Although the reaction is relatively slow (24 hours for development), it can be accelerated by the use of heat or moisture. Special ninhydrin chambers, which provide a hot and humid environment, allow for ninhydrin development in 20 minutes or less. When used for fingerprint development, the reaction works best on porous surfaces such as paper, and because amino acids are relatively stable, ninhydrin development works considerably well on old fingerprints. Figure 14 shows prints developed with ninhydrin.

Silver Nitrate Reaction

Chloride salts like sodium and potassium comprise a significant percentage of perspiration, and thus fingerprint residue. When silver nitrate reacts with any soluble chloride salt, the insoluble salt silver chloride is produced. The reaction occurs almost immediately. The silver chloride produced is a white solid that does not offer much contrast for fingerprint development. However, as the silver chloride remains exposed to ultraviolet light, it decomposes producing silver and chlorine gas. This produces a purple-black product that offers contrast for fingerprint development, as shown in Figure 15. Silver nitrate development works best on porous surfaces like paper.

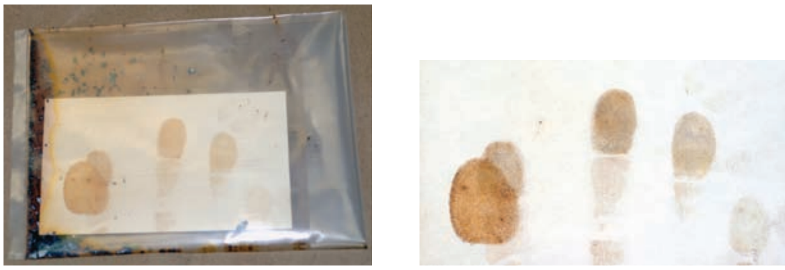
Iodine Fuming

Sublimation The direct phase change from a solid to a gas.

Iodine, in much the same way as solid carbon dioxide, undergoes a phase transition from solid to gas, skipping the liquid phase. This phenomenon is known as **sublimation**. Iodine is a purple solid under ambient temperature and pressure. When iodine crystals are heated, they will sublime, producing iodine vapors. These vapors are thought to be absorbed by the fingerprint residue so that they produce a transient amber-colored product, shown in Figure 16a.

Courtesy of Texas DPS Crime Laboratory Services

FIGURE 15 Fingerprints developed with silver nitrate.



Courtesy of Texas DPS Crime Laboratory Services

(a) (b)

FIGURE 16 Fingerprints (a) during iodine fuming and (b) after being treated with a starch fixative.

Over time, the amber color will fade. Techniques have been devised to fix the developed print. One technique employs the reaction of iodine with starch to produce a stable dark purple product, shown in Figure 16b. Iodine fuming is one of the oldest fingerprint development techniques; it works well on porous surfaces.

Superglue Fuming

In the late 1970s, it was discovered that superglue fumes, composed of cyanoacrylate monomers, would selectively polymerize (form polymers) on fingerprint residue found on smooth nonporous surfaces. The technique was first employed by the Criminal Identification Division of the Japanese National Police Agency in 1978. The technique was later introduced to the U.S. Army Crime Laboratory of Japan and was soon adopted by many crime laboratories nationally. It is presently one of the most popular fingerprint development techniques.

The polymerization of superglue monomers results in adhesion, and cyanoacrylates are commonly used for bonding purposes. The polymerization process is typically initiated by negatively charged water-soluble species (anions), which are found in fingerprint residue and are thought to preferentially initiate polymerization on their surface. This preferential initiation allows for the white–gray superglue polymer to form first on the fingerprint residue. The polymer not only offers modest contrast for fingerprint development but also aids in fingerprint preservation.

Items containing fingerprints to be developed are placed into a superglue fuming chamber, shown in Figure 17. Liquid superglue is poured into a container and slowly heated within the chamber on a hot plate to produce superglue fumes. The fumes saturate the air within the chamber and begin to polymerize on the fingerprint residue. Often the chamber is humidified. If the items containing fingerprints are not removed from the superglue fuming chamber in a timely fashion, polymerization may additionally occur on the surface resulting in "overfuming" and so jeopardize the development. Alternatively, superglue fumes may be produced by reducing the pressure inside the chamber.

Typically, analysts use fingerprint powders or dyes to enhance the contrast on the developed fingerprints. Most of the dyes used after superglue fuming are **fluorescent** dyes, which require the use of ultraviolet light for visualization. Superglue fuming played a role in the capture of the infamous Night Stalker of California, Richard Ramirez. Ramirez, suspected of having gone on a true murder spree in the mid-1980s, killed both young and old with no preferred murder weapon, location, or technique. His victims ranged in age from mid-twenties to mid-eighties. He was known to have beaten, shot, and/or stabbed his victims in addition to sexually assaulting them. From an abandoned car known to have been driven by the Night Stalker, police used superglue fuming to develop a single fingerprint that matched the fingerprint of Richard Ramirez. Ramirez was ultimately convicted of thirteen counts of murder, five attempted murders, eleven sexual assaults, and fourteen burglaries.

Phenolphthalin Reaction

Often fingerprints contain a trace amount of blood. Many reactions can be catalyzed by the **heme** portion of **hemoglobin** found in blood (shown in Figure 18) and have been used for the presumptive identification of blood. When used for fingerprint development of blood-containing fingerprints, the reactant molecule is converted to a colored product resulting in contrast. Because these reactions require heme as a **catalyst**, blood is not consumed, and the

Courtesy of Texas DPS Crime Laboratory Services

FIGURE 17 Fingerprints on an aluminum can are developed in a superglue fuming chamber.

Fluorescent Being able to produce visible light (of a longer wavelength) upon excitation with shorter wavelength ultraviolet light.

Heme An organic molecule, being a subunit of hemoglobin, with four nitrogen-containing rings surrounding an iron center.

Hemoglobin A moderately sized protein found in red blood cells responsible for oxygen transport.

Catalyst A substance used to lower the activation energy of a reaction, accelerating the reaction without itself being consumed.

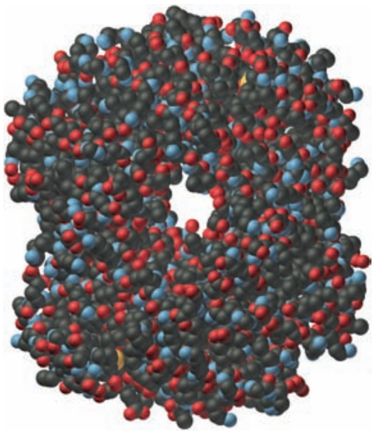


FIGURE 18 Structure of hemoglobin.

reactions are extremely sensitive. They have been used to develop latent fingerprints containing the slightest amount of blood.

Phenolphthalin is a molecule chemically related to phenolphthalein (a common chemical used in chemistry for acid–base reactions). Under ideal conditions, and in the presence of hydrogen peroxide and blood, colorless phenolphthalin will be converted to pink phenolphthalein. The reaction is often called the phenolphthalin or Kastle–Meyer reaction. Because compounds other than heme may also catalyze the reaction (potassium permanganate, rust, and some plant enzymes), the test is only presumptive for the presence of blood.

Reactions with chemicals other than phenolphthalin (leucomalachite green, tetramethylbenzidine, and ortho-tolidine) can also be catalyzed by heme and used to develop blood-containing fingerprints. All these chemicals produce a green-blue product in the presence of blood. The use of luminol is a popular test to locate trace amounts of blood, but it is not typically used for fingerprint development. It is a *chemiluminescent reaction*, producing light that can be seen in a dimmed room where blood is located. This technique can be used to determine hidden bloodstain patterns. *Bloodstain pattern analysis* is the examination and study of bloodstains (hidden or visible) for the purpose of crime scene reconstruction. Bloodstains can suggest where a crime occurred, what occurred, how it occurred, and a potential sequence of events.

CONCEPT CHECK B

1. __________ would work best for the preservation of fingerprints on smooth surfaces.
2. Blood is not consumed during the phenolphthalin reaction. (a) True, (b) False.
3. __________ reacts with α-amino acids found in fingerprint residue to produce a purple product.
4. __________ is a fingerprint development technique that produces an amber-colored transient product that can be fixed with __________.
5. __________ would work best for the development of fingerprints containing blood and generate a pink product.
6. __________ fingerprints are those created as the skin ridges of a finger remove some transferable material from a surface.
7. __________ is a fingerprint development technique that produces a white precipitate that changes color to a purple-black product when exposed to ultraviolet light.
8. Fingerprint powders may be applied with a brush, or when the powders contain iron, they may be applied with a(n) __________.
9. The polymerization reaction occurring during superglue fuming of a fingerprint is thought to be initiated by __________.

5 PRESUMPTIVE DRUG ANALYSIS

A police officer pulls over a car for speeding. While proceeding to the car, she sees the driver hurriedly put a plastic bag in the glove box. Suspecting that the driver has drugs in the car, she asks the driver to step out of the vehicle. The officer searches the vehicle and finds the plastic bag with nine other, similar bags, all containing a white powder. When asked what is in the bags, the driver responds, “Powdered sugar.” Suspicious that the driver is lying, but wise enough not to taste the unknown substance, she retains the bags for analysis.

What techniques are available to her to identify the substance quickly and presumptively on the scene? How can the identity of the substance in the bags ultimately be confirmed in the crime laboratory?

Most confirmatory analyses employed for drug identification are moderately time-consuming and require the use of expensive instrumentation such as a gas chromatograph-mass spectrometer or a Fourier transform infrared spectrophotometer. To save time and money, before conducting a confirmatory analysis (potentially resulting in inconclusive information), quick and inexpensive presumptive drug analyses are performed. These analyses direct the forensic scientist toward an appropriate confirmatory analysis that will yield the desired results the first time.

Color tests, sometimes called spot tests, are examples of presumptive drug tests used to probe questioned drug samples for their chemical properties. If chemical properties consistent with a known drug are discovered, a questioned drug sample can be *presumptively* identified. When conducting a color test, chemicals known to produce a colored product in the presence of a suspected drug are added to a small amount of the questioned sample. If the questioned sample contains the suspected drug, a colored product, having a color representative of the suspected drug, will be produced. The measured chemical property for drug identification is both its reactivity with the chemicals and its ability to produce the color-indicative product. For instance, cocaine produces a blue product when allowed to react with the chemical cobalt thiocyanate, and LSD produces a red-violet product when allowed to react with *p*-dimethylaminobenzaldehyde.

Many substances other than drugs will react with the chemicals used for presumptive drug identification and produce products of varying colors, or no color at all. The differing color (or lack of color) suggests that the questioned sample does not contain the suspected drug. Yet, many other substances will produce a product with the same representative color as the suspected drug. For example, in the presence of cobalt thiocyanate, lidocaine, benzocaine, and procaine all yield a blue-colored product similar to that of cocaine. For this reason, a positive color test is not confirmatory and simply directs the forensic scientist toward identification by limiting the possible number of drug candidates. For example, if a blue product is formed with cobalt thiocyanate, methamphetamine, heroin, and LSD can be excluded as possible identities for an unknown substance.

Color test reactions are commonly preformed in crime laboratories using **spot plates**. Spot plates are small ceramic or plastic dishes that contain several wells. Because most drug color tests are quite sensitive, requiring only a few micrograms of the sample being tested, the small wells of a spot plate are ideal for analysis. In addition, neighboring wells can be used to conduct **positive** (drug standard) and **negative** (no drug) **controls**. Side-by-side comparison of colors generated from the questioned sample and the control samples assist in positive identification.

Presumptive color tests, in addition to being performed in the crime laboratory, are commonly performed by police officers on the street in little plastic bags called Narcotic Field Test Kits. This is done to determine quickly on the scene if the police officer has enough *probable cause* for an arrest. The officer places the questioned substance in a bag containing ampoules of chemical reagents necessary for the presumptive identification of a particular drug and then breaks the ampoules within the bag, initiating the chemical reaction. The color of the product is observed. If the test is positive for the presumptive identification of a suspected drug, the test is typically performed a second time in the crime laboratory with controls for verification.

Many different presumptive color tests for drugs are available. Typically, different chemicals are used for each drug to be tested; therefore, the forensic

Color tests Tests used for the presumptive identification of drugs by probing a questioned sample for its chemical properties and visually examining a colored product.

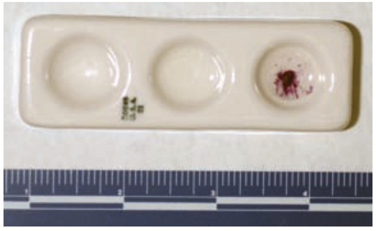
Spot plates Small ceramic or plastic dishes containing several wells, used for color test reactions.

Positive control A sample known to contain the compound in question, resulting in a positive result.

Negative control A sample known *not* to contain the compound in question, resulting in a negative result.

TABLE 2 Various Drug Color Tests

Test	Chemicals	Positive Results
Marquis	Formaldehyde and concentrated sulfuric acid	Amphetamines: brown orange Opium derivatives: purple
Scott Test	Cobalt thiocyanate, glycerine, hydrochloric acid, and chloroform	Cocaine derivatives: blue
Van Urk	*p*-Dimethylaminobenzaldehyde, concentrated hydrochloric acid, and ethanol	LSD: purple
Dillie-Koppanyi	Cobalt thiocyanate, methanol, and isopropylamine	Barbiturates: violet
Duquenois-Levine	Vanillin, acetaldehyde, ethanol, hydrochloric acid, and chloroform	Marijuana: purple in chloroform layer
Simon's	Sodium nitroprusside and sodium bicarbonate	Methamphetamine: deep blue



Courtesy of Texas DPS Crime Laboratory Services

FIGURE 19 Spot plate with controls for the Marquis test used to determine the presence of opiates.

chemist must propose a hypothesis regarding the identity of the substance prior to performing the presumptive test. Some chemicals, however, are used for more than one class of drugs. For example, the Marquis test, consisting of two chemicals (concentrated sulfuric acid and formaldehyde) yields a purple product for opiates like morphine, heroin, codeine, and oxycodone and an orange-red product for amphetamine and methamphetamine. Figure 19 shows a spot plate setup for the Marquis test to identify opiates. The center well has the negative control (no drug); the right-hand well has the positive control (codeine mixed with the Marquis reagent). The unknown substance will be mixed with the Marquis reagent and placed in the left-hand well for a color comparison with the other two wells.

Because the chemistry of most presumptive drug tests is complex, many reactions are not completely understood. In fact, most presumptive tests were developed by chance, when a certain chemical was added to a given drug and a colored product was generated without knowing exactly why. Subsequently, validations were performed to determine what else could yield a colored product when combined with that same chemical. Table 2 lists various drug color tests.

Courtesy of Texas DPS Crime Laboratory Services

FIGURE 20 Cocaine microcrystals under a polarized light microscope.

Microcrystalline tests, a special class of presumptive drug analyses, produce solid products. Typically the solid forms slowly, producing representative crystalline structures that may be viewed under the microscope with transmitted illumination (see Figure 20). To a trained expert, these tests are practically confirmatory. However, some controversy still exists regarding the applicability of microcrystalline tests. Many forensic chemists are not trained to recognize the characteristic crystalline structures. Identification of the target product is more complicated than simply observing a color. Consequently, even though well-developed microcrystalline tests are available for cocaine, amphetamine, heroin, and other drugs, many crime laboratories do not perform these tests.

6 SOIL ANALYSIS

Microcrystalline test Chemical analysis used for drug identification that produces representative solid crystals that can be seen under a microscope.

A body is found in a mountain canyon next to a riverbank. The victim is covered with mud and appears to have been dragged several yards. It is suspected the perpetrator was trying to dispose of the body in the river when it began to rain. Tire tracks are found leading toward and away from the riverbank. The tracks leading away from the riverbank are deeper and show signs of tires spinning, suggesting the individual may have been leaving in a hurry. The investigator notices that the muddy soil is rich in organic material and contains pollen and minerals unique to the area. The next day a suspect is located; he has a dirty truck with mud streaks on the side. Can the truck be linked to the location of the dead body? What properties of soil would be analyzed to make this connection?

Soil is a complex mixture of both organic and inorganic material. To most people, soil is simply dirt. It is anything closely associated with the Earth's crust that can be dug, plowed, or cultivated; it is the stuff upon which we build our homes and pave our roads; it is what erodes when it rains too hard and what provides food to an ever-increasing world population. However, to a forensic chemist, soil is much more than this. It is a hodgepodge of anything and everything ground up, disintegrated, or pulverized. It could be material rich in organic compounds and ideal for crops or simply pulverized rock or cement. A forensic soil analysis could include a wide range of substances from potting soil to safe insulation. Regardless of its actual identity, most techniques used for soil analysis are similar. All techniques require an understanding of common chemistry principles such as pH, heterogeneous mixtures, and density. Most soil analyses are performed by forensic chemists because geologists and mineralogists are rarely associated with crime laboratories.

During a soil analysis, the class characteristics of several soil samples from a known source are compared with those of a questioned sample. Rarely are individual characteristics found. Thus, when all the characteristics of a questioned sample match those of known samples, individualization *cannot* be assumed. However, just as with all items of evidence that simply contain class characteristics, exclusion is possible when the class characteristics of the known samples *do not match* the questioned sample.

If the location of the crime scene is not known, a questioned soil sample may hold information associated with the location of the crime scene. A trained forensic chemist (or geologist) familiar with the local geology may offer assistance in identifying regions containing soil with similar class characteristics that may potentially be the crime scene.

THE WORLD OF CHEMISTRY

Muddy Murder

Forensic geology proved key in solving one 1995 murder case in Colorado. In October of that year, Janice Hall and her husband of three months, John Dodson, were on a hunting trip in the mountains of western Colorado. On October 15, Janice Hall summoned nearby hunters for help, reporting that she had returned to her campsite to find her husband dead of gunshot wounds. Although at first glance it appeared to be a hunting accident, the evidence soon pointed to murder. When it was discovered that Janice's ex-husband, J. C. Lee, had been hunting nearby, he became a prime suspect. Lee had an alibi for the time in question; he also reported that a rifle and cartridges had been stolen from his camp that same day. The missing gun was a .308-caliber rifle, matching a shell casing and bullet found at the crime scene.

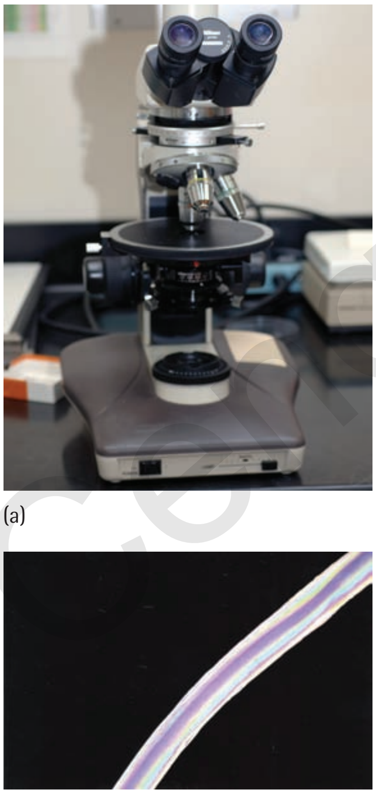
The rifle was never found; however, a pair of muddy coveralls worn by Janice Hall on the day of the murder turned out to be important evidence. Janice claimed that she had muddied the coveralls in the bog near her own camp. After years of fruitless investigation, a break in the case came when investigators asked a forensic scientist to analyze the dried mud on Janice's coveralls and compare it to soil samples collected from both campsites. As it turned out, the man-made pond at Lee's campsite was lined with bentonite, a clay not normally found in the area. When soil analysis revealed that the mud on Janice's coveralls contained bentonite, investigators knew that Janice had lied about the source of the mud, and that she had been at Lee's campsite at the time the rifle was stolen. This evidence proved convincing to jurors, and Janice Hall was convicted of murder. She is currently serving a life sentence.

Stereoscopic microscope Versatile microscope used to examine large and small objects; it has a magnification of approximately 10–60×

Polarized light microscope Sophisticated microscope employing the use of transmitted polarized light for illumination, with a magnification of approximately 40–400×

Courtesy of Texas DPS Crime Laboratory Services

FIGURE 21 Stereoscopic microscope.



(a)

(b)

Courtesy of Texas DPS Crime Laboratory Services

FIGURE 22 (a) A polarized light microscope and (b) a carpet fiber photographed under the microscope.

It is important that the known samples be collected in a manner representative of the questioned sample. For example, if the questioned sample, taken from the bottom of a suspect's shoe, is suspected of originating from the surface of a muddy field, then the known samples should be collected from the surface of the muddy field and not dug from the ground. However, if it is assumed that the suspect was digging a grave when he muddied his shoes, then the known samples *should* be dug from the ground.

Microscopic Analysis

A soil analysis often begins with a visual examination of several known soil samples. The natural variation of color, texture, and general appearance are all recorded. Investigators examine the color of the sample when it is both wet and dry and record all visual similarities and differences.

Next, they use a microscope to observe a small portion of each sample. The **stereoscopic microscope**, shown in Figure 21, magnifies the tiny surface features of the sample, aiding in the identification of vegetative matter like leaves common to the area, paint chips indicating soil found close to a barn or house, sawdust, bone chips, or any other minute items not identifiable to the naked eye. This is achieved by illuminating the surface of the sample and collecting the reflected light with the microscope. With a **polarized light microscope**, samples are illuminated by passing polarized light directly *through* the sample, allowing for analysis of internal features. Figure 22a shows a polarized light microscope, and Figure 22b shows a carpet fiber photographed under a polarized light microscope. This process involves oscillating electric fields of polarized light that propagate in a single plane. The light is produced by introducing a special filter (or polarizer) in the light path between the light source and the sample. As the polarized light passes through the sample, it interacts with the sample in ways that can be measured through careful observation. For example, crystalline solids have a uniform lattice structure at the atomic level. The orientation of their three-dimensional structure, with respect to the plane of propagation of polarized light, can produce different measurable interactions. These interactions are both class and individual characteristics of the crystalline solids. Because the minerals found in soil are frequently crystalline solids, the polarized light microscope can be used to determine mineral content, which in turn serves as a class characteristic of the entire soil sample.

Size Distribution

Because the individual particles in soil samples vary widely in size, investigators often find it difficult to determine the complete size distribution of a sample through a visual or microscopic analysis. In that case, they will pass the soil sample through a series of sieves (containers with a mesh or screen bottom) where the size of the mesh on each sieve differs. They are stacked together so that the sieve with the coarsest mesh is on the top and the finest mesh is on the bottom. The entire stack is mechanically or manually shaken for several minutes. The mass of soil retained in each sieve is then compared to the total mass of the sample that was introduced into the stack. The distribution of soil mass due to particle size is considered to be a class characteristic of the soil sample.

Density Comparison

As discussed in a previous chapter, density is the ratio of a substance's mass to volume.

$$\text{density} = \text{mass}/\text{volume} \qquad (1)$$

Density is typically expressed in units of grams per milliliter, or kilograms per liter. It is a physical property of a substance that does not change with amount. Physical and chemical properties of this nature are **intensive properties**. **Extensive properties**, such as mass or volume expressed independently, change as a function of amount. For example, as the amount of a glass sample is increased, both its mass and volume increase, but its density does not.

Intensive properties Physical and chemical properties of a substance that do *not* change with substance amount.

Extensive properties Physical and chemical properties of a substance that change with substance amount.

Density gradient A solution of chemicals containing a change in density from high to low and used to determine the density distribution of components found in a mixture.

Density is commonly used in forensic science when comparing items of evidence such as glass, plastic, wood, and soil. However, because soil is a complex mixture composed of many substances, each substance will have its own unique density. Ideally, the forensic scientist will use a density gradient to evaluate the distribution of densities comprising the soil mixture.

A **density gradient** can be prepared by carefully adding solutions of decreasing density to a glass container like a narrow glass tube or a graduated cylinder. Often bromoform (2.89 g/mL) and methanol (0.791 g/mL) are used to create the gradient, with pure bromoform on the bottom, pure methanol on the top, and decreasing bromoform/methanol mixtures from bottom to top. Because substances of a lesser density will float on top of substances of a greater density, the gradient described is quite stable. In fact, the longer the gradient sits, the more uniform is the transition from a lower density to higher density through the gradient. It is important to recognize that substances of a greater density will sink in substances of a lesser density, and substances of an equal density will neither sink nor float, but remain suspended in solution. This latter phenomenon is exploited during a soil density analysis.

If an unknown soil sample is poured into a density gradient, each substance comprising the soil sample will sink until it reaches a region in the density gradient where its density matches that of the gradient. What is produced is a visible profile of the distribution of densities of all substances found in the soil sample. The profile of a questioned soil sample can be compared with those of a known sample to determine soil type.

pH Comparison

Remember, pH is defined as the negative logarithm of hydronium ion (H_3O^+) concentration in an aqueous (water) solution.

$$\text{pH} = -\log[H_3O^+] \qquad (2)$$

When mixed with water, many of the compounds within a soil sample will produce hydronium ions. Because the amount of hydronium ions produced depends on soil composition, farmers often measure the pH of their soil in an attempt to monitor and regulate its value for optimal plant growth. Soil pH is commonly determined by forensic scientists during a soil comparison analysis after moistening the soil with a predetermined amount of water (often one part soil to one part water). The pH of the water from the soil is tested using pH indicators, litmus paper, or a pH meter, as shown in Figure 23. Soil pH is a class characteristic used for comparison.

Charles D. Winters

FIGURE 23 pH measurement devices.

7 THIN LAYER CHROMATOGRAPHY AND INK ANALYSIS

Suppose you just bought your very first car for $5000 and paid for it with a check. After several days, you notice that $5500 dollars was withdrawn from your account. You ask the bank to send you a copy of the check, and sure enough it reads “five thousand five hundred” instead of “five thousand.” The copy sent from the bank shows that someone has added the words “five hundred” and written over the first zero of the number to make it look like a

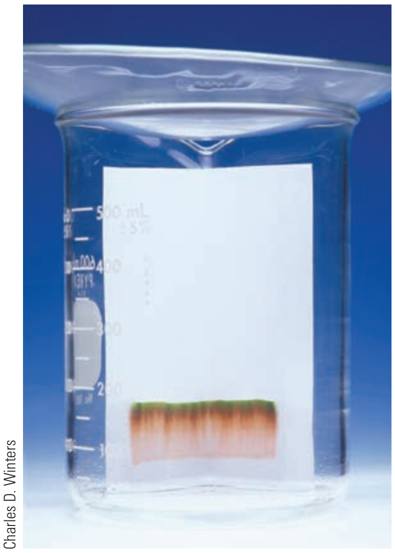


FIGURE 24 Compounds in ink are separated through paper chromatography, a process similar to thin layer chromatography.

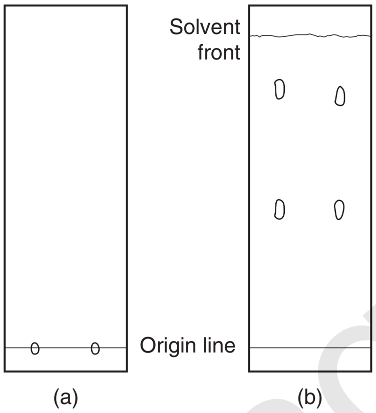


FIGURE 25 A spotted chromatographic plate (a) before and (b) after developing.

five. What can you do? Is there a way to determine if the ink used to write the words "five thousand" is the same used to write the words "five hundred"?

Chromatography, literally meaning color writing, is the process of separating compounds based on their unique and selective interactions. Many compounds have a tendency to become closely associated with other compounds through attractive forces, while others do not. For example, ethanol (the alcohol found in alcoholic beverages) will easily mix with water, while vegetable oil will not; there is no attraction. This attraction or tendency for association is often called *affinity*. Ethanol has a high affinity for water, while vegetable oil does not. Chromatography utilizes the differences in affinity of compounds for separation. For example, if two compounds are dissolved in a liquid, and the liquid (called the mobile phase) is allowed to pass over a fixed or immobile substance (called the stationary phase), the compound in the mobile phase with the greatest affinity for the stationary phase will find itself associating more with the stationary phase and not traveling as far or as quickly; thus, the compounds become separated, as shown in Figure 24.

In **thin layer chromatography** (TLC), the compounds to be separated are "spotted" onto a flat glass plate, coated with stationary phase, near the bottom of the plate but not at the bottom edge. The plate is placed vertically into a container with enough mobile phase to cover the bottom edge of the plate, but not enough to cover the locations of the spotted compounds (origin line). The mobile phase passes over the stationary phase through **capillary action**, which works in much the same way that a paper towel will become wet over time by simply placing one of its edges in a container of water. As the mobile phase comes into contact with the spotted compounds, it carries them over the stationary phase, and separation occurs, as illustrated in Figure 25.

In forensic science, TLC is commonly used to separate and compare drugs, fiber dyes, poisons, and inks. Most inks are composed of a mixture of colorful compounds, many of which can be separated using TLC. Two inks of a similar color and appearance may contain unique compounds that only become apparent after a TLC analysis. Often the dimensions of TLC plates are wide enough that several inks can be separated simultaneously. This allows the forensic scientist to prepare ink profiles of both known and questioned samples so that they can be compared side by side.

Chromatography A process of separating compounds using a stationary phase and a mobile phase.

Thin layer chromatography A type of chromatography employing a flat plate containing stationary phase over which a mobile phase passes due to capillary action.

Capillary action The ability of a liquid to travel against gravity due to adhesive interactions of the liquid with the inner walls of a capillary or channel.

CONCEPT CHECK C

1. Color tests are also called __________ tests.
2. Presumptive drug color tests only change color when the drug is present. (a) True, (b) False.
3. Density is an (intensive/extensive) property because it (does/does not) change with amount.
4. If a compound has a strong affinity for another compound it (will/will not) mix well with the compound.
5. As the pH of a sample increases, its hydronium ion concentration (increases/decreases).
6. If a substance of a lesser density than a liquid is placed directly into the liquid, it will (sink/float/remain suspended).
7. __________ can be used to separate compounds on a flat plate containing stationary phase.
8. Density gradients for soil analyses are commonly prepared with the chemicals __________ and __________.
9. Soil samples commonly have many individual characteristics. (a) True, (b) False.

8 CONCLUSIONS

Chemistry is an integral part of forensic science. Forensic scientists must understand chemistry principles, concepts, and techniques. However, they must also be well versed in all legal matters relevant to the occupation, like the criminal justice system, state and federal laws, and chain of custody. Most importantly, forensic scientists must have spotless criminal records and only exercise the highest ethical standards.

Upon completing an analysis, forensic scientists must be able to present their findings in a court of law in a manner understandable to the general public. This requires an extensive understanding of analysis techniques in addition to the ability to speak publicly and articulate ideas clearly. Forensic scientists work neither for the defense nor for the prosecution; they simply serve as advocates of the truth under all circumstances.

KEY TERMS

- α-amino acids
- Capillary action
- Catalyst
- Chemical properties
- Chromatography
- Class characteristics
- Classification
- Color tests
- Comparative analysis
- Confirmatory analysis
- Criminalist
- Extensive properties
- Density gradient
- Fingerprint development
- Fluorescent
- Forensic generalist
- Forensic history
- Forensic science
- Forensic specialist
- Fourier transform infrared spectrophotometer
- Gas chromatograph-mass spectrometer (GC-MS)
- Heme
- Hemoglobin
- Identification
- Individual characteristics
- Individualization
- Intensive properties
- Known sample
- Latent fingerprints
- Microcrystalline test
- Monomers
- Natural variation
- Negative control
- Negative fingerprints
- Physical evidence
- Physical match
- Physical properties
- Plastic fingerprints
- Polarized light microscope
- Polymers
- Positive control
- Powder dusting
- Presumptive analysis
- Proteins
- Questioned sample
- Sebum
- Scientific method
- Spot plates
- Sublimation
- Stereoscopic microscope
- Thin layer chromatography

THE LANGUAGE OF CHEMISTRY

Match the definition in the right-hand column with the correct term in the left-hand column.

1.	Affinity	a.	Single plane
2.	Positive control	b.	Composed of amino acids
3.	Catalyst	c.	Several possible origins
4.	Polarized light	d.	Single origin
5.	Plastic fingerprints	e.	Not consumed

6. Individualization
7. Reflected illumination
8. Natural variation
9. Proteins
10. Classification
11. Fluorescent
12. Capillary action
13. Monomer
14. Physical match

f. Travel against gravity
g. Used to visualize surface features
h. Attraction
i. Contains compound in question
j. Visible from ultraviolet light
k. Puzzle pieces
l. Molded into a soft surface
m. Range of characteristics
n. Used to make polymers

APPLYING YOUR KNOWLEDGE

1. Define forensic science and forensic history.
2. What are the two mentioned definitions of forensic? How are they related?
3. Look up and define adversarial system. Explain how debate is central to its definition.
4. Explain how legal truth is sought.
5. Search the Internet for "forensic" and find two websites that exclusively refer to the debate-related definition of the term.
6. Describe the role of a forensic scientist in an investigation.
7. List and define various types of evidence. What type of evidence does a crime laboratory analyze?
8. Do all crimes require the analysis of physical evidence? Explain.
9. Is chemistry the only discipline involved in forensic science? Explain.
10. The chapter suggests that forensic science includes disciplines such as odontology, anthropology, entomology, and pathology. What are these disciplines and how do they contribute to forensic science? (You will need to research this answer on the Internet.)
11. Describe the difference between a forensic generalist and a forensic specialist.
12. Define criminalistics in your own words.
13. Define a physical property and a chemical property.
14. Determine whether each of the following statements describes a physical or chemical property:
    (a) The fiber is blue.
    (b) The fiber dissolves in formic acid producing bubbles.
    (c) The fiber has a diameter of 10 micrometers.
    (d) The fiber has a trilobal cross section.
15. Determine whether each of the following statements describes a physical or chemical property:
    (a) The explosive is gray in color.
    (b) After detonation the explosive produced a large amount of white smoke.
    (c) The explosive burns very quickly.
    (d) The explosive contains trinitrotoluene.
16. Determine whether each of the following statements describes a physical or chemical property:
    (a) Black powder used with muzzle-loader firearms is not a fine powder but more of a collection of irregularly shaped flat particles.
    (b) As a means of identification, black powder generates a dark navy blue color in the presence sulfuric acid and diphenylamine.
    (c) Black powder burns much more quickly than smokeless powder.
    (d) Black powder is typically coated with a graphite glaze.
17. What is the typical order of a forensic analysis?
18. What is the difference between classification and individualization?
19. Explain how the steps involved in a forensic analysis are different for each item of evidence.
20. Would the same set of analyses be performed for the identification of all items of evidence? What about all drug evidence? Explain.
21. Discuss the importance of making an educated guess as to the identity of an item of evidence before beginning an analysis.
22. Discuss the difference between a presumptive and a confirmatory analysis.
23. What two instruments are commonly used by a forensic scientist for a confirmatory analysis? How does each instrument identify a compound or a mixture of compounds?
24. What is the purpose of a comparative analysis?
25. What is a class characteristic? Give several examples.
26. Define natural variation and discuss its importance in reference to a comparative analysis.

27. In reference to class characteristics, discuss the importance of not interpreting more into an analysis than what is being suggested.
28. Discuss the potential significance of a comparative analysis of an item of evidence only containing class characteristics.
29. What is an individual characteristic? Give several examples.
30. Discuss the difference between latent, negative, and plastic fingerprints.
31. Is the composition of fingerprint residue the same for every individual? Explain.
32. On what surfaces can fingerprints be developed using fingerprint powder?
33. How would a moist surface interfere with fingerprint development using fingerprint powder?
34. Discuss how fingerprint powder can be used to develop latent fingerprints.
35. On what surfaces does the ninhydrin reaction work best for fingerprint development?
36. How does the ninhydrin reaction develop fingerprints? With what does it react, and what is produced?
37. What is the difference between an α-amino acid and a protein?
38. With what substance found in perspiration does silver nitrate react?
39. How is contrast between the fingerprint and surface developed when using the silver nitrate reaction?
40. What is the appearance of the product when iodine vapors are absorbed by fingerprint residue?
41. Why must the iodine crystals be heated for fingerprint development?
42. What is the purpose of a starch solution when developing fingerprints with iodine fumes? What is the appearance of the product?
43. Discuss the process of fingerprint development using superglue.
44. Does superglue fuming alone offer significant fingerprint contrast? Explain.
45. What is often done subsequent to superglue fuming? Why?
46. In addition to fingerprint development what else does superglue fuming do to the fingerprint?
47. Why is the phenophthalin reaction so sensitive?
48. Discuss how the phenolphthalin reaction may be used to develop fingerprints.
49. What must the fingerprint contain in order to be developed using the phenolphthalin reaction? Be specific.
50. Could the phenolphthalin reaction develop fingerprints that do not contain blood? Explain.
51. What other tests (excluding phenolphthalin) have also been used for blood analysis and fingerprint development? What indicates a positive test for each?
52. What is bloodstain pattern analysis?
53. What is a chemiluminescent reaction and when might it be used in forensic science?
54. Briefly discuss the two types of presumptive drug tests.
55. What properties are analyzed when conducting a color test?
56. Is it possible for a color test to produce a colored product representative of a drug when the drug is not present? Explain.
57. Define and discuss the purpose of positive and negative controls.
58. Why are microcrystalline tests not used as frequently as color tests for presumptive drug identification?
59. Identify the chemicals used for the color testing of cocaine, methamphetamine, and LSD. What indicates the presence of each drug?
60. What is meant by the statement, known soil samples must be "collected in a manner representative of the questioned sample"?
61. Explain how a forensic scientist defines soil.
62. Can anything be done with a questioned soil sample if the location of the crime scene is *not* known? Explain.
63. Can a soil sample be exclusively linked to a single origin? Explain.
64. Discuss what may be determined when using a stereoscopic microscope for the analysis of soil.
65. Discuss what may be determined when using a polarized light microscope for the analysis of soil.
66. Which type of microscope may be used to determine mineral content? Explain.
67. Which type of microscope may be used for the analysis of a sample's surface features? Explain.
68. Which type of microscope may be used for the analysis of a sample's internal features? Explain.
69. How might a forensic scientist determine the particle size distribution of a soil sample?
70. Why is it important to measure the mass of a soil sample prior to introducing it into a stack of sieves?
71. If it is possible to decrease the size of soil sample particles due to excessive shaking, discuss why it would be important to shake the known and questioned samples in a stack of sieves for the same amount of time.
72. What is the difference between an intensive and an extensive property?
73. Discuss the production of a density gradient for soil analysis.

74. Why do soil particles remain suspended at different levels in a density gradient?
75. If two soil samples contain particles of similar densities, but their relative amounts are different, how would their density gradient profiles compare?
76. Define pH.
77. How might a forensic scientist determine soil pH?
78. Describe how two compounds become separated in chromatography.
79. How does the mobile phase travel over the stationary phase in thin layer chromatography?
80. How might a questioned ink sample be compared directly to a known ink sample?

CHEMISTRY ON THE WEB

- Federal Bureau of Investigation
  http://www.fbi.gov/
- Lightning Powder Company Technical Notes
  http://www.redwop.com/technotes.asp#2
- American Academy of Forensic Scientists
  http://www.aafs.org/
- Crime Library
  http://www.crimelibrary.com/criminal_mind/forensics/crimescene/1.html

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About the Author

David Collins received a B.S degree in chemistry at Weber State University (Ogden, Utah) in 1997, and a Ph.D. in analytical chemistry at Brigham Young University (Provo, Utah) in 2001. He has taught forensic science at Weber State University as a faculty member in the criminal justice department, and has developed a forensic program at Colorado State University—Pueblo. In addition, Dr. Collins has published several articles in respected analytical chemistry journals and a forensic science laboratory manual (Investigating Chemistry in the Laboratory); he also holds a U.S. patent. He was recently awarded the Colorado State University—Pueblo Excellence in Teaching Award for 2005. Presently, Dr. Collins lives in Rexburg, Idaho, with his wife and three children and teaches at Brigham Young University—Idaho in the chemistry department.

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