

chapter 11

Forensic Aspects of Arson and Explosion Investigations

Key Terms

accelerant

black powder

combustion

deflagration

detonating cord

detonation

endothermic reaction

energy

exothermic reaction

explosion

flammable range

flash point

glowing combustion

heat of combustion

high explosive

hydrocarbon

ignition temperature

low explosive

modus operandi

oxidation

oxidizing agent

primary explosive

pyrolysis

safety fuse

secondary explosive

smokeless powder (double-base)

smokeless powder (single-base)

spontaneous combustion

Learning Objectives

After studying this chapter you should be able to:

- List the conditions necessary to initiate and sustain combustion
- Recognize the telltale signs of an accelerant-initiated fire
- Describe how to collect physical evidence at the scene of a suspected arson or explosion

- Describe laboratory procedures used to detect and identify hydrocarbon and explosive residues
- Understand how explosives are classified
- List some common commercial, homemade, and military explosives

The Oklahoma City Bombing

It was the biggest act of mass murder in U.S. history. On a sunny spring morning in April 1995, a Ryder rental truck pulled into the parking area of the Alfred P. Murrah federal building in Oklahoma City. The driver stepped down from the truck's cab and casually walked away. Minutes later, the truck exploded into a fireball, unleashing enough energy to destroy the building and kill 168 people, including 19 children and infants in the building's day care center. Later that morning, an Oklahoma Highway Patrol officer pulled over a beat-up 1977 Mercury Marquis being driven without a license plate. On further investigation, the driver, Timothy McVeigh, was found to be in possession of a loaded firearm and charged with transporting a firearm.

At the explosion site, remnants of the Ryder truck were located and the truck was quickly traced to a renter—Robert Kling, an alias for Timothy McVeigh. Coincidentally, the rental agreement and McVeigh's driver's license both used the address of McVeigh's friend, Terry Nichols.

Outrage at the destruction of the Branch Davidian compound at Waco had spurred McVeigh and Nichols into planning the destruction of the federal building. Investigators later recovered McVeigh's fingerprint on a receipt for 2,000 pounds of ammonium nitrate, a basic explosive ingredient. Forensic analysts also located PETN residues on the clothing

McVeigh wore on the day of his arrest. PETN is a component of detonating cord. A jury took three days to decide McVeigh's guilt and then sentenced McVeigh to die by lethal injection.

Arson and explosions often present complex and difficult circumstances to investigate. Normally, these incidents are committed at the convenience of a perpetrator who has thoroughly planned the criminal act and has left the crime scene long before any official investigation is launched. Furthermore, proving commission of the offense is more difficult because of the extensive destruction that frequently dominates the crime scene. The contribution of the criminalist is only one aspect of a comprehensive and difficult investigative process that must establish a motive, the **modus operandi**, and a suspect.

The criminalist's function is rather limited; usually he or she is expected only to detect and identify relevant chemical materials collected at the scene and to reconstruct and identify igniters or detonating mechanisms. Although a chemist can identify trace amounts of gasoline or kerosene in debris, no scientific test can determine whether an arsonist has used a pile of rubbish or paper to start a fire. Furthermore, a fire can have many accidental causes, including faulty wiring, overheated electric motors, improperly cleaned and regulated heating systems, and cigarette smoking—which usually leave no chemical traces. Thus, the final determination of the cause of a fire or explosion must consider numerous factors and requires an extensive on-site investigation. The ultimate determination must be made by an investigator whose training and knowledge have been augmented by the practical experiences of fire and explosion investigation.

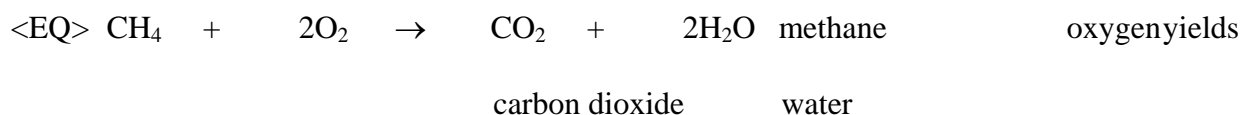
THE CHEMISTRY OF FIRE

Humankind's early search to explain the physical concepts underlying the behavior of matter al-

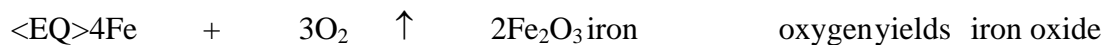
ways bestowed a central and fundamental role on fire. To ancient Greek philosophers, fire was one of the four basic elements from which all matter was derived. The alchemist thought of fire as an instrument of transformation, to be used for changing one element into another. One ancient recipe expresses its mystical power as follows: “Now the substance of cinnabar is such that the more it is heated, the more exquisite are its sublimations. Cinnabar will become mercury, and passing through a series of other sublimations, it is again turned into cinnabar, and thus it enables man to enjoy eternal life.”

Today, we know of fire not as an element of matter but as a transformation process during which oxygen is united with some other substance to produce noticeable quantities of heat and light (a flame). Therefore, any insight into why and how a fire is initiated and sustained must begin with the knowledge of the fundamental chemical reaction of fire—**oxidation**.

In a simple description of oxidation, oxygen combines with other substances to produce new products. Thus, we may write the chemical equation for the burning of methane gas, a major component of natural gas, as follows:



However, not all oxidation proceeds in the manner that one associates with fire. For example, oxygen combines with many metals to form oxides. Thus, iron forms a red-brown iron oxide, or rust, as follows:

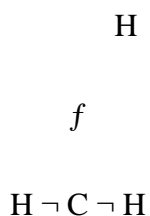


Yet chemical equations do not give us a complete insight into the oxidation process. We must consider other factors to understand all of the implications of oxidation or, for that matter, any

other chemical reaction. When methane unites with oxygen, it burns; but the mere mixing of methane and oxygen will not produce a fire, nor, for example, will gasoline burn when it is simply exposed to air. However, light a match in the presence of any one of these fuel–air mixtures (assuming proper proportions) and you have an instant fire. What are the reasons behind these differences? Why do some oxidations proceed with the outward appearances that we associate with a fire while others do not? Why do we need a match to initiate some oxidations while others proceed at room temperature? The explanation lies in a fundamental but abstract concept—**energy**.

Energy can be defined as the capacity for doing work. Energy takes many forms, such as heat energy, electrical energy, mechanical energy, nuclear energy, light energy, and chemical energy. For example, when methane is burned, the stored chemical energy in methane is converted to energy in the form of heat and light. This heat may be used to boil water or to provide high-pressure steam to turn a turbine. This is an example of converting chemical energy to heat energy to mechanical energy. The turbine can then be used to generate electricity, transforming mechanical energy to electrical energy. Electrical energy may then be used to turn a motor. In other words, energy can enable work to be done; heat is energy.

The quantity of heat from a chemical reaction comes from the breaking and formation of chemical bonds. Methane is a molecule composed of one carbon atom bonded with four hydrogen atoms:



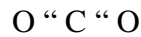
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An oxygen molecule forms when two atoms of the element oxygen bond:



In chemical changes, atoms are not lost but merely redistributed during the chemical reaction; thus, the products of methane's oxidation will be carbon dioxide:



and water:



This rearrangement, however, means that the bonds holding the atoms together must be broken and new bonds formed. We now have arrived at a fundamental observation in our dissection of a chemical reaction—that molecules must absorb energy to break apart their chemical bonds, and that they liberate energy when their bonds are reformed. The amount of energy needed to break a bond and the quantity of energy liberated when a bond is formed are characteristic of the type of chemical bond involved. Hence, a chemical reaction involves a change in energy content; energy is going in and energy is given off. The quantities of energies involved are different for each reaction and are determined by the participants of the chemical reaction.

All oxidation reactions, including the **combustion** of methane, are examples of reactions in which more energy is liberated than what is required to break the various bonds. This excess energy is liberated as heat and often as light and is known as the **heat of combustion**. Such reactions are said to be **exothermic**. Table 11–1 summarizes the heats of combustion of some important fuels in fire investigation.

Although we will not be concerned with them, some reactions require more energy than they will eventually liberate. These reactions are known as **endothermic reactions**.

Thus, all reactions require an energy input to start them. We can think of this requirement as an invisible energy barrier between the reactants and the products of a reaction (see Figure 11–1). The higher this barrier, the more energy required to initiate the reaction. Where does this initial energy come from? There are many sources of energy; however, for the purpose of this discussion we need to look at only one—heat.

The energy barrier in the conversion of iron to rust is relatively small, and it can be surmounted with the help of heat energy present in the surrounding environment at normal outdoor temperatures. Not so for methane or gasoline; these energy barriers are quite high, and a high temperature must be applied to start the oxidation of these fuels. Hence, before any fire can result, the temperature of these fuels must be raised to a value that will allow the heat energy input to exceed the energy barrier. Table 11–2 shows that this temperature, known as the **ignition temperature**, is quite high for common fuels. Once the combustion starts, enough heat is liberated to keep the reaction going by itself. In essence, the fire becomes a chain reaction, absorbing a portion of its own liberated heat to generate even more heat. The fire will burn until either the oxygen or the fuel is exhausted.

Table 11–1 Heats of Combustion of Fuels

Fuel	Heat of Combustion^a
Crude oil	19,650 Btu/gal
Diesel fuel	19,550 Btu/lb

Gasoline	19,250 Btu/lb
Methane	995 Btu/cu ft
Natural gas	128–1,868 Btu/cu ft
Octane	121,300 Btu/gal
Wood	7,500 Btu/lb
Coal, bituminous	11,000–14,000 Btu/lb
Anthracite	13,351 Btu/lb

^aBtu (British thermal unit) is defined as the quantity of heat required to raise the temperature of 1 pound of water 1°F at or near its point of maximum density.

Source: John D. DeHaan, *Kirk's Fire Investigation*, 2nd ed. Upper Saddle River, N.J.: Prentice Hall, 1983.

Normally, a lighted match provides a convenient igniter of fuels. However, the fire investigator must also consider other potential sources of ignition—for example, electrical discharges, sparks, and chemicals—while reconstructing the initiation of a fire. All of these sources have temperatures in excess of what is needed to meet the ignition temperature requirements of most fuels.

Although the liberation of energy explains many important features of oxidation, it does not completely explain all characteristics of the reaction. Obviously, although all oxidations liberate energy, they are not all accompanied by the presence of a flame; witness the oxidation of iron to rust. Therefore, one other important consideration will make our understanding of oxidation and fire complete: **the rate or speed at which the reaction takes place.**

We can picture a chemical reaction, such as oxidation, taking place when molecules combine or collide with one another. Essentially, the faster the molecules move, the greater the number of collisions between them and the faster the rate of reaction. Many factors influence the rate of these collisions. In our description of fire and oxidation, we consider only two: the physical state of the fuel and the temperature.

Table 11–2 Ignition Temperatures of Some Common Fuels

Fuel	Ignition Temperature, °F
Acetone	869
Benzene	928
Fuel oil #2	495
Gasoline (low octane)	536
Kerosene (fuel oil #1)	410
<i>n</i> -Octane	428
Petroleum ether	550
Turpentine	488

Source: John D. DeHaan, *Kirk's Fire Investigation*, 5th ed. Upper Saddle River, N.J.: Prentice Hall, 2002.

A fuel achieves a reaction rate with oxygen sufficient to produce a flame only when it is in the gaseous state, for only in this state can molecules collide frequently enough to support a flaming fire. This remains true whether the fuel is a solid such as wood, paper, cloth, or plastic, or a liquid such as gasoline or kerosene. How then does a liquid or solid maintain a gaseous reac-

tion? In the case of a liquid fuel, the temperature must be high enough to vaporize the fuel. The vapor that forms burns when it mixes with oxygen and combusts as a flame. The **flash point** is the *lowest* temperature at which a liquid gives off sufficient vapor to form a mixture with air that will support combustion. Once the flash point is reached, the fuel can be ignited by some outside source of temperature to start a fire. The ignition temperature is always considerably higher than the flash point. For example, gasoline has a flash point of -50°F ; however, an ignition temperature of 495°F is needed to start a gasoline fire. With a solid fuel, the process of generating vapor is more complex. Wood, or any other solid fuel, burns only when it is exposed to heat that is hot enough to decompose the solid into gaseous products. This chemical breakdown of solid material is known as **pyrolysis**. The numerous gaseous products of pyrolysis combine with oxygen to produce a fire. Here again, fire can be described as a chain reaction. A match or other source of heat initiates the pyrolysis of the solid fuel, the gaseous products react with oxygen in the air to produce heat and light, and this heat in turn pyrolyzes more solid fuel into volatile gases.

As we have seen from our discussion about gaseous fuel, air (oxygen) and sufficient heat are the basic ingredients of a flaming fire. There is also one other consideration—the gas fuel–air mix. Gaseous fuel and air burn only if their composition lies within certain limits. If the fuel concentration is too low (lean) or too great (rich), combustion does not occur. The concentration range between the upper and lower limits is called the **flammable range**. For example, the flammable range for gasoline is 1.3 to 6.0 percent.

Although a flaming fire can be supported only by a gaseous fuel, in some instances a fuel can burn without the presence of a flame. Witness a burning cigarette or the red glow of hot charcoals. These are examples of a phenomenon known as **glowing combustion** or *smoldering*. Here, combustion is taking place on the surface of a solid fuel in the absence of heat high enough to

pyrolyze the fuel. Interestingly, this phenomenon generally ensues long after the flames have gone out. Wood, for example, tends to burn with a flame until all of its pyrolyzable components have been expended; however, wood's carbonaceous residue continues to smolder long after the flame has extinguished itself.

We may now consider the conversion of iron to rust as an example of an extremely slow oxidation process, a situation that exists because of the inability of the iron atoms to achieve a gaseous state. For this reason, the combination of oxygen with iron to produce rust is restricted to the surface area of the metal exposed to air, a limitation that severely reduces the rate of reaction. On the other hand, the reaction of methane and oxygen is an example of oxidation in which all the reactants are in the gaseous state. Hence, this reaction proceeds rapidly, as reflected by the production of noticeable quantities of heat and light (a flame).

Most typically, the rate of a chemical reaction increases when the temperature is raised. The magnitude of the increase in rate with temperature varies from one reaction to another and also from one temperature range to another. For most reactions, a 10°C (18°F) rise in temperature doubles or triples the reaction rate. This observation explains in part why burning is so rapid. As the fire spreads, it raises the temperature of the fuel–air mixture, thus increasing the rate of reaction; this in turn generates more heat, again increasing the rate of reaction. Only when the fuel or oxygen is depleted will this vicious cycle come to a halt.

One rather interesting phenomenon often invoked by arson suspects as being the cause of a fire is **spontaneous combustion**. Actually, the conditions under which spontaneous combustion can develop are rather limited and rarely account for the cause of a fire. Spontaneous combustion is the result of a natural heat-producing process in poorly ventilated containers or areas. For example, hay stored in barns provides an excellent growing medium for bacteria whose activities

generate heat. If the hay is not properly ventilated, the heat builds to a level that supports other types of heat-producing chemical reactions in the hay. Eventually, as the heat rises, the ignition temperature of hay is reached, spontaneously setting off a fire.

Another known example of spontaneous combustion involves the ignition of improperly ventilated containers containing rags soaked with certain types of highly unsaturated oils, such as linseed oil. Heat can build up to the point of ignition as a result of a slow heat-producing chemical oxidation between the air and the oil. Of course, storage conditions must encourage the accumulation of the heat over a prolonged period of time. However, spontaneous combustion does not occur with hydrocarbon lubricating oils, and it is not expected to occur with most household fats and oils.

Until now we have referred only to oxidation reactions that rely on air as the sole source of oxygen. However, we need not restrict ourselves to this type of situation. For example, explosives are substances that undergo a rapid exothermic oxidation reaction, producing large quantities of gases. This sudden buildup of gas pressure constitutes an explosion. Detonation occurs so rapidly that oxygen in the air cannot participate in the reaction; thus, many explosives must have their own source of oxygen. Chemicals that supply oxygen are known as **oxidizing agents**. One such agent is found in black powder, a low explosive, which is composed of a mixture of the following chemical ingredients:

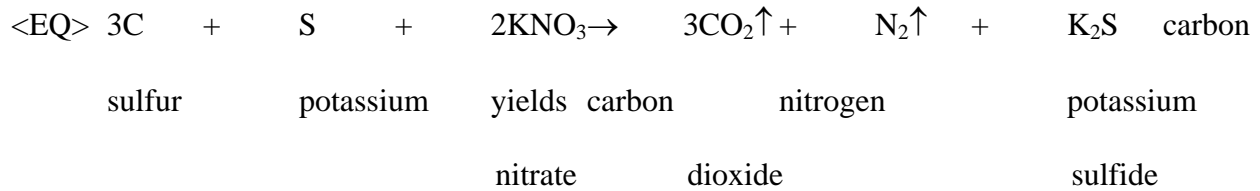
75 percent potassium nitrate (KNO_3)

15 percent charcoal (C)

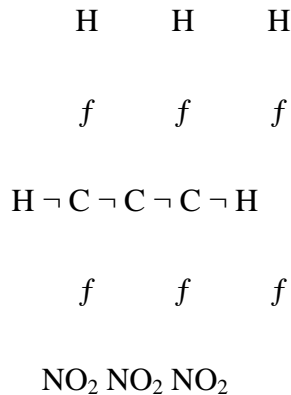
10 percent sulfur (S)

In this combination, oxygen containing potassium nitrate acts as an oxidizing agent for the char-

coal and sulfur fuels. As heat is applied to black powder, oxygen is liberated from potassium nitrate and simultaneously combines with charcoal and sulfur to produce heat and gases (symbolized by \uparrow), as represented in the following chemical equation:



Some explosives have their oxygen and fuel components combined within one molecule. For example, the chemical structure of nitroglycerin, the major constituent of dynamite, combines carbon, hydrogen, nitrogen, and oxygen:



When nitroglycerin detonates, large quantities of energy are released as the molecule decomposes, and the oxygen recombines to produce large volumes of carbon dioxide, nitrogen, and water.

In summary, three requirements must be satisfied if combustion is to be initiated and sustained:

1. A fuel must be present.
2. Oxygen must be available in sufficient quantity to combine with the fuel.

3. Heat must be applied to initiate the combustion, and sufficient heat must be generated to sustain the reaction.

SEARCHING THE FIRE SCENE

The arson investigator should begin examining a fire scene for signs of arson as soon as the fire has been extinguished. Time is constantly working against the arson investigator. Most arsons are started with petroleum-based **accelerants** such as gasoline or kerosene. Any petroleum residues that remain after the fire is extinguished may evaporate within a few days or even hours. Furthermore, safety and health conditions may necessitate that cleanup and salvage operations begin as quickly as possible. Once this occurs, a meaningful investigation of the fire scene will be impossible.

The need to begin an *immediate* investigation of the circumstances surrounding a fire even takes precedence over the requirement to obtain a search warrant to enter and search the premises. The Supreme Court, in explaining its position on this issue, stated in part:

... Fire officials are charged not only with extinguishing fires, but with finding their causes. Prompt determination of the fire's origin may be necessary to prevent its recurrence, as through the detection of continuing dangers such as faulty wiring or a defective furnace. Immediate investigation may also be necessary to preserve evidence from intentional or accidental destruction. And, of course, the sooner the officials complete their duties, the less will be their subsequent interference with the privacy and the recovery efforts of the victims. For these reasons, officials need no warrant to remain in a building for a reasonable time to investigate the cause of a blaze after it has been extinguished. And if the warrantless en-

try to put out the fire and determine its cause is constitutional, the warrantless seizure of evidence while inspecting the premises for these purposes also is constitutional....

In determining what constitutes a reasonable time to investigate, appropriate recognition must be given to the exigencies that confront officials serving under these conditions, as well as to individuals' reasonable expectations of privacy.¹

A search of the fire scene must focus on finding the fire's origin, which will prove most productive in any search for an accelerant or ignition device. In a search to determine the specific point of origin of a fire, the investigator may uncover telltale signs of arson. For instance, there may be evidence of separate and unconnected fires or the use of "streamers" to spread the fire from one area to another. For example, the arsonist may have spread a trail of gasoline or paper to cause the fire to move rapidly from one room to another. Additionally, the presence of containers capable of holding an accelerant or the finding of an ignition device ranging in sophistication from a candle to a time-delay device certainly will arouse suspicions of an arson-caused fire. Another telltale sign of arson is the existence of an irregularly shaped pattern on a floor or on the ground (see Figure 11-2) resulting from pouring an accelerant onto the surface. Investigators should simultaneously look for signs of breaking and entering and theft, and they should begin interviewing any eyewitnesses to the fire.

There are no fast and simple rules for identifying a fire's origin. Normally, a fire tends to move in an upward direction, and thus the probable origin is most likely closest to the lowest point that shows the most intense characteristics of burning. Sometimes as the fire burns upward, a V-shaped pattern forms against a vertical wall, as shown in Figure 11-3. However, many factors can contribute to the deviation of a fire from normal behavior. Prevailing drafts and winds;

secondary fires due to collapsing floors and roofs; the physical arrangement of the burning structure; stairways and elevator shafts; holes in the floor, wall, or roof; and the effects of the firefighter in suppressing the fire are all factors that the knowledgeable fire investigator must consider before determining conclusive findings. Because flammable liquids always flow to the lowest point, more severe burning found on the floor than on the ceiling may indicate the presence of an accelerant. If a flammable liquid was used, charring is expected to be more intense on the bottom of furniture, shelves, and other items rather than the top.

Once located, the point of origin should be protected to permit careful investigation. As at any crime scene, nothing should be touched or moved before notes, sketches, and photographs are taken. An examination must also be made for possible accidental causes, as well as for evidence of arson. The most common materials used by an arsonist to ensure the rapid spread and intensity of a fire are gasoline and kerosene or, for that matter, any volatile flammable liquid. Fortunately, only under the most ideal conditions will combustible liquids be entirely consumed during a fire. When the liquid is poured over a large area, it is highly likely that a portion of it will seep into a porous surface, such as cracks in the floor, upholstery, rags, plaster, wallboards, or carpet, where enough of it remains unchanged that it can be detected in the crime laboratory. In addition, when a fire is extinguished with water, the rate of evaporation of volatile fluids may be slowed, because water cools and covers materials through which the combustible liquid may have soaked. Fortunately, the presence of water does not interfere with laboratory methods used to detect and characterize flammable liquid residues.

The fire investigator's search for traces of flammable liquid residues may be aided by the use of a highly sensitive portable vapor detector or "sniffer" (see Figure 11-4). This device can rapidly screen suspect materials for the presence of volatile residues by sucking in the air surround-

ing the questioned sample. The air is passed over a heated filament; if a combustible vapor is present, it oxidizes and immediately increases the temperature of the filament. The rise in filament temperature is then registered as a deflection on the detector's meter. Of course, such a device is not a conclusive test for a flammable vapor, but it does provide the investigator with an excellent screening device for checking suspect samples at the fire scene. Another approach is to use dogs that have been trained and conditioned to recognize the odor of hydrocarbon accelerants.

The first fire-research laboratory in the United States has recently become operational. The Fire Research Laboratory, constructed by the U.S. government and located in Maryland, performs research on the determination of fire origin and cause, fire growth and spread, and fire-scene reconstruction. This facility provides investigators and researchers with the tools necessary to reconstruct and test key aspects of most fire scenarios encountered by fire investigators in the field. The laboratory can perform anything from small-scale fire tests to full-scale testing of residential structures. It has several large test cells (rooms) where full-scale test fires can be conducted.

COLLECTION AND PRESERVATION OF ARSON EVIDENCE

As a matter of routine, two to three quarts of ash and soot debris must be collected at the point of origin of a fire when arson is suspected. The collection should include all porous materials and all other substances thought likely to contain flammable residues. These include such things as wood flooring, rugs, upholstery, and rags. Specimens are to be immediately packaged in airtight containers so no loss of possible residues can occur through evaporation. New, clean paint cans with friction lids are good containers because they are low cost, airtight, and unbreakable and are

available in a variety of sizes (see Figure 11–5). Wide-mouthed glass jars are also useful for packaging suspect specimens, provided that they contain airtight lids. Cans and jars should be filled one-half to two-thirds full, leaving an air space in the container above the debris. Large bulky samples should be cut to size at the scene as needed so that they will fit into available containers. Plastic polyethylene bags are not suitable for packaging specimens because they react with hydrocarbons and permit volatile hydrocarbon vapors to be depleted.

The collection of all materials suspected of containing volatile liquids must be accompanied by a thorough sampling of similar but uncontaminated control specimens from another area of the fire scene. This is known as *substrate control*. For example, if an investigator collects carpeting at the point of origin, he or she must sample the same carpet from another part of the room, where it can be reasonably assumed that no flammable substance was placed. In the laboratory, the criminalist checks the substrate control to be sure that it is free of any flammables. This procedure reduces the possibility and subsequent argument that the carpet was exposed to a flammable liquid such as a cleaning solution during normal maintenance. In addition, laboratory tests on the unburned control material may help analyze the breakdown products from the material's exposure to intense heat during the fire. This is because common materials such as plastic floor tiles, carpet, linoleum, and adhesives can produce volatile hydrocarbons when they are burned. These breakdown products can sometimes be mistaken for an accelerant.

Fluids found in open bottles or cans must be collected and sealed. Even when such containers appear empty, the investigator is wise to seal and preserve them in case they contain trace amounts of liquids or vapors. At the same time, a thorough search of the scene should be undertaken for igniters. The most common igniter is a match. Normally, the match is completely consumed during a fire and is impossible to locate. However, there have been cases in which, by

force of habit, matches have been extinguished and tossed aside only to be recovered later by the investigator. This evidence may prove valuable if the criminalist can successfully fit the match to a book found in the possession of a suspect, as shown in Figure 11–6. In addition, an arsonist can construct many other types of devices to start a fire. These include a burning cigarette, firearms, ammunition, a mechanical match striker, electrical sparking devices, and a “Molotov cocktail.” Relatively complex mechanical devices are much more likely to survive the fire for later discovery. The broken glass and wick of the Molotov cocktail, if recovered, must be preserved as well.

One important piece of evidence is the clothing of the suspect perpetrator. If this individual is arrested within a few hours of initiating the fire, residual quantities of the accelerant may still be present in the clothing. As we will see in the next section, the forensic laboratory can detect extremely small quantities of accelerant materials, making the examination of a suspect’s clothing a feasible investigative approach. Each item of clothing should be placed in a separate airtight container, preferably a new, clean paint can.

The arson investigator must also be aware that accelerants present in soil and vegetation can be rapidly degraded by bacterial action. Freezing samples containing soil or vegetation is an effective way to prevent this degradation.

ANALYSIS OF FLAMMABLE RESIDUES

Criminalists are nearly unanimous in judging the gas chromatograph to be the most sensitive and reliable instrument for detecting and characterizing flammable residues. Most arsons are initiated by petroleum distillates such as gasoline and kerosene; these liquids are actually composed of a complex mixture of **hydrocarbons**. **Basically, the gas chromatograph separates the hydrocarbon components and produces a chromatographic pattern characteristic of a particular**

petroleum product.

The easiest way to recover accelerant residues from fire-scene debris is to heat the airtight container in which the sample is sent to the laboratory. When the container is heated, any volatile residue present in the debris is driven off and trapped in the container's enclosed airspace. The vapor or *headspace* is removed with a syringe, as shown in Figure 11-7. When the vapor is injected into the gas chromatograph, it is separated into its components, and each peak is recorded on the chromatogram. The identity of the volatile residue is determined when the pattern of the resultant chromatogram is compared to patterns produced by known petroleum products. For example, in Figure 11-8, a gas chromatographic analysis of debris recovered from a fire site shows a chromatogram similar to a known gasoline standard, thus proving the presence of gasoline. In the absence of any recognizable pattern, the individual peaks can be identified when the investigator compares their retention times to known hydrocarbon standards (such as hexane, benzene, toluene, and xylenes). At present, it is not possible to determine the brand name of a gasoline sample by gas chromatography or any other technique. Fluctuating gasoline markets and exchange agreements among the various oil companies preclude this possibility.

One major disadvantage of the headspace technique described earlier is that the size of the syringe limits the volume of vapor that can be removed from the container and injected into the gas chromatograph. To overcome this deficiency, many crime laboratories have begun to augment the headspace technique with a method called *vapor concentration*. One setup for accomplishing this analysis is shown in Figure 11-9. A charcoal-coated strip, similar to that used in environmental monitoring badges, is placed within the container holding the debris that has been collected from the fire scene.² The container is then heated to about 60°C for about one hour. At this temperature, a significant quantity of accelerant vaporizes into the container airspace. The

charcoal absorbs the accelerant vapor that it comes in contact with. In this manner, over a short period of time, a significant quantity of the accelerant will be trapped and concentrated onto the charcoal strip. Once the heating procedure is complete, the analyst removes the charcoal strip from the container and recovers the accelerant from the strip by washing it with a small volume of solvent (carbon disulfide). The solvent is then injected into the gas chromatograph for analysis. The major advantage of using vapor concentration with gas chromatography is its extreme sensitivity. By absorbing the accelerant into a charcoal strip, the forensic analyst can increase the sensitivity of accelerant detection at least a hundredfold over the conventional headspace technique.

An examination of Figure 11-8 shows that identifying an accelerant, such as gasoline, by gas chromatography is an exercise in pattern recognition. Typically, a forensic analyst compares the pattern generated by the sample to chromatograms from accelerant standards obtained under the same conditions. The pattern of gasoline, as with many other accelerants, can easily be placed in a searchable library. But on occasion, discernible patterns are not attainable by gas chromatography. There may be a mixture of accelerants, or the accelerant residue may be mixed with heat-generated breakdown products of materials burning at the fire scene, making a gas chromatographic pattern difficult if not impossible to interpret. In these cases, gas chromatography combined with mass spectrometry (see pp. 150–153) has proven to be a valuable technique for solving difficult problems in the detection of accelerant residues.

Complex chromatographic patterns can be simplified by passing the separated components emerging from the gas chromatographic column through a mass spectrometer. As each component enters the mass spectrometer, it is fragmented into a collection of ions. The analyst can then control which ions will be detected and which ones will go unnoticed. In essence, the mass spec-

trometer acts as a filter allowing the analyst to see only the peaks associated with the ions selected for a particular accelerant. In this manner, the chromatographic pattern can be simplified by eliminating extraneous peaks that may obliterate the pattern.³ The process is illustrated in Figure 11–10.

TYPES OF EXPLOSIVES

The ready accessibility of potentially explosive laboratory chemicals, dynamite, and, in some countries, an assortment of military explosives has provided the criminal element of society with a lethal weapon. Although politically motivated bombings have received considerable publicity worldwide, in the United States most bombing incidents are perpetrated by isolated individuals rather than by organized terrorists. Unfortunately for society, explosives have become an attractive weapon to criminals bent on revenge, destruction of commercial operations, or just plain mischief.

Most bombing incidents involve the use of homemade explosives and incendiary devices. The design of such weapons is limited only by the imagination and ingenuity of the bomber. Like arson investigation, bomb investigation requires close cooperation of a group of highly specialized individuals trained and experienced in bomb disposal, bomb-site investigation, forensic analysis, and criminal investigation. The criminalist must detect and identify explosive chemicals recovered from the crime scene as well as identify the detonating mechanisms. This special responsibility concerns us for the remainder of this chapter.

Like fire, an explosion is the product of combustion accompanied by the creation of gases and heat. However, the distinguishing characteristic of an explosion is the rapid rate at which the reaction proceeds. The sudden buildup of expanding gas pressure at the origin of the explosion

produces the violent physical disruption of the surrounding environment. Consider, for example, the effect of confining an explosive charge to a relatively small, closed container. On detonation, the explosive almost instantaneously produces large volumes of gases that exert enormously high pressures on the interior walls of the container. In addition, the heat energy released by the explosion expands the gases, causing them to push on the walls with an even greater force. If we could observe the effects of an exploding lead pipe in slow motion, we would first see the pipe's walls stretch and balloon under pressures as high as several hundred tons per square inch. Finally, the walls would fragment and fly outward in all directions. This flying debris or shrapnel constitutes a great danger to life and limb in the immediate vicinity.

On release from confinement, the gaseous products of the explosion suddenly expand and compress layers of surrounding air as they move outward from the origin of the explosion. This blast effect, or outward rush of gases, at a rate that may be as high as 7,000 miles per hour creates an artificial gale that can overthrow walls, collapse roofs, and disturb any object in its path. If a bomb is sufficiently powerful, more serious damage will be inflicted by the blast effect than by fragmentation debris.

The speed at which explosives decompose varies greatly from one to another and permits their classification as high and low explosives. In a low explosive, this speed is called the *speed of deflagration* (burning). This is characterized by very rapid oxidation that produces heat, light, and a subsonic pressure wave. In a high explosive, it is called the *speed of detonation*. **Detonation** refers to the creation of a supersonic shock wave within the explosive charge. This shock wave causes the chemical bonds of the explosive charge to break apart, leading to the new instantaneous buildup of heat and gases.

Low explosives, such as black and smokeless powders, decompose relatively slowly at rates

that vary up to 1,000 meters per second. Because of their slow burning rates, they produce a propelling or throwing action that makes them suitable as propellants for ammunition or skyrockets. However, the danger of this group of explosives must not be underestimated, because when any one of them is confined to a relatively small container, it can explode with a force as lethal as that of any known explosive. High explosives include dynamite, TNT, PETN, and RDX. They detonate almost instantaneously at rates from 1,000 to 8,500 meters per second, producing a smashing or shattering effect on their target.

Low Explosives

The most widely used explosives in the low-explosive group are black powder and smokeless powder. The popularity of these two explosives is enhanced by their accessibility to the public. Both are available in any gun store, and black powder can easily be made from ingredients purchased at any chemical supply house as well. **Black powder** is a relatively stable mixture of potassium nitrate or sodium nitrate, charcoal, and sulfur. Unconfined, it merely burns; it is used as a medium for carrying a flame to an explosive charge. A safety fuse usually consists of black powder wrapped in a fabric or plastic casing. When ignited, a sufficient length of fuse will burn at a rate slow enough to allow a person adequate time to leave the site of the pending explosion. Black powder, like any other low explosive, becomes explosive and lethal only when it is confined.

The only ingredients required for a low explosive are fuel and a good oxidizing agent. Thus, the oxidizing agent potassium chlorate, for example, when mixed with sugar, produces a popular and accessible explosive mix. When it is confined to a small container—for example, a pipe—and ignited by the flame of a safety fuse, this mixture can explode with a force equivalent to a stick of 40 percent dynamite. Some other commonly encountered ingredients that may be com-

bined with chlorate to produce an explosive are carbon, sulfur, starch, phosphorus, and magnesium filings. Chlorate mixtures may also be ignited by the heat generated from a chemical reaction. For instance, sufficient heat can be generated to initiate combustion when concentrated sulfuric acid comes in contact with a sugar–chlorate mix.

The safest and most powerful low explosive is smokeless powder. This explosive usually consists of nitrated cotton or nitrocellulose (single-base powder) or nitroglycerin mixed with nitrocellulose (double-base powder). The powder is manufactured in a variety of grain sizes and shapes, depending on the desired application.

Another form of low explosive is created when a considerable quantity of natural gas escapes into a confined area and mixes with a sufficient amount of air. If ignited, this mixture results in simultaneous combustion and sudden production of large volumes of gases and heat. In a building, walls are forced outward by the expanding gases, causing the roof to fall into the interiors, and objects are thrown outward and scattered in erratic directions with no semblance of pattern.

Mixtures of air and a gaseous fuel will explode or burn only within a limited concentration range. For example, the concentration limits for methane in air range from 5.3 to 13.9 percent. In the presence of too much air, the fuel becomes too diluted and does not respond to efforts to ignite it; on the other hand, if the fuel becomes too concentrated, ignition is prevented because there is not enough oxygen to support the combustion. Mixtures at or near the upper concentration limit (“rich” mixtures) explode; however, some gas remains unconsumed because there is not enough oxygen to complete the combustion. As air rushes back into the origin of the explosion, it combines with the residual hot gas and a fire is produced that is characterized by a *whoosh* sound. This fire is often more destructive than the explosion that preceded it. Mixtures near the lower end of the limit (“lean” mixtures) generally cause an explosion without accompa-

nying damage due to fire.

High Explosives

The sensitivity of a high explosive provides a convenient basis for its classification into two groups. The first group, primary explosives, are ultrasensitive to heat, shock, or friction, and under normal conditions detonate violently instead of burning. For this reason, they are used to detonate other explosives through a chain reaction and are often referred to as *primers*. Primary explosives provide the major ingredient of a blasting cap and include lead azide, lead styphnate, and diazodinitrophenol. Because of their extreme sensitivity, these explosives are rarely used as the main charge of a homemade bomb.

The second group, secondary explosives, are relatively insensitive to heat, shock, or friction, and normally burn rather than detonate if they are ignited in small quantities in open air. This group comprises the majority of high explosives used for commercial and military blasting. Some common examples of noninitiating explosives are dynamite, TNT (trinitrotoluene), PETN (pentaerythritol tetranitrate), RDX (cyclotrimethylenetrinitramine), and tetryl (2,4,6-trinitrophenylmethylnitramine).

It is an irony of history that the prize most symbolic of humanity's search for peace—the Nobel Peace Prize—should bear the name of the developer of one of our most lethal discoveries—dynamite. In 1867, the Swedish chemist Alfred Nobel, searching for a method to desensitize nitroglycerin, found that when kieselguhr, a variety of diatomaceous earth, absorbed a large portion of nitroglycerin, it became far less sensitive but still retained its explosive force. Nobel later decided to use pulp as an absorbent because kieselguhr was a heat-absorbing material. Thus, pulp dynamite was the beginning of what is now known as the straight dynamite series, the gradations of which are specified according to the percentage of nitroglycerin used. These dyna-

mites are used when a quick shattering action is desired. Present-day straight dynamites also include sodium nitrate, which furnishes oxygen for complete combustion, along with a small percentage of a stabilizer—for example, calcium carbonate. The strength rating of a straight dynamite is designated by the weight percentage of nitroglycerin in the formula: a 40 percent straight dynamite contains 40 percent, a 60 percent grade contains 60 percent, and so forth. However, the concept that the actual blasting power developed by different strengths is in direct proportion to the percentage markings is erroneous. A 60 percent straight dynamite, rather than being three times as strong as a 20 percent, is only one and one-half times as strong.

In recent years, nitroglycerin-based dynamite has all but disappeared from the industrial explosives market. Commercially, these explosives have been replaced mainly by *ammonium nitrate-based explosives*, that is, *water gels*, *emulsions*, and *ANFO explosives*. These explosives mix oxygen-rich ammonium nitrate with a fuel to form a low-cost and very stable explosive. Typically, water gels have a consistency resembling that of set gelatin or gel-type toothpaste. They are characterized by their water-resistant nature and are employed for all types of blasting under wet conditions. These explosives are based on formulations of ammonium nitrate and sodium nitrate gelled with a natural polysaccharide such as guar gum. Commonly, a combustible material such as aluminum is mixed into the gel to serve as the explosive's fuel.

Emulsion explosives differ from gels in that they consist of two distinct phases, an oil phase and a water phase. In these emulsions, a droplet of a supersaturated solution of ammonium nitrate is surrounded by a hydrocarbon serving as a fuel. A typical emulsion consists of water, one or more inorganic nitrate oxidizers, oil, and emulsifying agents. Commonly, emulsions contain micron-sized glass, resin, or ceramic spheres known as *microspheres* or *microballoons*. The size of these spheres controls the explosive's sensitivity and detonation velocity.

Ammonium nitrate soaked in fuel oil is an explosive known as *ANFO*. Such commercial explosives are inexpensive and safe to handle and have found wide applications in blasting operations in the mining industry. Ammonium nitrate in the form of fertilizer makes a readily obtainable ingredient for homemade explosives. Indeed, in an incident related to the 1993 bombing of New York City's World Trade Center, the FBI arrested five men during a raid on their hideout in New York City, where they were mixing a "witches' brew" of fuel oil and an ammonium nitrate-based fertilizer.

Triacetone triperoxide (TATP) is a homemade explosive that has been used as an improvised explosive by terrorist organizations in Israel and other Middle Eastern countries. It is prepared by reacting the common ingredients of acetone and hydrogen peroxide in the presence of an acid catalyst such as hydrochloric acid. TATP is a friction- and impact-sensitive explosive that is extremely potent when confined in a container such as a pipe. The 2005 London transit bombings were caused by TATP-based explosives and provide ample evidence that terrorist cells have moved TATP outside the Middle East. A London bus destroyed by one of the TATP bombs is shown in Figure 11-11.

No discussion of high explosives would be complete without a mention of military high explosives. In many countries outside the United States, the accessibility of high explosives to terrorist organizations makes them very common constituents of homemade bombs. RDX, the most popular and powerful military explosive, is often encountered in the form of a pliable plastic of doughlike consistency known as *composition C-4* (a U.S. military designation).

TNT was produced and used on an enormous scale during World War II and may be considered the most important military bursting charge explosive. Alone or in combination with other explosives, it has found wide application in shells, bombs, grenades, demolition explosives, and

propellant compositions. Interestingly, military “dynamite” contains no nitroglycerin but is actually composed of a mixture of RDX and TNT. Like other military explosives, TNT is rarely encountered in bombings in the United States.

PETN is used by the military in TNT mixtures for small-caliber projectiles and grenades. Commercially, the chemical is used as the explosive core in a detonating cord or *primacord*. Instead of the slower-burning safety fuse, a detonating cord is often used to connect a series of explosive charges so that they will detonate simultaneously.

Unlike low explosives, bombs made of high explosives must be detonated by an initiating explosion. In most cases, detonators are blasting caps composed of copper or aluminum cases filled with lead azide as an initiating charge and PETN or RDX as a detonating charge. Blasting caps can be initiated by means of a burning safety fuse or by an electrical current (see Figure 11–12).

Homemade bombs camouflaged in packages, suitcases, and the like are usually initiated with an electrical blasting cap wired to a battery. An unlimited number of switching-mechanism designs have been devised for setting off these devices; clocks and mercury switches are favored. Bombers sometimes prefer to employ outside electrical sources. For instance, most automobile bombs are detonated when the ignition switch of a car is turned on.

COLLECTION AND ANALYSIS OF EXPLOSIVES

The most important step in the detection and analysis of explosive residues is the collection of appropriate samples from the explosion scene. Invariably, undetonated residues of the explosive remain at the site of the explosion. The detection and identification of these explosives in the laboratory depends on the bomb-scene investigator’s skill and ability to recognize and sample

the areas most likely to contain such materials.

The most obvious characteristic of a high or contained low explosive is the presence of a crater at the origin of the blast. Once the crater has been located, all loose soil and other debris must immediately be removed from the interior of the hole and preserved for laboratory analysis.

Other good sources of explosive residues are objects located near the origin of detonation. Wood, insulation, rubber, and other soft materials that are readily penetrated often collect traces of the explosive. However, nonporous objects near the blast must not be overlooked. For instance, residues can be found on the surfaces of metal objects near the site of an explosion. Material blown away from the blast's origin should also be recovered because it, too, may retain explosive residues. All personnel involved in searching the bomb scene must take appropriate measures to avoid contaminating the scene, including dressing in disposable gloves, shoe covers, and overalls.

The entire area must be systematically searched, with great care given to recovering any trace of a detonating mechanism or any other item foreign to the explosion site. Wire-mesh screens are best utilized for sifting through debris. In pipe-bomb explosions, particles of the explosive are frequently found adhering to the pipe cap or to the pipe threads, as a result of either being impacted into the metal by the force of the explosion or being deposited in the threads during the construction of the bomb. **One approach for screening objects for the presence of explosive residues in the field or the laboratory is the ion mobility spectrometer (IMS).** A portable IMS is shown in Figure 11–13.

This handheld detector uses a vacuum to collect explosive residues from suspect surfaces. Alternatively, the surface suspected of containing explosive residues is wiped down with a Teflon-coated fiberglass disc and the collected residues are then drawn into the spectrometer off the

disc. Once in the IMS, the explosive residues are vaporized by the application of heat. These vaporized substances are exposed to a beam of electrons or beta rays (see p. 172) emitted by radioactive nickel and converted into electrically charged molecules or ions. The ions are then allowed to move through a tube (drift region) under the influence of an electric field. A schematic diagram of an IMS is shown in Figure 11–14. Ions move at different speeds depending on their size and structure. The preliminary identification of an explosive residue can be made by noting the time it takes the explosive to move through the tube. Used as a screening tool, this method rapidly detects a full range of explosives, even at low detection levels. However, all results need to be verified through confirmatory tests. The IMS can detect plastic explosives as well as commercial and military explosives. More than 10,000 portable and full-size IMS units are currently used at airport security checkpoints, and more than 50,000 handheld IMS analyzers have been deployed for chemical-weapons monitoring in various armed forces.

All materials collected for examination by the laboratory must be placed in airtight sealed containers and labeled with all pertinent information. Soil and other soft loose materials are best stored in metal airtight containers such as clean paint cans. Debris and articles collected from different areas are to be packaged in separate airtight containers. Plastic bags should not be used to store evidence suspected of containing explosive residues. Some explosives can actually seep through the plastic.

When the bomb-scene debris and other materials arrive at the laboratory, everything is first examined microscopically to detect particles of unconsumed explosive. Portions of the recovered debris and detonating mechanism, if found, are carefully viewed under a low-power stereoscopic microscope in a painstaking effort to locate particles of the explosive. Black powder and smokeless powder are relatively easy to locate in debris because of their characteristic shapes and col-

ors (see Figure 11–15). However, dynamite and other high explosives present the microscopist with a much more difficult task and often must be detected by other means.

Following microscopic examination, the recovered debris is thoroughly rinsed with acetone. The high solubility of most explosives in acetone ensures their quick removal from the debris. Once collected, the acetone extract is concentrated and analyzed using color spot tests, thin-layer chromatography (TLC), high-performance liquid chromatography (HPLC; see p. 138), and gas chromatography/mass spectrometry (see pp. 150–153). The presence of an explosive will be indicated by a well-defined spot on a TLC plate with an *R_f* value corresponding to a known explosive—for example, nitroglycerin, RDX, or PETN. The high sensitivity of HPLC also makes it very useful for analyzing trace evidence of explosives. The HPLC operates at room temperature and hence does not cause explosives, many of which are temperature sensitive, to decompose during their analysis. When a water-gel explosive containing ammonium nitrate or a low explosive is suspected, the debris should be rinsed with water so that water-soluble substances (such as nitrates and chlorates) will be extracted. Table 11–3 lists a number of simple color tests the examiner can perform on the acetone and water extracts to screen for the presence of organic and inorganic explosives, respectively.

Table 11–3 Color Spot Tests for Common Explosives

Substance	Reagent		
	Griess ^a	Diphenylamine ^b	Alcoholic KOH ^c
Chlorate	No color	Blue	No color
Nitrate	Pink to red	Blue	No color

Nitrocellulose	Pink	Blue-black	No color
Nitroglycerin	Pink to red	Blue	No color
PETN	Pink to red	Blue	No color
RDX	Pink to red	Blue	No color
TNT	No color	No color	Red
Tetryl	Pink to red	Blue	Red-violet

^aGriess reagent: Solution 1—Dissolve 1 g sulfanilic acid in 100 mL 30% acetic acid. Solution 2—Dissolve 0.5 g *N*-(1-naphthyl) ethylenediamine in 100 mL methyl alcohol. Add solutions 1 and 2 and a few milligrams of zinc dust to the suspect extract.

^bDiphenylamine reagent: Dissolve 1 g diphenylamine in 100 mL concentrated sulfuric acid.

^cAlcoholic KOH reagent: Dissolve 10 g of potassium hydroxide in 100 mL absolute alcohol.

When sufficient quantities of explosives are recoverable, confirmatory tests may be performed by either infrared spectrophotometry or X-ray diffraction. The former produces a unique “fingerprint” pattern for an organic explosive, as shown by the IR spectrum of RDX in Figure 11–16. The latter provides a unique diffraction pattern for inorganic substances, as exemplified by the diffraction patterns for potassium nitrate and potassium chlorate, shown in Figure 6-11.

An explosive “taggant” program has been proposed to further enhance a bomb-scene investigator’s chances of recovering useful evidence at a postexplosion scene. Under this proposal, tiny color-coded chips the size of sand grains would be added to commercial explosives during their manufacture. Some of these chips would be expected to survive an explosion and be capable of recovery at explosion scenes. To aid in their recovery, the chips are made both fluorescent and

magnetic sensitive. Hence, investigators can search for taggants at the explosion site with magnetic tools and ultraviolet light.

The taggant chip is arranged in a color sequence that indicates where the explosive was made and when it was produced (see Figure 11–17). With this knowledge, the explosive can be traced through its distribution chain to its final legal possessor. The taggant colors are readily observed and are read with the aid of a low-power microscope.

There are no plans to institute a taggant program for commercial explosives in the United States. In Europe, only Switzerland has adopted a taggant program; thus, it is extremely doubtful that taggants will be found in any significant number of bombing incidents in the foreseeable future. Interestingly, the International Civil Aviation Organization has mandated that a volatile taggant be added to plastic explosives during their manufacture in order to facilitate the detection of these explosives. Programs are now under way to tag commercial C–4 with the volatile chemical known as DMNB (2,3-dimethyl-2,3-dinitrobutane).

Forensics at Work

The Crash of TWA Flight 800

Though the crash of TWA Flight 800 was ultimately not proven to be an act of terrorism, the initial investigation revealed the difficulties investigators can expect to encounter in recovering explosive residues at bombing scenes. For example, in spite of the large quantities of explosive used, investigators encountered extreme difficulties in recovering explosive residues at both the World Trade Center (1993) and Oklahoma federal building bombing sites.

The Search: The TWA Plane Crash

Three weeks after the Atlantic Ocean swallowed a flaming Boeing 747, investigators continue to

explore a prevailing theory that the downfall of Trans World Airlines Flight 800 was caused by a bomb. But their complicated mission is made all the more complex by the very water in which much of the plane rests.

Investigators say they are still concerned that the extended submersion in saltwater might have an effect on telltale chemical traces that a bomb would have left on airplane aluminum, plastic containers, luggage—and anything else from the jumbo jet's front end, where, investigators theorize, the explosion that downed the aircraft took place. More than 80 percent of the airplane remains scattered on the ocean floor, 120 feet down.

Their worry has heightened the sense of urgency in recovering debris from the water, said Joseph Cantamessa Jr., an F.B.I. special agent in charge. "It's the reason we have been so impatient about getting the evidence in the lab for testing."

Christopher Ronay, the former head of the Federal Bureau of Investigation's explosives unit and now president of the Institute of Makers of Explosives in Washington, D.C., said investigators have cause for concern. "Your explosive residue," he said, "adheres to all sorts of materials—to carpet fibers and upholstery and plastics, and it can be trapped in the surface material through all sorts of means. And certainly water washes away some kinds of residues."

But the July 17 explosion of Flight 800, which killed all 230 people on board, remains a puzzle in many pieces. As Mr. Ronay and others point out, the airplane may or may not have been brought down by a bomb. And if a bomb was the cause, the explosive material could have been one of several kinds. And depending on the kind of explosive, ocean water could either wash away the chemical residue or have little effect.

Dr. Jesse L. Beauchamp, a chemistry professor at the California Institute of Technology in Pasa-

dena, said: “It goes without saying that any traces of explosives that were present on wreckage would likely be partially removed—not entirely removed—by continued exposure to saltwater. But it depends on the type of explosives.”

Mr. Ronay, who helped coordinate the bureau’s successful investigation into the fatal explosion of Pan Am Flight 103 over Lockerbie, Scotland, in 1988, expressed confidence in the F.B.I. laboratory’s sophisticated equipment and in Tom Thurman, his successor as chief of the explosives unit and the case agent in the Lockerbie investigation.

Mr. Thurman and his team of forensic specialists have been examining the recovered airplane debris at a hangar in Calverton, L.I. In general they are concentrating on two avenues of inquiry: finding any explosive’s chemical residue, and searching for pockmarks, tearing and other signs found on items that were near the explosion, often called “witness material.”

In an explosion, a chemical reaction transforms the explosive material into gas. But some of that material is merely scattered, albeit in microscopic fragments. And that is what the forensic investigator seeks.

“There’s almost always some residue,” said Dr. Jimmie Oxley, a professor of chemistry at the University of Rhode Island. “And you look for something abnormal in the chemical analysis, something that shouldn’t be there.”

Dr. Oxley, who is a consultant to the F.B.I. and the Bureau of Alcohol, Tobacco and Firearms, said that investigators undoubtedly are rinsing airplane parts with an organic solvent to see if there is organic material that would not normally be present. “If you found traces of a military explosive such as RDX, which is not water soluble, it would have no reason for possibly being there,” she said. “So now you have positive evidence.”

But the ocean presents another variable. “On the other hand, if you never find anything at all, you can’t draw any conclusions,” Dr. Oxley said. “Now you’ve got to look at a lot of other things. There are explosive materials that could have been used that are water soluble. There is ammonium nitrate fuel oil, which is water soluble except for the oil. And this stuff has been bathing down there for a long time.”

Even in the case of ammonium nitrate fuel oil, or ANFO, the material used in last year’s deadly bombing of a Federal building in Oklahoma City, the investigators would expect to find traces of insoluble materials used to detonate the mixture.

Investigators in Calverton are using tools such as a gas chromatograph, which separates organic components, and a mass spectrometer, which identifies each component by its molecular weight. But Mr. Ronay said that more in-depth analysis is being done at the F.B.I. laboratory in Washington where, he said, there are specific instruments to use on specific explosives.

“Their equipment is so sensitive that it can track material in parts per trillion,” he said. “I don’t think a shark can smell blood in the water to that degree.”

Still, Mr. Ronay acknowledged the difficulty that his former colleagues face. “It’s such a big, big project,” he said. “And you might never find the right piece.”

That would force investigators to focus on the other avenue of inquiry—the hunt for a specific kind of tear in metal, or the pitting in a piece of luggage that might have been near the source of an explosion.

“If they never find the residue, the experts will probably characterize the damage and make some estimates regarding the kind of explosive that was used,” Mr. Ronay said. “But if you find residue, you don’t need to guess.”

Source: Dan Barry, “Saltwater’s Ill Effects Depend on Bomb Type,” *New York Times*, August 7, 1996, p. B-5. Copyright © 1996 by the New York Times Company. Reprinted with permission.

Chapter Summary

The arson investigator needs to begin examining a fire scene for signs of arson as soon as the fire has been extinguished. The search of the fire scene must focus on finding the fire’s origin. Some telltale signs of arson include evidence of separate and unconnected fires, the use of “streamers” to spread the fire from one area to another, and evidence of severe burning found on the floor as opposed to the ceiling of a structure. At the suspect point of origin of a fire, porous materials should be collected and stored in airtight containers.

When a fire occurs, oxygen combines with a fuel to produce noticeable quantities of heat and light (flames). If combustion is to be initiated and sustained, a fuel must be present, oxygen must be available, heat must be applied to initiate the combustion, and sufficient heat must be generated to sustain the reaction. A fuel achieves a reaction rate with oxygen sufficient to sustain a fire only when it is in the gaseous state.

In the laboratory, the gas chromatograph is the most sensitive and reliable instrument for detecting and characterizing flammable residues. Most arsons are initiated by petroleum distillates such as gasoline and kerosene. The gas chromatograph separates the hydrocarbon components and produces a chromatographic pattern characteristic of a particular petroleum product. By comparing select gas chromatographic peaks recovered from fire-scene debris to known flammable liquids, a forensic analyst may be able to identify the accelerant used to initiate the fire.

Explosives are substances that undergo a rapid oxidation reaction with the production of

large quantities of gases. This sudden buildup of gas pressure constitutes an explosion. The speed at which explosives decompose permits their classification as high or low explosives. The most widely used low explosives are black powder and smokeless powder. Among the high explosives, primary explosives are ultrasensitive to heat, shock, or friction and provide the major ingredients found in blasting caps. Secondary explosives normally constitute the main charge of a high explosive. Nitroglycerin-based dynamite has all but disappeared from the industrial explosive market and has been replaced by ammonium nitrate-based explosives (such as water gels, emulsions, and ANFO explosives). In many countries outside the United States, the accessibility of military high explosives to terrorist organizations makes them very common constituents of homemade bombs. RDX is the most popular and powerful of the military explosives.

The entire bomb site must be systematically searched with great care given to recovering any trace of a detonating mechanism or any other item foreign to the explosion site. Objects located at or near the origin of the explosion must be collected for laboratory examination. Typically, in the laboratory, debris collected at explosion scenes is examined microscopically for unconsumed explosive particles. Recovered debris may also be thoroughly rinsed with organic solvents and analyzed by testing procedures that include color spot tests, thin-layer chromatography, high-performance liquid chromatography, and gas chromatography/mass spectrometry.

Review Questions

1. True or False: The absence of chemical residues always rules out the possibility of arson.

2. The combination of oxygen with other substances to produce new chemical products is called _____.

3. True or False: All oxidation reactions produce noticeable quantities of heat and light.

4. _____ is the capacity for doing work.
5. Burning methane for the purpose of heating water to produce steam in order to drive a turbine is an example of converting _____ energy to _____ energy.
6. The quantity of heat evolved from a chemical reaction arises out of the _____ and _____ of chemical bonds.
7. Molecules must (absorb, liberate) energy to break their bonds and (absorb, liberate) energy when their bonds are reformed.
8. All oxidation reactions (absorb, liberate) heat.
9. Reactions that liberate heat are said to be _____.
10. Excess heat energy liberated by an oxidation reaction is called the _____.
11. A chemical reaction in which heat is absorbed from the surroundings is said to be _____.
12. True or False: All reactions require an energy input to start them. _____
13. The minimum temperature at which a fuel burns is known as the _____ temperature.
14. A fuel achieves a sufficient reaction rate with oxygen to produce a flame only in the (gaseous, liquid) state.
15. The lowest temperature at which a liquid fuel produces enough vapor to burn is the _____.
16. _____ is the chemical breakdown of a solid material to gaseous products.

17. _____ is a phenomenon in which a fuel burns without the presence of a flame.
18. The rate of a chemical reaction (increases, decreases) as the temperature rises.
19. _____ describes a fire caused by a natural heat-producing process.
20. Oxidizing agents supply _____ to a chemical reaction.
21. Three ingredients of black powder are _____, _____, and _____.
22. True or False: An immediate search of a fire scene can commence without obtaining a search warrant. _____
23. A search of the fire scene must focus on finding the fire's _____.
24. True or False: The probable origin of a fire is most likely closest to the lowest point that shows the most intense characteristics of burning. _____
25. The collection of debris at the origin of a fire should include all (porous, nonporous) materials.
26. _____ containers must be used to package all materials suspected of containing hydrocarbon residues.
27. The most sensitive and reliable instrument for detecting and characterizing flammable residues is the (gas chromatograph, infrared spectrophotometer).
28. The identity of a volatile petroleum residue is determined by the (size, pattern) of its gas chromatogram.
29. True or False: The major advantage of using the vapor concentration technique in combination with gas chromatography is its extreme sensitivity for detecting volatile residues from fire-scene evidence. _____

30. True or False: A forensic analyst typically compares the gas chromatographic pattern generated from a fire scene sample to a library of patterns in order to identify the accelerant.

31. The criminalist (can, cannot) identify gasoline residues by brand name.

32. Rapid combustion accompanied by the creation of large volumes of gases describes a(n)

_____.

33. Explosives that decompose at relatively slow rates are classified as _____ explosives.

34. _____ explosives detonate almost instantaneously to produce a smashing or shattering effect.

35. The most widely used low explosives are _____ and _____.

36. A low explosive becomes explosive and lethal only when it is _____.

37. True or False: Air and a gaseous fuel burn when mixed at any concentration range.

38. High explosives can be classified as either _____ or _____ explosives.

39. The blasting power of different dynamite strengths (is, is not) in direct proportion to the weight percentage of nitroglycerin.

40. True or False: The most common commercial explosives incorporate ammonium nitrate.

41. The most widely used explosive in the military is _____.

42. The explosive core in detonating cord is _____.

43. A high explosive is normally detonated by a(n) _____ explosive contained within a

blasting cap.

44. An obvious characteristic of a high explosive is the presence of a(n) _____ at the origin of the blast.
45. The most important step in detecting explosive residues is the _____ of appropriate samples from the explosion scene.
46. Unconsumed explosive residues may be detected in the laboratory through a careful _____ examination of the debris.
47. Debris recovered from the site of an explosion is routinely rinsed with _____ in an attempt to recover high-explosive residues.
48. Once collected, the acetone extract is initially analyzed by _____, _____, and _____.
49. The technique of _____ produces a unique absorption spectrum for an organic explosive.
50. The technique of _____ provides a unique diffraction pattern for the identification of the inorganic constituents of explosives.

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Modus Operandi

An offender's pattern of operation.

Oxidation

The combination of oxygen with other substances to produce new substances.

Energy

The combined ability or potential of a system or material to do work. Some forms of energy are heat energy, chemical energy, and electrical energy.

Combustion

Rapid combination of oxygen with another substance accompanied by the production of noticeable heat and light.

Heat of Combustion

The heat evolved when a substance is burned in oxygen.

Exothermic Reaction

A chemical transformation in which heat energy is liberated.

Endothermic Reaction

A chemical transformation in which heat energy is absorbed from the surroundings.

Ignition Temperature

The minimum temperature at which a fuel will spontaneously ignite.

Flash Point

The minimum temperature at which a liquid fuel produces enough vapor to burn.

Pyrolysis

The decomposition of organic matter by heat.

Flammable Range

The entire range of possible gas or vapor fuel concentrations in air that are capable of burning.

Glowing Combustion

Burning at the fuel–air interface. Examples are a red-hot charcoal or a burning cigarette.

Spontaneous Combustion

A fire caused by a natural heat-producing process in the presence of sufficient air and fuel.

Oxidizing Agent

A substance that supplies oxygen to a chemical reaction.

Accelerant

Any material used to start or sustain a fire. The most common accelerants are combustible liquids.

Hydrocarbon

Any compound consisting only of carbon and hydrogen.

Explosion

A chemical or mechanical action resulting in the rapid expansion of gases.

High Explosive

An explosive with a velocity of detonation greater than 1,000 meters per second. Examples include dynamite and RDX.

Low Explosive

An explosive with a velocity of detonation less than 1,000 meters per second. Examples include black powder and smokeless powder.

Deflagration

A very rapid oxidation reaction accompanied by the generation of a low-intensity pressure wave that can disrupt the surroundings.

Detonation

An extremely rapid oxidation reaction accompanied by a violent disruptive effect and an intense, high-speed shock wave.

Black Powder

Normally, a mixture of potassium nitrate, carbon, and sulfur in the ratio 75/15/10.

Safety Fuse

A cord containing a core of black powder. It is used to carry a flame at a uniform rate to an explosive charge.

Smokeless Powder (Single-Base)

An explosive consisting of nitrocellulose.

Smokeless Powder (Double-Base)

An explosive consisting of a mixture of nitrocellulose and nitroglycerin.

Primary Explosive

A high explosive that is easily detonated by heat or shock.

Secondary Explosive

A high explosive that normally must be detonated by a primary explosive.

Detonating Cord

A cordlike explosive containing a core of high-explosive material, usually PETN; also called primacord.

FBI agents and New York State police guard the reconstruction of TWA Flight 800.

Source: Mark Lennihan, AP Wide World Photos

Figure 11–1 An energy barrier must be hurdled before reactants such as methane and oxygen can combine with one another to form the products of carbon dioxide and water.

Figure 11–2 Irregularly shaped pattern on the ground resulting from a poured ignitable liquid. *Courtesy Franklin County Crime Scene Unit, North Carolina*

Figure 11–3 Typical V patterns illustrating upward movement of the fire. *Courtesy John Lentini*

Figure 11–4 Portable hydrocarbon detector. *Courtesy Sirchie Finger Print Laboratories, Inc., Youngsville, N.C., www.sirchie.com*

Figure 11–5 Various sizes of paint cans suitable for collecting debris at fire scenes. *Courtesy Sirchie Finger Print Laboratories, Inc., Youngsville, N.C., www.sirchie.com*

Figure 11–6 Three matches (Spec. 3, 4, 5) discarded at the scene of an arson are each shown to fit into a matchbook (Spec. 1) found in the suspect’s possession. Such evidence provides a strong link between the crime scene and the suspect. *Courtesy New Jersey State Police*

Figure 11–7 Removal of vapor from an enclosed container prior to gas chromatographic analysis.

Figure 11–8 (top) Gas chromatograph of vapor from a genuine gasoline sample. (bottom) Gas chromatograph of vapor from debris recovered at a fire site. Note the similarity of the known gasoline to vapor removed from the debris. *Courtesy New Jersey State Police*

Figure 11–9 Apparatus for accelerant recovery by vapor concentration. The vapor in the enclosed container is exposed to charcoal, a chemical absorbent, where it is trapped for later analysis.

Figure 11–10 Chromatogram of a residue sample collected at a fire scene (A) shows a pattern somewhat like that of gasoline (B). However, a definitive conclusion that the unknown

contained gasoline could be obtained only after extraneous peaks were eliminated from the unknown by the use of GC/MS (C).

Figure 11–11 A London bus destroyed by a TATP-based bomb. *Courtesy AP Wide World Photos*

Figure 11–12 Blasting caps. The left and center caps are initiated by an electrical current; the right cap is initiated by a safety fuse.

Figure 11–13 A portable ion mobility spectrometer used to rapidly detect and tentatively identify trace quantities of explosives. *Courtesy GE Ion Track, Wilmington, Mass. 01887*

Figure 11–14 Schematic diagram of an ion mobility spectrometer. A sample is introduced into an ionization chamber, where bombardment with radioactive particles emitted by an isotope of nickel converts the sample to ions. The ions move into a drift region where ion separation occurs based on the speed of the ions as they move through an electric field.

Figure 11–15 Samples of smokeless powders.

Figure 11–16 Infrared spectrum of RDX.

Figure 11–17 Cross-section of a taggant. The color sequence of the recovered taggant is observed with the aid of a low-power microscope. The colors are then matched to a color code to yield information about the plant of manufacture, production lot, and purchasers of the explosive material.

¹ *Michigan v. Tyler*, 436 U.S. 499 (1978).

² R. T. Newman et al., “The Use of Activated Charcoal Strips for Fire Debris Extractions by Passive Diffusion. Part 1: The Effects of Time, Temperature, Strip Size, and Sample Concentration,” *Journal of Forensic Sciences* 41 (1996): 361.

³ M. W. Gilbert, “The Use of Individual Extracted Ion Profiles versus Summed Extracted Ion Profiles in Fire Debris Analysis,” *Journal of Forensic Sciences* 43 (1998): 871.