An Introduction to Forensic Science: The Science of Criminalistics

CHAPTER 14
Forensic Arson and Explosives

Confidential Correspondence

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II. CHEMICAL EVIDENCE

Chapter 14: Forensic Arson and Explosives

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Chapter 14.1: Forensic Fire and Explosives Investigations

“The most tangible of all visible mysteries - fire.” Leigh Hunt (1784–1859)

Learning Goals and Objectives

Forensic Investigations may deal with the causes of fires and explosions. In this chapter, you will need to understand the following concepts:

- What is fire and what are the roles of the components in the fire tetrahedron;
- What type of information is part of a fire investigation;
- What is meant by arson and what are some of the telltale clues to intentional fires;
- What are the common explosives used today and how are they classified;
- How are the identities of explosives determined in the laboratory

Introduction

Fire has been both a boon and a threat to human civilization since the beginning of recorded history. While providing heat and a means of preparing safe food, it also presented clear threats. Many cities, such as Rome, London, Chicago and New York, all have experienced devastating fires in their histories. In the Middle Ages, William the Conqueror required that all fires be covered after a specified time in the evening – a practice known as “couvre feu” or “cover the fire”, giving rise to our modern term “curfew”. From this need to protect people and property, fire investigations remain an important aspect of forensic science today. The need to protect people and property has contributed to the continued development of increasingly sophisticated and effective tools, processes and analyses for the investigation of crimes and events involving fire and explosions.

Investigations into the cause and nature of fires and explosions require careful observation and reliance upon forensic scientific analysis to unravel the chain of events leading to the fire. While fires and explosions release large quantities of energy, traces of their origins can surprisingly remain long after the fires have been extinguished. Fires and explosion investigations explore the physical and chemical components that help to explain how these events occurred.

Fire Basics

In order to understand how forensic evidence can provide critical insights into the cause and events surrounding a fire or explosion, we first need to understand the basics of fire and combustion. Fire is defined as the rapid oxidation of substances through combustion reactions with the release of energy, often in the form of heat and light, and the formation of chemical products. Specifically, burning is an exothermic chemical reaction (a reaction that gives off energy) that occurs between a fuel and an oxidant. An oxidant is simply a chemical that can either transfer oxygen atoms to

Figure 14.1.1. House fires combine four necessary ingredients to deliver large amounts of energy very rapidly (www.thatsfloriduh.com/?p=1419).

Figure 14.1.2. Oxidation and Reduction reactions (http://ict4us.com/r.kuijt/en_oxidation_reduction.htm)
or remove electrons from another chemical compound (Figure 14.1.2). In combustion reactions, the fuel reacts with the oxidant to form new compounds where each element in the fuel is combined with the oxidant. A variety of oxidants are possible but, in most cases, the oxidant in fires of forensic interest is atmospheric oxygen (O₂) and the most common fuels are organic compounds, especially compounds composed primarily of carbon and hydrogen called hydrocarbons. In these reactions, oxygen combines with each element in the fuel, carbon and hydrogen, to give off carbon dioxide (CO₂) and water (H₂O) vapor as products (Figure 14.1.3), as illustrated in the following equations for representative hydrocarbons:

General Hydrocarbon Combustion: Fuel(s) + Oxygen(g) -----> CO₂(g) + H₂O(g) + Energy

Methane:  
\[ \text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) + \text{Energy} \quad \Delta H^\circ \text{comb.} = -54.0 \text{ kJ/g} \]

Gasoline:*  
\[ \text{C}_8\text{H}_{18}(g) + \frac{25}{2} \text{O}_2(g) \rightarrow 8 \text{CO}_2(g) + 9 \text{H}_2\text{O}(g) + \text{Energy} \quad \Delta H^\circ \text{comb.} = -47.3 \text{ kJ/g} \]

Wood:*  
\[ \text{C}_6\text{H}_{10}\text{O}(s) + 6 \text{O}_2(g) \rightarrow 6 \text{CO}_2(g) + 5 \text{H}_2\text{O}(g) + \text{Energy} \quad \Delta H^\circ \text{comb.} = -15.0 \text{ kJ/g} \]

[*approximate chemical formulas for gasoline and wood(cellulose) are shown here]

During burning, some of the potential energy that is stored in the chemical bonds of the molecules that make up the fuel is released. The energy generated in this process can take the form of heat, light, sound, mechanical, or other forms of energy. In natural organic fuels, for example, energy from the sun is first captured by plants and stored in the chemical bonds of the molecules that the plants make, such as glucose, cellulose, oils, and many others. Generally, energy is released.
(exothermic) when chemical bonds form and required (endothermic) when bonds are broken. This may seem “backwards, but energy is usually released only when new, stronger bonds are formed to make products. In photosynthesis, for example, plants break apart the very strong bonds of carbon dioxide and water to make new chemical bonds in the production of glucose and oxygen molecules, as shown in Equation 14.1 – an energetically uphill process (Figure 14.1.4.). The energy needed to break the CO₂ and H₂O bonds is supplied to the plants from sunlight. During combustion, the strong bonds of the CO₂ and H₂O products (the reverse of Equation 14.1) are reformed to release the energy stored in the glucose and oxygen.

\[6\text{H}_2\text{O}(l) + 6\text{CO}_2(g) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\ \text{O}_2(g)\]

Equation 14.1

This process is similar to storing energy in a book by placing it on a high shelf. Energy is required to lift the book to the shelf and is stored by virtue of the position of the book (potential energy). The energy can be released by pushing the book off the shelf – converting the stored potential energy into the kinetic energy of motion. In an analogous fashion, energy is stored in the chemical bonds of the product molecules from photosynthesis. This energy may later be recovered by oxidizing the

### What is a Flame?

When a fire occurs, hot gases are produced from the combustion of the fuel. These hot gases can emit visible light when high energy electrons from the heated molecules cool to lower energies, emitting a photon of visible light (see Chapter 12).

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### Fire from the Sky!

When the German airship Hindenburg burned on May 6, 1937 near Lakehurst, New Jersey, over 7 million cubic feet of hydrogen gas that was used to keep the ship afloat combined with oxygen:

\[2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\ \text{H}_2\text{O}(g) + \text{Energy} \quad \Delta H^\circ_{\text{comb.}} = -484\ \text{kJ/mol}\]

This explosion and fire lasted just 34 seconds, liberated over 2.1 billion kJ of energy and produced 160,600 Kg of water (as vapor)(did it all go away as vapor or was there a little Hindenburg shower?). This is equivalent to 160,600 liters of liquid water (~42,500 gal of water) and about the electrical energy needs for 100 average US homes for a year (10^{12} J) – all released in 34 seconds you already referenced this 34 second up above or less. Fire investigators are still trying to piece together what happened to cause the catastrophic results. Theories include both accidental and intentional causes.
glucose and oxygen back into CO$_2$ and H$_2$O to provide the energy needed by the plant. Of course, glucose may also be transformed into other molecules by the plant (e.g., linked together to make cellulose), consumed as food by other organisms, or modified through other processes, such as in the geological and chemical processes that led to the formation of fossil fuels. When these compounds burn as fuels, the long-stored solar energy is finally released in the heat and light that we observe, as illustrated in the cycle shown in Figure 14.1.5.

Each type of fuel generates a characteristic amount of energy on burning, called the heat of combustion for the compound, denoted as $\Delta H^\circ_{\text{comb}}$.

When given in kJ/g, as shown for the reactions above (1 kJ = 1000 Joules of energy or about the energy in a burning match), the larger the $\Delta H^\circ_{\text{comb}}$ value, the more energy that is generated per gram of fuel. From this we can see that methane can deliver over 3½ times the amount of energy given off by an equal amount of wood. Heats of formation are also often given in kJ per mole of compound burned.

Oxidation reactions are among the most common of all chemical reactions on Earth. Oxygen is one of the few elements known to form compounds with every other element in the periodic table. Everything around us undergoes oxidation reactions to some extent, but why do some chemicals explode, other burn rapidly, some burn slowly and even others appear to be relatively unreactive? The answer has largely to do with the energy requirements and rates of chemical reactions, important considerations to understand for combustion and explosive reactions.
Most chemical reactions require an input of energy to get the process started, even if the products are lower in energy than the reactants, liberating heat when the reaction occurs. In other words, even if the reaction is an energetically downhill process it requires a “push” to get started. The energy that must be given to get a reaction going is called the **activation energy** of the reaction ($E_{\text{Act}}$, Figure 14.1.6). This is similar to the energy necessary to start a roller-coaster going or a rock rolling downhill. We must first put in sufficient energy to get the coaster car to the top of the first hill (the activation energy) and, once there, the coaster continues on its own until the end of the ride. If not enough energy is added to push the car to the top of the hill, it will roll back to where it started and not go on to the end point. It’s the same with chemical reactions – enough energy must be added to the reaction to get it over the energy “hill” of the activation energy so that it can proceed to products – the addition of an insufficient amount of energy will not initiate the reaction and it will just “roll” back to the beginning as unreacted starting materials. Often, this activation energy is required to break chemical bonds in the starting molecules to allow new bonds to form, such as breaking the C-H bonds in the oxidation of methane to form the new C=O bonds in carbon dioxide. The higher the activation energy, the more energy is needed to get a chemical reaction started.

For example, in Figure 14.1.7, the energy profiles for two reactions are shown – one reaction having a much higher activation energy than the other ($E_{\text{Act}} \text{ Reaction 1} > E_{\text{Act}} \text{ Reaction 2}$). Reaction 1 would require much more energy to added than reaction 2 for it to reach the top of the energy “hill” and have the reaction initiated. Some reactions have sufficiently low activation energies that room temperature is sufficient to provide the needed energy to start the reaction. Other reactions require the input of larger amounts of energy that must be provided by an outside source, such as the energy generated by friction when rubbing a match on sandpaper, from directly heating the compound, by providing a hot flame or spark, or even from light energy. Finally, some reactions have activation barriers that are so high that very large amounts of energy are required to start the process, such as...
the oxidation of gold or the burning (oxidation) of atmospheric nitrogen (N₂). Each compound has its own unique activation barrier to oxidation that must be overcome (see auto-ignition temperature below).

Chemical reactions represent a change in matter. Starting materials are converted into products at a specific rate – the amount of change that happens in a given amount of time. The main explanation of why some chemicals explode while others burn only slowly comes from considering the rates of chemical reactions. Explosive reactions happen at a very fast rate while combustion reactions may occur much more slowly. A number of important factors contribute to the observed rate of a chemical reaction including activation energy, concentration, temperature, molecular orientation (how tow molecules come together), the presence of a catalyst, and the reaction medium. On the molecular level, these factors combine to effectively control how many reacting molecules come together during a time span with just the right orientation and enough energy to cause the reaction to occur – a concept called the collision model (Figure 14.1.8). The more collisions of molecules or atoms with the right features at a time, the faster the rate.

Increasing the concentration of the reactants leads to more productive collisions (collisions leading to products) by crowding the reactants more tightly together and forcing them to collide more frequently. For example, heating steel wool in the air with about 21% oxygen causes it to glow and be slowly oxidized, as shown in Figure 14.1.9. Taking the steel wool that has been heated to the same temperature and placing it into a pure oxygen atmosphere, however, causes it to burst into flames and react much faster. The observed differences in this example are caused by simply changing the concentration of the oxygen in the two experiments. Similarly, in burning solid objects, such as wood or paper, increasing the surface area of the solid effectively increases the concentration or amount of oxygen that can reach the fuel, thereby increasing the rate. For example, a solid phone book...
burns rather slowly while a shredded book – where much more oxygen is available to the fuel surface – burns rapidly (Figure 14.1.10). As the concentration of combustion products increase, however, the oxidation reaction tends to slow because they “blanket” the surface, effectively reducing the amount of surface available for reaction.

Changing the temperature of a reaction also greatly affects its rate. Roughly, the rate of a chemical reaction doubles for every ten degrees C that the temperature is raised. Increasing the temperature increases the kinetic energy of the molecules – the molecules move faster. This means that more molecular collisions occur per unit of time and have enough energy for a productive reaction to occur. This temperature effect is particularly important in considering the spread of fires. As a fire burns, energy is given off to the surroundings largely as heat. This heat increases the temperature of the fuel and air mixture, in turn speeding up the oxidation reaction. This cyclic process continues with added heat increasing the burning rate to give off even more heat that, once again, increases the temperature until the fuel, oxidant or other component is changed or consumed (Figure 14.1.11). Once the fire starts and the cycle begins, it can very rapidly accelerate from the buildup of heat from the exothermic the combustion process.

Sometimes, a chemical called a catalyst is present that can greatly affect the rate of a reaction. A catalyst is a compound that lowers the activation energy of a chemical reaction, thereby increasing its rate, without being consumed in the reaction. Catalysts function in a variety of ways by helping to bring the reacting molecules together in such a way that leads to productive reactions. Catalysts can weaken bonds in reactants, hold molecules in the right orientations for reactions to occur or alter the path of a chemical reaction. Frequently, burn-rate catalysts (compounds that modify the rate of the combustion reaction) are added to explosives and propellants to increase the combustion rate for a specific purpose. For example, iron oxide (Fe₂O₃) can be added to ammonium perchlorate solid rocket propellants (NH₄ClO₄ – called an AP-type propellant), such as used in the space shuttle’s solid rocket booster and in many improvised propelled weapons. These catalysts increase the rate of the combustion reaction and deliver more propulsion per unit of time. Sulfur or other compounds are sometimes added to gunpowder to similarly increase the rate of combustion of the powder. Catalysts may also be added to reduce, control, or suppress combustion, including in certain types of fire-retardant additives found in fabrics, building materials, and fire-extinguishers. Detecting the minute presence of these catalysts in explosive residues can provide a great deal of information about their point of manufacture, primary intended use, and how they were employed in the observed blast.

In actuality, combustion reactions are very complex chemical processes that often do not result solely in the reaction products shown by the idealized chemical reactions above. The incomplete combination of hydrocarbon fuels with oxygen can give carbon monoxide (CO) as the major product instead of carbon dioxide. In fact, the major cause of fire-related deaths comes not from direct burns or heat but from toxic vapors, such as carbon monoxide and smoke (Figure 14.1.12). Additionally, common impurities in fuels, especially sulfur and nitrogen-containing compounds, can combine to give various oxides, such as SO₃ and NO₃. If temperatures are high enough, even the usually very inert atmospheric nitrogen (N₂) can also
combine with oxygen to give a variety of dangerous nitrogen oxides (around 1% of products formed in hot fires). As an illustration, some of the additional reactions that are possible when natural gas (mostly methane) and its common impurities are burned include:

\[
\begin{align*}
\text{CH}_4(g) + 2 \text{O}_2(g) & \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) + \text{Energy} \quad \Delta H^{\circ}\text{comb.} = -882 \text{ kJ/mol} \\
2 \text{CH}_4(g) + 3 \text{O}_2(g) & \rightarrow 2 \text{CO}(g) + 4 \text{H}_2\text{O}(g) + \text{Energy} \quad \Delta H^{\circ}\text{comb.} = -1782 \text{ kJ/mol} \\
\text{N}_2(g) + \text{O}_2(g) & \rightarrow 2 \text{NO}(g) + \text{Energy} \quad \Delta H^{\circ}\text{comb.} = -90.3 \text{ kJ/mol} \\
\text{N}_2(g) + 2 \text{O}_2(g) & \rightarrow 2 \text{NO}_2(g) + \text{Energy} \\
\text{S}(g) + \text{O}_2(g) & \rightarrow 2 \text{SO}_2(g) + \text{Energy} \quad \Delta H^{\circ}\text{comb.} = -296.8 \text{ kJ/mol} \\
\end{align*}
\]

…and other reactions are also possible depending upon the impurities in the fuel.

When the rate of the reaction is slow, some combustion reactions can still occur through flameless reactions. **Smoldering** (or glowing combustion) is the slow, lower temperature combustion of compounds without a flame, often to give incomplete combustion products (largely carbon monoxide from organic compounds). Wood, cellulose, cotton, tobacco, plastics, dust and humus are typical substances that can support long-lasting smoldering reactions. Smoldering materials can eventually lead to the initiation of fires, especially in furniture, clothing and bedding, from tobacco and similar sources. Smoldering also happens at the end of a fire event after all of the volatile flammable materials have been driven off of solid fuels, such as wood. This is the case seen in fireplaces when the flames are gone but the coals continue to glow red-hot for a long time (Figure 14.1.13). Oxidation reactions are still occurring at the surface of the wood, just at a relatively slow rate since the oxygen cannot penetrate beyond the surface into the fuel.

**Fire Initiation, Growth, Decay, and Suppression**

In order for a fire to begin, grow, and continue, four basic components are required. The close relationship between these four elements is often depicted in the fire tetrahedron, as shown in Figure 14.1.14. These components are heat, oxygen (oxidant), fuel and a chemical chain reaction:

- **Heat:** In order for a fire to start and be sustained, a critical temperature (similar to an activation energy) must be first achieved and then maintained. If the temperature drops below this value, the fire will soon go out. The

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Flash Point</th>
<th>Auto-ignition Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>-43°C</td>
<td>246°C</td>
</tr>
<tr>
<td>Diesel Fuel</td>
<td>62°C</td>
<td>210°C</td>
</tr>
<tr>
<td>Vegetable Oil</td>
<td>327°C</td>
<td>~650°C</td>
</tr>
<tr>
<td>Paper</td>
<td>232°C</td>
<td>450°C</td>
</tr>
<tr>
<td>Wood</td>
<td>~300°C</td>
<td>300°-450°C</td>
</tr>
<tr>
<td>Methane</td>
<td>-221°C</td>
<td>537°C</td>
</tr>
<tr>
<td>Ethanol (70%)</td>
<td>16°C</td>
<td>363°C</td>
</tr>
</tbody>
</table>

**Spontaneous Combustion?**

Throughout history, there have been claims that people, animals, and property have spontaneously been consumed by fire that started without any apparent external source of ignition. While human spontaneous combustion has not been verified, there are instances when an object can build up enough heat to reach the auto-ignition point. For example, the microbial decay of hay or similar materials in an enclosed, non-ventilated space can generate enough heat to reach the auto-ignition point of the fuel. Similarly, cloth soaked with certain oils, such as linseed oil, and sealed in a container can generate enough heat from a slow oxidation process to reach the auto-ignition point of the cloth, setting off a spontaneous fire. Spontaneous combustion without an external heat source or spark is exceedingly rare, however, and not a common source of fires.
most common fire-fighting medium, water, acts simply to reduce the temperature of a fire by absorbing large amounts of heat energy in its phase transition from liquid to gaseous water. Two values are defined to help understand the temperatures needed for the combustion of a specific fuel. The **auto-ignition temperature** (or kindling point) is the minimum temperature at which a substance will spontaneously ignite **without** an external source of ignition (spark), as shown in Figure 14.1.15. From a chemical standpoint, once the temperature is high enough to overcome the **activation energy** necessary for the combustion reaction to occur (the auto-ignition temperature), a compound can spontaneously combust. At temperatures below the auto-ignition point, there is not enough energy for the material to oxidize without some external stimulus. Once begun, heat generated from the oxidation reaction of the fuel then maintains the temperature necessary to support combustion. The **flash point** of a fuel is the lowest temperature at which it will vaporize sufficiently to form an ignitable mixture with air that will combust when an ignition source is supplied (e.g., a spark or flame). If the temperature of a burning fire drops below the flash point of the fuel, the fire will cease burning and extinguish. Each substance has its own characteristic auto-ignition and flash point temperatures and examples of these values for several common fuels are given in Table 14.1.1. The flash point for a compound is usually well below the auto-ignition temperature, meaning that the temperature needed to ignite a fire with a spark is much lower than the spontaneous combustion point. It is useful to note as an example the very low flashpoint of methane (-221°C) relative to its high auto-ignition temperature (+537°C), a difference of over 750°C! The energy needed to start a combustion reaction can be provided by heat generated by friction (e.g., lighting a match), a spark, electrical discharge, or other means.

**Figure 14.1.15.** Turpentine (a liquid distilled from pine trees, largely C₇H₁₆) has an auto-ignition point of 253°C. This means that it will not burst into flames without an ignition source at temperatures below 253°C (www.reptox.cstt.qc.ca/Documents/SIMDUT/GuideAng/Htm/GuideAng08.htm).

**Figure 14.1.16.** Ethylene (C₂H₄) has a lower flammability limit of 2.7% ethylene (97.3% air) and an upper flammability limit of 36% ethylene (64% air). As long as the concentration is either below or above that air-fuel mixture, there is no fire/explosion risk. If, however, the concentration is between these limits, an explosion could occur if a spark is provided (www.reptox.cstt.qc.ca/Documents/SIMDUT/GuideAng/Htm/GuideAng08.htm).
• **Oxygen/Oxidizer**: An oxidizer, by far most often oxygen (O₂) from the air, is needed for a fire to begin and continue. The fuel and the gaseous oxygen must come into contact and mix *in the gas phase* for the combustion reaction to occur. The relative amounts of oxygen and fuel in the gaseous mixture is called the **air-fuel ratio**. There are threshold limits of air-fuel mixtures, referred to as the **flammability limits**, which are required for combustion. Beyond these limits, combustion cannot be sustained, such as illustrated in Figure 14.1.16. This is the case where there is either too much oxygen or too little fuel present in the mixture (lean mixture) or too much fuel and too little oxygen (rich mixture). For example, the lower flammability limit for methane is about 5% methane, the lowest concentration of methane in air that can sustain a flame, and the upper limit of flammability is about 15%. If the concentration of methane is in the range of 5% to 15%, combustion (explosion) can occur. Outside of these limits the mixture is safe and does not burn even when a flame is available. The air–fuel ratio describes the *gaseous* mixture based upon the percentage of the compound mixed with air and it should be remembered that air is only about 21% oxygen, the rest is composed of inert gases such as nitrogen (~78%) and argon (~1%) (Figure 14.1.17). Additionally, none of the solid or liquid components of fuel are considered in the ratio, just the

**Figure 14.1.17.** Composition of the air on Earth (en.wikipedia.org/wiki/File:Atmosphere_gas_proportions.svg).

**Figure 14.1.18.** The structure of nitroglycerine, a major component of dynamite and cordite, contains both fuel components (C₃H₅O₃) and oxidizer components (NO₃) within the same molecule such that no external oxygen source is needed for detonation to occur:

![Radical chain reaction propagating reaction](image)

**Figure 14.1.19.** Radical chain reaction propagating (continuation) steps: the small dots represent valence (outermost) electrons and the larger spheres (labeled A, B, and C) represent atoms or molecules. Note that species with a pair of electrons are labeled non-radical while those with unpaired, single electrons are labeled as radicals (JTS).
gaseous portions.

Decreasing the amount of oxygen available to a flame will cause it to burn more slowly while increasing the oxygen content, within the flammability limits, increases the rate of combustion. Fanning a flame or providing ventilation essentially delivers more oxygen to the flame, causing it to burn faster.

In the case of explosives, the oxidizer often is not atmospheric oxygen but rather another compound added as the oxidant. Atmospheric oxygen (~21% of air) just can’t supply oxygen fast enough to an explosive compound to generate the extremely fast chemical reactions that characterize explosions. Instead, an oxidizer is added either to the explosive mixture or incorporated into the explosive compound itself so that it has both fuel and oxidizer portions fused into a single molecule. Nitroglycerine, shown in Figure 14.1.18, is a good example of an explosive that contains both oxidizer and fuel components within the same molecule. Black powder, in contrast, uses a separate compound added to the mixture, potassium nitrate (“salt peter”), that serves as the oxidant.

- **Fuel**: Fuel, as we define it relative to fire and explosives, is any material that stores chemical energy that can be extracted through combustion reactions. Fuels may be in any physical state; solid, liquid, or gas. The burning process with oxygen, however, must occur in the gas phase and, therefore, occurs near the interface between the gaseous oxygen and the solid or liquid fuels. For example, a solid or liquid must first be heated sufficiently for combustible gases to be given off that can be rapidly mixed with and be oxidized by the gaseous oxygen in the air. In other words, the fuel must also be a gas in order to react with the gaseous oxidant, oxygen. The flash point of a fuel is the temperature at which the solid or liquid fuel generates enough volatile gas products to create a concentration of these gases within the flammability limits for combustion for the fuel. Most common fuels come from biological sources: biofuels or fossil fuels. Biofuels are those that come from any carbon source that can be readily replenished and are termed a renewable resource (e.g., plants, microorganisms, animals – wood, cloth, vegetable oils, and fats are examples). Fossil fuels are hydrocarbons (C_xH_y compounds) that are derived from the ancient remains of fossilized plants and animals, such as petroleum, various oils, coal, natural gas, and tars. Fossil fuels are a non-renewable resource since the supply is not replenished – it takes millions of years to convert biological matter into these fossil fuels. Other fuel sources, although not as commonly encountered, are derived from mineral and other inorganic sources.

- **Chemical Chain Reaction**: Combustion reactions occur through a complex chemical process called a radical chain reaction. A radical is a molecule or atom that has an unpaired electron in its outermost (valence) shell. Usually, nature tries to pair all electrons in molecules to form stable species.
and, because of this, radicals tend to be very reactive intermediate compounds that try to pair up their electrons by pulling electrons from other molecules. When a radical encounters a non-radical molecule or atom, it reacts by grabbing (abstracting) an electron from that non-radical molecule. The original radical then becomes a more stable non-radical species while the original non-radical molecule becomes a radical [Sounds confusing, but think of it like this – if you had no money and your friend has $1, you could borrow the $1 from them, leaving them now without money (where you started) and you now have $1 (where they started)]. This is illustrated schematically in Figure 14.1.19. The process of a radical pulling an electron from a non-radical to create a new non-radical and a radical can continue in a long series of reactions called a chain reaction, similar to that shown in Figure 14.1.19. These highly reactive radical intermediates can continue to pull non-radical molecules apart, leading to new products – in the case of combustion, to the observed oxidized products.

Combustion actually consists of many simultaneous different radical chain reactions, usually initiated by oxygen-based radicals. Molecular oxygen ($O_2$), actually more correctly called dioxygen, is a very unusual molecule in that its most stable form is a diradical (it has two unpaired electrons in its lowest energy form). The high initiation temperatures required for combustion come from the need to convert the stable oxygen diradical into a very reactive electron spin-paired state. This latter, highly reactive form of oxygen then can then abstract a hydrogen atom and other fragments from the fuel molecules to give a variety of new radicals, including HOO radical, called the hydroperoxide radical (the dot by the formula indicates an unpaired electron making it a radical). The radicals formed at the high temperatures of combustion continue the radical chain reaction process (Figure 14.1.20) until either the fuel is consumed or the temperature drops too low to produce the necessary radicals to continue the chain reaction.

![Figure 14.1.21. Development stages of a typical fire – the vertical axis is temperature and the horizontal axis is time](http://cfbt-us.com/wordpress/?p=759).

### Types of Fires

In the US, fires are classified into groupings depending upon the source of fuel. The classification of the fire is used to determine the best way to suppress the fire. The categories of fires are:

- **Class A fire**: Ordinary combustibles such as wood, paper, cloth, trash, cardboard, and PVC;
- **Class B fire**: Flammable liquid or gaseous fuels such as benzene, gasoline, oil, butane, propane, and natural gas;
- **Class C fire**: Involving live electrical equipment, often caused by short circuits or overheated electrical cables;
- **Class D fire**: Combustible metals and alloys, such as iron, aluminum, sodium, and magnesium;
- **Class K fire**: Cooking media that contain vegetable or animal fat and oils.
Most of these radicals are so short-lived, however, that they cannot be detected but nonetheless lead to the observed combustion products. Anything that can inhibit the formation of radicals or remove these radicals from the combustion mixture can effectively shut down the combustion process.

**Fire Dynamics**

In order for a fire to start and grow, all four of the components of the fire tetrahedron must be present in the right form. Conversely, to stop a fire, one or more of these basic ingredients must be removed. Different firefighting materials and techniques are aimed at reducing or eliminating one of these four components:

- **Heat Suppression**: The most common firefighting agent is water. Water largely acts to cool the fire by absorbing large amounts of energy. Compounds that cool the fire can help to bring it under control.

- **Oxidant Suppression**: Carbon dioxide and sodium bicarbonate (solid extinguisher) act to smother the fire by removing oxygen from the equation. This typically requires large amounts of CO$_2$ to be effective, as much as 75% of the surface of the fuel must be covered with CO$_2$ to suppress the fire in some instances. CO$_2$ is denser than air so it settles to the lowest point to blanket the low-lying fire. Since it does not support combustion and displaces oxygen from the neighborhood of the fuel, it serves as an effective extinguisher. Because of the toxicity of CO$_2$, however, it is most often employed on smaller fires. In enclosed areas, inert gases such as nitrogen can also be used to remove the oxidant by displacing the oxygen – although this can be very dangerous for any people trapped in the contained space from the lack of oxygen to breath.

- **Fuel Suppression**: Typically, removal of the fuel occurs by either physically isolating the fuel source or interrupting the flow of fuel into the fire, such as turning off a gas valve.

- **Chain Reaction Suppression**: A common type of fire extinguisher uses a substance called Halon as the active fire suppressant, one of a family of halomethane compounds such as CBrF$_3$ (Halon 1301) and CBrClF$_2$ (Halon 1211). Halon acts at high temperatures to produce halogen atom radicals (e.g., fluorine, chlorine, bromine, or iodine) that rapidly react with radicals produced in the combustion chemical chain reaction, such as the hydrogen radical (H). Removing the chain-continuing radicals interrupts the combustion process, terminating the fire even when sufficient heat, fuel and oxygen are present.
Fires often present a predictable pattern of development and damage. Understanding how a “normal” fire behaves gives key insights when investigating fires that may have been set intentionally. Fires usually develop through four stages (Figure 14.1.21):

- **Incipient Stage**: The first stage usually is invisible to a viewer but involves the generation and accumulation of the volatile and combustible gases necessary to support combustion.

- **Smoldering/Growth Stage**: Small amounts of visible smoke may be visible at the beginning of this stage as the heat and mixture of fuel and oxidizer reaches a point to support active combustion, initially a relatively slow rate. As this oxidation reaction continues (smoldering), the temperature rises, increasing the rate of the oxidation reaction. The heat can be transferred by a number of means including radiation, convection, diffusion and conduction (Figure 14.1.22). Initially, the fire’s growth is controlled by the properties of the fuel but, as the fire grows, it becomes controlled by the amount of oxygen present, often called ventilation-controlled fire growth. The reaction rate doubles as the temperature rises about every 10°C, leading to a rapid growth cycle for the fire. To continue to grow, a fire must spread beyond the initial point of ignition to incorporate additional fuel. The “movement” of a fire follows well-understood patterns that can help decipher the initial source and primary cause of a fire.

- **Full Development/Active Fire Stage**: The critical combination of all the necessary elements must be in place to lead to a raging fire. A flashover may take place leading into this stage. A flashover is the rapid transition to a fully developed fire by the nearly simultaneous ignition of all the flammable materials within an enclosed space. It occurs when the surfaces in an enclosed space are rapidly heated to the auto-ignition temperature, igniting the large amounts of unburned flammable gases that have accumulated from the pyrolysis of the surfaces (Figure 14.1.23). During the full development stage, firefighters are always conscious of the possibility of an explosive backdraft event, especially later in this stage. A

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**Figure 14.1.24.** The difference in the heat release rate on the orientation of the fuel. In this study, the HRR of standing and lying down pine trees were measured. Note from the graph that the HRR for Tree 5 (black line), the one lying on its side, is much slower than for the other vertically oriented trees (Source: Madrzykowski, D. (2008). Impact of a Residential Sprinkler on the HRR of a Christmas Tree Fire. NIST: Gaithersburg, MD).
backdraft is possible when a fire burns in an enclosed space and uses up much of its oxygen supply, starving the fire of oxygen and causing it to decrease when it still with plenty of gaseous fuel. The backdraft can then occur, often explosively, when oxygen is rapidly reintroduced to the room that has accumulated unburned fuel (from lack of O₂), such as by opening a window or from a roof collapse, leading to a sudden increase of oxygen leading to a flash of combustion.

- **Decay**: This is the final stage of the fire when either the fuel is consumed or, due to firefighting efforts, one or more of the elements in the fire tetrahedron have been removed. After the active flames have been extinguished, the fire may continue to smolder for days.

When dealing with a fire, investigators consider the variables that led to the rate at which heat was released during the fire. This important quantity is called the **Heat Release Rate**, or HRR. The variables that affect the HHR include the size of the area burning, the identity of the fuel, the moisture content of the fuels, the surface area available for combustion (see Figure 14.1.10), the orientation of the burning materials (e.g., lying on the floor, standing vertically, on the walls, or elevated off of the floor, Figure 14.1.24), the method for heat transfer (see Figure 14.1.22), and how efficiently the materials themselves burn. All of these combine to give an estimate of how much heat should be released from a given fire. Unusual features observed, such as a fire hotter in some places than would be expected, can provide fire investigators important information about the source, progression, materials, and nature of the fire.

**Fire Investigation**

With an understanding of the basics of fire initiation, development and behavior, fire investigators are often asked to piece together evidence to explain the cause and actions of the fire. There are several reasons for this type of

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**Some Common Arson Accelerants**

Arsonists have been known to use many different accelerants when setting fires. Some of the most commonly employed are (f.p. = flash point and AIT = auto-ignition temperature):

- **Acetone** (C₃H₆O, f.p. -20°C, AIT 465°C): Acetone is a very volatile liquid with a strong odor that is used as a solvent in varnish, cosmetics, and nail polish remover.

- **Alcohols** (Methyl (wood, CH₃OH, f.p. 12°C, AIT 484°C), Ethyl (grain, C₂H₅OH, f.p. 13°C, AIT 365°C), and Isopropyl (rubbing, C₃H₇OH, f.p. 12°C, AIT 399°C) alcohols): These colorless liquids are readily available and find many uses including in beverages, industrial solvents, cleaning materials, and windshield wiper fluids.

- **Carbon Disulfide** (CS₂, f.p. -30°C, AIT 100°C): CS₂ is a colorless liquid with the odor of rotten eggs and is used in the manufacture of rayon and nylon, the vulcanization of rubber and resins, along with uses as a solvent. Because of its low auto-ignition point it can spontaneously combust when in contact with hot steam pipes.

- **Camping Stove Fuel** (various hydrocarbons, f.p. -33°C, auto-ignition temp. not reported): These light fuels are distilled from petroleum processing and commonly available as fuel sources for camping stoves and lanterns.

- **Ethyl Ether** (C₂H₅OC₂H₅, f.p. -45°C, AIT 180°C): Ether is a very volatile, low boiling compound (b.p. 34°C) that can form explosive peroxides upon standing or exposure to light. It is a common organic solvent.

- **Fuel Oils** (e.g., C₉–C₂₃ compounds, such as kerosene, home heating oil, f.p. range from 42°C to 96°C, AIT ranges from 210° to 260°C): Very commonly available materials but tend to burn slower due to their somewhat lower volatilities.

- **Gasoline** (mixture of hydrocarbons, f.p. -43°C, AIT 280°C): Very flammable and readily available, gasoline is the most common of all accelerants employed by arsonists.

- **Mineral Spirits** (mixed hydrocarbons, f.p. 40°C, AIT 245°C): Commonly employed as paint thinner.

- **Turpentine** (C₁₀H₁₆, f.p. 32° to 46°C, AIT 253°C): Commonly used as a paint thinner and in varnishes, soaps, linoleum flooring, and polishes.
Investigation. The first is to determine the cause of the fire to help prevent future similar events from happening elsewhere as well as to make sure that the specific fire will not reoccur. The second is to determine if the fire arose from a “natural” or accidental cause or was due to someone’s unlawful actions, whether through negligence or intent. Fires arising from either negligence or intent can lead to criminal prosecution and the investigator’s work forms the foundation of any court case brought forward.

**Arson** is the criminal act of intentionally setting fire without lawful consent. Arson may be part of other crimes such as covering a homicide, destroying property for insurance fraud, or eliminating questionable records. It may also be determined to be a hate crime, a crime of revenge, or terrorism, among other possibilities. An important part of any investigation is determining if there was a motive for setting the fire. The most common reason for arson is to destroy property to collect insurance money, especially when it would be hard to sell of otherwise collect money for the specific property (see inset box “Insurance Fraud through Arson”).

Arson investigations usually begin with a direct examination of the fire scene. Investigators must work as quickly after the fire has been extinguished as is safely possible since fire-related evidence can be very transient and short-lived. The combined action of the fire itself and the results of efforts to put out the fire can destroy evidence that might be crucial to the investigation. Working carefully but quickly afterwards can help preserve key evidence.

In order to start a fire, an arsonist must somehow arrange the components of the fire tetrahedron to facilitate the rapid initiation and growth of a fire. This might involve gathering ignitable fuel together, providing a heat or ignition source, or adding compounds specifically to facilitate fire initiation.
Insurance Fraud Through Arson

Intentionally setting fire to property for the purpose of collecting insurance money is believe to be the number one reason for arson. Insurance companies must defend themselves through civil proceedings using the arson defense to avoid paying a settlement.

In order to avoid paying, an insurance company must successfully prove arson through “clear, cogent, and convincing evidence” (US Supreme Court). The burden of proof is on the insurance company and they must positively prove the case against the owner (the presumption is that the owners are innocence of arson and guilt must be proven). The insurer must prove that the owner committed arson of the property by either direct (physical) or circumstantial evidence. Court precedent requires that the insurer must prove: (1) evidence of arson by someone, (2) motive for the fire by the owner, and (3) evidence implicating the owner (called “opportunity” evidence).

For example, a claim of arson was upheld in court (Thomure v. Truck Insurance Exchange, 8th Circuit, 1986) on the following grounds:

1. **Evidence of arson**: proof was given that accelerants were poured throughout the house and intentionally lit;
2. **Motive**: the insured was in severe financial difficulty and the property had been unsuccessfully for sale for several years;
3. **Opportunity evidence**: all the inhabitants of the house were unusually away at the time of the fire, the home had been insured for twice its purchase price value, and the owners had claimed very large sums for destroyed personal items. Additionally, the owners had moved household furnishings, firewood, parked cars, and the pet dog well away from the home just before the fire and had stored four gallons of kerosene in a clothes closet.

The court deemed that there was sufficient physical and circumstantial evidence to support the insurance company’s claim of arson with the intent to defraud.

![Figure 14.1.28.](image-url) The unusual burn pattern of heavily burned wood interspersed with unburned wood is evidence that a liquid accelerant was poured on a floor and leaked down onto the supporting joists. The fire burned where it leaked between the floorboards and, where it did not contact the wood, little burning was observed.

 accelants). An evidence-based demonstration of arson requires investigators to show that somehow one or more of the fire tetrahedron’s components have been altered inappropriately or criminally to facilitate a fire. It is important to note that failing to find any natural or accidental cause of a fire is not an acceptable legal argument for determining arson as the cause of the fire. Many cases have shown that this line of reasoning does not withstand the rigors of trial.

Many arson fires involve the use of accelerants to set fires. In fire investigations, accelerants are defined as compounds, often hydrocarbons, which facilitate the initiation and/or growth of a fire, but do not necessarily serve as a fuel. This is a somewhat different definition than the usual usage of the chemical term...
“accelerant” which refers to a catalyst that alters the rate of a chemical reaction without being consumed itself in the reaction (the accelerant is, therefore, technically not a fuel since it is unchanged at the end of the reaction). Nonetheless, common fire-related usage makes little distinction between an accelerant and a fuel and the term is usually meant to describe any added substance that promotes a fire. A list of commonly employed accelerants, along with some of their properties, is given in the box “Some Common Arson Accelerants.” The use of accelerants can cause a fire to start faster, burn hotter, and consume the fuel in a different pattern than a typical, naturally occurring fire. Investigators look for traces of these accelerants that remain after the fire as direct physical evidence of arson (see below).

Investigators often begin by interviewing the fire-fighters responding to the blaze, especially asking about any unusual behavior of the fire, even if it is a vague feeling that the fire simply did not behave as they had expected. Clues that might more directly suggest arson include multiple points of origin of the fire, the presence of accelerants, unusual burn patterns, quantity and color of the smoke, disabled fire-suppression systems (e.g., sprinklers, hydrants, hoses, etc.), unusual ventilation arrangements, and the condition of the fire scene.

The color of the smoke can help investigators learn what was burning and assess whether the smoke is consistent with fuels normally found in the structure. For example, gasoline tends to produce a yellow flame with thick black smoke while wood produces a yellow or red flame with gray or brown smoke (Figure 14.1.25). If firefighters observe thick black smoke coming from a building when they arrive, this could be an indication that gasoline was involved. If the building would not normally be expected to contain gasoline, such as a residential structure, this would suggest further investigation.

Arsonists often know that increasing the supply of oxygen to a fire accelerates its rate of combustion (similar to blowing on glowing kindling in a fireplace or campfire to start the fire). Finding doors and windows propped open or unusual openings cut into walls or ceiling might suggest the work of an arsonist. Likewise, finding fire-fighting or fire-suppression equipment disabled or missing that might allow the fire to grow unchecked and slow the fire-fighting response provides further evidence of arson.

Investigators especially look at the burn patterns left behind by the fire. Finding multiple places where the fire seems to have simultaneously originated or multiple explosions or flashovers is unusual with a natural fire. Additionally, “natural” fires tend to spread and build in well-recognized...
patterns. Deviations from these patterns can be evidence for arson. For example, finding a linear burn pattern, such as shown in Figure 14.1.26, indicates the use of an accelerant that was poured over the floor and then ignited. An “inverted cone” burn pattern (Figure 14.1.27) is another indication of an unusual burn pattern associated with arson accelerant use. Accelerants poured on floors can leak underneath the floor tiling or floor boards to show an unusual burn pattern when the tiles or floor boards are removed for inspection, as illustrated in Figure 14.1.27). Other significant findings can include localized “rusting” (oxidation) on metal items, finding accelerant containers in or near the fire scene, a detectable odor of gasoline, soot plumes in unexpected places, shifted furniture or other flammable items “stacked” together as fuel sources, and other unusual features. Investigators also look to see if specific items had been removed from the scene prior to the fire, especially sentimental and valuable items. This type of action clearly shows premeditated planning for setting the fire. Sometimes, evidence of accelerant use can come from the injuries sustained by the arsonist at the fire. Arsonists who use ignitable fluids can be badly burned on their hands, face and legs in patterns that could be consistent with accelerant use (Figure 14.1.29).

Commercially available hand-held hydrocarbon detectors, sometimes called “sniffers”, can be useful in screening a fire scene for the possible presence of any accelerants (Figure 14.1.30). These devices typically function by continuously sampling the air and monitoring the temperature of an internal hot filament for increases in temperature from the presence of oxidizable compounds in the sampled air.

Investigators often use photographers and/or personal observations at the scene to “watch the watchers” – to observe any bystanders, voluntary helpers, witnesses or victims who might be familiar or behave unusually. Some types of arsonists like to watch fire-fighting operations, even helping or video-taping the results of their efforts.

Determining the point or points of origin of a fire is very important. Looking for the deepest charring is not a good method for determining the origin, contrary to popular notion. Instead,
identifying fire plumes, such as shown in Figure 14.1.31, determining the path of the spread of the fire, and witness information can help locate sources.

Arson investigations are very tricky matters to do correctly. They require very careful observation, reliance upon tested scientific methods and validation, trained experts with experience in understanding fire behavior, and a complete openness to all possibilities. Investigators need to follow the process of the scientific method, be slow and deliberate in coming to a conclusion, and support their conclusion with evidence and logical reasoning. Wrongful convictions and improper findings are damaging to all involved, including those diligent investigators who exercise the proper, competent, and honest methods for investigating fires.

The Fire Scene: Collecting Fire Evidence

A fire scene is most properly considered to be a crime scene until it has been shown to be otherwise. Because of this, all of the general care and practices in dealing properly with any potential crime scene must be observed, as outlined in Chapter Two. The most important first consideration must be the safety of the responders, any victims and property owners, and the general public. First responders must deal effectively with any potential threats, including rendering assistance to victims, communicating any dangers to the public, establishing a safe perimeter, and other steps to make the scene safe – usually by extinguishing the fire and removing any possibility of re-ignition. Care must be given to the possible presence of any dangerous incendiary devices that might remain after the fire and present a real safety threat.

Once the scene is deemed safe, other standard crime scene processing steps then need to be quickly established. The scene must be carefully documented, especially photographically, noting the position and identification of all items of evidence, burn patterns, and fire damage. Proper warrants are usually needed for any extensive searches beyond quick searches to establish that the fire scene is no longer dangerous. Proper chain of custody procedures, searching methods, and site control are critical for ensuring that any evidence collected at the site will be admissible in court. Investigators should search carefully for any types of physical evidence that might include incendiary devices (including matches, torches, lighter, firearms, and others, Figure 14.1.32), impression evidence (e.g., footprints, fingerprints, tool marks, etc.), the location and pattern of debris, the presence of any trace evidence (e.g., hair, fibers, clothing, chemical residues, odors, etc.), and any unusual structural arrangements and burn patterns, as described...
previously. To the extent possible, potential evidence should be protected and left unmoved until it can be properly documented, catalogued, and collected. It is important, of course, to limit the use of gasoline-powered and similar equipment to avoid contamination of the evidence with gasoline that might be confused as an accelerant associated with arson. If possible, the clothing from a suspect should also be treated as evidence since it may be contaminated with accelerant.

A variety of types of evidence can be collected from a fire-scene. Usually, any evidence collected is placed in air-tight metal containers to trap volatile gasses in the container. These containers can later be analyzed to see if traces of accelerants or unusual fuels can be found. Typical containers for storing fire evidence are shown in Figure 14.1.33. Care must be taken to prevent any contamination of the samples and keep them in as close to the original condition as possible until they reach the laboratory. Accelerants are most often trapped in porous materials, such as wood, cloth, carpeting, and similar. Collecting these types of samples in suspected points of origin are important as often the best source of accelerants.

**Analyzing Fire Evidence in the Laboratory**

One of the most commonly used tools for the laboratory analysis of fire evidence involves the chemical detection of accelerants collected from the fire scene. This is most often done using GC-Mass Spectrometry (GC/MS). The gas chromatograph separates the many components of the sample and the mass spectrometer is then used to identify each component. This type of analysis is important since most accelerants are quite similar in chemical composition and consist of complex mixtures of many compounds. A GC/MS analysis is required to determine which specific accelerant was employed by identifying the presence and amount of each component in the mixture.

There are several ways commonly employed for obtaining a sample for the GC/MS analysis. One method uses a solvent to extract any possible accelerants from the sample. The problem with this method is that it does not concentrate the sample and requires the use of relatively large amounts of solvent (usually CS$_2$). A second method gently heats the contents of the sealed evidence container to drive any trapped volatile gasses in the sample into the gas phase. A syringe is then inserted into the top of the can and a volume of the head-space air removed and injected into the GC/MS for analysis.

Several improved methods have been developed that use an adsorbent, such as activated charcoal, to capture and concentrate any volatile accelerants present in the evidence. When the contents of the container are heated, the trapped volatile gasses are captured by an activated charcoal sample placed in the container. The charcoal serves to concentrate these gasses that can are then be
recovered by washing it with a solvent (CS$_2$) and injecting the extract into the GC/MS for analysis. A more recent method called solid-phase microextraction (SPME) utilizes a polymer-coated silica fiber (SiO$_2$) to concentrate the volatile components. After absorbing the gasses, the silica fiber is then placed into the GC instrument directly and heated to release the volatile materials. Typical gas chromatograms for the common accelerants of lighter fluid and gasoline, collected on a silica fiber, are shown in Figures 14.1.34 and 14.1.35, respectively. The “fingerprint” patterns of the GC, coupled with the identification of each component, provide powerful evidence for the presence of accelerants at the fire scene.

**Wrongful Conviction? The Willingham Case**

In December of 1991, a fire ran through the Willingham home in Corsicana, Texas, killing the Willingham’s three daughters. Cameron Todd Willingham, the children’s father, escaped with only minor burns. Prosecutors charged Willingham with setting the fatal fire to cover up alleged abuse of the children, despite positive evidence for the abuse. Cameron Willingham was convicted based upon arson evidence presented and executed on Feb. 17th, 2004.

After his execution, there have been major probes into the forensic fire evidence. Experts on both sides of the issue are currently debating the strengths and weaknesses of the evidence presented. An unprecedented commission has been set up by the State of Texas to examine the claims and report and the case remains controversial to date. Read the information available about the case and formulate your own conclusions concerning the case.

**Fiery Love Letters.**

In 2002, Terry Barton was employed by the U.S. Forest Service, when she burned a love letter from her estranged husband in the forest, setting off a wildfire outside of Denver. Barton, whose job was to spot illegal fires, called in the blaze to authorities on June 8th of 2002. Before it could be extinguished, the fire burned 138,000 acre of forest and destroyed 133 houses and one business. Investigators found the remains of burnt matches and a letter mailed to Barton at the source of the fire. Barton was arrested, convicted, and sentenced to two concurrent six year terms in prison. The judge, however, refused to require her to pay the government $14.6 million in restitution to cover the costs of the fire-fighting and restoration in the Pike Peak National Forest, as the prosecution had requested.