Arson and Explosives

- Chemistry of Fire

Introduction

- Arson and explosions often present complex and difficult circumstances to investigate due to the fact that the perpetrator has thoroughly planned the act, is not present during the act, and the destruction is so extensive.
- The criminalist's function is limited to detecting and identifying relevant chemical materials collected at the scene and reconstructing and identifying ignitors or detonating mechanisms.

The Chemistry of Fire

- Chemically, fire is a type of oxidation, which is the combination of oxygen with other substances to produce new substances.
- To start fire, the minimum temperature needed to spontaneously ignite fuel, known as ignition temperature, must be reached.
- The heat evolved when a substance burns is known as heat of combustion.
- An additional factor, besides the liberation of energy, needed to explain fire is the rate or speed at which the oxidation reaction takes place.

The Chemistry of Fire

- A fuel will achieve a reaction rate with oxygen sufficient to produce a flame only when it is in the gaseous state.
- A liquid burns when the temperature is high enough to vaporize it (flash point), while a solid must be hot enough to decompose into gaseous products (pyrolysis).
- Glowing combustion or smoldering is burning at the fuel-air interface, such as a cigarette.
- Spontaneous combustion, which is rare, is the result of a natural heat-producing process in poorly ventilated containers or areas.

Introduction

- Arson crimes are hard to solve.
- Only 17% of cases in 2003 ended in arrest.
- Vandalism is the leading cause of arson.
- An estimated 25% of arson fires are drug related.

The Fire Triangle
Fuel

• Organic Fuels (most common)
  – wood & paper
  – petroleum products & fossil fuels
    • hydrocarbons
• Inorganic Fuels
  – elemental
    • alkali metals, magnesium, hydrogen, phosphorus
  – metal salts like azide

• Most important attribute
  – energy stored in bonds of the molecule
  – with proper “encouragement” bonds broken releasing this energy
  – exothermic combustion reaction
• \( 
  \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} 
\) – releases 51.6 kJ/gram fuel

Heat

• Input energy (activation energy)
  – excites molecule causing bonds to break
• Activation energy is typically applied in the form of heat

Oxygen

• Most combustion reactions are oxidation processes
  – oxygen is a good electron acceptor
  – oxygen is a good oxidizing agent
    • takes electrons from other materials
• Oxygen itself is not flammable
  – the fuel burns not the oxygen

Activation Energy

• All reactions require an initial input of energy to start them
• The energy barrier that must be surmounted before any bonds can be broken

Activation Energy

• Some reactions have a low energy barrier
  – iron to rust
  – energy in the environment sufficient
• Some reactions have a high energy barrier
  – gasoline to carbon dioxide & water
  – the flame from a match sufficient
    • match is most common arson igniter
Activation Energy

• Spontaneous combustion is rare
• For a material to spontaneously burst into flames, it must be continually generating heat in a poorly-ventilated area
  – barn filled with hay
    • bacteria produce heat as a metabolism by-product which is not dissipated from center of stack
    • smolder ---> flames

Terminating the Burn

• Cut off oxygen supply
  – smother fire with water, blanket, or carbon dioxide
• Allow fuel source to be totally consumed
• Reduce temperature
  – water
  – atmospheric conditions

Oxidation: The Heart of Fire

• Fire is the result of an oxidation reaction.
  – Oxidation: a chemical reaction between a substance and oxygen
  – “Slow” oxidation reactions: processes such as rusting or bleaching
  – “Fast” oxidation reactions: rapid release of heat such as combustion or fire
  – “Extremely fast” oxidation reactions: explosions

How Are Flames Produced?

• Molecules of fuel must be in gaseous state to produce a flame
• Molecules of fuel must be mixed with a sufficient quantity of air for reaction to sustain itself
• Liquid fuels must be volatilized before they can burn
  – the higher the temp the more molecules converted to gaseous state

Factors That Influence the Intensity of a Fire

• The intensity of the fire increases as the rate of chemical reaction increases
• Three ways to increase or decrease the rate of chemical reaction:
  – Manipulate the temperature
  – Change the concentration of reactants
  – Add a catalyst
• With arson, focus on temperature, state of fuel, concentration of reactants, use of accelerants

Factors That Influence the Intensity of a Fire

• The effect of temperature
  – Fuel will produce a flame only when sufficient molecules exist in gaseous state
  – Temperature must be high enough to vaporize liquid fuels
Factors That Influence the Intensity of a Fire

- Flash point: the minimum temperature at which a liquid fuel will produce enough vapor to burn
  - Flammable liquids: flash points < 100 °F
  - Combustible liquids: flash points ≥ 100 °F
  - Once a liquid reaches its flash point, fuel can be ignited by an outside source of heat
  - Ignition temperature is higher than flash point

Factors That Influence the Intensity of a Fire

- Accelerants: materials used to start or sustain a fire
  - Liquid accelerants form flammable or explosive vapors at room temperature.
  - Wood or plastic materials will burn when heated to a temperature that is hot enough to decompose the solid and produce combustible gaseous products.

Factors That Influence the Intensity of a Fire

- The effect of concentration
  - If the ratio of gaseous fuel to air is too low or too high, the mixture will not burn
  - Flammable range: the concentration of gaseous fuel that will support combustion
  - Lower explosive limit: lowest concentration that will burn
  - Upper explosive limit: highest concentration that will burn

Factors That Influence the Intensity of a Fire

- The effect of concentration
  - The rate of a chemical reaction increases as the temperature rises.
  - As fire burns, it raises the temperature of the fuel–air mixture, which increases the rate of reaction.
  - In most structural fires, oxygen from air is a necessary reactant to keep the fire burning.

The Sequence of Events During a Fire

- Incipient stage
  - Stage begins with ignition of fire
  - Gases rise in the room
  - Oxygen dives to the bottom of the flames
  - Fire produces a characteristic “V” pattern on vertical surfaces

The Sequence of Events During a Fire

- Free-burning stage
  - Fire consumes more fuel and intensifies
  - Flames spread upward and outward
  - Dense layer of smoke and fire gases accumulate near ceiling
  - At a temperature of 1100 °F, all fuels in the room ignite (flashover)
  - Entire structure becomes engulfed in flames
The Sequence of Events During a Fire

• Smoldering stage
  – All fuel is consumed and the fire’s open flames disappear
  – If oxygen suddenly enters the area, the soot and fire gases can ignite with explosive force, producing a backdraft

Liquid Fuels

Flash Point

• The lowest temperature at which a flammable liquid gives off sufficient vapor to support a flame
• The presence of vapor is necessary but not sufficient for ignition
  – vapor must combine in proper proportion with oxygen-containing air
• Volatile liquids require a low temp to vaporize some molecules

Ignition Temperature

• The temperature which inputs sufficient energy to surmount the activation energy
• Ignition temp is always considerably higher than the flash point
  – gasoline
    • flash point: -50°F
      – defines the temp which the bulk of the liquid must reach to produce vapor
    • ignition temp: 495°F
      – temp required to start gasoline burning

Liquid Fuels

• Liquids never burn by themselves
• Fire takes place in the vapor phase at the surface of the liquid
• Exception
  – nitroglycerine
    • both fuel & oxygen are present in the compound

Hydrocarbon Accelerants

• Hydrocarbons
  – Composed of two elements: carbon and hydrogen
• Alkanes (from simple to complex):
  methane, ethane, propane, butane
  – As the carbon chains in an alkane grow longer, the properties of the members change with increasing molecular weight
• Structural isomers: compounds that have the same molecular formula but different structures
Hydrocarbon Accelerants

• Petroleum
  – Main source of most organic compounds used by industry
  – Crude petroleum is sent to a refinery and separated into fractions (fractional distillation)
  – Each fraction contains a different mix of hydrocarbons, so the presence of certain hydrocarbons in fire debris may indicate that a certain accelerant was used

Different Accelerants

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<td>Jet-A-Fuel</td>
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Solid Fuels

Pyrolysis

• To produce a flame from a burning solid, molecules at the surface of the solid must be transformed directly to a gas
• Heat can decompose complex molecules (wood) into smaller, more volatile molecules
  – pyrolysis
• Decomposition products react with oxygen

A Wood Fire

• Three types of reactions occur simultaneously
  – gas combustion (flames)
  – pyrolysis sustained by the heat of the flames
  – glowing surface combustion (smoldering)

Smoldering

• Uncombined carbon can’t burn with a flame because the heat liberated in its oxidation is lower than the heat required for its vaporization
  – smoldering embers
    • still oxidizing slowly analogously to rusting process
• Fresh source of oxygen will re-ignite the flaming reaction if pyrolizable fuel is present
The Crime Scene

Collection of Evidence

The Fire Scene

- The arson investigator needs to begin examining a fire scene for signs of arson as soon as the fire has been extinguished.
- Experience shows that most arsons are started with petroleum-based accelerants.
- The necessity to begin an immediate investigation even takes precedence over the requirement to obtain a search warrant.
- The search of the fire scene must focus on finding the fire’s origin, which may be most productive in any search for an accelerant or ignition device.

The Fire Scene

- 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, due to a flammable liquid.
- Normally, a fire has a tendency to move in an upward direction, and thus the probable origin will most likely be the lowest point showing the most intense characteristics of burning.
- Fortunately, combustible liquids are rarely entirely consumed during a fire.

The Fire Investigation

Questions to Be Asked

- What was the heat source?
- What was the fuel?
- What provided the oxygen supply?

Answers

- Oxygen supply almost always atmospheric — wind patterns & air drafts may be important in determining the origin & progress of the fire
  - usually done by a trained fire investigator
- Fuel is usually fairly obvious
- Laboratory useful in analyzing the evidence relating to heat source
Accidental or Incendiary?
- Evidence of an ignition device
- Evidence of accelerant or ignitable fluid

Determining the Origin and Cause of a Fire
- Point of origin:
  - Place where the fire started
  - Typically the site of greatest damage
- Investigators often work from exterior to interior, and from the areas of least damage to greatest damage

Determining the Origin and Cause of a Fire
- Burn patterns: physical marks and char that remain after a fire
  - Lines or darkened areas record the boundaries between different levels of heat and smoke.
  - The direction the fire traveled can be determined from burn holes in walls or ceilings.
  - Remains of damaged material may provide clues about the source of the fire.
  - Measuring the depth and extent of charring may help estimate the duration of the fire.

Determining the Origin and Cause of a Fire
- Burn pattern geometry: shapes on the walls or floors may indicate handling of accelerants
  - “V” pattern: accelerants from a container
  - Hourglass pattern: pool of burning liquid
  - Pour pattern: burn in the middle of a room
  - Trailer pattern: burn pattern that resembles a flowing stream; liquid was spread from one location to another

Determining the Origin and Cause of a Fire
- Melting of materials
  - Investigator can estimate temperatures of the fire by examining melted objects
  - Melted objects assist in determining the intensity and duration of the heating, the extent of heat movement, and the relative rate of heat release from fuels

Determining the Origin and Cause of a Fire
- Discolored metals
  - Discoloration indicates that the fire was extremely hot
  - Metals retain their discoloration even after the fire ends and they cool down
**Indicators of Arson**

- **Charring of floor surfaces**
  - Area of burned floor adjacent to unburned floor is a reliable sign of liquid accelerant
  - Accelerant can often be detected in the corners of a room or along the base of a wall
- **Containers**
  - Liquid containers are evidence
  - They may indicate use of a liquid accelerant

**Indicators of Arson**

- **Odors (from liquid accelerants)**
  - Many evaporate quickly, so evidence must be collected immediately.
  - Contaminated areas can be detected with ultraviolet violet light or a hydrocarbon detector.
  - Specially trained dogs can detect accelerant residues.

**Collection and Preservation of Arson Evidence (1 of 3)**

- **At the scene:**
  - Search for, identify, record, and photograph all evidence and note its location in a sketch.
  - Photograph and document the condition of doors, windows, and locks.
  - Look for accelerant residues at the edges of burn pattern.

**Collection and Preservation of Arson Evidence (2 of 3)**

- **Collect debris suspected of containing accelerants and place it in clean metal paint cans**
- **Metal paint cans are used for two reasons:**
  - Plastic will absorb the compounds and may ruin the sample
  - Cans are airtight and will preserve volatile vapors

**Collection and Preservation of Arson Evidence (3 of 3)**

- **In the laboratory:**
  - Open evidence storage units as briefly and infrequently as possible to minimize escape of vapors.
  - The nature of the debris may dictate that the examiner carry out a certain type of test.

**Collecting Evidence**

- **Ignitable fluids are very volatile requiring care in collection**
- **Collect a large quantity of ash & soot for suspected point of origin**
  - may contain remnants of unburned or partially burned ignitable fluid
- **Partially burned or unburned porous material should also be collected**
Collecting Evidence

• Evidence should be collected in airtight, solvent-resistant containers
  – new metal paint cans
  – not plastic containers
    • might react with evidence fluids
  – polyester bags that are chemically resistant

Substrate Samples

• Many household materials are hydrocarbon-based
• Important to collect substrate samples of materials similar to those from point of origin for comparison
  – look for presence of different substances at point of origin than in other samples
• Suspect’s clothing may contain fluid residue

Ignition Devices

• Can be ordinary devices
  – cigarette
  – match
• May have had electric or mechanical sparking devices

Fire Patterns

• V-pattern
  – fire moves upward spreading from its origin
    • point of origin does not imply arson, but gives a good starting place for evidence collection
• Ribbon pattern
  – fire follows the path of ignitable fluid spread before ignition

Arson Investigation

The Forensic Laboratory

What’s the Question?

• Legal Question
  – “Did someone purposefully set the fire, and if so who?”
• Since most materials don’t easily ignite, an arsonist will often employ an ignitable fluid to start the fire
• Presence of an ignitable fluid does not, in and of itself establish the legal crime of arson
### Laboratory Collection Methods

#### Headspace
- Simplest collection technique
- Material collected in an airtight can is gently warmed inducing a vapor which rises to occupy the empty top space.
- A sampling device such as a syringe is used to puncture the can and collect a sample of the headspace.

#### Analysis of Flammable Residue
- Heated headspace sampling
  - Examiner puts a piece of fire debris in a special metal container
  - Container is heated
  - Syringe is used to puncture the rubber septum and remove a small sample of the vapor
  - Vapor is injected into the gas chromatograph
  - Only a small portion can be sampled

- Passive headspace diffusion
  - Small strip of carbon fiber mat is suspended in a container with the debris
  - Container is heated to turn liquid accelerant into vapor
  - Charcoal (carbon) strip absorbs the vapor and concentrates it
  - Accelerant is extracted from carbon strip

- Solid-phase microextraction
  - Replaces carbon fiber mat with a solid-phase absorbent bonded to the fiber
  - Material is inserted into a container of fire debris via a hollow needle
  - Container is heated
  - Absorbent material is withdrawn from the can and inserted into a gas chromatograph

#### Adsorption/Elution
- Hydrocarbon vapors are collected & concentrated on an adsorptive strip
  - charcoal-coated teflon
- Strip placed in container with the evidence
- Container warmed to release vapors which are adsorbed by the charcoal on the strip
- Strip eluted with a small quantity of solvent
  - increases possible detection by 100X
Laboratory Analysis

Gas Chromatography

Analysis of Flammable Residue

- Gas chromatography
  - Used to separate and detect complex mixtures of volatile organic compounds
  - Distributes compounds of a mixture between an inert-gas mobile phase and a solid stationary phase
  - Individual components produce symmetrically shaped peaks
  - Area under each peak is proportional to the concentration of that component

Analysis of Flammable Residue

- Gas chromatography
  - Some arsonists use a mixture of accelerants
  - To overcome this problem, a GC may be attached to a mass spectrometer
  - Mass spectrum indicates which components of the evidence sample are contained in a certain accelerant

Interpretation of Results

- Look for the pattern resulting from the chromatographic separation of the compounds making up the mixture
- Patterns produced by known petroleum distillates are kept on file in the laboratory
- If possible comparisons are made with suspect objects

Same Substance Different Sources

What Information Can Be Obtained?

- Can classify the substance by the complex pattern of peaks
  - gasoline vs. paint thinner
- Can’t usually determine the gas station the particular sample came from
- Difficult sufficiently prove common origin of evidence & reference sample
  - sample from can in suspect’s car
Classification of Hydrocarbons

- n-Heptane
  - 7 carbon straight-chain alkane
  - total of 8 isomers having formula of $\text{C}_7\text{H}_{16}$

Some Petroleum Distillate Chromatograms

Explosions

- Explosives are substances that undergo a rapid oxidation reaction with the production of large quantities of gases.
- It is this sudden buildup of gas pressure that constitutes the nature of an explosion.
- The speed at which explosives decompose permits their classification as high or low explosives.
- The most widely used explosives in the low-explosive group are black powder and smokeless powder.
- Black powder is a mixture of potassium or sodium nitrate, charcoal, and sulfur.
- Smokeless powder consists of nitrated cotton (nitrocellulose) or nitroglycerin and nitrocellulose.

The Explosive Market

- In recent years, nitroglycerin-based dynamite has all but disappeared from the industrial explosive market and has been replaced by ammonium nitrate-based explosives (i.e., 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, often encountered in the form of pliable plastic known as C-4.
**Explosion**

- Like fire, explosion is a product of combustion
  - produces the same by-products
    - heat
    - light
- Distinguishing characteristics of explosives
  - the rapid rate at which the reaction proceeds

**Explosives**

- Rapid rate facilitated by incorporating both the fuel & the oxygen into the same solid substance
  - ensures immediate availability of the oxygen to the fuel

**Explosives**

- Main damage from explosives from
  - flying shrapnel
    - rapidly expanding gases create extreme pressure on the walls of the container bursting container
  - self-propagating wave
    - caused by rapidly expanding gases compressing the surrounding air
    - can reach speeds of 7000 mph

**History of Explosives**

- Alfred Nobel
  - first major research into explosives
  - manufacturer of nitroglycerine
    - unsafe to handle in pure form
    - much more stable when absorbed into diatomaceous earth
      - doesn't explode until specifically detonated
      - dynamite
    - also invented smokeless powder

**Classification of Explosives**

- Often the only difference between a reaction proceeding as an explosion rather than a fire is its confinement in a small space
- Classes
  - low explosives
  - high explosives

**Low Explosives**

- Rate is called speed of deflagration
  - produces a subsonic pressure wave
  - reaction is relatively controlled
  - reaction has a predictable burn rate
    - useful for propelling or throwing objects
  - Best known use for low
**Black Powder**
- consists of charcoal, sulfur & potassium or sodium nitrate
- combination of charcoal & sulfur is the fuel
- oxygen is contained within the NO₃ (nitrate) ion

**Smokeless Powder**
- Most commonly used powder today
- Two types
  - “Single-base” gunpowder
    - contains only nitrocellulose
  - “Double-base” gunpowder
    - contains nitroglycerine mixed with nitrocellulose
    - the carbon containing cellulose or glycerin part is the fuel while the nitro part contains the oxygen

**Other Low Explosives**
- Natural gas
  - explodes if allowed to leak from a pipe for some time before being ignited
- Very fine organic powders
  - flour
    - grain elevator explosions

**High Explosives**
- The chemical bonds making up the unstable compound oxidize at extremely rapid rate releasing huge amounts of energy in microseconds
  - produces a supersonic shock wave
  - speed of detonation
  - self-propagating shock wave rips apart the chemical bonds in the explosive, initiating a chain reaction of more heat & expanding gases

**High Explosives**
- Two subcategories
  - initiating explosives
  - non-initiating explosives

**Non-initiating Explosives**
- Relatively stable
  - will simply burn if small quantities are ignited in the open
  - most commercial & military explosives
    - dynamite
    - TNT (trinitrotoluene)
    - PETN (pentaerythritol tetranitrate)
    - RDX
Non-initiating Explosives

- Ammonium nitrate-based explosives
  - typically consist of oxygen-rich ammonium nitrate combined with some highly flammable fuel
  - water gels
    - mixed with highly combustible inorganic substance
      - aluminum
  - emulsions
    - mixed with hydrocarbon fuel
      - typically an oil

Home-made Explosives

- ANFO
  - ammonium nitrate soaked in fuel oil
  - both ingredients readily available as innocuous items
- Believed to be the explosive used in
  - World Trade Center bombing
  - Oklahoma City bombing

Initiating Explosives

- The slightest mechanical disturbance will cause a violent detonation
- Primarily inorganic compounds
  - lead azide
  - lead styphnate
  - mercury fulminate
- Used as primers in blasting caps
  - used to detonate the main explosive charge

The Crime Scene

- Bomb pieces are widely scattered
  - pieces are usually very small
- Scene must be systematically searched in an organized pattern
  - wire-mesh screens are used to sift through the debris
- The origin of an explosive blast is usually obvious
  - a crater surrounded by debris

Two Categories of Evidence

- Ignition Device
  - often survives the blast in pieces
- Undetonated explosive
  - found on fragments of the bomb container
  - adhering to objects in objects in the vicinity of the blast

Collection of Evidence

- EGIS system (screening tool)
  - collects vapors from surface of objects
  - GC analysis
- Explosives often take the form of a fine dust
  - collect in airtight containers
    - metal cans
    - plastic bags
    - improperly packaged explosives can contaminate an entire evidence room's worth of evidence
Collection and Analysis

• 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.
• Often a crater is located at the origin and loose soil and other debris must be preserved from its interior for laboratory analysis.
• One approach for screening objects for the presence of explosive residues in the field or laboratory is the ion mobility spectrometer (IMS).

Collection and Analysis

• Preliminary identification of an explosive residue using the IMS can be made by noting the time it takes the explosive to move through a tube. A confirmatory test must follow.
• All materials collected for the examination by the laboratory must be placed in sealed air-tight containers and labeled with all pertinent information.
• Debris and articles collected from different areas are to be packaged in separate air-tight containers.
• It has been demonstrated that some explosives can diffuse through plastic and contaminate nearby containers.

Back at the Lab

• Typically, in the laboratory, debris collected at explosion scenes will be 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.
• Confirmatory identification tests may be performed on unexploded materials by either infrared spectrophotometry or X-ray diffraction.