

CHEMICAL FORENSIC EVIDENCE IN FIRE/EXPLOSION CAUSATION ANALYSIS

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ABSTRACT

Fire and explosion scenes often have the potential to contain crucial chemical evidence. Unlike visual evidence often used in causation analysis chemical evidence is hidden. This evidence may be physically hidden under debris and ash, or may be masked in the samples taken for laboratory analysis. It can even be hidden in plain sight – as unusual characteristics certain materials can take on under unusual conditions.

When evidence is hidden in the samples, only with carefully selected analytical techniques and data interpretation will the causation become evident. The complex dynamics of a fire and/or explosion can affect chemical species in remarkable ways. Chemicals and their combustion or pyrolysis by-products may interact, vaporize, become coated by, or absorbed by other materials during an incident, making them easily overlooked by the inexperienced investigator. Other times an understanding of complex chemical interactions is crucial to determining the cause of an incident. Knowledge of the physical and chemical characteristics and behaviors of the materials involved in an incident often under atypical pressure, temperature and oxidative regimes can lead to an awareness of the physical and chemical processes that occurred and played a causative role in the incident.

Case examples are utilized to consider where chemical forensic evidence was crucial at arriving at a causation determination.

INTRODUCTION

The analysis of fire/explosion incidents has over time moved to a more solid scientific foundation. It is often the case that simple scenarios are relatively easy to discern based on observation of the scene and interviewing witnesses. There are other cases that are potentially far more complex and require careful scientific analysis. While it is often the case that various mechanical engineering simulations and analysis are needed, chemical forensic evidence is often a critical component in these complex cases. Sometimes this evidence is dependent on careful sampling and laboratory analysis. In other cases a deeper understanding of the complexities of how materials react and interact as chemicals in atypical oxidative, pressure and/or temperature conditions is needed.

ANALYTICAL TECHNIQUES TO UNCOVER HIDDEN EVIDENCE

There are a wide variety of analytical techniques used in chemical forensic analysis of materials sampled at the scenes of fires and explosions. Some of the most common are reviewed in this section. Perhaps the most important thing to remember is that data interpretation by a skilled analyst is imperative. Reliance on analysts not familiar with fire investigation samples or reliance on computer automated data interpretation can lead to erroneous or conflicting conclusions that may not stand up during litigation to a more detailed review.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is most often used to identify or confirm the identity of materials taken from a fire scene. While most useful for organic materials it can also be useful in determining some inorganic materials. Its greatest limitation is that it usually requires a pure or nearly pure sample. It does not work well for

complex mixtures. Further, for solid samples it will only determine the composition of the outermost layer of a material. Because materials often volatilize and recondense during a fire samples can be coated with thin layers that are not representative of the underlying matrix. Figures 1 and 2 show two different FTIR spectra of the same sample taken before and after scraping a surface layer from the sample. This was a microscopic sample found inside of a medical oxygen cylinder that proved critical for determining the source of fuel in a fire that occurred inside the oxygen cylinder regulator.

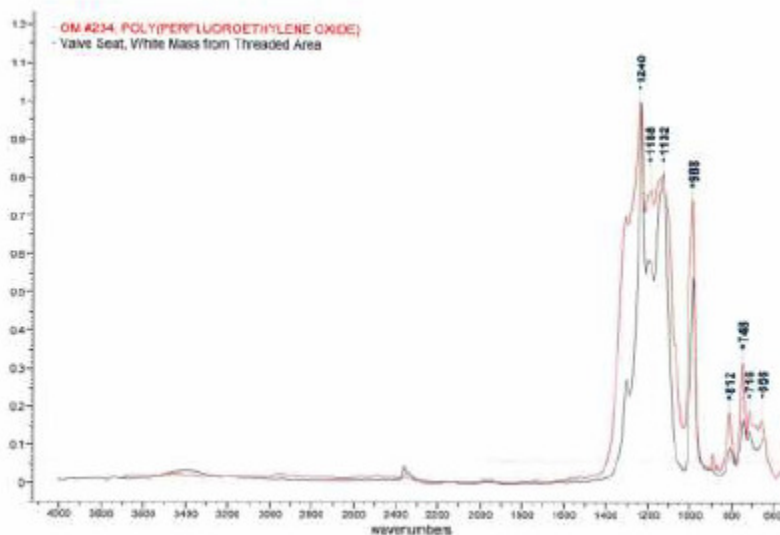


Figure 1 - Spectral Overlay of White Mass Removed From Valve Seat Retainer – Pre-abrasion (Black) and Poly (perfluoroethylene oxide) (Purple)

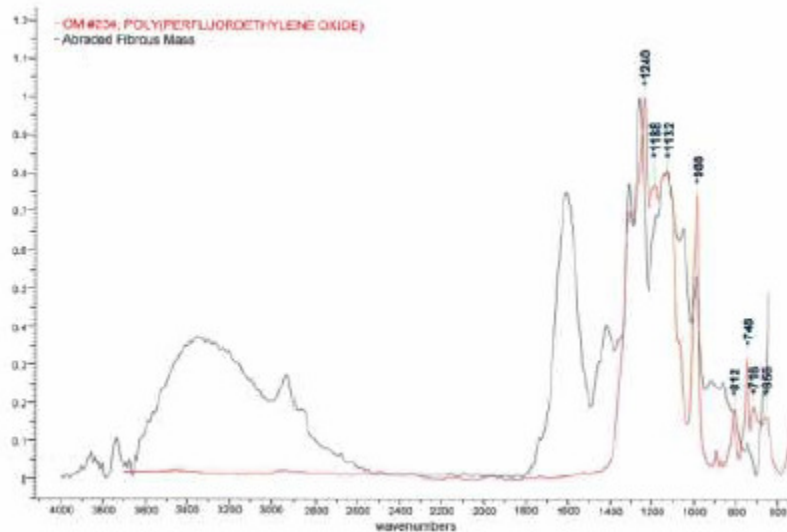


Figure 2 - Spectral Overlay of Abraded White Mass Removed From Valve Seat Retainer (Black) and Poly (perfluoroethylene oxide) (Purple)

Gas Chromatography-Mass Spectrometry (GC-MS)

GC/MS is a binary analytical technique that uses gas chromatography to separate samples that can be volatilized (heated to become a gas) followed by mass spectroscopy to identify a component of a mixture. This is a powerful technique for dealing with complex mixtures or trace amounts of compounds that may have been deposited or even formed during a fire/explosion event. Computerized identification

of compounds, while a powerful aid, are too often relied upon in their entirety by labs and analysts. Different compounds can produce very similar mass spectra and in complex chromatograms compounds that coelute can further complicate proper identification of constituents. An experienced analyst knows how and when to recognize problems and still make use of the data using specialized techniques to deal with these complications. Figures 3, 4 and 5 show reference spectra for three different organic compounds. Even to the untrained eye it is easy to see how a computer might misidentify a real sample that contained one of these compounds. Proper identification of the compound could play a critical role in determining the source of the sample.

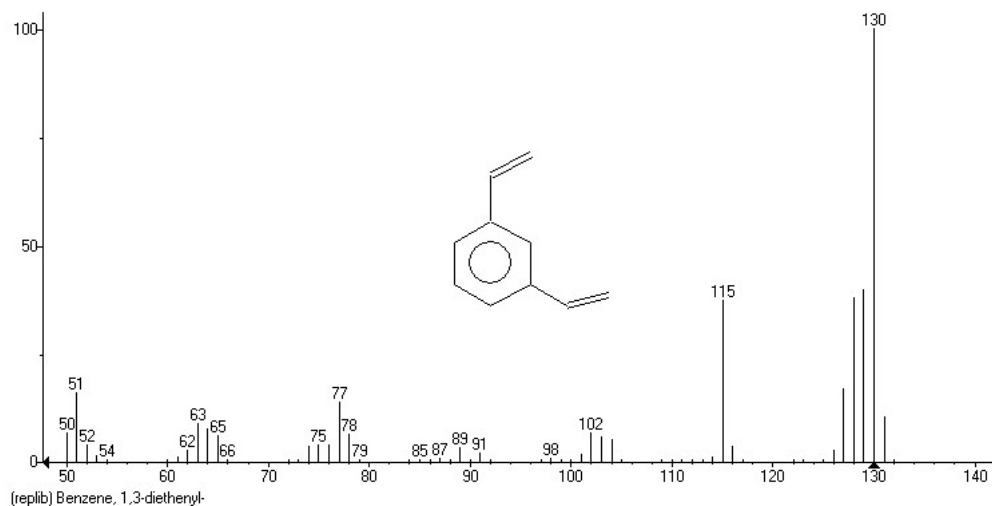


Figure 3 – Benzene, 1,3-diethyl-

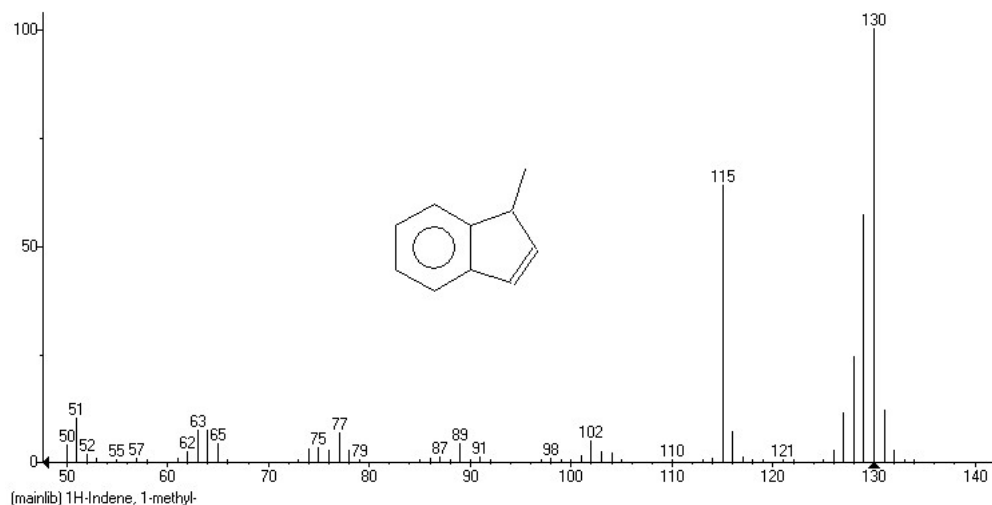


Figure 4 – 1H-Indene, 1-methyl-

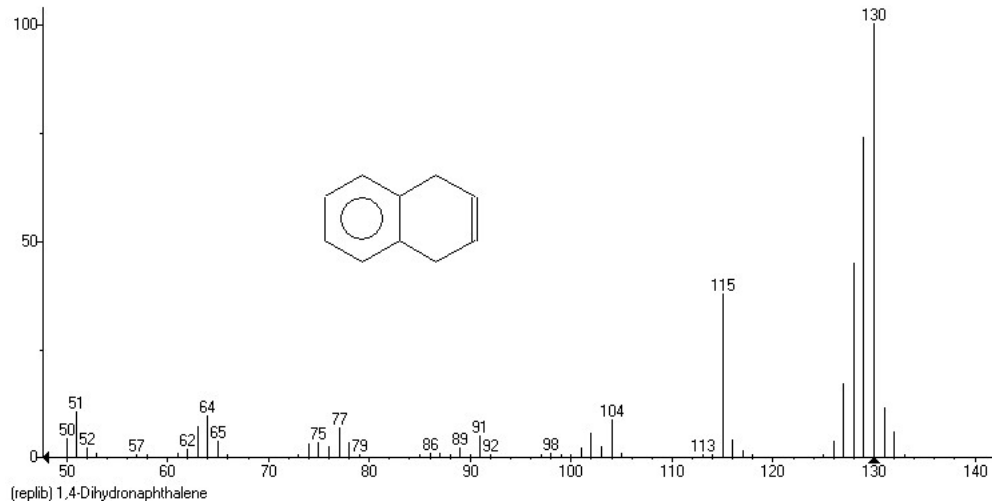


Figure 5 -1,4-Dihydronaphthalene

Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

SEM-EDX is another combination of two analytical techniques that are often but not necessarily used together. SEM is actually a method for imaging extremely small samples. It can be helpful in using the morphology of a sample in identifying the source of a material. As an example there are extensive libraries of SEM images for different types of cellulosic materials that can prove useful in forensic investigations. EDX is used by itself at a macroscopic level or with SEM at the microscopic level to determine the elemental composition of a sample. SEM techniques are limited when determining lighter elements in the periodic table but very powerful in the determination of trace metals. It does not suffer from many of the sample digestion problems that other elemental/metal testing methods have but it is another technique that is limited to the surface of samples. On a macroscopic scale this limitation is easily overcome with sample grinding and analysis of the resulting fine particulate. For microscopic samples this surface testing is often desirable. Sometimes samples are cross-sectioned and then analyzed using this technique to determine the depth to which something had penetrated the material – either leading up to an event or during the event.

Thermogravimetric Analysis (TGA)

TGA is a method that involves slowly heating a sample and constantly monitoring the weight of the sample. As the sample burns, volatilizes or pyrolyzes depending on containment conditions the TGA curve can be used to characterize the sample. This technique is most often used to assist in identifying polymers but can have other uses during fire/explosion investigations. A related technique called DSC (differential scanning calorimetry) monitors the energy absorption or release of a sample during heating. This method is also often used to help identify polymers but can also be useful in looking at potential energetic reactions that may have been involved in fire/explosion incidents.

WHERE CAN CHEMICALS AND CHEMICAL EVIDENCE HIDE?

Before one chooses what type of analysis to perform on a given sample the actual choice of samples from an incident scene must be undertaken. Beyond the obvious samples such as residue in a container at or close to the source of the incident there can be important samples in other locations.

Smoke and combustion/pyrolysis byproducts from an incident are often absorbed into plastics and silicones that may be proximate or distant from the event. For example silicone compounds used to seal gasket materials or that make up caulking compounds are highly absorbent for the types of compounds produced in fires/explosions. Plastics such as PVC, especially the soft versions made for tubing, are also absorbent of these compounds. Analyzing these samples using thermal desorption onto a SPME (Solid

Phase Microextraction) fiber with subsequent GC/MS may provide the information critical for some causation determinations.

During a fire there are many compounds being evaporated or formed that can condense onto surfaces. Using FTIR or other methods to determine the composition of samples gathered during an investigation can create misleading results if this fact is not taken into consideration as was previously illustrated in the section on FTIR.

There are times when it is the unexpected retained sample that provides the critical information needed to understand a fire/explosion. For example when sampling liquid residual material from a container such as a drum involved in a fire/explosion don't forget to sample the entire cross-section of the container including any solid debris that may be on the bottom of the container. We have seen at least one example where that solid debris was critical in determining causation.

Sometimes an event may be due to the reaction between two or more substances. Such reactions will often leave byproducts of that reaction. Don't just look for the compounds that can cause such reactions. They may have been completely consumed in the incident. Instead sampling and testing for reaction byproducts may be needed to understand the cause of the incident and the sequence of events leading up to it.

ATYPICAL CONDITIONS THAT CAN BE INVOLVED IN FIRES AND EXPLOSIONS

Too often when determining causation of fires/explosions that involve chemicals, investigators limit their information to that found on a Safety Data Sheet (SDS). While information on an SDS can be valuable it must usually be considered a starting point. Often the causation determination will require a deeper understanding and knowledge of the chemistry and reaction potential of a material. In general if commonly understood precautions had been sufficient the incident would not have happened in the first place. That means a deeper dive into the technical literature to understand the reactivity of potential chemical agents under atypical conditions.

Oxidants

There are sources of oxygen other than oxygen gas and oxidizers other than oxygen. Many investigators are likely already familiar with mineral oxidizers such as perchlorate compounds that can react violently with many hydrocarbons, but did you know that both water and CO₂ can provide the oxygen needed for some fires/explosion? In the case of water both oxygen and fuel (from the hydrogen in the water molecule) can be part of the incident – often creating a secondary explosion. Metals such as sodium will react violently with water creating both fires and explosions as an example. Oxygen is not even needed in any form – chlorine is also a very common oxidizer the source of which may be something as simple as chemicals used to maintain water quality in a swimming pool. Even nitrogen can become an oxidizer under the right circumstance. Fires involving titanium or zirconium metal can use nitrogen gas as the oxidizer. Some fires can be made worse if sprayed with a CO₂/water or even a nitrogen gas extinguisher.

Combustion vs. Pyrolysis

Sometimes it is important to understand if an incident was occurring under oxidizing or reducing conditions – or perhaps in the absence of an oxidizer. That is when a clear understanding of the difference between combustion and pyrolysis byproducts (generally gasses and their condensates) can be critical. When a fuel burns the gasses produced, even under incomplete combustion, can be very different if the fuel is being heated to the point where it chemically breaks down and vaporizes but is not undergoing oxidation. When looking at combustion residue via GC/MS it is important to be aware of this difference. An excellent reference for considering pyrolysis gas signatures is *Pyrolysis-GC/MS Book of Synthetic Polymers* by Shin Tsuge¹.

Other Atypical Conditions

Sometimes fires and explosions happen with materials not considered dangerous because of atypical pressure, temperature or oxidative conditions. Some of us can remember the tragic Apollo 1 fire. Pure oxygen at pressures above atmospheric pressure caused materials in the cabin that were not normally flammable to become highly flammable, resulting in the death of three US astronauts working to see us to the moon. It is often difficult during a fire/explosion investigation to determine if atypical conditions existed at the time of the incident. It may be necessary to perform calculations or simulations of conditions leading up to an incident to determine the full potential of atypical conditions or if they in fact existed.

CASE EXAMPLES

Two case examples are provided to help understand how chemical forensics can be critical in determining the cause of an incident.

Pool Chlorinator Explosion

During the investigation of a pool chlorinator explosion samples of silicone grease residue from pieces of the exploded pool chlorinator were analyzed using GC/MS. The analysis revealed a number of chlorinated hydrocarbons as well as other hydrocarbons typically found in pool water system such as those derived from sun block lotion. This information proved critical in understanding that the explosion was not mechanical in nature but in fact the result of a hydrocarbon contaminant such as gasoline or break fluid finding its way into the system – likely having accumulated in the sand filter and then flushed suddenly into the chlorinator when turned on after routine maintenance.

Railcar explosion

On February 18, 2018, a rail car containing toluene diisocyanate still bottoms exploded on a siding at a plant in Indiana as seen in Figure 6. The National Transportation Safety Board (NTSB) report failed to identify the specific series of events that resulted in the explosion. During litigation over insurance claims relative to the incident, further examination of the data and information gathered during the NTSB investigation, coupled with an understanding of atypical conditions, was performed. Identification of atypical conditions that were present prior to the explosion allowed the determination of the specific series of events that blocked the pressure relief valve and resulted in the build up of pressure inside the rail car to the point of the explosion.

Specifically, excessive heat applied to the materials in the car in an unsuccessful attempt to unload the car resulted in a run-away dimerization reaction that generated CO₂ gas. As the pressure built in the car the manual release of building pressure caused the material to violently boil (like pulling a vacuum on water at room temperature) splashing the high viscosity material in the car into the pressure relief valve opening which was exposed to winter temperatures in Indiana. This blocked the pressure relief valve and pressure gauges. Continued dimerization eventually caused the rail car to exceed its design pressure and violently rupture, sending hot flaming material over a wide area and causing extensive damage to the plant.



Figure 6 – Essroc plant after the accident; #1 indicates pre-accident position of UTLX 643593; #2 indicates location of bulk of tank car after the accident. (Photo courtesy of Logansport Pharos-Tribune newspaper)

CONCLUSION

The investigation of chemical evidence from a fire/explosion scene requires more than a laboratory. Critical decisions on the samples and analysis to be performed along with skilled interpretation of the raw lab data plays an important role in determining causation. Fire and explosion environments often create chemical signatures/byproducts that are unique and not typically seen by most laboratories. Even the preparation of a sample at the microscopic level can have a big outcome in helping to settle a difficult case. Atypical conditions that may have existed in or just prior to a fire/explosion may need to be understood at quite literally the molecular level in order to properly determine causation. As a fire and explosion investigator, especially if there is potentially conflicting information or inconclusive information consider the use of chemical forensics in aiding in your investigation – that decision could be very important in resolving an issue and foxing out hidden evidence.

ABOUT THE AUTHOR

David Gossman has a B.S. and M.S. in Interdisciplinary Physical Science, is a Fellow of the American Institute of Chemists (FAIC) and is a Certified Fire and Explosion Investigator (CFEI). He is President, Gossman Consulting, Inc., President, ChemRight Laboratories, Inc., Chief Investigator, Gossman Forensics (a division of ChemRight Laboratories, Inc.), Owner, Hidden Bluffs Farm and Sole Proprietor, TreeFarmProducts.com. He has been Manager, Cement Kiln Services for Safety Kleen Corp.; Manager, Business Development for McKesson EnviroSystems; and Technical Director for Systech Corp. During his professional scientific career, he developed a large number of the commercially available systems for recycling/reusing industrial wastes. Over the last seventeen years he has provided expert witness and investigation services in matters of fires, explosions, chemical releases, personal injury, enforcement actions and similar issues related to litigation support. Prior to entering the hazardous

waste management field in 1980, he held a faculty position at the Michigan State University Heavy Ion Laboratory where he worked as an instrumentation engineer. He is currently serving on the American Institute of Chemists Editorial Review Board. He is on various committees for ASTM International including: Air Quality; Waste Management; Molecular Spectroscopy and Separation Science; Occupational Health and Safety; and Environmental Assessment, Risk Management and Corrective Action. Over the years David Gossman has been involved in the process of developing, reviewing and approving numerous ASTM standards. He is a member of the American Chemical Society, the American Association for the Advancement of Science, the International Society of Environmental Forensics, the National Fire Protection Association, the National Association of Fire Investigators, the Forensic Expert Witness Association and is an Associate Member of the American Bar Association (ABA)-Section of Environment, Energy & Resources and Section of Tort Trial & Insurance Practice. He is a licensed Private Investigator and is on the Technical Advisory Board of Core Technology Development Group, LLC. He is a named inventor on five patents granted by the US Patent Office.

ENDNOTES

- ¹ Tsuge, Shin, Pyrolysis-GC/MS Book of Synthetic Polymers, Elsevier, New York, (2011).