Alice Delia, Ph.D.
April 2016

Fire VOCs – The New Frontier in Post-Fire Assessments

Introduction

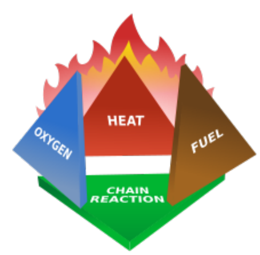
Fire and smoke produce a very complex mixture of chemicals and particulates. The particulate methods now in use do not account for the variability and complexity of fire situations.

More importantly, there aren't any VOC or chemical methods specific to fire situations. Some chemical measurements are made, e.g., for acrolein, but they are not consistent and in the case of acrolein, the value is limited. Acrolein has both high volatility and high reactivity – meaning there will be a high concentration immediately after a fire but it's unlikely to persist for weeks or months as other VOCs will.

Much work has been done to identify both the type and the specific chemical compounds produced in fire and smoke. Numerous studies have focused on identifying the chemical compounds present but have not gone beyond that. Evaluating the presence of these compounds and what that means in terms of the amount of post-fire contamination is the missing component.

There are many more types, or classes, of chemical compounds than particulate matter. The oxidation process and incomplete combustion that are characteristic of fire create an extraordinary variety of chemical products in a state between the original material and the carbon dioxide and water which are the results of complete combustion. In many cases, these intermediate chemical products go on to react with other chemical compounds, further complicating the mixture.

About Fire



Fire is a chemical oxidation process where fuel, heat, and oxygen combine to initiate the fire process and the heat released feeds back into the fuel and oxygen which releases more heat. This creates a chain reaction that sustains the fire until one or more of the components are used up or removed.

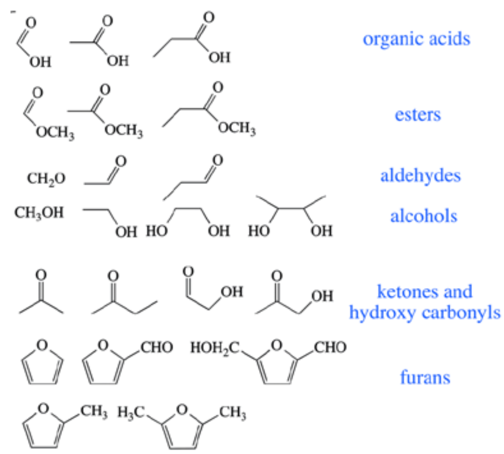
Hundreds of reaction products are created during and after a fire. The soot, char, and ash that make up the particulate portion of these products are the most noticeable. They are responsible for the visual staining so characteristic of fire. However, there are hundreds of chemical compounds released as well. Some dissipate quickly and are not a long-term contamination concern; others can linger for weeks, months, or even years, causing concern about chronic effects and uncertainty regarding the efficacy of the cleanup or remediation process.

Chemical Products of Fire

Every fire is unique, with a combination of different fuel to burn, environmental conditions, fire conditions, etc. So it's not surprising that the byproducts of this complex process are often so inconsistent.

Both fire and the chemical compounds produced go through several stages. Initially, most of the chemical reaction products are present but high concentrations of small reactive compounds are dominant. Most common are carbon monoxide and dioxide, formaldehyde, acrolein, cyanide, and other small molecules. These typically dissipate quickly due to their high reactivity and volatility.

Larger and less reactive compounds, although smaller in concentration, remain over a longer period of time and are the cause of many post-fire complaints. These include almost every chemical class – a lot of oxygenated compounds like aldehydes, esters, acids, and alcohols, aromatics like benzene and heavier compounds like polycyclic aromatic hydrocarbons (PAHs), as well as a range of hydrocarbons created by lower temperature processes or remnants of the original fuel material.



Chemical Class	Examples	
Hydrocarbons	Branched alkanes/alkenes, cyclic alkanes/alkenes	
Aldehydes	Formaldehyde, acetaldehyde, acrolein	
Phenols	Methyl phenols (cresols), Methoxy methyl phenols (creosols)	
Aromatics	Benzene, toluene, xylenes, styrene	
PAHs	Naphthalene, acenaphthylene, phenanthrene	

In addition to the many chemical classes produced during fire, there are other properties that must be considered.

- The specific fuel material, i.e., what burns, primarily determines the distribution of the chemical contamination.
    - Wildfires are characterized by the burning of plant material, or biomass. Although there are many variations in the specific plant material affected, (e.g., trees, grasses, brush, dead or decaying matter, etc.), all share the basic cell structure and the breakdown of

the cell walls, primarily involving cellulose and lignin, produces a chemical mixture with some core similarities.
  - Indoor fires tend to have more variety in the fuel. Although many indoor fires involve wood or other cellulose-based materials, which produce a similar chemical mixture as wildfires, other materials like plastic, synthetic fibers, and building materials contribute as well and sometimes dominate. In these cases the chemical signature can be quite different and may be more difficult to identify.
- Specific fire conditions can shift the distribution of the chemical products by changing the heat and oxygen characteristics. For example, a lower temperature fire is likely to produce a lot more smoke than a higher temperature fire. Also, the lower temperature fire does not provide as much energy for chemical reactions, leading to a mixture that looks a lot more like the initial fuel materials than the more fully oxidized reaction products.
- Environmental conditions have a big effect on how long post-fire contamination remains. As ventilation increases the chemical concentration in the air decreases, essentially diluting the concentration. Temperature and humidity have an opposite effect where higher temperature and humidity will shift the equilibrium to emission so on warm, humid days the smoky odor may be noticeable whereas it may not be in colder weather.
- The volatility of these chemical compounds is key in understanding the effects they might have. Fundamentally, volatility is a measure of how much of a substance will vaporize – so high volatility means there will be a lot in the air and low volatility means there will be relatively little in the air. Permanent gases, like CO and CO_2, are highly volatile. Heavier volatile organics and semi-volatile organics have increasingly lower concentrations in the air and larger concentrations in liquid or solid form respectively.
- Other sources that contain fire indicator VOCs are a concern and can make it more difficult to determine the exact origin of these VOCs. For example, it's very difficult to differentiate the contributions of a kitchen fire where cabinetry burned from those of a wood burning fireplace in the same home.

These factors and conditions make it impossible to measure all the chemical materials produced from a fire directly, therefore chemical compounds that can be used as a signature of that fire must represent the rest of the chemical compounds produced by the fire that are not measured.

Fire VOC Indicators

Despite the many studies of fire and smoke events, a meaningful chemical profile has not been developed. This is partly due to the large variety of sampling and analysis methods. Certain chemical compounds may be included or excluded from the list of possible compounds because of the limitations of the sampling media and instrument response. However, a more critical factor is the lack of incorporation of “real” data into the fire-specific data. Many of the chemical compounds produced during or after a fire event are common to many other sources and activities and so are not useful in identifying fire-specific contamination.

A thorough understanding of chemical compounds typical of non-fire sources and activities is necessary to evaluate whether a particular VOC would be effective in identifying fire contamination. For example, although formaldehyde would be an excellent short-term fire indicator, other sources such as solid and engineered wood, other building products, decay, personal care and cleaning products, etc. make it impossible to apportion formaldehyde to these diverse sources in a meaningful way.

There are three essential criteria that must be used to evaluate the effectiveness and applicability of any potential fire indicator VOC.

Universality

There really aren’t any truly universal VOC fire indicators. The fuel material and fire conditions vary too widely to use only one VOC fire indicator. Therefore, a panel of fire indicators has a better chance of accurately predicting the presence of fire contamination.

Volatility

In order to be effective, fire VOC indicators must encompass a range of volatilities – from high, i.e., light compounds, such as acrolein, to medium volatility, such as cresols, to low volatility, i.e., heavy compounds, such as polycyclic aromatic hydrocarbons. A range of volatilities is critical to track the dissipation and/or removal of fire contamination. As time goes by, the high to moderate volatility compounds will dissipate, leaving only the lower volatility compounds. However, a relatively fresh or concentrated fire will have a high concentration of the high to moderate volatility compounds relative to the lower volatility compounds.

Detectability

Many technologies are available to measure chemical compounds and each has its own advantages and disadvantages. No matter which technology is selected, it is imperative that the target analytes have good detection properties, e.g., selective, unambiguous, quantifiable. Since many of these chemical compounds may be present at concentrations less than 1 part per billion (ppb), it is also essential that the analytical technique be able to achieve sub-ppb detection limits.

The Fire Panel

With all these factors and restrictions in mind, it's possible to evaluate the extensive data for the best possible indicators. Since the criteria are so restrictive, the chemical compounds are separated into primary and secondary indicators based on their ability to meet the three essential criteria of universality, volatility, and detectability.

Primary

The primary indicators are those that best meet all the essential criteria. There are many more chemical compounds that can provide valuable information about other aspects of fire contamination.

- Cresols (o, m, p)
- Creosol
- Guaicol
- 4-Ethylguaicol
- Acenaphthylene

Secondary

Secondary indicators do not fully meet one or more of the essential criteria but can be used to support fire identification as well as other parameters such as fuel material or projected dissipation profile.

- Acrolein
- Acetonitrile
- Salicaldehyde
- 2-Furaldehyde
- 2,4-Dimethylphenol
- Biphenyl
- Naphthalene
- 2-Methylnaphthalene

Since so many things can affect fire processes and the background environment is typically unknown, at least two Primary indicators should be present to signify the presence of fire residues. The distribution of specific fire VOCs, as well as selected situation-specific VOCs, can provide valuable information about the type of fuel material and the possible effects of post-fire contamination.

References

1. National Fire Protection Association. All About Fire. http://www.nfpa.org/press-room/reporters-guide-to-fire-and-nfpa/all-about-fire (accessed January, 2015).
2. Heitmann, K.,; Wichmann, H.; Bahadir, M.; Gunschera, J.; Schulz, N.; Salthammer, T. Chemical Composition of Burnt Smell Caused by Accidental Fires: Environmental Contaminants. *Chemosphere* **2011,** *82*, 237-243.
3. Heitmann, K.,; Wichmann, H.; Bahadir, M. Chemical Causes of the Typical Burnt Smell After Accidental Fires. *Anal. Bioanal. Chem.* **2009**, *395(6)*, 1853-65.
4. Schauer, J.J.; Kleeman, M.J.; Cass, G.R.; Simoneit, B.R.T. Measurement of Emissions from Air Pollution Sources. 3. C1-C29 Organic Compounds from Fireplace Combustion of Wood. *Environ. Sci. Technol.* **2001**, *35*, 1716-1728.
5. CDC Agency for Toxic Substances and Disease Registry (ATSDR); http://www.atsdr.cdc.gov/ (accessed January, 2014).
6. US EPA Air Toxics. http://www.epa.gov/ttn/atw/ (accessed January, 2014).
7. US Fire Administration. https://www.usfa.fema.gov/data/statistics/ (accessed March 2016).