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ANALYSIS OF WILDFIRE AND STRUCTURE FIRE COMBUSTION RESIDUES

Microscopy Methods and Other Considerations

BY DANIEL M. BAXTER, RUSS CRUTCHER, BRAD KOVAR, AND LARRY WAYNE

The collection of samples as part of a wildfire or structure fire investigation typically has two related goals. The first goal is to determine whether the particle types or concentrations, or the ratio of combustion-generated residues, indicate an atypical impact above background. If analysis shows that the particles and residues are greater than background, the second goal comes into play: to determine whether the impact—defined by the assemblage of particles found—is more likely to be associated with a specific fire event or with a site-specific background condition identified by the investigator.

As described in AIHA's *Technical Guide for Wildfire Impact Assessments for the Occupational and Environmental Health and Safety Professional*, these goals can be achieved only by preserving the in-situ sample integrity of the deposited particles for direct light (optical) microscopical analysis without introducing significant sample alteration or particle loss. The ultimate reliability of analytical results produced by the laboratory depends on the use of sampling and analytical methods that preserve the sampled particles' chemical and physical properties, including their size, morphology, and deposition patterns. It is also vital that the methods do not alter, destroy, or inhibit the detection of the collected combustion particles or residues.

WILDFIRE VS. STRUCTURE FIRE PARTICLES

Wildfires can generate a wide range of vegetative combustion particles and lofted burned soil debris. The particles are generally classified into three generic categories:

- Soot, also called "black carbon," is a fine carbonaceous material with aciniform structure produced during incomplete combustion. The distinguishing features of aciniform morphology are grape-like clusters or open branch-like structures. Although soot is produced in great abundance in a wildfire, it is not a common constituent of settled wildfire residues.
- Wildfire char comprises large, irregular, mostly carbonaceous fragments of burned vegetation from leaves, twigs, and bark.
- Wildfire ash is the decarbonized residue of cellulose material. It typically comprises soluble mineral salts, carbonates, oxides, insoluble plant phytoliths, and noncombustible compounds.

See Figure 1 for images of these materials. More information is available from the *Technical Guide for Wildfire Impact Assessments for the Occupational and Environmental Health and Safety Professional*.

Wildfire smoke damage investigations rely on sampling methods and analytical procedures designed to identify specific characteristics of the primary wildfire particle categories including char and ash. The presence of particles such as burned plant phytoliths and plant structures, burned soil or clays, and other vegetative structures can help identify the type and source of the fire. Based on the analytical experience of the authors of this article, over 95 percent of the burned particles associated with a wildfire range in size from approximately 2 µm to 5,000 µm (5 millimeters). The average size of the wildfire char, ash, and other particles found as infiltrated settled debris indoors ranges from approximately 2 µm to 50 µm.

Wildfire particles and surface depositional patterns can be identified and quantified by collecting surface tape-lift samples of the settled dust and then analyzing the particles with a light microscope equipped with simultaneous reflected light (dark field) and transmitted or polarized light imaging capabilities covering a magnification range of 50x–500x. The primary identification of vegetative char, ash, and other optically opaque particles is obtained by a direct light microscopical examination of their morphological and reflected light surface properties.

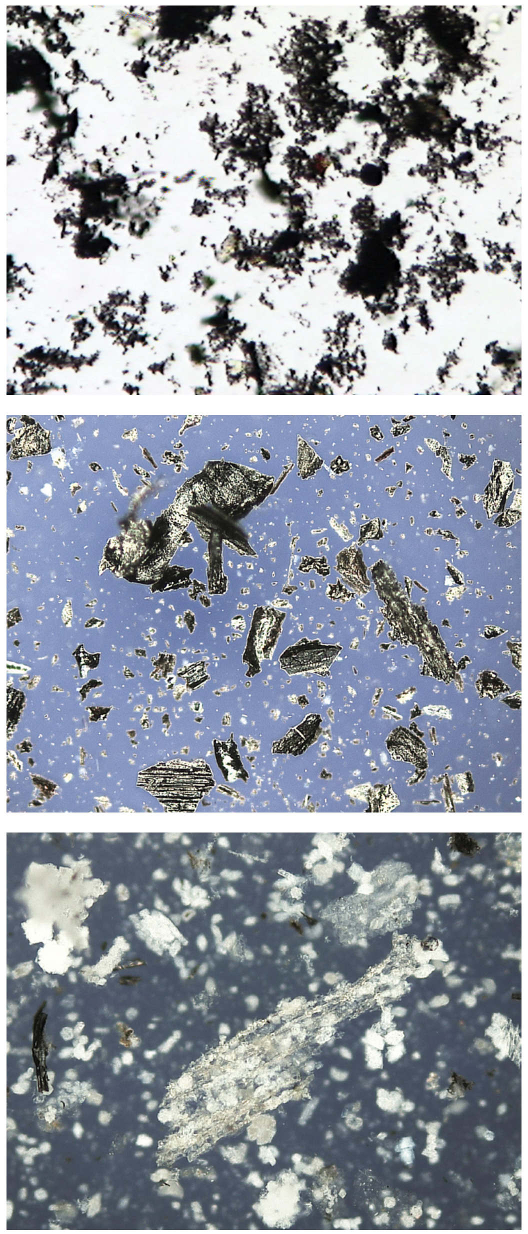

Figure 1. Examples of wildfire particles: soot (top, approximately 600x), char (middle, approximately 200x), and ash (bottom, approximately 400x). Images courtesy of Daniel M. Baxter, Russ Crutcher, Brad Kovar, and Larry Wayne.

Structure fires contain different organic and inorganic fuel sources and can include a mixture of burned construction materials, furniture, cloth, decorative materials, paint, metal corrosion, foodstuffs, cooking oils, and other materials common to the indoor environment. The particle classifications include soot, vegetative and non-vegetative char (from wood, paper, and fabrics), cellulosic ash, melted organic debris, and corrosion (that is, oxidized particles from metals, paint, and so on). The distinction between what would be classified as char or ash in structure fires is more complex than in wildfires. See Figure 2 for examples of particles from structure fires.

Smoldering fires can generate copious amounts of organic compounds that condense as large aciniform soot clusters and—when these compounds come into contact with cooler surfaces such as walls and ceilings—chaining patterns and organic films. These characteristically uniform "indicator" patterns can only be observed when collected on tape-lift samples where the spatial integrity of the sample is preserved. In our experience, the unique settled burned char and ash particles found in structure fires range in size from 1 µm to 5,000 µm. Their depositional patterns, especially for soot condensates, can range from 5 µm to several millimeters. These properties can also be identified by using a combination of tape-lift sampling and a properly equipped light microscope.

ASTM METHOD D6602-13 AND CARBON BLACK

Some investigators and laboratories have mistakenly cited ASTM method D6602-13, *Standard Practice for Sampling and Testing of Possible Carbon Black Fugitive Emissions or Other Environmental Particles, or Both*, as a standard method for the analysis of wildfire and structure fire residues, which it is not. Like other wipe-sampling methods, ASTM D6602-13 has a limited application for wildfire and structure fire investigations because it alters particle deposition and sometimes the particles themselves.

Because of the wide range of fuel sources, temperatures, and oxygen availability found in wildfires and structure fires, the resulting combustion particles and organic condensates are complex mixtures of particles from materials fully and partially combusted that can contain a wide range of physical, morphological, and chemical properties. Many of these particles are mechanically fragile, soluble, or altered by the use of wipes, as noted in ASTM 6602 section 7.3.2. The procedures used to recover the residues from the wipe, and exposure to vacuum and heating by the electron beams used in analyses performed by transmission electron microscopy (TEM) or scanning electron microscopy (SEM), further damage or remove many of the particles required to identify a wildfire or structural fire source, as noted in ASTM D6602-13 section 4.1.

In addition, ASTM D6602-13 is intended only "for distinguishing ASTM type carbon black, in the N100 to N900 series, from other environmental particulates," as stated in section 1.1. Carbon black—the common name for several types of manufactured, amorphous carbon products mainly used as filler in tires, plastics, paints, inks, and as a color pigment—is very different from particles generated during wildfires and structure fires.

The residues generated during structure fires and wildfires can contain high concentrations of soluble minerals in addition to both volatile and soluble organic compounds not found in manufactured carbon black. The particles of burned materials and organically derived aggregates found in these fires are significantly larger (5–1,000 µm) than carbon black particles and can easily be altered or destroyed by using the sample collection, sample preparation, or analytical procedures prescribed by the ASTM D6602-13 method.

Section 1.2 of ASTM D6602-13 stresses the importance of proficiency in the identification of carbon black but states that only a "general knowledge" of other environmental particles is necessary. Further, section 4.2 states that "use of the [polarized light microscopy] analysis is not mandatory when the [transmission electron microscopy] analysis finds no aciniform aggregates resembling carbon black." The only technical reference mentioned in ASTM D6602-13 is *Carbon Black: Science and Technology* edited by Jean-Baptiste Donnet, and this book addresses only carbon black. How the light microscope is used to identify particle sources is not mentioned or alluded to in ASTM D6602-13, which is designed to analyze the disaggregated aciniform morphology of the sub-micron (1-300 ηm) manufactured primary carbon black particles (also called nodules) using TEM.

The identifying properties of combustion particle residues can include their concentration, assemblage distribution, and deposition patterns found on sampled surfaces. The amounts of soluble and semi-volatile organic compounds and of inorganic chemical residues are also instrumental in the formation of recognizable surface depositional patterns, especially in structure fires. These combined properties are critical to determine the extent of potential contamination, characterize the source of the combusted material, and interpret the extent of exposure. The use of wipes in ASTM 6602-13 alters, destroys, or removes these patterns entirely. For manufactured carbon black, the unstable impurities and organic compounds from well-defined fuels are removed through heating during the manufacturing process.

As described in a 2013 paper in *Environmental Pollution*, carbon black products are typically manufactured in reduced oxygen environments at controlled temperatures above 2,400 F, which results in very high concentrations of inert elemental carbon. During the manufacturing process, carbon black forms para-crystalline carbon with a high surface-area-to-volume ratio containing negligible polycyclic aromatic hydrocarbons (PAHs). This makes the individual particles more well-defined and highly inert—and dissimilar to the wide range and composition of organically derived soot condensates and char particles that are generated at uncontrolled lower temperatures (400 to 2,000 F) commonly found in wildfires and structure fires. Although both carbon black and soot have aciniform morphology, they are physically and chemically distinct substances, as demonstrated by a 2001 paper in the *AIHA Journal*.

Figure 2. Examples of structure fire particles: soot chaining patterns (top, approximately 600x); cardboard char (middle, approximately 200x), and melted wire insulation debris (bottom, approximately 200x). Images courtesy of Daniel M. Baxter, Russ Crutcher, Brad Kovar, and Larry Wayne.

Table 1. Characteristics of Carbon Black Manufacturing

Chemical Process	Manufacturing Method	Main Raw Materials
Thermal-oxidative decomposition	Furnace black process	Aromatic oils natural gas
	Degussa gas black process	Coal tar distillates
	Lamp black process	Aromatic oils or mineral oil
Thermal decomposition	Thermal black process	Natural gas (or mineral oils)
	Acetylene black process	Acetylene

Sources: **bit.ly/epcarbonblack** and **bit.ly/carbonblackoec** (PDF).

Table 1, summarized from information in the 2013 *Environmental Pollution* paper and in a 2015 resource published by Orion Engineered Carbons, characterizes some of the processes used to manufacture carbon black.

THOROUGH, ACCURATE ANALYSIS

The analysis of wildfire and structure fire residues is reliably performed using a combination of direct (tape-lift) sampling and specific light microscopy methods. The ASTM D6602-13 TEM method and wipe sampling procedures were specifically developed for the collection and analysis of the primary sub-micron nodules associated with carbon black, a manufactured material produced under highly controlled conditions. In addition to differences in how they are produced, carbon black and products of uncontrolled combustion are distinctly different in their structure and morphology, concentration of organic compounds, and response to solvents and thermal treatment. Therefore, using the ASTM D6602-13 method for the evaluation of other types of combustion particles is fraught with physical and chemical limitations that can result in both their under-reporting and non-detection. The ASTM wipe sampling and analysis methodologies do not result in a reliable analysis of wildfire or structural fire debris. They destroy or remove the larger, fragile combustion particles and depositional patterns associated with a wildfire or structure fire event.

Electron microscopy (TEM and SEM) analyses cannot be directly compared with the quantitative estimates obtained by light microscopy analysis. Electron microscopy and energy dispersive X-ray analysis (EDS) may be useful as a secondary tool to differentiate or confirm the composition of resilient particles that may interfere with the identification of the very small char or ash combustion particles observed during the light microscopy analysis.

There are well established procedures for using a light microscope (equipped with reflected and transmitted light, bright field, dark field, and polarized light capability) to accurately analyze the optical properties of combustion particles that are characteristic of a wildfire or structure fire. A thorough analysis must include a simultaneous examination of all reflected and transmitted light properties of combustion particles and their characteristic deposition patterns. The presence or absence of specific indicator or signature particles characteristic of the type of fire can also help confirm the source or origin of the fire. A transmitted polarized light microscope typically used for asbestos analysis does not provide sufficient information for this purpose. The appropriate use and limitations of these procedures are described in the *Technical Guide for Wildfire Impact Assessments for the Occupational and Environmental Health and Safety Professional*. Combustion particle analysis can be provided directly from tape-lift samples. The combined use of tape-lift sampling and light microscopy is the preferred combustion particle analysis procedure prescribed by the AIHA *Technical Guide* and is the current industry-accepted methodology. ❺

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RESOURCES

AIHA: *Technical Guide for Wildfire Impact Assessments for the Occupational and Environmental Health and Safety Professional* (April 2018).

AIHA Journal: "Carbon Black and Soot: Two Different Substances" (March 2001).

Air Pollution Control Association: "Light Microscopy as an Analytical Approach to Receptor Modeling" in *Receptor Models Applied to Contemporary Pollution Problems* (1983).

ASTM International: Method D6602-13(2018), *Standard Practice for Sampling and Testing of Possible Carbon Black Fugitive Emissions or Other Environmental Particulate, or Both* (2018).

Environmental Pollution: "Carbon Black vs. Black Carbon and Other Airborne Materials Containing Elemental Carbon: Physical and Chemical Distinctions," **bit.ly/epcarbonblack** (October 2013).

Marcel Dekker Inc.: *Carbon Black: Science and Technology* (1993).

The Microscope: "Thermally Modified Calcium Oxalate Phytoliths as Markers for Biomass Fire Sources" (2020).

Orion Engineered Carbons: "What Is Carbon Black?" **bit.ly/carbonblackoec** (PDF, 2015).

The Synergist: "The ABC's of Wildfire Residue Contamination Testing: Post Fire Assessments of the Indoor Environment, **bit.ly/syn1117wildfire** (November 2017).

Wiley: "Sampling of Surface Dust in Buildings" in *Indoor Environment: Airborne Particles and Settled Dust* (2003).

Wiley Blackwell: *Fire on Earth: An Introduction* (2014).