THE LIMITATIONS OF USING THE ASTM 6602-13 METHOD FOR THE ANALYSIS OF WILDFIRE AND STRUCTURE FIRE RESIDUES

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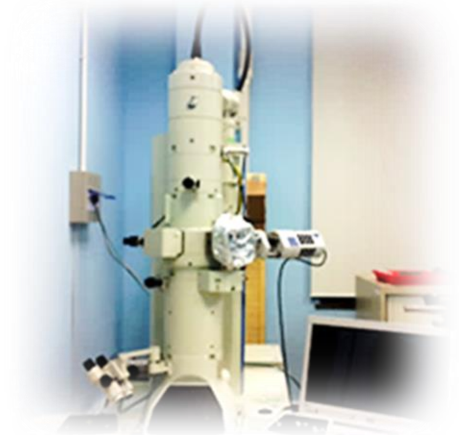

THE LIMITATIONS OF USING THE ASTM 6602-13 METHOD FOR THE ANALYSIS OF WILDFIRE AND STRUCTURE FIRE RESIDUES

Daniel M. Baxter, Environmental Analysis Associates, Inc.

1.0 INTRODUCTION

This white paper clarifies the appropriate use and limitations of the ASTM D6602-13 "*Standard Practice for Sampling and Testing of Possible Carbon Black Fugitive Emissions or Other Environmental Particulate, or Both*[1]". It addresses the limitations of using the ASTM method as a procedure for the analysis of combustion residues generated by wildfires and structure fires. A general explanation of how the sample collection and preparation methods impact the reliability of Optical or Electron Microscopy analysis of wildfire and structure fire residues is explained in an Environmental Analysis Associates, Inc. White Paper entitled **"***The Analysis of Fire Residue Particles Using Optical Microscopy – An Overview of Method Advantages, Limitation, and Fire-related Particle Terminology*[3]".

The ASTM 6602-13 method was specifically designed to analyze the disaggregated <u>aciniform morphology of the individual sub-micron carbon black particles.</u> The Method clearly states on the first page "*Section 1. Scope, 1.1 This practice covers sampling and testing for distinguishing ASTM type carbon black, in the N100 to N900 series, from other environmental particulates".* Carbon black is a manufactured material designed to have a specific size range, specific surface area, and inert chemical properties that specifically excludes the presence of non-resilient particles and residual organic compounds and PAH's. Non-resilient particles are defined in this paper as the partially burned materials that become physically fragile, semi-volatile, and/or semi-soluble and are altered or destroyed by the sample collection method, laboratory sample preparation, and/or analysis procedures. Resilient particles are combustion materials that will not be significantly altered in their physical, chemical, or morphological composition by the sample preparation or analysis method.

The ASTM TEM preparation and analysis procedures work well together for the analysis of manufactured carbon black. The procedures remove or reduce the presence of non-resilient or non-carbon black soot particles with similar morphology as they are considered unwanted contaminant or interferences to the methods' specific goal of determining the presence or absence of carbon black. The advantages of the Method for the detection of carbon black directly limit its' usefulness when applied to the analysis of other non-engineered combustion particles. These limitations have caused significant confusion and misuse of the method for other purposes (such as the detection of wildfire and structure fire residues). This white paper summarizes the sections of the ASTM sample preparation and analysis procedures that clearly define the applicability of the ASTM method is for the analysis of "resilient" (or non-brittle) end-product particles that have negligible residual organics, and are both non-volatile and non-soluble. As a result, using the ASTM 6602 method (especially the wipe sampling, and solvent preparation procedures) to assess the lower temperature and uncontrolled residues found in wildfires and structure fires will produce inherently unreliable results.

2.0 THE CHEMISTRY OF MANUFACTURED CARBON BLACK

Carbon black, lamp black, and thermal black is produced by a controlled reaction of a hydrocarbon fuel such as oil, coal, vegetative matter, or gas with a limited supply of combustion air at temperatures ranging from 2,400 to 2,800°F[7]. These controlled processes increase the surface area, reduce the particle size, and remove unwanted residual organic compounds making the material usable for various manufacturing applications. "*The terms carbon black and soot have often been used interchangeably despite the fact that soot by definition is an undesired byproduct of incomplete combustion of fossil fuels and biomass. Watson and Valberg (2001) demonstrated that CB and soot are physically and chemically distinct substances*[9]*"*. The differences between the physical and chemical properties of carbon black, other fugitive emission sources, including biomass burning representative of wildfire residues are summarized below in Table 2[9].

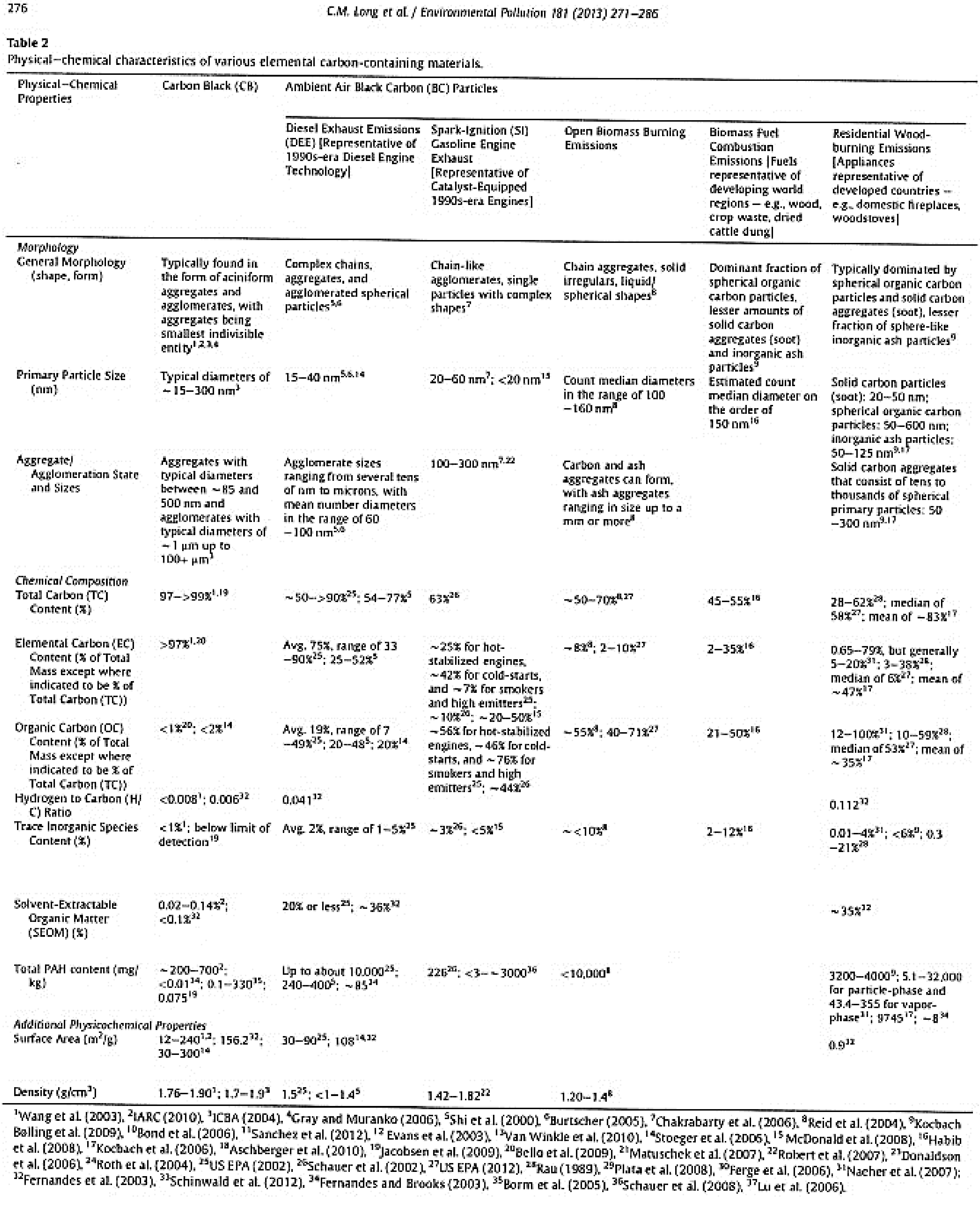

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Table 2
Physical–chemical characteristics of various elemental carbon-containing materials.

Physical–Chemical Properties	Carbon Black (CB)	Ambient Air Black Carbon (BC) Particles				
		Diesel Exhaust Emissions (DEE) [Representative of 1990s-era Diesel Engine Technology]	Spark-Ignition (SI) Gasoline Engine Exhaust [Representative of Catalyst-Equipped 1990s-era Engines]	Open Biomass Burning Emissions	Biomass Fuel Combustion Emissions [Fuels representative of developing world regions – e.g., wood, crop waste, dried cattle dung]	Residential Wood-burning Emissions [Appliances representative of developed countries – e.g., domestic fireplaces, woodstoves]
Morphology						
General Morphology (shape, form)	Typically found in the form of aciniform aggregates and agglomerates, with aggregates being smallest indivisible entity[1,2,3,4]	Complex chains, aggregates, and agglomerated spherical particles[5,6]	Chain-like agglomerates, single particles with complex shapes[7]	Chain aggregates, solid irregulars, liquid/spherical shapes[8]	Dominant fraction of spherical organic carbon particles, lesser amounts of solid carbon aggregates (soot) and inorganic ash particles[9]	Typically dominated by spherical organic carbon particles and solid carbon aggregates (soot), lesser fraction of sphere-like inorganic ash particles[9]
Primary Particle Size (nm)	Typical diameters of ~15–300 nm[3]	15–40 nm[5,6,14]	20–60 nm[7]; <20 nm[15]	Count median diameters in the range of 100–160 nm[8]	Estimated count median diameter on the order of 150 nm[16]	Solid carbon particles (soot): 20–50 nm; spherical organic carbon particles: 50–600 nm; inorganic ash particles: 50–125 nm[9,17]
Aggregate/Agglomeration State and Sizes	Aggregates with typical diameters between ~85 and 500 nm and agglomerates with typical diameters of ~1 µm up to 100+ µm[3]	Agglomerate sizes ranging from several tens of nm to microns, with mean number diameters in the range of 60–100 nm[5,6]	100–300 nm[7,22]	Carbon and ash aggregates can form, with ash aggregates ranging in size up to a mm or more[8]		Solid carbon aggregates that consist of tens to thousands of spherical primary particles: 50–300 nm[9,17]
Chemical Composition						
Total Carbon (TC) Content (%)	97–>99%[1,19]	~50–>90%[25]; 54–77%[5]	63%[26]	~50–70%[8,27]	45–55%[16]	28–62%[28]; median of 58%[27]; mean of ~83%[17]
Elemental Carbon (EC) Content (% of Total Mass except where indicated to be % of Total Carbon (TC))	>97%[1,20]	Avg. 75%, range of 33–90%[25]; 25–52%[5]	~25% for hot-stabilized engines, ~42% for cold-starts, and ~7% for smokers and high emitters[25]; ~10%[26]; ~20–50%[15]	~8%[8]; 2–10%[27]	2–35%[16]	0.65–79%, but generally 5–20%[31]; 3–38%[28]; median of 6%[27]; mean of ~47%[17]
Organic Carbon (OC) Content (% of Total Mass except where indicated to be % of Total Carbon (TC))	<1%[20]; <2%[14]	Avg. 19%, range of 7–49%[25]; 20–48[5]; 20%[14]	~56% for hot-stabilized engines, ~46% for cold-starts, and ~76% for smokers and high emitters[25]; ~44%[26]	~55%[8]; 40–71%[27]	21–50%[16]	12–100%[31]; 10–59%[28]; median of 53%[27]; mean of ~35%[17]
Hydrogen to Carbon (H/C) Ratio	<0.008[1]; 0.006[32]	0.041[32]				0.112[32]
Trace Inorganic Species Content (%)	<1%[1]; below limit of detection[19]	Avg. 2%, range of 1–5%[25]	~3%[26]; <5%[15]	~<10%[8]	2–12%[16]	0.01–4%[31]; <6%[9]; 0.3–21%[28]
Solvent-Extractable Organic Matter (SEOM) (%)	0.02–0.14%[2]; <0.1%[32]	20% or less[25]; ~36%[32]				~35%[32]
Total PAH content (mg/kg)	~200–700[2]; <0.01[34]; 0.1–330[35]; 0.075[19]	Up to about 10,000[25]; 240–400[6]; ~85[34]	226[26]; <3–~3000[36]	<10,000[8]		3200–4000[9]; 5.1–32,000 for particle-phase and 43.4–355 for vapor-phase[31]; 9745[17]; ~8[34]
Additional Physicochemical Properties						
Surface Area (m²/g)	12–240[1,2]; 156.2[32]; 30–300[34]	30–90[25]; 108[14,32]				0.9[32]
Density (g/cm³)	1.76–1.90[1]; 1.7–1.9[3]	1.5[25]; <1–1.4[5]	1.42–1.82[22]	1.20–1.4[6]		

[1]Wang et al. (2003), [2]IARC (2010), [3]ICBA (2004), [4]Gray and Muranko (2006), [5]Shi et al. (2000), [6]Burtscher (2005), [7]Chakrabarty et al. (2006), [8]Reid et al. (2004), [9]Kocbach Bølling et al. (2009), [10]Bond et al. (2006), [11]Sanchez et al. (2012), [12] Evans et al. (2003), [13]Van Winkle et al. (2010), [14]Stoeger et al. (2006), [15] McDonald et al. (2008), [16]Habib et al. (2008), [17]Kocbach et al. (2006), [18]Aschberger et al. (2010), [19]Jacobsen et al. (2009), [20]Bello et al. (2009), [21]Matuschek et al. (2007), [22]Robert et al. (2007), [23]Donaldson et al. (2006), [24]Roth et al. (2004), [25]US EPA (2002), [26]Schauer et al. (2002), [27]US EPA (2012), [28]Rau (1989), [29]Plata et al. (2008), [30]Ferge et al. (2006), [31]Nacher et al. (2007); [32]Fernandes et al. (2003), [33]Schinwald et al. (2012), [34]Fernandes and Brooks (2003), [35]Borm et al. (2005), [36]Schauer et al. (2008), [37]Lu et al. (2006).

The differences between carbon black, open biomass burning particles (consistent with wildfire particles), and “traditional” diesel exhaust particulate are illustrated in Figure 4 below[9].

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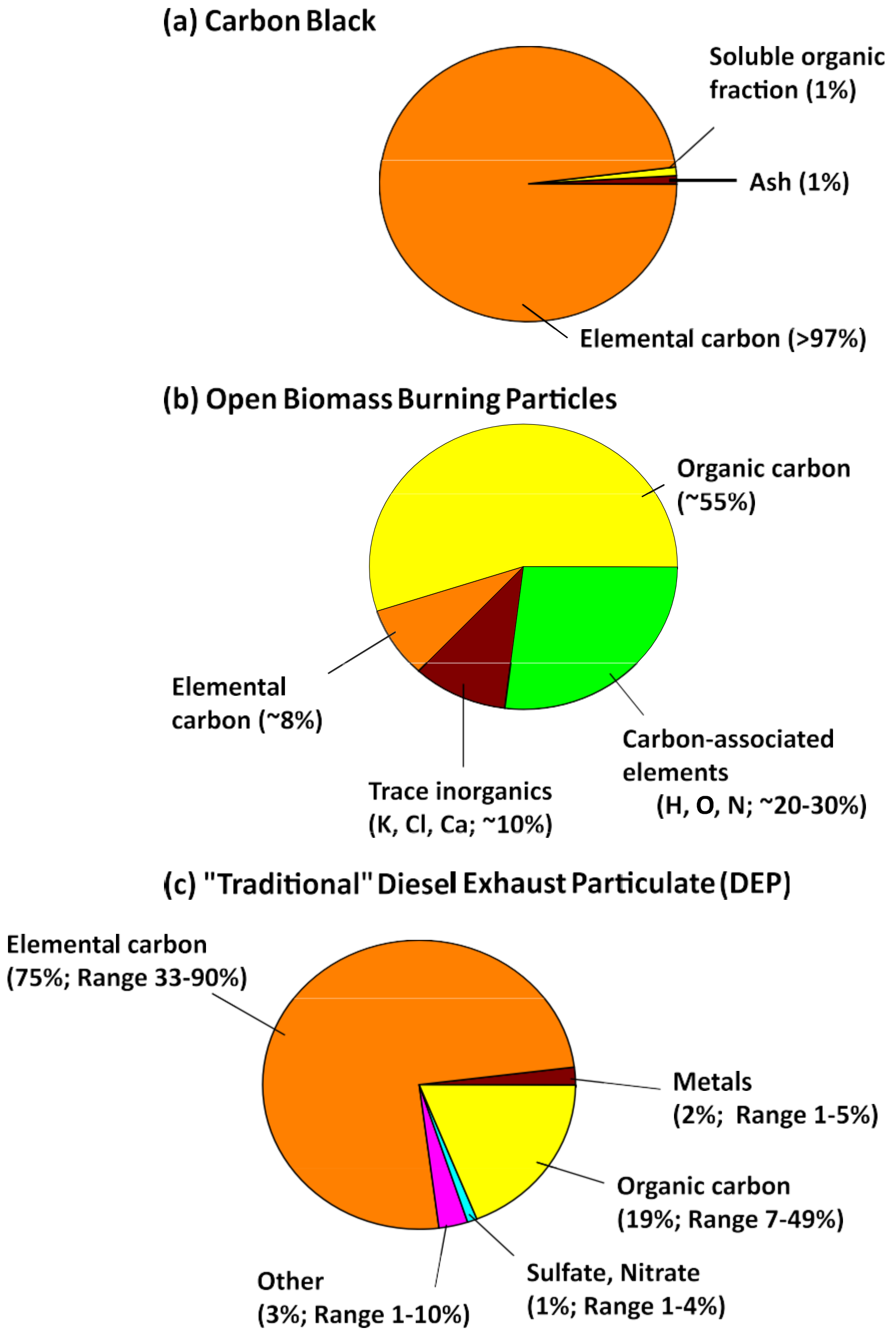


Fig. 4. Comparison of chemical composition among different elemental carbon-containing particles. Elemental carbon-containing particles include (a) carbon black (data from Watson and Valberg, 2001) and two dominant forms of black carbon or “soot”, namely (b) particulate emissions from open biomass burning (data from Reid et al., 2004) and (c) “traditional” diesel exhaust particulate representative of 1990s-era diesel engine technologies (data from US EPA, 2002).

Carbon black is “produced” at high temperatures above 2,400^{o}F and is dissimilar to the wide range and composition of soot condensates and char particles that are generated at uncontrolled lower temperatures (400 to 2,000^{o}F) commonly found in wildfires and structure fires. Carbon black and diesel emissions are primarily composed of elemental carbon (>75% and >97% respectively), while open biomass burning particles contain very low concentrations of elemental carbon (~8%) and are primarily “organic” carbon with different volatility and solubility characteristics. Carbon black is mainly used as fillers in tires, plastics, paints, and inks; and as a color pigment. There are various processes used for the manufacture of carbon black including but limited to the following:

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

Carbon black is dissimilar to "soot" as it is manufactured to form para-crystalline carbon with a high surface-area-to-volume ratio containing negligible polycyclic aromatic hydrocarbon (PAH) content. This makes the individual particles a more well-defined highly resilient end product.

3.0 THE CHEMISTRY OF WILDFIRE AND STRUCTURE FIRE RESIDUES

Because of the wide range of fuel and temperatures found in wildfires and structure fires, the resulting combustion particles and condensates are complex mixtures of fully combusted (burned) particles, partially burned non-resilient particles containing a range of soluble and semi-volatile organic compounds, and unburned particles.

Wildfire Particles

Wildfires generate a wide range of vegetative combustion particles and lofted soil debris. The particles are generally classified as three main categories defined as soot, char, and ash. The "soot" particles are typically condensate particles from the organic fuels that are blown off in the crown of a wildfire. They are not a common constituent of the settled and infiltrated wildfire residues unless the structure is relatively close to the burn zone. The burned vegetation from a wildfire can be characterized by the char and ash particles, and specific identifiable indicator or signature particles such as the types of plant phytoliths, plant structures, burned soil / clays, burned pollen grains, plant trichomes, and other vegetative structures. The majority of these particles can be identified and quantified by using a properly equipped Optical Microscope with simultaneous reflected light (dark field) and transmitted / polarized light imaging capabilities covering a range of 50x - 500x. A transmitted Polarized Light Microscope (PLM) used by itself is inadequate for combustion particle analysis.

Structure Fire Particles

Structure fires contain a mixture of cellulose and construction materials, melted plastics, oils, and synthetic fibers. The lower temperatures in smoldering fires typically generate copious amounts of organic compounds that condense on the cooler interior surfaces forming characteristic aciniform "soot" clusters and chaining patterns; as well as organic film deposits. These characteristically uniform "indicator" patterns can only be observed when collected on tape-lift samples where the spatial integrity of the sample is preserved. The burned char and ash particles found in structure fires can also be characterized by recognizable indicator or signature particles that can include burned or melted plastics, paper, construction materials, corrosion, and paint. Again, the majority of these particles and their depositional patterns can be identified by using a properly equipped Optical Microscope.

Because an unknown percentage of fire-related particles contain non-resilient (i.e. fragile, brittle, soluble, and semi-volatile compounds with an unstable particle morphology), the sampling, sample preparation, and analysis methods suggested in the ASTM 6602 Method may alter, destroy, or remove them entirely from the sample. The ASTM Method requires significant physical and chemical manipulation procedures that were specifically designed to selectively only retain and concentrate the fine resilient particles consistent with carbon black. The Method was never intended for the analysis of the wide range of other non-resilient particles found in oxygenated lower temperature fires.

4.0 EXCERPTS FROM THE ASTM 6602-13 METHOD

The appropriate use of the ASTM 6602-13 Method is described in numerous sections of the document. The following excerpts clearly show the Method is specifically intended for the analysis of *carbon black*, and differentiating carbon black *from other environmental particulates*. The Method does not cover or even address the comprehensive Optical Microscopy identification requirements for the analysis of wildfire or structure fire particles. The Optical portion of the ASTM method is only *"a screening test method that provides an overview of the bulk composition of the sample through examination under a light microscope*". The method only provides examples of sample analysis performed using low power stereo reflected light microscopy and transmitted light Bright Field and Polarized Light Microscopy (PLM) prepared in refractive index oil 1.550, a procedure typically used for the analysis of asbestos and other crystalline minerals. Because the method is designed for the analysis carbon black, it does not address the accepted analysis protocols for the analysis of soot, char, or ash found in wildfires or structure fires. These methods rely on the accepted use of high power (100-500x) reflected light dark field microscopy (in addition to PLM analysis using transmitted light) as prescribed by other methods such as the 2018 "*AIHA Technical Guide For Wildfire Impact Assessments*[4]".

Section 1. Scope

Section 1.1 Page 1, line 2 — *This practice covers sampling and testing for distinguishing ASTM type carbon black, in the N1000 to N900 series, from other environmental particulates.*

Section 1.2 Page 1, line 1 — *This practice requires some degree of expertise on the part of the microscopist. For this reason, the microscopist must have adequate training and on-the-job experience in identifying the morphological parameters of carbon black and general knowledge of other particles that may be found in the environment.*

Comment: It requires more than *"general knowledge of other particles"* to identify wildfire or structure fire particles.

Section 2. Reference Documents

Section 2 Page 1, line 3	D1619 *Test Methods for Carbon Black – Sulfur Content*
Section 2 Page 1, line 4	*D3053 Terminology Relating to Carbon Black*
Section 2 Page 1, line 5	*D3849 Test Method for Carbon Black – Morphological Characterization of Carbon Black Using Electron Microscopy*

Comment: All reference methods refer to the analysis of carbon black and not other fire combustion particles.

Section 3. Terminology

Section 3.1.5 Page 2, line 3 — *char – a particulate larger than 1um made by the incomplete combustion which may deagglomerate or disperse by ordinary techniques, may contain material which is not black, and may contain some of the original materials' cell structure, minerals,* *ash, cinders, and so forth.*

Comment: This definition is clearly aimed at the differentiation of fine carbon black after being dispersed and broken up in a liquid and not the actual identification of the source material as deposited on the surface. Settled char particles infiltrating into buildings from wildfires and structure fires typically range in size from 5µm to 5,000µm.

Section 3.1.3 Page 1, line 18

carbon black, - an engineered material, primarily composed of elemental carbon, obtained from the partial combustion or thermal decomposition of hydrocarbons, existing in the form of aggregates of aciniform morphology which are composed of spheroidal primary particles characterized by uniformity of primary particle sizes within a given aggregate and turbostratic layering within the primary particles.

Section 3.1.12 Page 2, line 1

Soot – a submicron black powder generally produced as an unwanted by-product of combustion or pyrolysis. It consists of various quantities of carbonaceous and inorganic solids in conjunction with adsorbed and occluded organic tars and resin.

Comment: The ASTM Method clearly states that *soot* is different than *carbon black*. The *soot, unwanted by-products,* and the important in situ depositional characteristics associated with wildfire or structure fire particle condensates are destroyed when using the ASTM sample preparation methods that prescribe the use of wipe sampling, solvent disaggregation, ultrasonication, and include the low vacuum and sample heating encountered when performing Electron Microscopy. The presence of soot particles associated with a wildfire or structure fire **event,** cannot be differentiated from fugitive emission particles based solely on their sub-micron micro-structure of the primary particle or "nodule" alone. It requires the microscopic observation of the larger in situ spatial and depositional "condensed" patterns of aciniform clusters and chains (5µm to 500+µm). These agglomerate and aggregate patterns are illustrated in Fig 3[9].

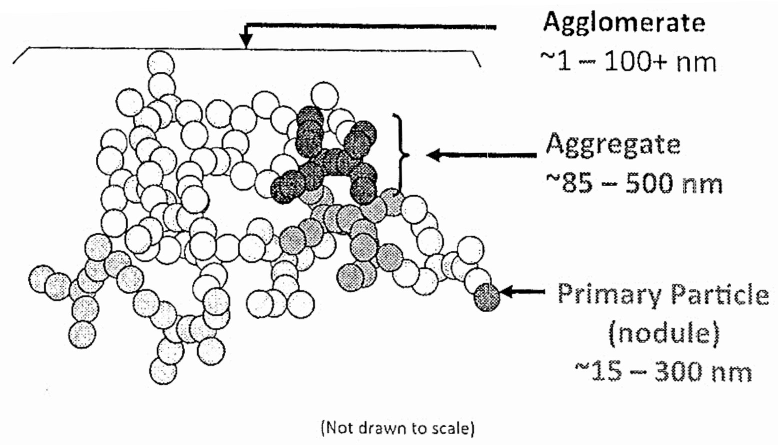
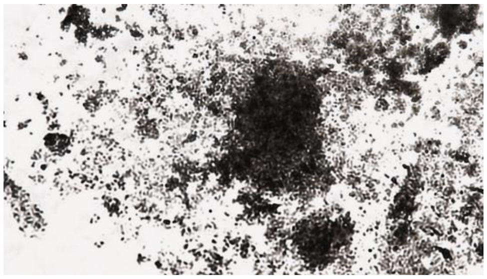
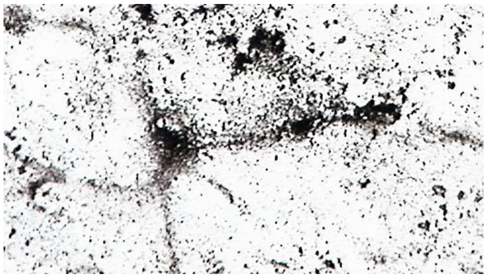


Fig. 3. Structure of carbon black. (Adapted with permission from Gray and Muranko (2006). Copyright 2006 Lippincott Williams & Wilkins, Inc.) Size ranges represent approximate diameters of typical CB structural entities, as reported in ICBA (2004).

These patterns can be observed with a direct examination of the impacted surface, or tape lift samples collected directly from the surface. Examples of agglomerated soot clusters and chaining patterns deposited during a structure fire are shown below:


Structure fire inter-related soot cluster patterns ~ 600x


Structure fire chaining patterns ~ 600x

Section 3.1.12.1 Page 1, line 1

Discussion – .... Soot may have several carbon morphologies. Examples of soot are carbon residues from diesel and gasoline engines, industrial flares, sludge pits, burning tires, and so forth.

Comment: There is no mention of wildfire or structure fire residues as a part of carbon soot residue analysis in this method. Only "fugitive" emissions are discussed.

Section 4. Summary of Practice

Section 4.1 Page 2, Line 2

"This practice describes the procedures and protocols to follow in order to collect fugitive emission/environmental samples and identify the classes of particulate present including materials consistent or inconsistent with manufactured carbon black (referred to simply as carbon black)."

Section 4.1 Page 2, Line 9

"*However, PLM analysis cannot differentiate between carbon black and soots (black carbons) that may come from sources in the environment.*

Comment: This caution clearly states that PLM analysis by itself (and as collected and prepared using the ASTM Method) cannot be used to differentiate soot from carbon black or other environment sources. This statement is true because the ASTM Method is based on the analysis of the primary sub-micron particles or "nodules", and was never intended to analyze the in situ depositional patterns of larger (5-500+µm) soot aggregates that are characteristic of wildfires or structure fires.

Section 4.1 Page 2, Line 14

"Because the preparation steps for the TEM analysis eliminates certain types of particles and concentrations only the fine (small) particles from the sample, The TEM analysis alone cannot be used to estimate the amount of carbon black or other type in the whole sample".

Comment: This caution clearly states that the TEM analysis method selectively *eliminates certain types of particles,* and concentrates the remaining fine particles that may be consistent with carbon black. It also states that this preparation method precludes the ability of the method to quantify the amount of carbon black, or any other constituent in the sample.

Section 4.2 Page 2, Line 5

The TEM analysis is critical in determining if the collected sample is consistent or inconsistent with carbon black. Use of the TEM analysis is mandatory in determining whether a sample is positive for carbon black.

Comment: This caution clearly states that the TEM analysis method is mandatory for the positive confirmation or identification of carbon black. The Method does not state that TEM analysis is mandatory for the confirmation of other *soot* or combustion by-products.

Section 5. Significance and Use

Section 5.1 Page 2, Line 6

Soot is formed as an unwanted by-product of composition and consequently varies widely with the type of fuel and combustion conditions. Carbon black on the other hand, is purposely produced under a controlled set of conditions. Therefore, it is important to be able to distinguish carbon black from soot, as well as other environmental contaminations.

Comment: This definition clearly states that the intended "use" of the method is to differentiate *carbon black* (if present) from the presence of other environmental *soot* particles.

Section 7. Examination by Light Microscopy

Section 7.1 Page 3, Line 2

Summary of Test Method – This method is screening test method that provides an overview of the bulk composition of the sample through examination under a light microscope. This portion of the method is mandatory except in cases where the TEM examination gives no positive results for aciniform aggregates resembling carbon black…..

Comment: This portion of the method is contradictory and confusing. If Light Microscopy is a *screening test that provides an overview*, why would it only be *mandatory* if the primary (confirmatory) TEM method is negative and *gives no positive results for aciniform aggregates resembling carbon black*? This statement implies that the TEM analysis is performed before the initial optical screening examination. This statement is further confused by the next except shown below.

Section 7.1 Page 4, Line 7

It is important to note that the results obtained by the light microscopy technique cannot be considered as conclusive for identifying the presence of carbon black.

Comment: The ASTM Optical Microscopy section shows the method is designed to screen the sample for aciniform aggregates resembling carbon black only. However, why perform optical microscopy at all if the confirmatory test for carbon black requires TEM?

Section 7.2 Apparatus

Section 7.2.1 Page 4, Line 1

Light Stereomicroscope, capable of at least 40x magnification.

Section 7.2.2 Page 4, Line 1

Polarized Light Microscope, equipped with objectives at least in the 10 to 40x range of magnification.

Section 7.3.2 Page 4, Line 1

Inspect the tape-lift sample with a polarized light microscope using ***both transmitted and reflected light.***

Section 7.3.3 Page 4, Line 1

Inspect the wipe sample with a stereobinocular microscope.

Section 7.3.4 Page 4, Line 1

Place the glass slide sample on a polarized light microscope and examine with transmitted (both direct and with cross polars) ***and reflected light.***

Comment: The Apparatus and Procedure Sections are confusing and contradictory regarding the optical microscopic capability required for the analysis. Section 7.2 (Apparatus) states in Section 7.2.1 the use of a "*Light Stereomicroscope, capable of at least 40x magnification*", and the use in Section 7.2.2 of a "*Polarized Light Microscope, equipped with objectives at least in the 10 to 40x range of magnification*". This is different than what is stated in Section 7.3.2 where the method specifies a PLM microscope equipped with both transmitted and reflected light capabilities. This capability requires a combined or dual source high power microscope with both transmitted and reflected light sources, and objective lenses capable of both transmitted and reflected light imaging. This same contradictory information is present in Sections 7.3.3 and 7.3.4 for the examination of wipe samples using the stereo-binocular microscope (7.3.3) and examination by PLM using both transmitted and reflected light (7.3.4). Based Section 7.3.4, page 5, line 11 below, any reference to the use of reflected light likely refers to the use of a low power stereo-binocular bright field microscope.

Section 7.3.2 Page 4, Line 8 — *The tape lift generally preserves the integrity of particle aggregates without smearing that tends to occur when using the wipe sampler.*

Comment: This section confirms that when the spatial integrity of particles is important, the tape lift sampling procedure is better suited than wipe sampling.

Section 7.3.4 Page 5, Line 11 — *"It is helpful to observe the sample using different lighting conditions, that is, top, bottom, and side lighting. This inspection is performed in order to ascertain if carbon black, other black particles, and nonblack particles are present."*

Comment: Again, another confusing section on Optical Microscopy. This language and use of top and side lighting is usually associated with low power stereomicroscopy, not PLM analysis.

8. Examination by Transmission Electron Microscopy

Section 8.1 Page 5, Line 1 — "Summary of Test Method:"

Section 8.1.1 Page 5, Line 1 — "*This test method is a mandatory evaluation of the aciniform materials present in the sample to determine primarily if their morphology is consistent with grape-like or branch-like structures typically associated with carbon black and soots."*

Section 8.1.2 Page 5, Line 1 — *"The sample is extracted into element-free chloroform or acetone by sonication. The resulting suspension is deposited onto a prepared carbon substrate attached to a 200 – 300 mesh copper grid."*

Section 8.3.1 Page 6, Line 1 — *"Snip off an appropriate soiled portion of the polyester wipe / cotton ball with a clean pair of scissors and place in a freshly cleaned test tube or vial."*

Section 8.3.2 Page 6, Line 1 — *"Add 1 to 4* cm^3 *of chloroform or acetone to a test tube or 10 to 20*cm^3 *to a glass vial until the entire sample is totally immersed in liquid.*

Section 8.3.3 Page 6, Line 3 — *"Ultrasonicate a sufficient amount of time (typically 10 min) to disperse the material. If the sample under examination is not dispersed well, re-prepare the sample using more ultrasonic energy or dilute the suspension."*

8.3.5 Page 6, Line 1

*“Using a volumetric pipette, deliver from 5 - 10*mm^3 *(ul) of the suspension onto the center of the grid and let the solvent evaporate.”*

Comment: The preparation procedures described in Sections 8.3–8.3 require the wipe sample to be sonicated in a solvent (acetone or chloroform) to disaggregate and resuspend the agglomerated dust. This process destroys the integrity of non-resilient particles and dissolves and removes the semi-soluble soot particles. At the same time, the remaining carbon black particles (or other fine particles with similar resilient properties) are theoretical uniformly resuspended so that very small aliquots (requiring very large serial dilutions of over 1,000-fold) can be transferred to a sample grid (2mm in diameter) and analyzed by the TEM.

8.3.7 Page 6, Line 1

“Place the grid on the microscope sample holder and insert the holder into the column. A typical accelerating voltage of 80KV is sufficient for carbon black. Determine an appropriate magnification for the particles between 5000 and 100000x magnification.”

Comment: The sample preparation procedures and magnification ranges specified are clearly designed to analyze the morphology of the individual carbon black particles or nodules, and not the original agglomerates or aggregates present. The suggested accelerating voltage of 80KV (80,000 volts) used for the TEM analysis can generate particle temperatures ranging from >200ºF to <3,000ºF[10, 11] depending on a combination of the electron beam accelerating voltage and current, the particle mass and size, thermal conductivity, and the elapsed time the particles are exposed to the electron beam. Between the low vacuum required by the TEM, and the temperature of particles when illuminated by the electron beam, a significant percentage of the semi-soluble or semi-volatile “soot” (non-carbon black) particles originally present can become heat altered, melted, or volatilized from the sample entirely.

8.4 Material Identification

8.4.1 Page 6, Line 1

“Classify the aggregates as being consistent with or inconsistent with the morphology of aciniform material. Carbon black and some soot(s) are considered to be aciniform. ASTM reference carbon blacks are available.”

Comment: The analysis or identification of other soot(s) is not prescribed by the ASTM Method, only defining if the aggregates are consistent inconsistent with carbon black.

9.4 Scanning Electron Microscopy – X-ray Analysis:

9.4.1 Page 7, Line 1

“Summary of the Test Method – This test method uses Scanning Electron Microscopy (SEM) and X-ray analysis (EDS) to eliminate some particles as consistent with carbon black based on their morphology and chemical composition”.

9.4.3.5 Page 8, Line 1

“It is important to note that the results obtained by this SEM-EDS (or WDS) technique cannot be considered as conclusive for identifying the presence of carbon black”.

Comment: Section 9.4 of the Method confirms that the SEM can differentiate some soot particles from carbon black based upon their morphology and elemental chemistry, but is not conclusive for the identification of carbon black. The method does not address the fact that the SEM analysis also suffers from the same fundamental operational limitations as the TEM analysis. Soot particles (from low temperature fire sources) may also be lost in the sample preparation and/or SEM analysis.

ANNEXES (Mandatory Information)

Figures A1l.2 – A1.7 Page 9-12 *PLM photograph of low temperature combustion soot, and other particles 1.55 RI Cargille, using transmitted light.*

Comment: The photograph shows only one mode of illumination (transmitted light) for the analysis of low temperature combustion soot and other particles. There are no examples of, or references to the use of high power (100x–500x) reflected light illumination.

Figures A2.8 – Page 20 *TEM image and X-ray Spectrum of California Wildfire Soot*

Comment: The method does provide one image and X-ray spectra of "soot" from a wildfire. This X-ray spectra is characteristic of the very small "resilient" particles that would remain following the TEM sample preparation and analysis procedures. The more common Potassium and Magnesium rich non-resilient and/or soluble residues more characteristic of a wildfire would not be detected, and no examples are provided in the Method.

5.0 CONCLUSIONS

This summary of the ASTM 6602-13 Method shows the intended use is for the selective sampling, preparation, and analysis of manufactured carbon black particles. Other remaining particles with similar resilient properties are simply viewed as an unwanted by-product of the analysis. By design, the wipe sample collection and preparation portions of the ASTM Method specifically eliminate or minimize the presence of other non-resilient *soot* or aciniform particles that might interfere with the analysis of carbon black. The wipe sampling portion of the method relies on mechanical force, the use of solvents (acetone or chloroform), and ultrasonication to intentionally breakup the particles in the sample so only the residual fine and disaggregated particles remain. The only other environmental particles remaining in the prepared samples will have a similar resiliency and fine particle morphology that are preserved as a contaminant in the samples. These remaining particles are further subjected to the high vacuum and elevated temperature of the SEM or TEM electron beam. This is the exact opposite of what is required to detect and analyze the fragile non-resilient combustion particles, and the in situ depositional patterns found on indoor surfaces as a direct result of a wildfire, structure fire, or proteinaceous fire.

As stated in the ASTM Method, "*Use of the TEM analysis is mandatory in determining whether a sample is positive for carbon black*". This statement is only accurate for the positive identification of *carbon black*. It is not applicable to other forms of environmental carbonaceous soot, and including wildfire or structure fire combustion particles. An accurate analysis cannot be performed using the ASTM TEM preparation and/or analysis procedures because of their incompatibility with the non-resilient chemical and physical properties of oxygenated fire residues generated by the uncontrolled burning of a wide range of potential fuels.

There are well established Optical Microscopy procedures (requiring the use of high quality transmitted and reflected light objective lenses) that can accurately analyze the full-size range (1µm - 2,000µm) of the settled combustion particles and condensed soot agglomerates characteristically found in wildfires and structure fires. These include the simultaneous (high power 100-500x) analysis of characteristic transmitted and reflective properties of aciniform soot (and their characteristic deposition patterns), char, ash, and specific indicator particles typical of the type of fire.

These analyses can be provided directly from tape lift samples where the spatial integrity, semi-volatility, and solubility of all particles is preserved. A standard PLM microscope typically used for asbestos analysis is inadequate by itself when used for the analysis of combustion residues. The Optical Microscopy reference images provided in ASTM Method Annexes use transmitted light PLM analysis only with the slide samples prepared in refractive index oil 1.55. They are inadequate as an aid for the identification of common wildfire or structure fire combustion particles, and that was never the purpose for their inclusion in the ASTM 6602-13 Method.

Finally, the ASTM 6602-13 Method (including the sample collection, sample preparation, and analysis procedures) is incompatible with, and was never designed to be used as a method for the analysis of wildfire or structure fire combustion particles. The Method was specifically optimized for the analysis of the residual “elemental” carbon end product residues formed at high controlled temperatures, while at the same time eliminating the unwanted “organic” carbon byproducts formed at lower temperatures. As a result, any attempt to apply this method specifically to the lower temperature “organic” carbon wildfire or structure fire combustion particles (especially soot condensate particles) is unpredictable and therefore inherently unreliable.

6.0 REFERENCES

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