Designation: D6602 – 13

Standard Practice for
Sampling and Testing of Possible Carbon Black Fugitive Emissions or Other Environmental Particulate, or Both[1]

This standard is issued under the fixed designation D6602; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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.

1.2 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. In support of this analysis, Donnet's book[2] is highly recommended to be used as a technical reference for recognizing and understanding the microstructure of carbon black.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1619 Test Methods for Carbon Black—Sulfur Content

D3053 Terminology Relating to Carbon Black

D3849 Test Method for Carbon Black—Morphological Characterization of Carbon Black Using Electron Microscopy

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *aciniform*—shaped like a cluster of grapes.

3.1.1.1 *Discussion*—The spheroidal primary particles of carbon black are fused into aggregates of colloidal dimension forming an acinoform morphology.

3.1.2 *aciniform carbon*—colloidal carbon having a morphology consisting of spheroidal primary particles (nodules) fused together in aggregates of colloidal dimension in a shape having grape-like clusters or open branch-like structures

3.1.3 *carbon black, n*—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.

3.1.3.1 *Discussion*—Particle size and aggregate size (number of particles per aggregate) are distributional properties and vary depending on the carbon black grade. Transmission electron micrographs shown in Annex A2 demonstrate that while particle and aggregate sizes vary greatly within a given grade of carbon black, the primary particle size is essentially uniform within an individual aggregate.

3.1.4 *chain of custody*—a document describing the condition of a sample during its collection, analysis, and disposal.

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

3.1.6 *fugitive dust*—transitory, fleeting material comprised of particulates foreign to the surface of deposition.

3.1.7 *fungus, sooty mold, mildew, biofilm*—particulates from a superficial growth that grows on living and decaying organic matter.

3.1.8 *mineral dust*—naturally occurring inorganic particulates inherent to the area such as soil minerals.

3.1.9 *pollen*—particulates from a mass of microspores in a seed plant.

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[1] This practice is under the jurisdiction of ASTM Committee D24 on Carbon Black and is the direct responsibility of Subcommittee D24.66 on Environment, Health, and Safety.

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[2] Hess, W.M. and Herd, C.R., *Carbon Black Science and Technology*, Edited by Donnet, J.B., Bansal, R.C., and Wang, M.J., Marcel Dekker, Inc., New York, NY, 1993, pp. 89–173.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.1.10 *rubber dust*—finely divided soft particulates abraded from rubber.

3.1.11 *sample*—a small fractional part of a material or a specified number of objects that are selected for testing, inspection, or specific observations of particular characteristics.

3.1.12 *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 resins.

3.1.12.1 *Discussion*—The carbonaceous portion also is colloidal and often has the aciniform morphology. 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.

3.1.13 *sticky tape*—a section of tape with a sticky, solvent-soluble adhesive used in the collection of particles from surfaces.

3.1.14 *surface*—the outer surface, facing, or exterior boundary of an object capable of supporting carbon and other fugitive and natural occurring dusts and particulates.

3.1.15 *turbostratic*—a type of graphitic crystallographic structure in which there is no symmetry along the z-axis.

3.2 *Acronyms:*

3.2.1 *EDS*—energy dispersive spectroscopy associated with SEM and TEM for the identification of elemental composition,

3.2.2 *LM*—light microscope,

3.2.3 *PLM*—polarizing light microscope,

3.2.4 *SEM*—scanning electron microscope,

3.2.5 *TEM*—transmission electron microscope.

3.2.6 *WDS*—wavelength dispersive spectroscopy associated with SEM and TEM for the identification of elemental composition.

NOTE 1—Standard terminology relating to carbon black can be found in Terminology D3053.

4. Summary of Practices

4.1 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). A semi-quantitative estimate of the percentage of each type of surface particulate component is determined using polarized light microscopy (PLM). However, PLM analysis cannot differentiate between carbon black and soots (black carbons) that may come from many sources in the environment. Therefore, transmission electron microscopy (TEM) analysis is mandatory in determining whether a sample contains carbon black. Because the preparation steps for the TEM analysis eliminates certain types of particles and concentrates only the fine (small) particles from the sample, the TEM analysis alone cannot be used to estimate the amount of carbon black or other particle type in the whole sample. Either the PLM or TEM analysis may be done first.

4.2 Section 6 provides guidelines for proper sampling and handling of fugitive emission/environmental samples. Sections 8 and 9 describe the analysis of the sample using polarized light microscopy (PLM) and transmission electron microscopy (TEM). 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. The use of the PLM analysis is not mandatory when the TEM analysis finds no aciniform aggregates resembling carbon black. Section 9 describes additional ancillary techniques that may be included in a sample analysis for purposes of providing supporting information as to the nature of the sample material. These are situation-dependent methods and can provide critical identification information in certain cases.

4.3 A block diagram is presented in Fig. 1 to give a possible scheme to follow in performing this analysis. However, it should be noted that this diagram is a suggestion, not a requirement. Either the PLM or TEM analysis may be performed first.

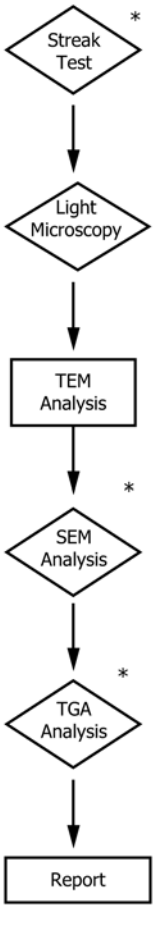

FIG. 1 Block Diagram of Suggested Analysis Scheme for Samples

5. Significance and Use

5.1 There are a variety of darkening agents that contribute to air and surface contamination in industrial, urban and rural environments. Biofilms (fungal and algal), soil minerals, plant fragments, rubber fragments, metal corrosion and soot are common darkening agents. Soot is formed as an unwanted by-product of combustion 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 contaminants.

6. Sampling

6.1 The area to be sampled should be representative of the contaminated area. For sampling, choose an area that appears to contain black particulates. In some situations, the same general surface can be used for gathering all test samples for each property site location or area.

6.2 *Equipment:*

6.2.1 *Polyester Wipes* (Texwipe Alphasat syntheic fiber wipes in 70 % alcohol/30 % DI water or equivalent).

6.2.2 *Sticky tape* (Scotch Crystal Clear Tape, No. 25 or equivalent).

6.2.3 *Polyethylene Ziploc Bags.*

6.2.4 *Standard Glass Microscope Slides.*

6.3 Samples are to be collected by the following two techniques (wipe and tape) in accordance with 6.3.1 and 6.3.2. Precautions should be taken to carefully collect, handle, and transport samples in a manner that will not cause further contamination.

6.3.1 *Technique I: Wipe Sampling*—Collect the wipe sample by wiping the surface to be sampled with a polyester wipe to remove surface particulates and solids. Light pressure on the wipe should be sufficient. Make sure that enough of an area has been wiped to load the surface of the wipe. Place the exposed wipe in a ziploc bag and label.

6.3.2 *Technique II: Tape Sampling*—Prepare a tape-lift slide by applying an appropriate length of tape to a clean glass microscope slide, leaving a tab for easy removal of the tape. Remove particulates and solids from surfaces by removing the tape from the prepared slide and applying it to the surface to be sampled. Carefully remove the tape and place back across the glass microscope slide. Take care not to overload the tape.

6.3.3 All collected samples must be clearly identified at the time of collection.

6.4 At the time of sample collection, complete a sampling record (Table 1) and also complete a chain of custody record (Table 2).

6.5 This practice does not preclude examination of samples collected by other means than the preceding, such as polyethylene glove wipes, filter paper, samples of clothing, material scraped directly from the surface of interest, and so forth, or a large sample taken in other containers at a spill site. However, these samples always require thorough identification taken at the time of sample collection.

6.6 It is advisable in the case of repeated incidents to clean the surface between sampling.

7. Examination by Light Microscopy

7.1 *Summary of Test Method*—This method of examination is a 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 TEM examination gives no positive results for aciniform aggregates resembling carbon black and there is no request for a semi-quantitative analysis of the other components in the sample. In addition, there are special situations where other information such as a torn bag near a carbon black manufacturing site strongly suggests that the black particulate being sampled is carbon black. In this case, a TEM analysis may be sufficient to confirm the presence of carbon black without the mandatory PLM analysis. 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.

7.2 *Apparatus:*

7.2.1 *Light Stereomicroscope,* capable of at least 40× magnification.

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

7.2.3 *Refractive Index Liquids including Meltmount,* 1.662 or 1.55 RI Cargille liquid or equivalent.

TABLE 1 Example Sampling Record

Sample Identification Number: ____

Sample Location: ____

Date of Sampling: ____

Comments:

____
____
____
____
____
____
____
____
____.

TABLE 2 Example Chain of Custody Record

	Sample ID	Date Sampled	Sampled By	Comments		
1.						
2.						
3.						
4.						
5.						

	Sample Number	Relinquished By	Received By	Time	Date	Reason for Change:
1.						
2.						
3.						
4.						
5.						

Comments: ______________________________

7.2.4 *Scissors or Safety Razor Blades, or both.*

7.2.5 *Glass Slides.*

7.2.6 *Glass Cover Slips.*

7.2.7 *Microscope Camera* (Polaroid, 35 mm, or digital).

7.2.8 *Tungsten Needles.*

7.2.9 *Forceps.*

7.2.10 *Reference Slides of Particles Found in Dust Samples.*

7.2.11 *Fiber-Optic Light Source,* for reflected light examination.

7.3 *Procedure:*

7.3.1 Inspect the tape-lift with a stereobinocular microscope. Note regions of interest where either jet black or dark particles are visible.

7.3.2 Inspect the tape-lift with a polarized light microscope using both transmitted and reflected light. The tape lift will preserve intact colonies of fungal material (biofilm) if present. If the sampled surface is weathered paint, pigment lifted from the surface will not obscure or hinder identification of biofilm constituents, as is often the case with wipe samples. Aciniform soot will appear as opaque, jet black aggregates of particles displaying a dull reflection in top light. The tape lift generally preserves the integrity of the particle aggregates without the smearing that tends to occur when using the wipe sampler.

7.3.3 Inspect the wipe sample with a stereobinocular microscope. With a clean razor blade, cut out a small square section (~1 cm) of a representative portion of the wipe, including an area of black staining if present. Using two clean tweezers, agitate, twist, and scrape the square section of the wipe over a clean microscope slide to dislodge particle from the wipe and on to the slide. If fine black particles coat some of the fibers of the wipe, pull some of them out and mount them separately. It may also be possible to transfer dark particulate from the wipe to a microscope slide using a tungsten needle. Add a drop of immersion oil to the preparation (oil having a refractive index of 1.55 works well) and place a cover slip over it.

7.3.4 Place the glass slide sample on the polarized light microscope and examine with transmitted (both directly and with crossed polars) and reflected light. Aciniform soot will appear as aggregates of jet black particles exhibiting dull reflection. While observing with the microscope, lightly press the coverslip with a needle. If the aggregates are carbon soot or carbon black, they will likely deform inelastically and/or disperse. If an aggregate deforms elastically, it is likely a rubber particle which contains carbon black as an additive. Estimate the percentage of each component from Table 3 and record. The identification of environmental particles and classification into categories by PLM has been published (**1**).[4] The microscopist relies on his/her training, experience and reference to various published articles and books about particle characteristics (**2-8**). Some representative PLM images of particles in the common darkening agent classes of soot, fungal growth (biofilms), soil minerals, plant fragments and rubber particles are shown in Annex A1. Estimate the percentage of each type of component found from the list in Table 3 and record. 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.

TABLE 3 Particulate Work Sheet For Light Microscopy of Environmental Samples

Component	Estimated Percentage (by volume or area)
Pollen	
Fungal, Mold, Biofilm	
Soil Minerals	
Soot (which may include aciniform carbon, fine char & carbon black)	
Coal ash (Fly ash)	
Plant Fragments	
Paint	
Insect Parts	
Rust/Metal Flakes	
Rubber	
Coal/Coke	
Other	

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[4] The boldface numbers in parentheses refer to a list of references at the end of this standard.

7.3.4.1 The semi-quantitative visual estimate of percentages of particles in a sample is a well known technique that has been used for many years by geologists, paleontologists, and asbestos analysts (**9-14**). Analysts learn to perform calibrated visual estimates by studying comparison charts where a known percentage of the particles in the chart has been filled in with dots or other dark figures. Fig. 2 shows a representative comparison chart used for calibrating analysts in semi-quantitative visual estimation. Samples of known composition made from known volumes of various components are also used to 'calibrate' an analyst. Particles are examined by PLM at magnifications ranging from 100 to 400×. Particles are characterized and identified by PLM on the basis of their optical properties, including, but not limited to: *(1)* birefringence/bireflectance, *(2)* color, *(3)* morphology/surface texture, *(4)* physical dispersal in mountant, and *(5)* refractive index relative to mountant. Carbon black, as observed by PLM, is typically black opaque aggregates or agglomerates that vary in dimension based on the type or manufacturer. Various soots may have a similar appearance by PLM. (Constituent particles of aggregates are best observed with the TEM.) The aggregates/agglomerates do not have a characteristic reflectance but the aciniform morphology may be apparent. Perform Kohler illumination for PLM periodically by the project microscopist. Calibrate the graticule scale micrometer once upon installation and again with the microscope if the microscope is moved from its initial position.

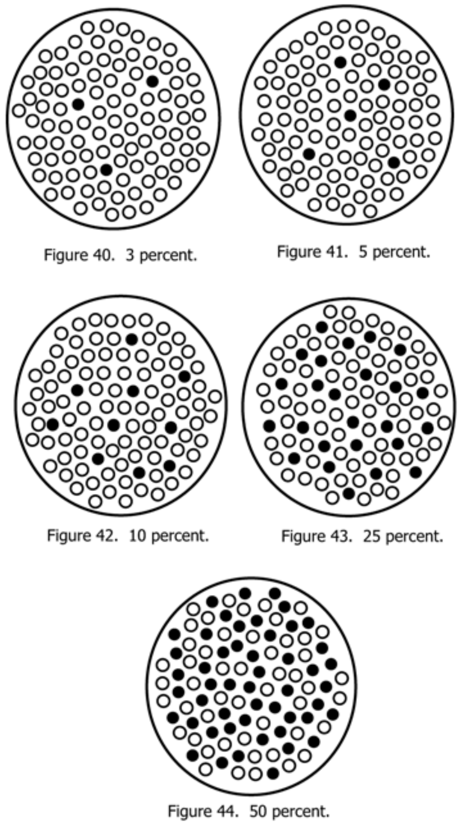


Figure 40. 3 percent.

Figure 41. 5 percent.

Figure 42. 10 percent.

Figure 43. 25 percent.

Figure 44. 50 percent.

FIG. 2 Comparison Chart Showing Known Percentages of Particles (3)

7.3.5 It is highly recommended that the various types of particles present be documented as needed with photomicrographs (with the aid of the microscope camera).

7.3.6 Photographs of known samples of some or all of the particulates listed in Table 3 should be made for reference and comparison if needed. Collect these samples from the area in question. Other environmental contaminants may be collected for comparisons if desired.

7.3.7 There is no requirement on the least amount of particles required for valid observation due to the variance in population of particles.

NOTE 2—An ancillary method may be used for PLM preparation that includes the following:
(1) For examination by PLM, dissolve the tape-lift adhesive with organic solvents (for example, toluene, xylene, or chloroform).
(2) Extract particles from the adhesive through mechanical shaking or sonication.
(3) Transfer an aliquot onto a slide containing a drop of refractive index liquid, for example, 1.55 or 1.660, on a microscope slide and cover with a coverslip.

The procedures used to prepare wipe samples for analysis include the following:
(1) Roll a tungsten needle, wetted with organic solvent, (for example, toluene, xylene, or chloroform), across surface of the wipe.
(2) Transfer a representative sampling of all particles from the needle to a drop of refractive index liquid, that is 1.660, on a glass microscope slide and cover with a coverslip.

8. Examination by Transmission Electron Microscopy (TEM)

8.1 *Summary of Test Method:*

8.1.1 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. In order to discriminate discrete morphological parameters, the resolving power of a TEM is required. In addition to TEM examination, the ancillary methods in accordance with Section 9 may provide supporting information as to the nature and amount of the material.

8.1.2 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 or 300-mesh copper grid. The grid is placed into the transmission electron microscope (TEM) and representative fields are examined. The aciniform materials are then evaluated for overall morphology.

8.2 *Apparatus and Chemicals:*

8.2.1 *Transmission Electron Microscope (TEM),* equipped with a suitable camera. Energy or wavelength dispersive analysis is highly recommended but not mandatory.

8.2.2 *Ultrasonic Bath or Ultrasonic Probe,* of satisfactory power to disperse the particles.

8.2.3 *Copper TEM Grids,* 3-mm 200 or 300-mesh, with carbon substrate.

8.2.4 *Scissors.*

8.2.5 *Glass 1 Dram Vials with Cap or Glass Test Tubes,* 10 by 85 mm, or *Glass Vial*, 3 by 5 cm.

8.2.6 *Pipettes,* disposable.

8.2.7 *Chloroform,* spectrophotometric grade.

8.2.8 *Acetone,* spectrophotometric grade.

8.3 *Procedure:*

8.3.1 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.

8.3.2 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.

8.3.3 An ultrasonic probe or bath may be used to disperse the material into liquid. If an ultrasonic probe is used, set the vial into a container filled with ice and water. 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.

8.3.4 Place a copper grid with the carbon substrate upward on a filter membrane. Place the filter membrane in a hood.

8.3.5 Using a volumetric pipette, deliver from 5 to 10 mm^3 (µL) of the suspension onto the center of the grid and let the solvent evaporate. When the liquid drop is placed on the grid it overlaps onto the filter paper resulting in a spot size that is larger than the size of the grid.

8.3.6 If the spot is exceptionally light, repeat 8.3.5 with additional drops until a stain is seen on the filter paper or a maximum of 20 drops are applied. Stopper the remaining suspension and place in the hood.

8.3.7 Place the grid on the microscope sample holder and insert the holder into the column. A typical accelerating voltage of 80 KV is sufficient for carbon black. Determine an appropriate magnification for the particles between 5000 and 100 000× magnification.

8.4 *Material Identification:*

8.4.1 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 in nature (**15-22**). ASTM reference carbon blacks are available for comparison (**23**). A standard reference diesel exhaust aciniform carbon is also available from the National Institute of Standards and Technology (NIST) (**24**). Reference particles of coal and coke are also available from NIST (**24**).

NOTE 3—It is highly recommended to take into consideration the grades of carbon black manufactured in the area sampled. If acinoform material is found in the sample, it is advisable to also examine possible manufactured carbon blacks from the area to be used as controls versus the environmental sample.

8.4.2 If the aggregates are aciniform, then continue with the identification process. Examine the overall morphology of the aggregate in the magnification range of 30 000× to 50 000× and examine the microstructure of the primary particles in the range of 100 000×. In support of the analysis, it is recommended to generate photomicrographs of representative fields. Refer to Annex A1 to aid in particle identification.

8.4.3 Elemental identification of the aciniform material is highly recommended but not mandatory. It is accomplished using an X-ray system associated with the electron microscope. The aciniform particles of soot and carbon black are mostly carbonaceous but may contain small amounts of other elements.

8.4.4 *Morphology of Aggregates:*

8.4.4.1 Assess how the primary particles are joined together in the aggregates, that is, the dimensions (diameter and length) of the necks between primary particles. In carbon black aggregates, the dimensions of the particle necks are smaller than the diameter of the primary particles. Whereas, in some soots, the necks have similar dimensions to the primary particles, thereby making it difficult to distinguish one primary particle from the next. The following are used to determine if the aggregates are consistent with carbon black:

(1) the majority of aggregates contain well-defined primary particles,

(2) the diameter and length of the primary-particle necks are smaller than the primary-particles,

(3) the individual aggregates contain a narrow range of primary particle sizes, and

NOTE 4—To rule out the presence of carbon black, at least one of the above parameters should not be satisfied.

8.4.4.2 The preponderance of carbon black aggregates contain well-defined fairly uniform primary particles. Typically, the perimeter of the primary particles in carbon black appears fairly smooth when viewed at a magnification of 100 000× to 500 000×. Whereas, in certain soots a significant fraction of the primary particle perimeters are rough, somewhat jagged, having an etched-like appearance, suggesting that the particles are inconsistent with carbon black.

8.4.4.3 The size of the primary particles within an aggregate should fall in the size range from 10 to 100 nm for furnace grades and from 200 to 500 nm for thermal grades. If these conditions are not satisfied, the material is said to be inconsistent with carbon black. One method for measuring the diameters of primary particles in aciniform aggregates found in environmental samples has been published (**25**).

8.4.4.4 Representative micrographs should be generated at an appropriate magnification and furnished in support of the analysis. See Annex A2 for reference photomicrographs to aid with carbon black identification.

8.5 Record the results of analysis of at least 5 aciniform aggregates or at least 5 grid openings. Classify each aggregate as consistent or inconsistent with carbon black based on morphology. Include information about elemental composition and primary particle size parameters if determined.

8.5.1 If both the PLM and TEM analyses including elemental composition and primary particle size parameters have been performed, it is possible to calculate an approximate percentage of carbon black in the sample by multiplying the ratio of aggregates consistent with carbon black (morphology, elemental composition and size) to total aggregates analyzed by the percentage of black carbon (soot) determined by PLM.

9. Ancillary Methods for Support Data

9.1 This section is provided to include methods of sample analysis that are situation-dependent and, in some cases, can provide critical supporting information that is useful in identification.

9.2 *TEM X-ray Analysis:*

9.2.1 *Summary of Test Method*—This test method is a semi-quantitative measure of the sulfur content in individual components suspected to be carbon black by energy (EDS) or wavelength dispersive spectrometry (WDS) to determine if an individual component in the sample has an appropriate sulfur to carbon ratio consistent with commercially produced carbon black. In addition, this test method allows other non-carbon components besides sulfur to be identified, which, if present, may constitute the basis for the sample to be inconsistent with carbon black. In this test method, individual compounds in the samples are examined in either a transmission electron microscope equipped with energy or wavelength dispersive analysis equipment and tested for elemental composition in order to determine if specific particles have the same sulfur ratios as carbon black.

9.2.2 Follow the procedure in accordance with 8.3.1 – 8.3.7 for the sample preparation. The sample is extracted into element-free chloroform or acetone by sonication. Check the liquid by putting a drop mount on a carbon grid and performing a TEM x-ray analysis. A small silicon peak has been seen in some spectrophotometric grade chloroforms. Additional information about sulfur determination can be found in Test Methods D1619.

9.2.3 Isolate the specific particle in question and center the beam on the particle.

9.2.4 Following the manufacturer's instructions for the energy dispersive equipment attached to the microscope, determine the elemental composition versus one or more of the ASTM carbon black reference standards or reference samples from potential local sources which have known sulfur contents. In addition, determine if other non-carbon components besides sulfur are present in significant amounts. Carbon blacks contain about 97 to 99.5 % carbon and sulfur content ranges from 0 % in thermal and acetylene blacks to 0.5 to 2 % sulfur in typical furnace-grade carbon blacks. The percent of sulfur in a carbon black is highly dependent on the percent of sulfur in the feedstock oil and this should be taken into consideration. Soots, depending on their source, may contain greater than 2 % sulfur, which distinguishes them from carbon black. However, some soots may contain <2 % sulfur, which can make them more difficult to distinguish from carbon black. Determine if the specific particles have extraneous components not normally found in carbon black.

9.3 *Streak Test Method:*

9.3.1 *Summary of Test Method*—In this test method, a lens tissue is wiped across a surface and the tissue is then visually examined for black streaks. The streak test method may give an indication of the presence of newly deposited carbon black, soots, molds, and some natural occurring particulates. A positive streak test method does not identify the streak as carbon black, since carbon soots and other particulate materials including some 'sooty' molds can also give a positive streak test.

9.3.2 *Apparatus:*

9.3.2.1 *Polyester Wipes or Cotton Balls.*

9.3.2.2 *Optical Lens Tissue.*

9.3.3 *Procedure*—Form a cylinder (about 15 by 40 mm) from 1 or more balls of polyester or cotton. Wrap lens tissue around the elongated roll and wipe the elongated roll across about one-foot length of surface. Use one continuous motion. Observe the tissue for streaking. Soft facial tissue such as "Kleenex" may also be used on smooth surfaces. Fresh carbon black and most soots will leave a streak on the tissue from individual particles. Place the tissue in a plastic bag and label for possible future examinations.

NOTE 5—Particulate-gathering materials should be kept in sealed bags or containers to protect them from exposure to foreign particulates and contamination.

9.3.4 It is important to note that the results obtained by this streak test cannot be considered as conclusive for identifying the presence of carbon black.

9.4 *Scanning Electron Microscopy – X-ray Analysis:*

9.4.1 *Summary of 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. The SEM-EDS may also be helpful in identifying some darkening agent particles as biological material, minerals or rust/corrosion metallic particles.

9.4.2 *Apparatus and Chemicals:*

9.4.2.1 *Carbon Sticky Tape or Double Side Sticky Cellophane Tape or Carbon Adhesive Material.*

9.4.2.2 *SEM Sample Mounts.*

9.4.2.3 *Carbon Evaporator or Gold Sputter-Coater.*

9.4.2.4 *Carbon Black Standard(s),* in accordance with Test Methods D1619.

9.4.3 *SEM Procedure:*

9.4.3.1 Attach the sticky tape sample collected to an SEM sample mount with double-sided sticky tape or transfer some of the particulate collected onto carbon adhesive material attached to an SEM sample mount. Be careful not to damage the sample.

9.4.3.2 Label the sample mount appropriately and then put the sample in the carbon evaporation system and give the sample a light carbon coating in order make it conductive.

NOTE 6—Some samples or situations do not require that the sample be coated before analysis.

9.4.3.3 Place the sample in the SEM and view at 100 to 500×. Observe several fields until a representative field is firmly in mind. Photograph this area and then select certain particles of interest to test by X-ray analysis.

9.4.3.4 Using the manufacturer's instructions for the EDS or WDS equipment, determine the elements present in the particles of interest. The sulfur content may be quantified by comparing intensity of the sulfur peak in the sample to that of a known sulfur content carbon black standard. It is also useful to test known samples of the suspect material such that the spectrum of the known may be used as a "fingerprint" reference for comparison purposes. In addition, determine if other noncarbon components besides sulfur are present in significant amounts.

9.4.3.5 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.

9.5 *Thermogravimetric Analysis:*

9.5.1 *Summary of Test Method*—This test method is a quantitative measure of the volatile organic content of carbon samples by use of thermogravimetric techniques. This test method can only be applied to samples confirmed by electron microscopy to be primarily aciniform carbon (95 %) or samples where the volatile content of the components other than carbon are known or can be accounted for. This test method allows the distinction between the types of particulate carbon to be determined as carbon blacks are quite low in volatile organic content (<8 %) whereas soots are normally high in volatile organic content (>20 %). Test samples collected on glass fiber pads are heated in nitrogen to 550°C to determine the volatile organic content and then heated in air to 800°C to determine the mass of particulate carbon in order to calculate the percent of volatiles in the particulate carbon.

9.5.2 *Apparatus:*

9.5.2.1 *Thermogravimetric analyzer* (TGA), with sensitivity of ±0.001 mg.

9.5.2.2 *Glass Fiber Filter Pad.*

9.5.2.3 *Tweezers.*

9.5.3 *Procedure:*

9.5.3.1 First test an unexposed piece of the glass fiber filter pad (blank) on the TGA to determine the mass loss due to the pad material at 550°C under nitrogen (50 cm^3/min) and at 650°C under air (50 cm^3/min). Begin heating at 50°C at a rate of 10°C/min. Before inserting the blank, sample zero the microbalance of the TGA with the heating chamber closed. Open the heating chamber and then with tweezers insert the blank onto the microbalance pan. Close the heating chamber. Ensure that nitrogen flow is at 50 cm^3/min. Starting at 50°C, heat to 550°C at 10°C/min and record the mass loss of the blank in nitrogen. Allow the instrument to cool below 350°C then switch to air at 50 cm^3/min. Heat from 350 to 650°C at 10°C/min and record.

9.5.3.2 Repeat 9.5.3.1 for the sample in question and record the mass loss of the sample in nitrogen and the mass loss of the sample in air.

9.5.3.3 Calculate the volatile content using the following equation:

$$\% \text{ volatiles} = \frac{(\text{mass loss of sample in nitrogen} - \text{mass loss of blank in nitrogen})}{(\text{mass loss of sample in air} - \text{mass loss of blank in air})} \times 100 \quad (1)$$

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

10. Report

10.1 Report the following information for each sample:

10.1.1 A Chain of Custody Record (Table 2 or equivalent).

10.1.2 A Sampling Information (Table 1 or equivalent).

10.1.3 Observation from the PLM and TEM analysis (Sections 7 and 8).

10.1.3.1 Include necessary supporting photomicrographs.

10.2 In addition, report any additional analysis performed as consistent or inconsistent with carbon black and report any additional observations and data obtained from those analyses which may include one or more of the following:

10.2.1 TEM X-ray Analysis (9.2).

10.2.2 Streak Test (9.3).

10.2.3 Scanning Electron Microscopy (9.4).

10.2.4 Thermogravimetric Analysis (9.5).

ANNEXES

(Mandatory Information)

A1. PLM

A1.1 Scope

A1.1.1 Several example photomicrographs (Figs. A1.1-A1.7) taken with a digital camera mounted on an Olympus BH-2 polarized light microscope are attached to show examples of some common darkening agents. The photomicrographs are provided here as general examples.

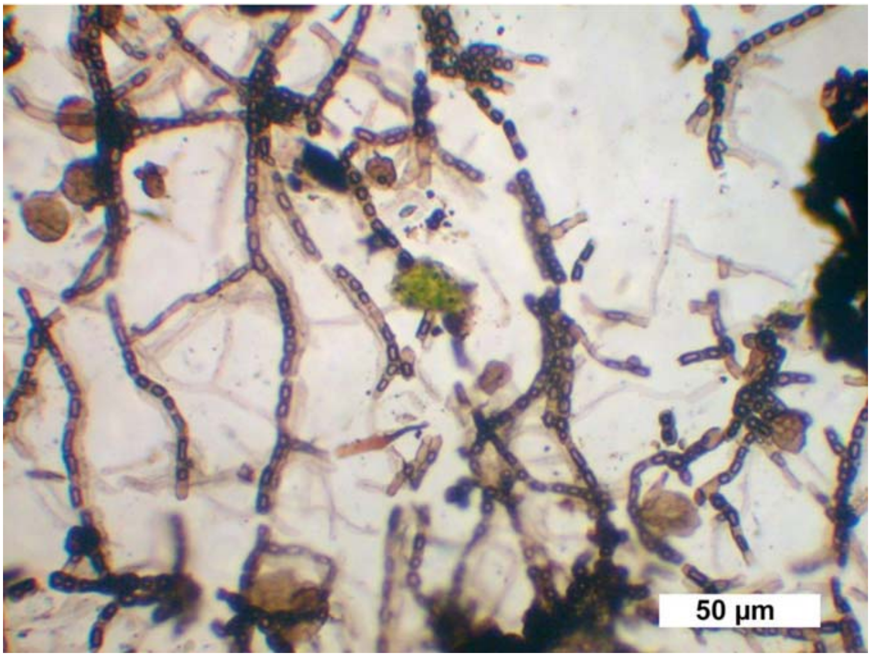


FIG. A1.1 PLM photograph of biofilm, from tape-lift, transmitted light

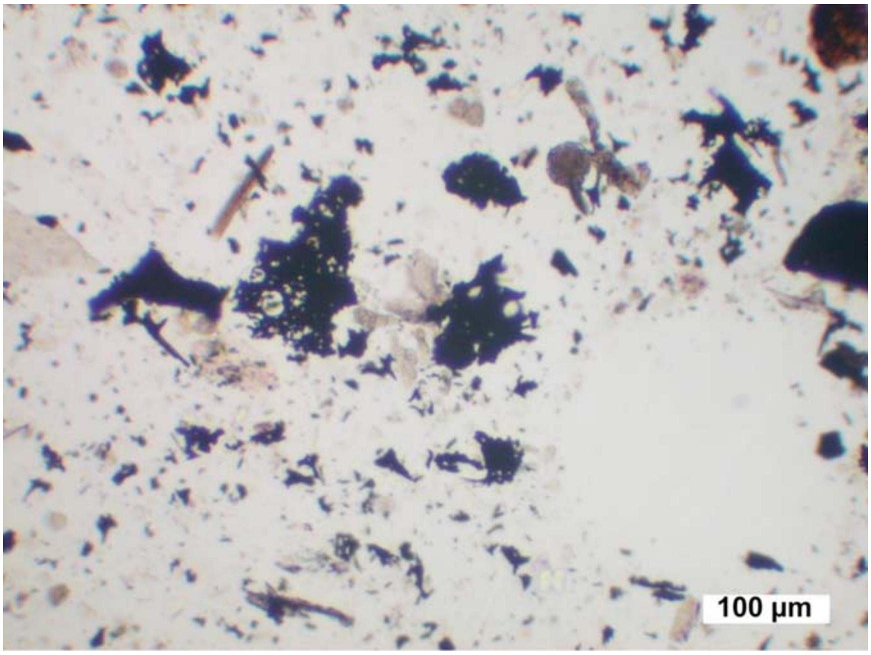


FIG. A1.2 PLM photograph of low temperature combustion soot, 1.55 RI Cargille liquid, transmitted light

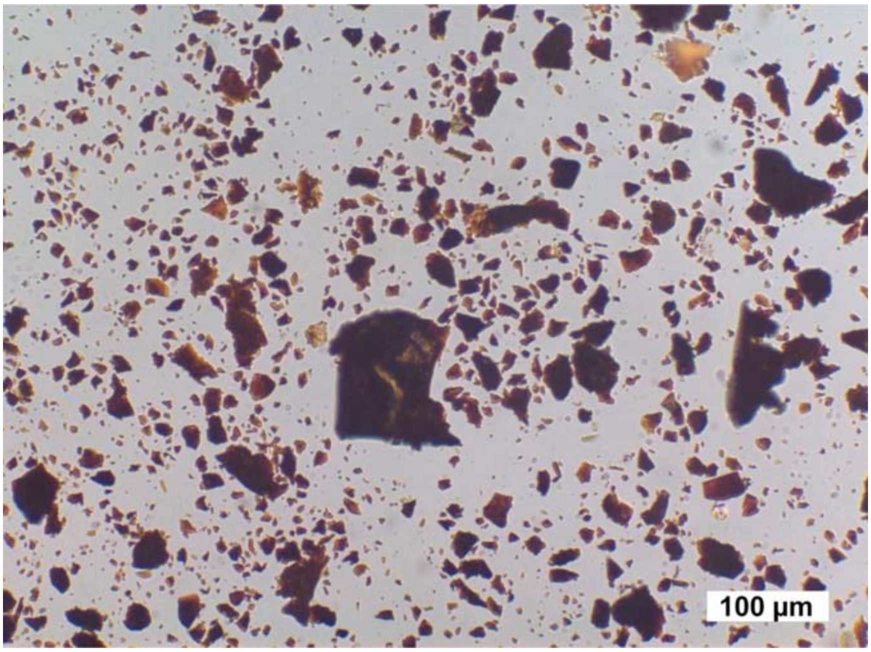


FIG. A1.3 PLM photo of coal dust, 1.55 RI Cargille liquid, transmitted and reflected light

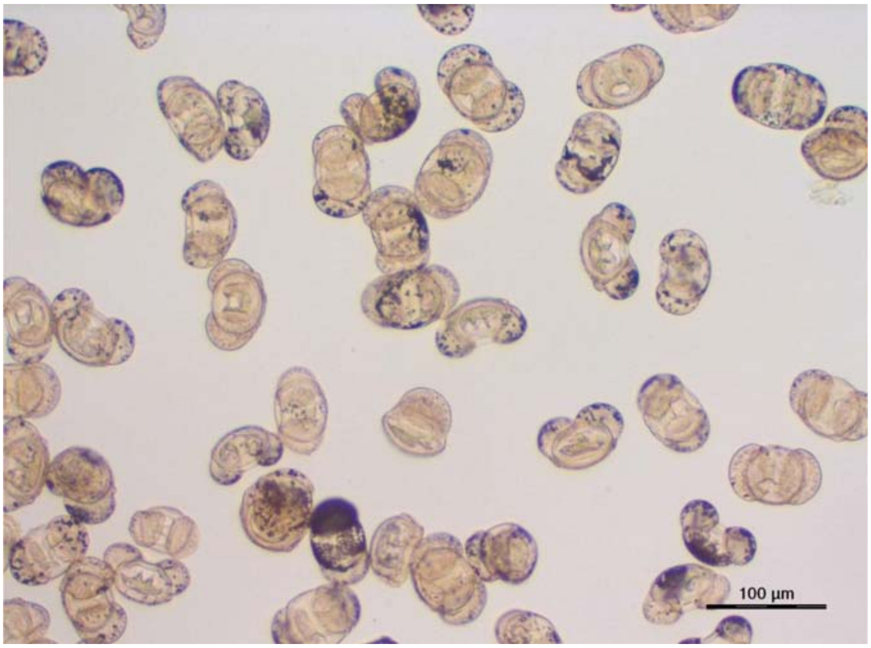


FIG. A1.4 PLM photo of pollen (Loblolly Pine), 1.55 RI Cargille liquid, transmitted light

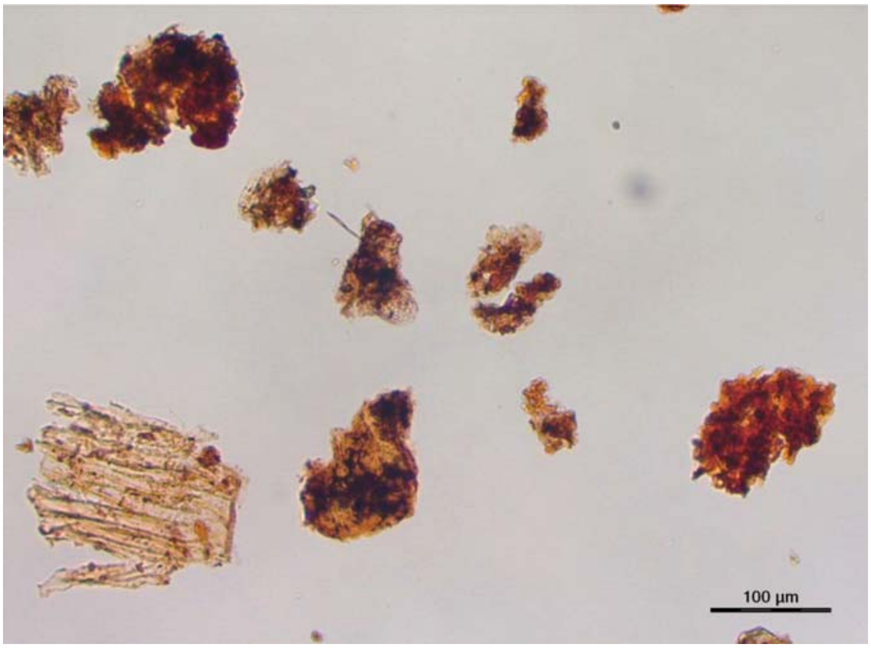


FIG. A1.5 PLM photo of plant fragments, 1.55 RI Cargille liquid, transmitted light

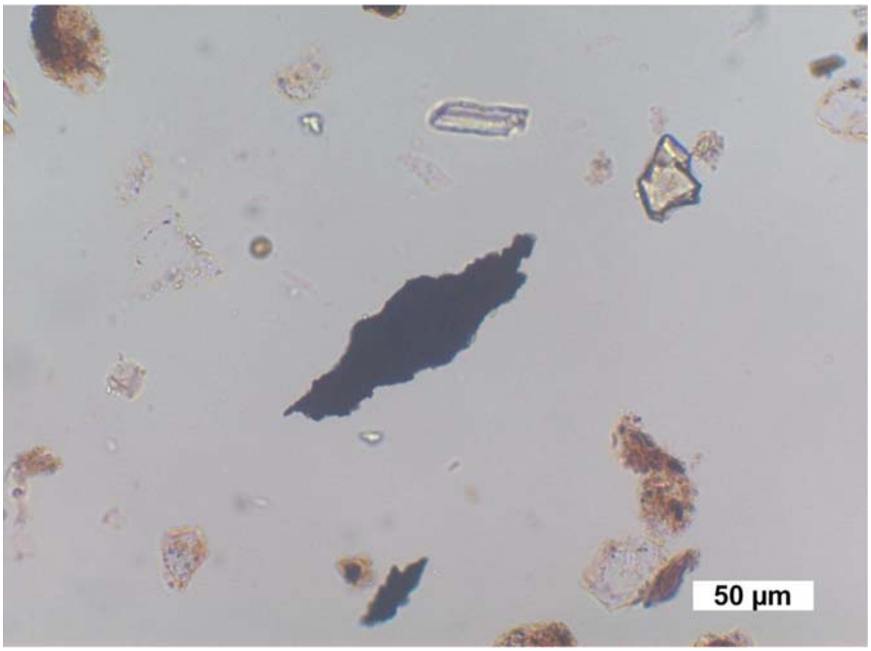


FIG. A1.6 PLM photo of rubber particle, 1.55 RI Cargille liquid, transmitted light

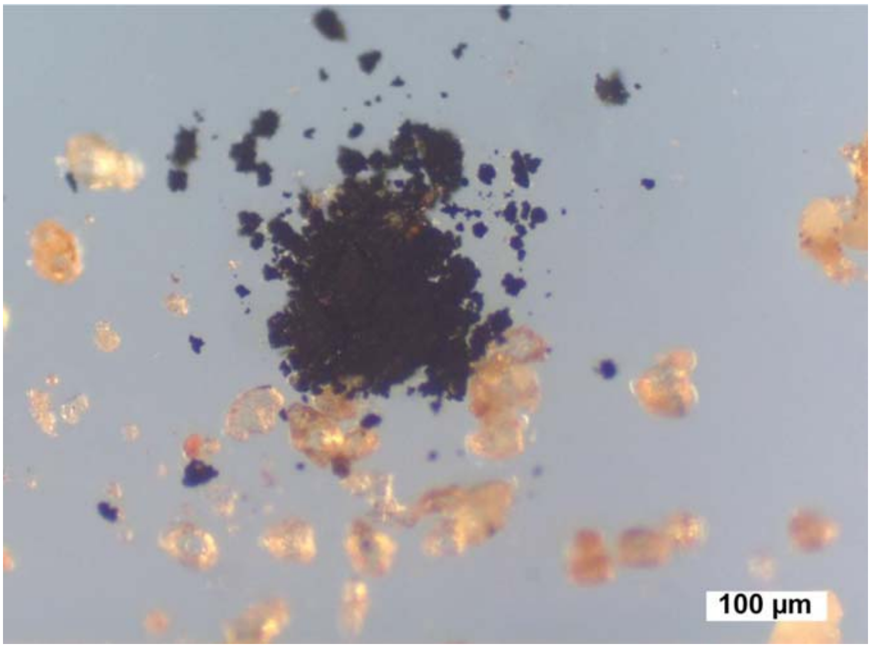
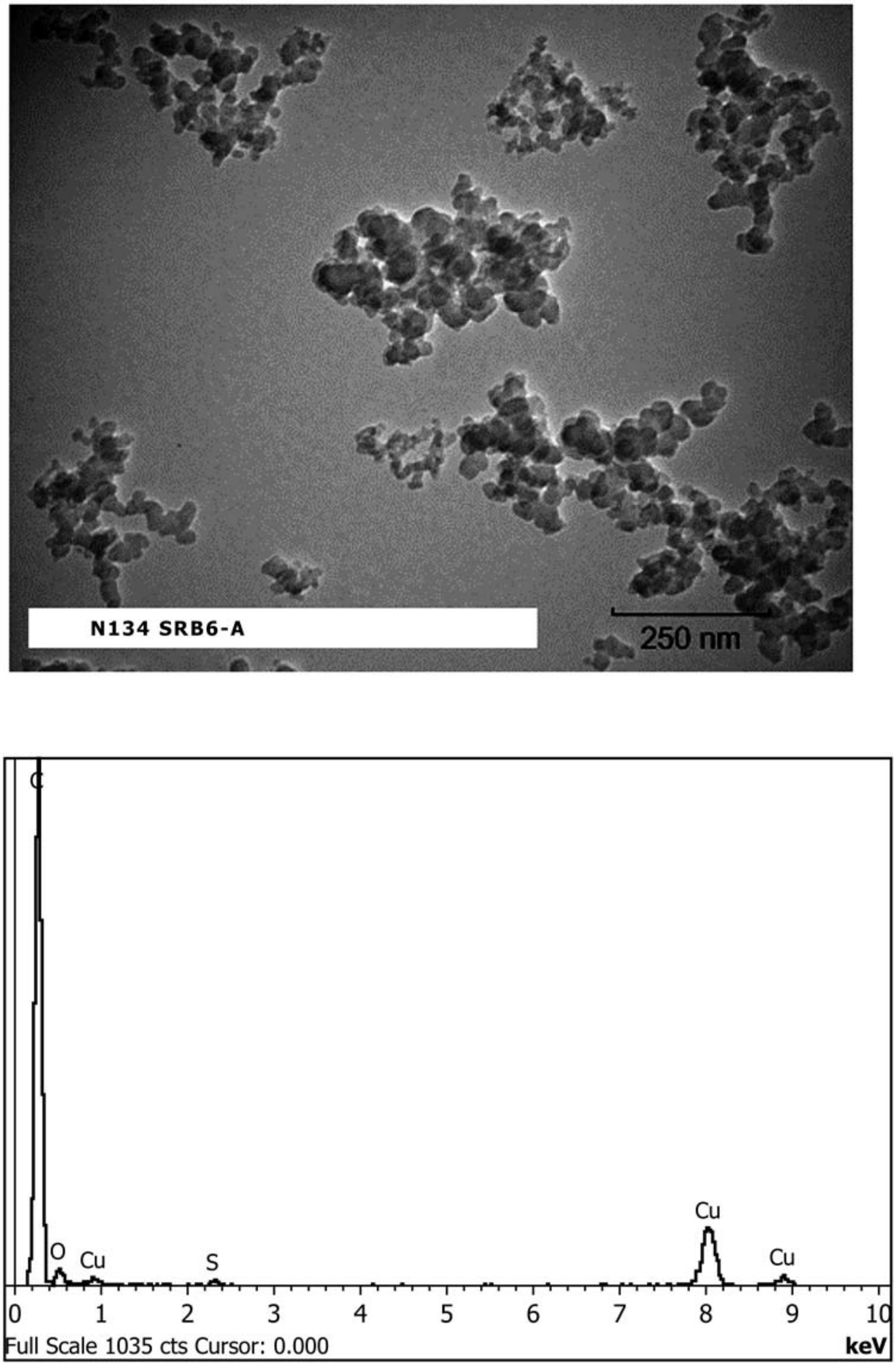


FIG. A1.7 PLM photo of aciniform soot, 1.55 RI Cargille liquid, from tape-lift, transmitted light

A2. ACINIFORM MORPHOLOGY OF SOOTS AND CARBON BLACK

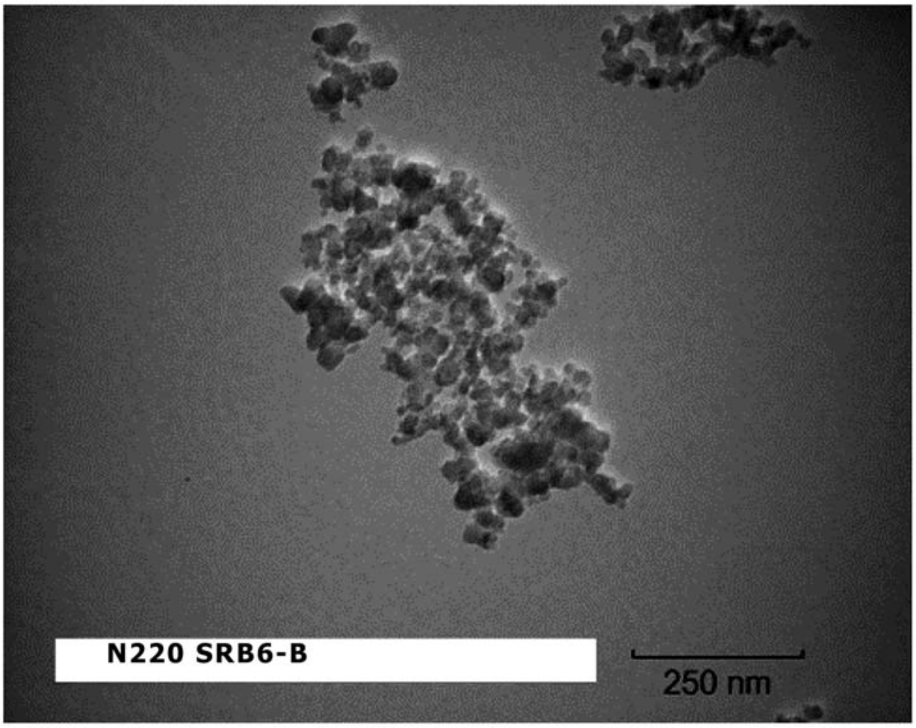
A2.1 Scope

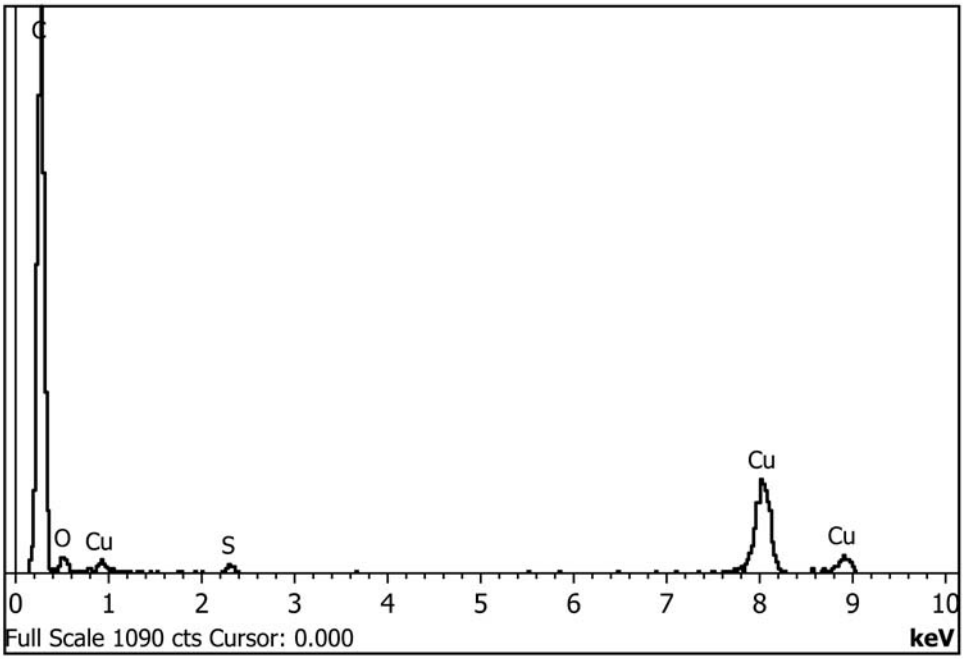
A2.1.1 The aciniform morphology that appears like a cluster of grapes is the characteristic morphology of soots, carbon black, and several other materials. Several example photomicrographs (Figs. A2.1-A2.9) taken with a transmission electron microscope are attached for comparison purposes. The photomicrographs are to be provided here as general examples. When possible reference samples collected locally can be used for comparisons in the laboratory. The shape, size, and number of primary nodules can vary in individual aciniform carbon aggregates. Interpretation based on a single aggregate should be done with caution.



NOTE 1—Scale = 250 nm

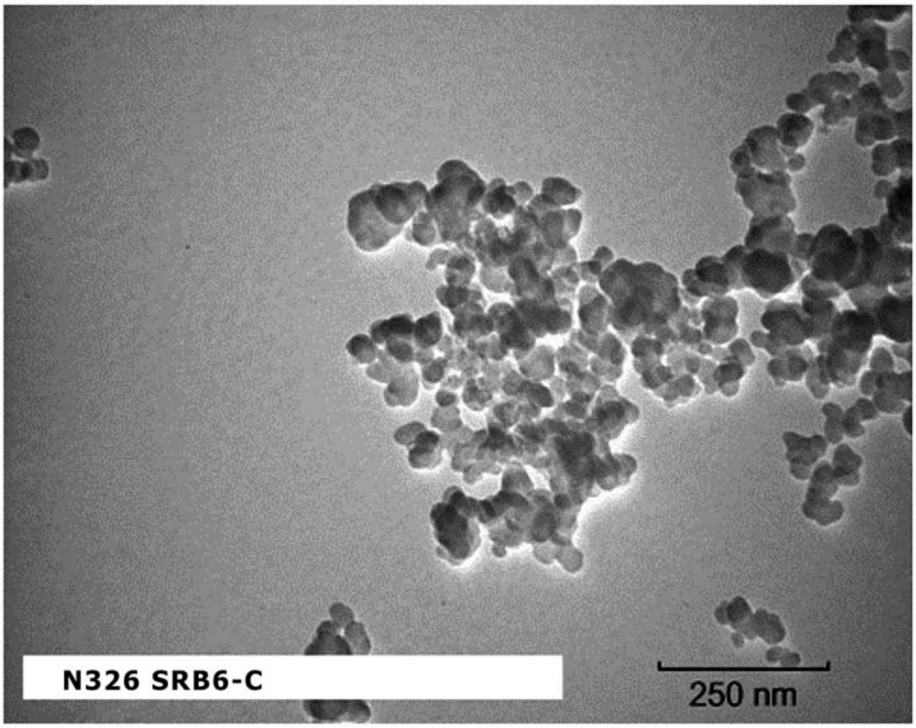
FIG. A2.1 TEM image (above) and X-ray Spectrum (below) of ASTM SRB6-A carbon black N134

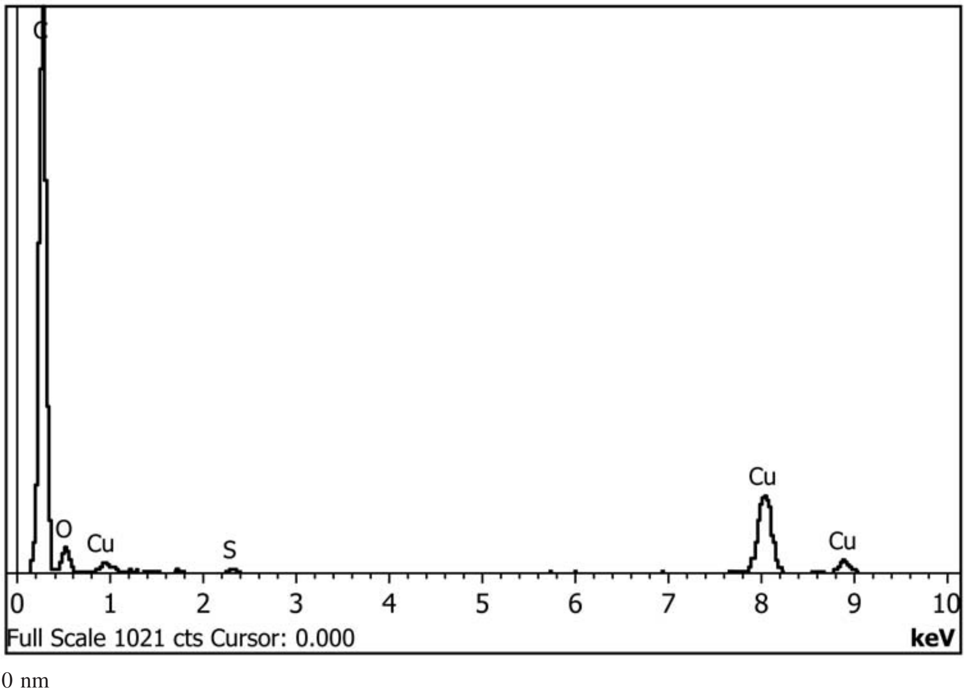




NOTE 1—Scale = 250 nm

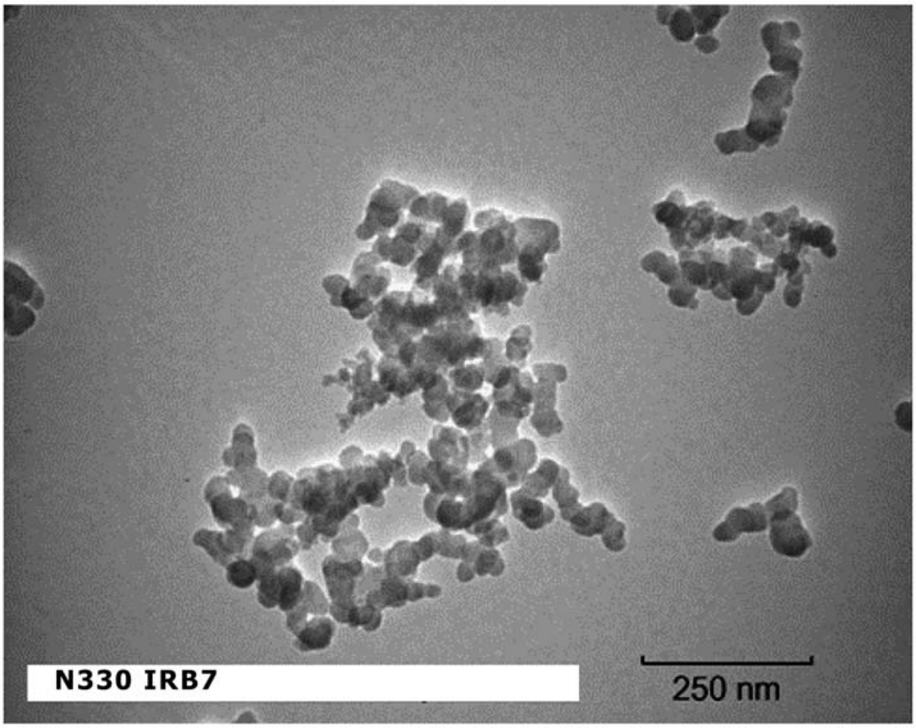
FIG. A2.2 TEM image (above) and X-ray Spectrum (below) of ASTM SRB6-B carbon black N220

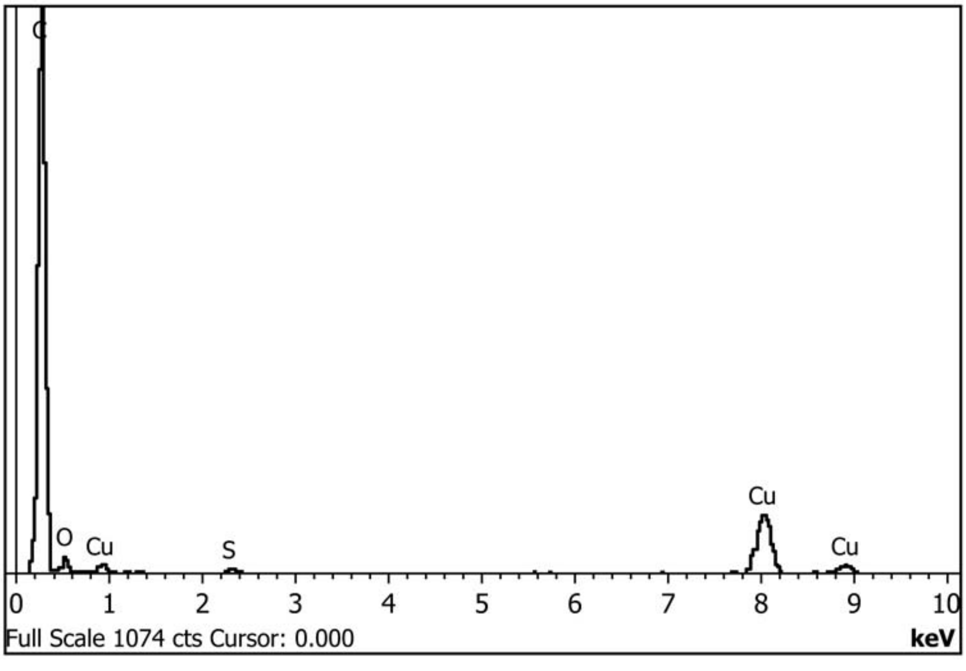




NOTE 1—Scale = 250 nm

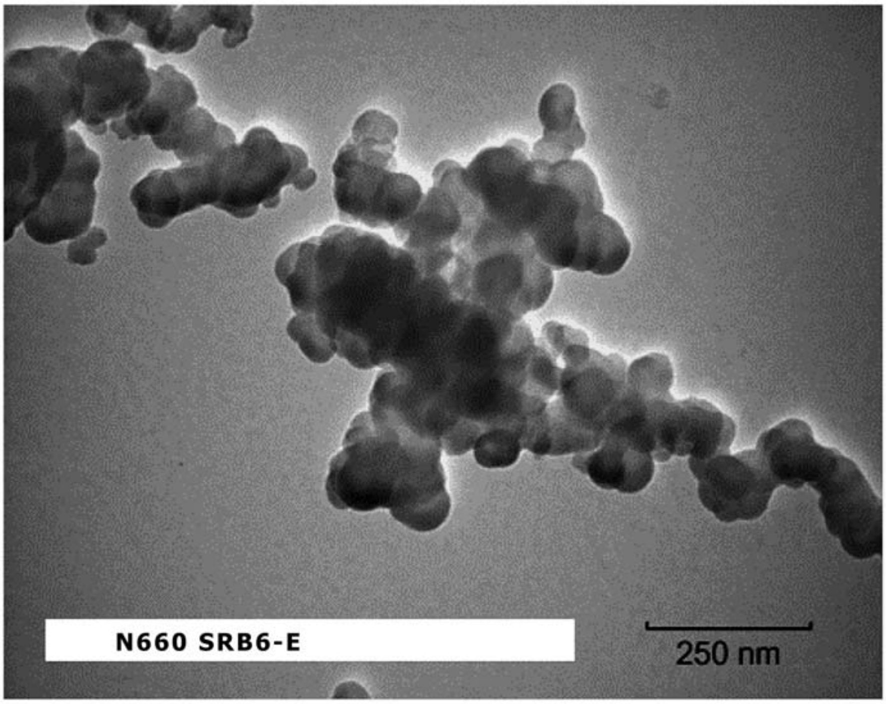
FIG. A2.3 TEM image (above) and X-ray Spectrum (below) of ASTM SRB6-C carbon black N326

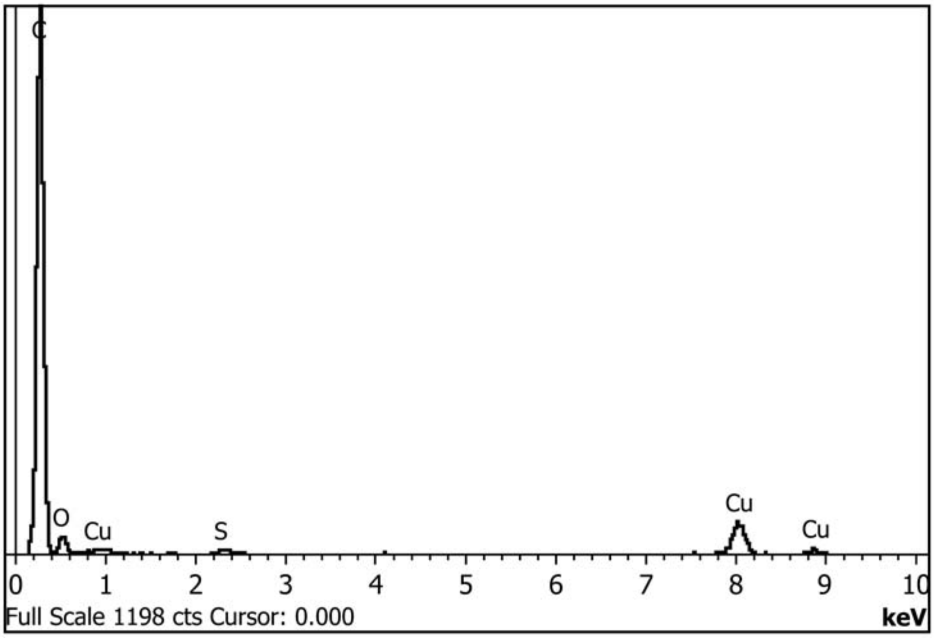




NOTE 1—Scale = 250 nm

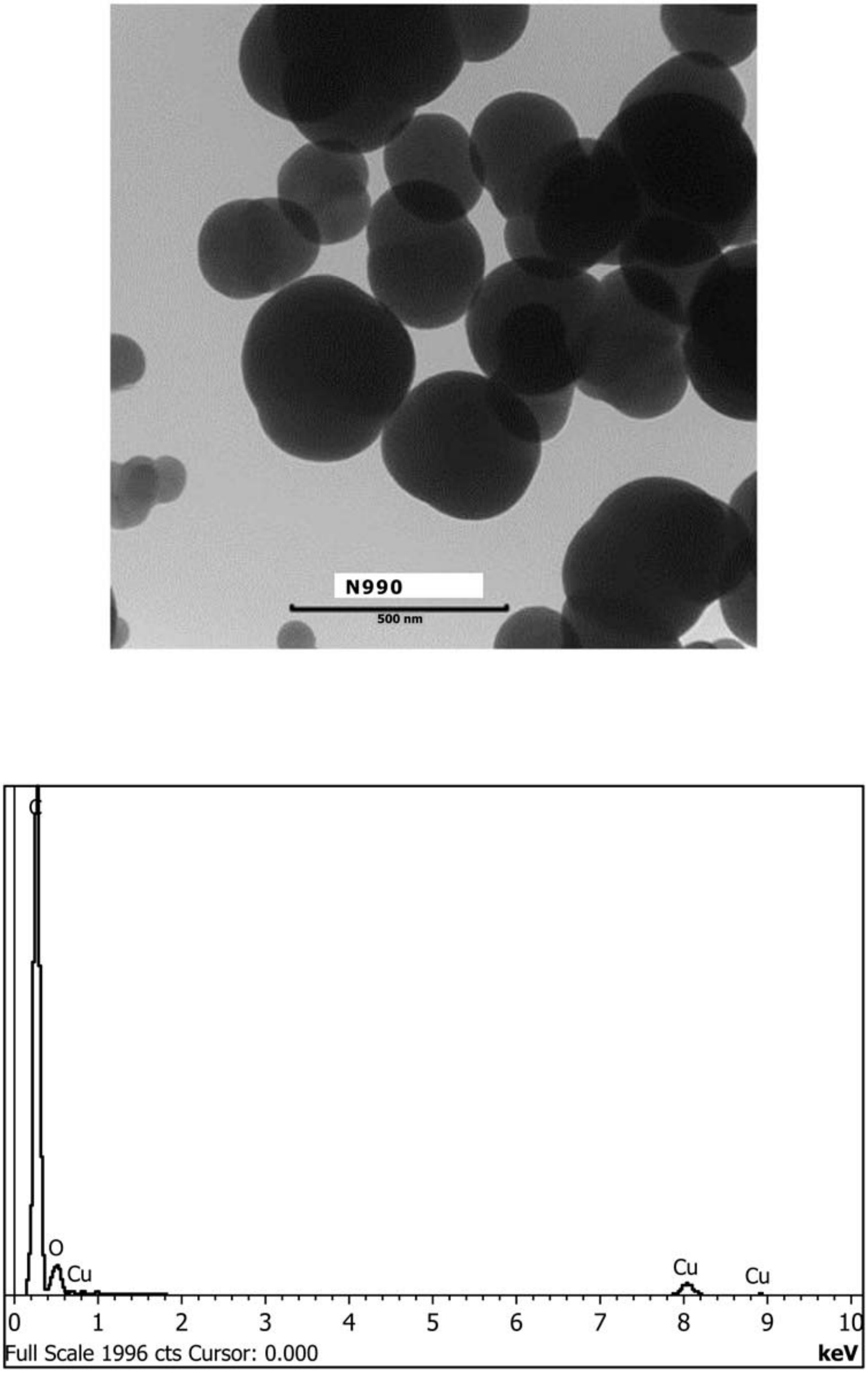
FIG. A2.4 TEM image (above) and X-ray Spectrum (below) of ASTM IRB7 carbon black N330





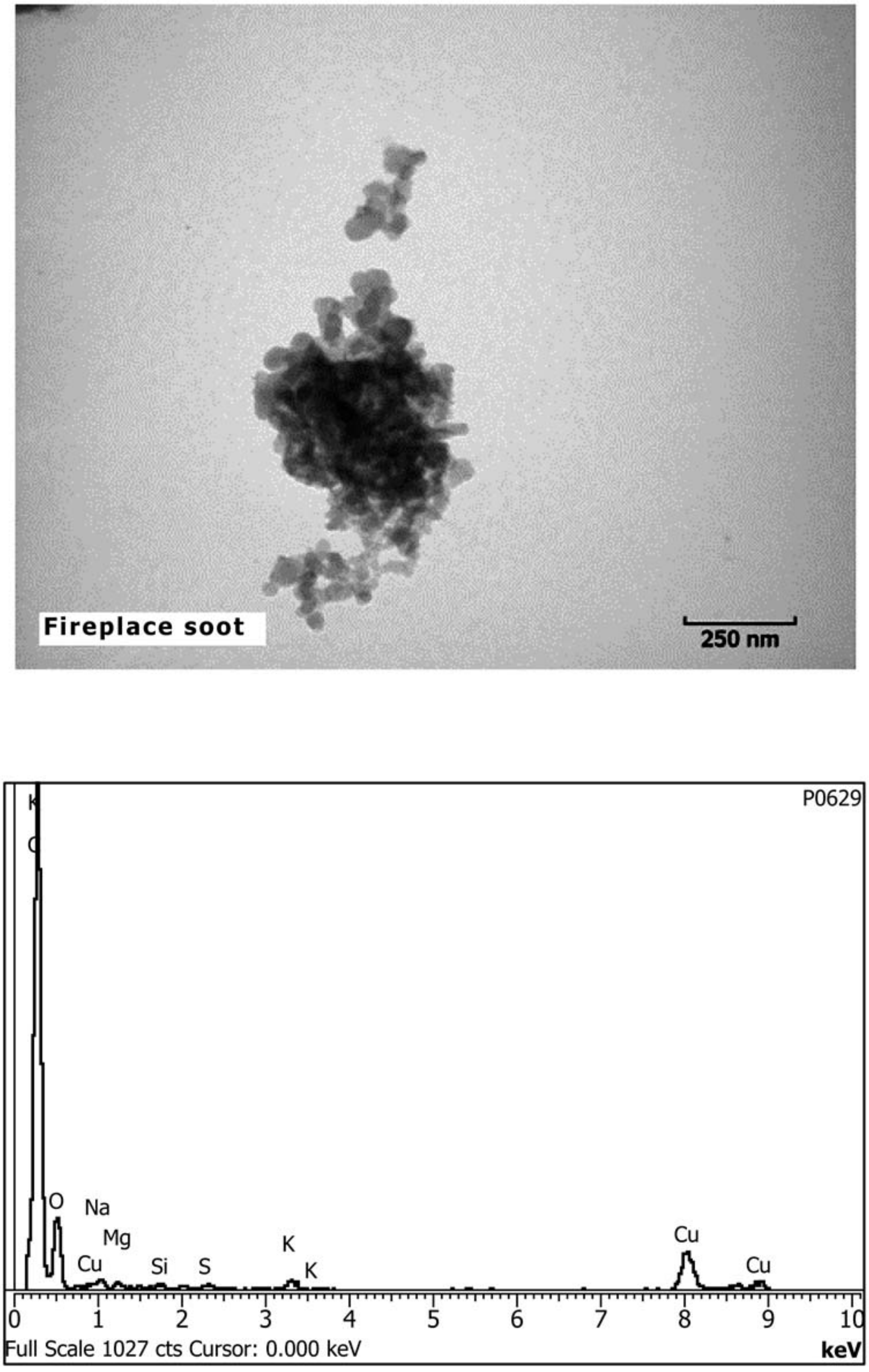
NOTE 1—Scale = 250 nm

FIG. A2.5 TEM image (above) and X-ray Spectrum (below) of ASTM SRB6-E carbon black N660



NOTE 1—Scale = 500 nm (Thermax, Cancarb, LTD)

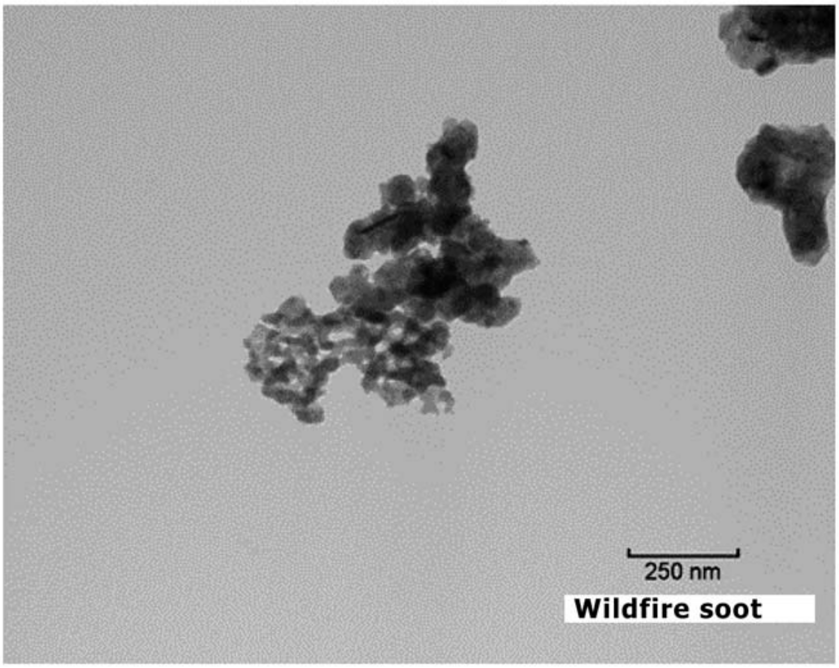
FIG. A2.6 TEM image (above) and X-ray Spectrum (below) of carbon black N990

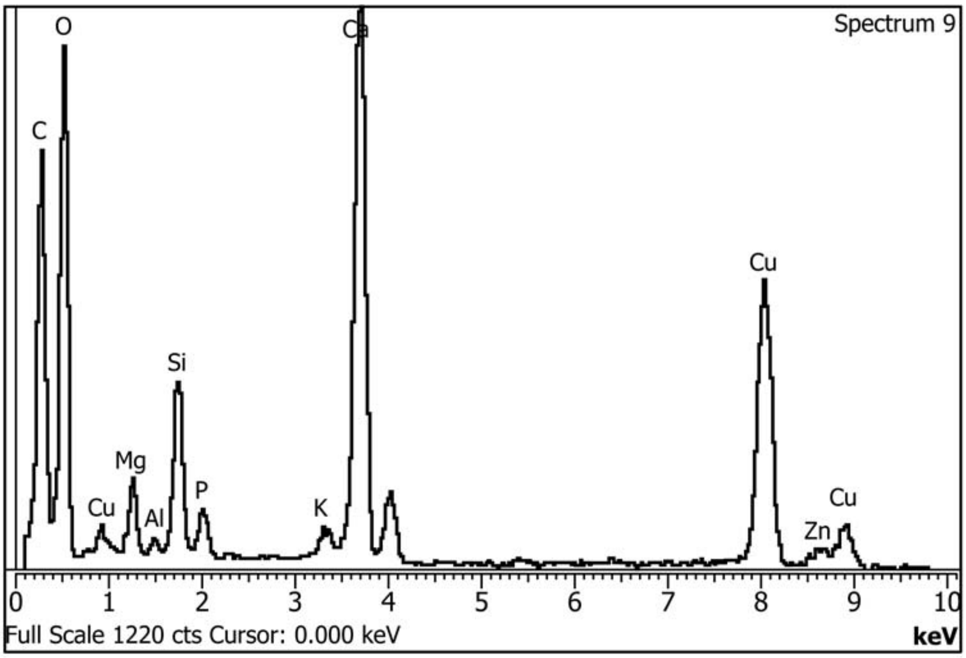


NOTE 1—Scale = 250 nm

NOTE 2—Soots from uncontrolled combustion may vary considerably. This figure illustrates one possibility.

FIG. A2.7 TEM image (above) and X-ray Spectrum (below) of Fireplace Soot

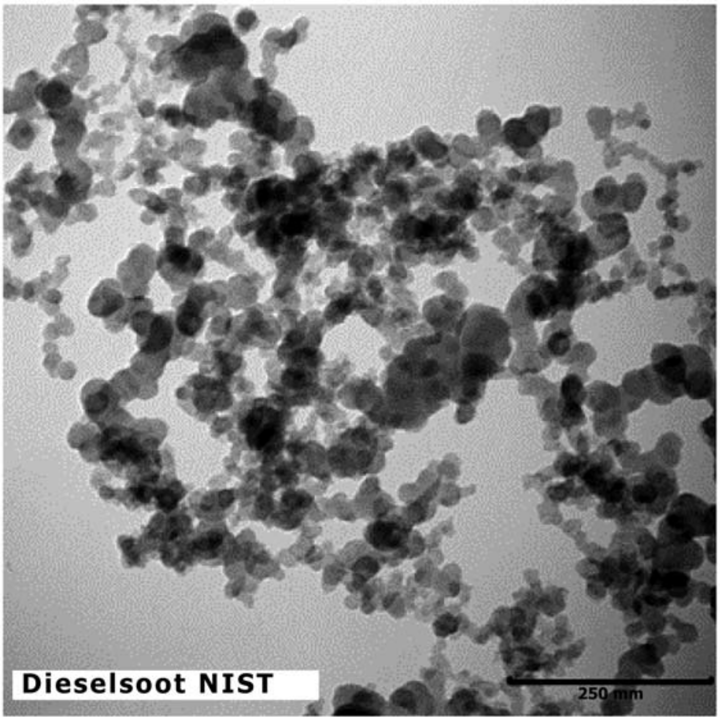


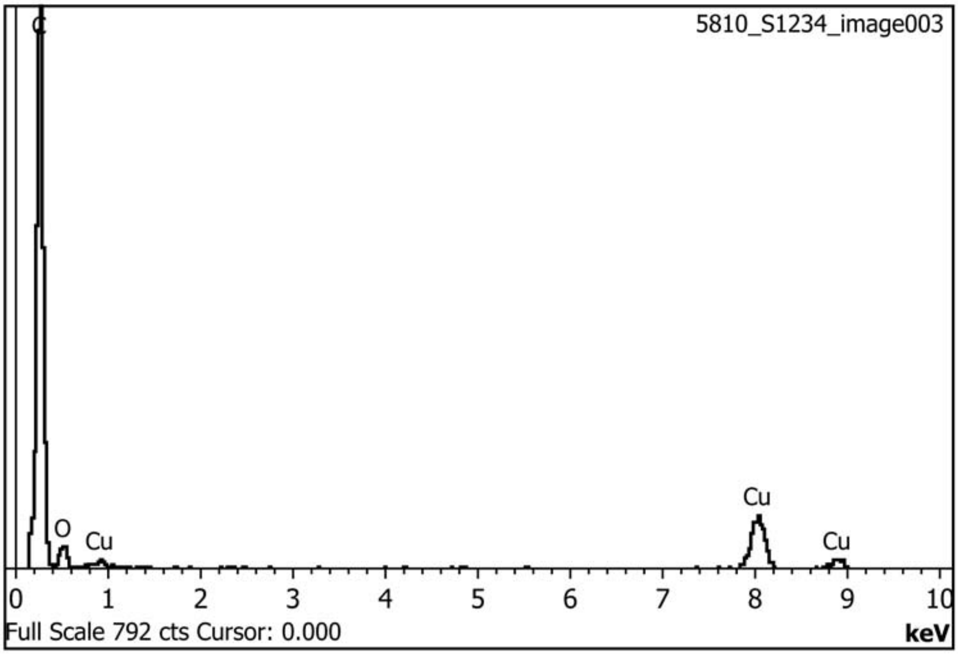


NOTE 1—Scale = 250 nm

NOTE 2—Soots from uncontrolled combustion may vary considerably. This figure illustrates one possibility.

FIG. A2.8 TEM image (above) and X-ray Spectrum (below) of California Wildfire Soot





NOTE 1—Scale = 250 nm

FIG. A2.9 TEM image (above) and X-ray Spectrum (below) of NIST Diesel Soot

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