



Designation: D 6602 – 03

## Standard Practice for Sampling and Testing of Possible Carbon Black Fugitive Emissions or Other Environmental Particulate, or Both<sup>1</sup>

This standard is issued under the fixed designation D 6602; 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 ( $\epsilon$ ) 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 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information.

1.3 *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.*

1.4 This practice requires some degree of expertise on the part of the microscopist. For this reason, the microscopist must have adequate training and substantial on-the-job experience in identifying the morphological parameters of carbon black. In support of this analysis, Donnet's book<sup>2</sup> is highly recommended to be used as a technical reference for recognizing and understanding the microstructure of carbon black.

### 2. Referenced Documents

- 2.1 *ASTM Standards:*  
D 1619 Test Methods for Carbon Black—Sulfur Content<sup>3</sup>  
D 3053 Terminology Relating to Carbon Black<sup>3</sup>  
D 3849 Test Method for Carbon Black—Morphological Characterization of Carbon Black Using Electron Microscopy<sup>3</sup>

### 3. Terminology

#### 3.1 Definitions of Terms Specific to This Standard:

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

3.1.2 *Aciniform Carbon*—colloidal carbon having a morphology consisting of spheroidal primary carbon particles fused together in aggregates of colloidal dimension in a shape like grape clusters, where the primary particles are comprised of turbostratic layers.

3.1.3 *carbon black*—a submicron black carbon powder commercially produced under controlled conditions by burning hydrocarbons in insufficient air; it is composed of colloidal carbon of well-defined aciniform morphology (see Annex A1) with a minimum of tars and other extraneous materials.

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  $\mu\text{m}$  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*—particulates from a superficial growth that grows on living and decaying organic matter.

3.1.8 *mineral and urban dust*—airborne, naturally occurring inorganic particulates inherent to the area.

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

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

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee D24 on Carbon Black and is the direct responsibility of Subcommittee D24.81 on Carbon Black Microscopy and Morphology.

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<sup>2</sup> 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.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 09.01.

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.

NOTE 1—Standard terminology relating to carbon black can be found in Terminology D 3053.

**4. Summary of Practice**

4.1 This practice describes the procedures and protocols to follow in order to collect fugitive emission/environmental samples and identify if these samples contain materials consistent or inconsistent with manufactured carbon black (referred to simply as carbon black).

4.2 Section 6 provides guidelines for proper sampling and handling of fugitive emission/environmental samples. Section 7 describes the analysis of the sample using transmission electron microscopy (TEM). This analysis is critical in determining if the collected sample is consistent or inconsistent with carbon black. Use of this analysis is mandatory in applying this practice. Section 8 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 scheme is a suggestion, not a requirement.

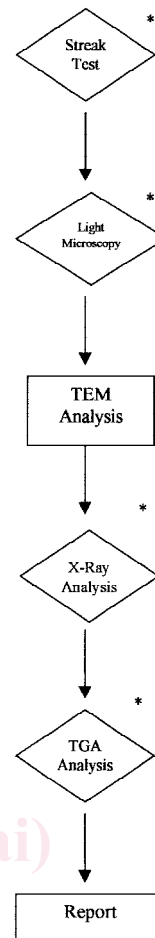
**5. Significance and Use**

5.1 Particulate emissions are major contributors to air contamination in industrial and urban environments. 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 must be representative of the contaminated area. For sampling, choose an area that appears to contain black particulates. The same general surface should be used for gathering all test samples for each property site location.

6.2 *Equipment:*



\* - Test is optional

**FIG. 1 Block Diagram of Suggested Analysis Scheme for Samples**

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

6.2.2 *Polyester/Cotton Balls or Glass Fiber Pads.*

6.2.3 *Petri Dishes or Polyethylene Bags.*

6.3 Samples are to be collected by two primary techniques in accordance with 6.3.1 and 6.3.2. Precautions should be taken to carefully collect, handle, and transport samples in a manner to not cause further contamination.

6.3.1 Remove particulates and solids from surfaces by placing an appropriate length of sticky tape on the surface to be sampled. Carefully remove the tape and place across a petri dish opening or in a polyethylene bag. All samples collected must be clearly identified at the time of collection. These samples may be used for later examination by microscopy and X-ray samples.

6.3.2 Collect the other type of sample by rubbing the surface to be sampled with a polyester ball or glass fiber filter pad with a light back-and-forth motion to remove surface particulates and solids. Do not try to remove “old” or aged contaminants from the surface. Light pressure on the ball or pad should be sufficient. Use the polyester ball or fiber pad to wipe an area of approximately 100 cm<sup>2</sup>. Place the exposed ball (or pad) in a plastic bag and label.

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6.3.3 All collected samples must be clearly identified at the time of collection. Measure the surface area sampled to the nearest  $\pm 0.25 \text{ cm}^2$  (each measurement has to be taken to the nearest  $\pm 0.5 \text{ cm}$ ) and record the measurement in Table 1. These samples may be used for microscopy and TGA analysis. Please note that if TGA analysis is a possibility, the samples should be collected on the fiber pad instead of the polyester ball.

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

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, 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 Transmission Electron Microscopy (TEM)**

*7.1 Summary of Test Method:*

7.1.1 This test method is a mandatory evaluation of the overall morphology of the particles present in the sample to determine primarily if their morphology is consistent with the unique grape cluster or acinoform, morphology of carbon black and soots. In order to discriminate discreet morphological parameters, the resolving power of a TEM is required. In addition to TEM examination, the ancillary methods in accordance with Section 8 may provide supporting information as to the nature and amount of the material.

7.1.2 The sample is extracted into chloroform by sonication. The resulting suspension is deposited onto a prepared 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.

*7.2 Apparatus and Chemicals:*

7.2.1 *Transmission Electron Microscope*, equipped with a 35-mm camera.

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

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

7.2.4 *Scissors*.

7.2.5 *Glass Test Tubes*, 10 by 75 mm, or *Glass Vial*, 3 by 5 cm.

7.2.6 *Pipettes*, disposable.

7.2.7 *Chloroform*, spectrophotometric grade.

7.2.8 *Polyester Balls or Glass Fiber Filter Pad*.

*7.3 Procedure:*

7.3.1 Snip off an appropriate soiled portion of the polyester/cotton ball or fiber filter pad with a clean pair of scissors and place in a freshly cleaned test tube or vial.

7.3.2 Add 1 to 4  $\text{cm}^3$  of chloroform to a test tube or 10 to 20  $\text{cm}^3$  to a glass vial until the entire sample is totally immersed in chloroform.

7.3.3 An ultrasonic probe or bath may be used to disperse the material into chloroform. 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. Add this additional volume to Sonication Volume (L) in Table 3.

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

7.3.5 Using a volumetric pipette, deliver from 5 to 10  $\text{mm}^3(\mu\text{L})$  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.

7.3.6 If the spot is exceptionally light, repeat 7.3.5 with additional drops. Place the remaining suspension back into the test tube, stopper, and place in the hood.

**TABLE 1 Chain of Custody Record**

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

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

Comments: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_



**TABLE 2 Sampling and Meteorology Record**

Sample Identification Number: \_\_\_\_\_

Complainant: \_\_\_\_\_

Date of Complaint: \_\_\_\_\_

Complainant Phone Number: \_\_\_\_\_

Complainant Address: \_\_\_\_\_

Nature of Complaint (What, when, where):  
 \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

Weather Data (Wind speed and direction during time of occurrence):  
 \_\_\_\_\_

Source of Weather Data:  
 \_\_\_\_\_

Plant Upsets Reported (During time of occurrence):  
 \_\_\_\_\_  
 \_\_\_\_\_

Other Area Environmental Releases (During time of occurrence):  
 \_\_\_\_\_  
 \_\_\_\_\_

**TABLE 3 Quantitative TEM Analysis Results**

NOTE 1—Result (R) and sensitivity need to be calculated in accordance with the procedure in 8.4.4.

A	B	D	I		L	V	S	R	
Grid Opening Area, $\mu\text{m}^2$	Number of Grid Openings Examined	Spot Diameter, mm	Carbon Black Aggregates Counted	Area of One Carbon Black Aggregate,	Sonication Volume, $\text{cm}^3$	Suspension Volume, $\text{cm}^3$	Surface Area Samples, $\text{cm}^2$	Result, %	Sensitivity, %

7.3.7 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 5 000 and 100 000 $\times$  magnification. In some cases, higher magnification is an additional benefit to aid in the characterization process.

**7.4 Particle Identification:**

7.4.1 Classify the particles as being consistent with or inconsistent with the morphology of aciniform material. Carbon black and some soot(s) are considered to contain aciniform carbon.

7.4.2 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.

7.4.3 Elemental identification of the acinoform material is assumed to be predominately carbonaceous. If this is not known, this can be accomplished using an X-ray detector

**TABLE 4 Common Particulates in Environmental Samples**

Particulate carbon (soots or carbon black, or both)
Vegetation char and ash
Mineral/urban dust
Pollen
Mold/mildew/fungus
Rubber dust
Other unknown

associated with the electron microscope. If the aciniform particles are not carbonaceous, then proceed to the report section.

7.4.4 If the particles are aciniform and carbonaceous in nature, then continue with the particle identification process. Examine the aggregate morphology by observing the particles between 10 000 $\times$  to 100 000 $\times$  magnifications and preferably, generate photomicrographs of representative fields. Refer to Annex A1 to aid in particle identification. In the case of aciniform carbon, 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. These particles are fused together to form colloidal aggregates.

#### 7.4.5 Morphology of Aggregates:

7.4.5.1 Assess how the carbon primary particles are joined together in the aggregates, that is, the dimensions (diameter and length) of the necks between primary particles. The preponderance of carbon black aggregates contain well-defined, fairly uniform, primary particles. Typically, in higher structure 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 particle from the next particle. The following are used to determine if the particles are inconsistent with carbon black:

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

(2) the diameter and length of the primary-particle necks have similar dimensions as the primary-particles, and

(3) the individual aggregates contain a wide range of primary particle sizes. If the particles are inconsistent with carbon black, then proceed to the Report section. If the particles are consistent with carbon black then continue with the particle identification process.

7.4.5.2 Typically, the perimeter of the primary particles in carbon black appear 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. If this is the case, then proceed to the Report section. If the particles are consistent with carbon black then continue with the particle identification process.

7.4.5.3 Assess the microstructure of the primary particles. In general, carbon blacks have more ordered, concentric, surface parallel orientation of graphitic layers in the primary particles than certain soots. Representative micrographs should be generated at an appropriate magnification and furnished in support of the analysis. See Figs A1.1 to A1.14 for reference photomicrographs to aid with carbon black identification. The final report should be written referencing Section 9.

## 8. Ancillary Methods for Support Data

8.1 This section is provided to include methods of sample identification that are situation-dependent (primarily based on the results of the TEM examination in Section 7) and, in questionable cases, can provide critical supporting, sometimes “fingerprinting,” information that is useful in identification.

### 8.2 Streak Test Method:

8.2.1 *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 soots and other particulate materials also give a positive streak test.

#### 8.2.2 Apparatus:

8.2.2.1 *Polyester or Cotton Balls.*

8.2.2.2 *Optical Lens Tissue.*

8.2.3 *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 2—Particulate-gathering materials should be kept in sealed bags or containers to protect them from exposure to foreign particulates and contamination.

### 8.3 Examination by Light Microscopy:

8.3.1 *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 method, while useful, is not mandatory and results obtained by this technique cannot be considered as conclusive for identifying the presence of carbon black.

#### 8.3.2 Apparatus:

8.3.2.1 *Light Stereomicroscope*, capable of 40 to 60× magnification.

8.3.2.2 *Polarized Light Microscope*, equipped with objectives in the 10 to 50× range of magnification.

8.3.2.3 *Meltmount*, 1.662 D.

8.3.2.4 *Scissors.*

8.3.2.5 *Glass Slides.*

8.3.2.6 *Glass Cover glass.*

8.3.2.7 *Microscope Camera* (Polaroid, 35 mm, or video).

8.3.2.8 *Organic Solvents.*

8.3.2.9 *Tungsten Needles.*

8.3.2.10 *Forceps.*

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

#### 8.3.3 Procedure:

8.3.3.1 Snip off a representative portion of the sample tape from the length of tape with a clean pair of scissors and place sticky side toward the glass cover which contains Meltmount. Prepare a glass slide with Meltmount and sandwich the tape between the cover and the glass slide.

8.3.3.2 Set the glass slide with the sample and cover on a hot plate and gently rock and press the cover down on the glass slide to dispel the air bubbles from the tape. Remove from the hot plate and gently hold the cover glass in place until cool.

8.3.3.3 Place the glass slide sample on the stereo light microscope stage and examine. 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.

8.3.3.4 Place the glass slide sample on the polarized light microscope and examine with transmitted light as required. Examine with single and crossed polars. Estimate the percentage of each component from Table 3 and record. 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. (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.

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

8.3.3.6 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.

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

NOTE 3—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, 1660, 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.

#### 8.4 Quantitative TEM Analysis:

8.4.1 *Summary of Test Method*—Having previously determined that the sample has aciniform material consistent with carbon black by TEM (Section 7), this quantitative TEM test method provides an estimation of the amount of surface area occupied by this material. Several assumptions are made in applying this test method as listed in 8.4.5.

#### 8.4.2 Apparatus and Chemicals:

8.4.2.1 *Transmission Electron Microscope*, equipped with a 35-mm camera.

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

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

8.4.2.4 *Scissors*.

8.4.2.5 *Glass Test Tubes*, 10 by 75 mm or *Glass Vial*, 3 by 5 cm.

8.4.2.6 *Pipettes*, disposable.

8.4.2.7 *Chloroform*, spectrophotometric-grade.

8.4.2.8 *Polyester Balls or Glass Fiber Filter Pad*.

8.4.2.9 *Volumetric Syringe or Pipette*, capable of delivering 5 to 10 mm<sup>3</sup>(μL).

8.4.3 *Procedure*:

8.4.3.1 Snip off the entire soiled portion of the polyester/cotton ball or fiber filter pad with a clean pair of scissors and place in a freshly cleaned test tube or vial.

8.4.3.2 Add 1 to 4 cm<sup>3</sup> of chloroform to a test tube or 10 to 20 cm<sup>3</sup> to a glass vial until the entire sample is totally immersed in chloroform. Record the amount of chloroform added (L) in Table 3.

8.4.3.3 An ultrasonic probe or bath may be used to disperse the material into chloroform. If an ultrasonic probe is used, set the vial into a container filled with ice and water. Ultrasonicate a sufficient amount of time to disperse the material. If the sample under examination, is not dispersed well, then re-prepare the sample using more ultrasonic energy or dilute the suspension. Add this additional volume to Sonication Volume (L) in Table 3.

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

8.4.3.5 Using a volumetric pipette, deliver from 5 to 10 mm<sup>3</sup>(μL) of the suspension onto the center of the grid and let 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. Record the volume of the suspension (V) dropped onto the grid in Table 3.

8.4.3.6 Remove the grid from the filter paper and measure the diameter of the spot to the nearest ±1 mm. Record the diameter of the spot (D) in Table 3.

8.4.3.7 If the spot is exceptionally light, repeat 7.3.5 with additional drops and record total volume used. Add this additional volume to (V) in Table 3. Place the remaining suspension back into the test tube, stopper, and place in the hood.

8.4.3.8 Place the grid on the microscope sample holder and insert it into the column. A typical accelerating voltage of 80 kV is sufficient for carbon black. Determine an appropriate magnification for the particles between 5 000 and 100 000×. In some cases, higher magnification is an additional benefit to aid in the characterization process.

8.4.3.9 Place the grid into the TEM and examine in accordance with the following parameters. Examine a minimum of 3 fields per grid openings and tally the number of carbon black aggregates. If the object per structures count exceeds 100, stop the examination and report the results accordingly. If the object per structures count is less than 100, continue the examination until at least 100 objects per structures are counted and that grid opening of the 100<sup>th</sup> object per structures has been fully examined.

8.4.3.10 Report the number of grid openings examined (B) in Table 3. If the sample contains carbon black, report the number of aggregates that are consistent with carbon black (I) in Table 3.

8.4.3.11 Calculate in accordance with 8.4.4 and report the amount of area occupied by carbon black and sensitivity of the analysis in Table 3.

8.4.3.12 If no carbon black aggregates are found, report less than 0.001 %.

NOTE 4—The number in 8.4.3.12 was obtained in accordance with the calculation procedure of 8.4.4 based on a conservative assumption that less than 1 carbon black aggregate was present and had an aggregate area of 60 000 nm<sup>2</sup>; sonication volume used 10 cm<sup>3</sup>; suspension volume used 0.005 cm<sup>3</sup>; three 200-mesh grid openings were examined; and the sampled area equaled 100 cm<sup>2</sup>.

8.4.4 *Calculation*—Calculate as follows:

$$C = T * A * B \quad (1)$$

$$G = (3.14159 * (D/2)^2)/F \quad (2)$$

$$H = (C/G) * 100 \quad (3)$$

$$J = (I/H) * 100 \quad (4)$$

$$P = ((J * L)/V) * 1000 \quad (5)$$

$$R = T * ((P * Q)/S) * 100 \quad (6)$$

where:

*A* = area of Grid Opening, usually available by the manufacture, nm<sup>2</sup>,

*B* = number of grid openings examined, obtained from 8.4.3.8,

*C* = area of grid examined, cm<sup>2</sup>

*D* = spot diameter, diameter of the liquid drop placed onto the filter paper where the TEM grid rests in the middle of the spot; spot diameter is obtained from 8.4.3.6, measured to ±1 mm,

*F* = conversion factor that converts the area from mm<sup>2</sup> to um<sup>2</sup>,  $F = 10^6$ ,

*G* = spot area, cm<sup>2</sup>, area of the spot that was obtained by placing one or multiple liquid drops of the suspension onto the filter paper, (see 8.4.3.5),

*H* = area of spot examined, %,

*I* = number of carbon black aggregates counted, obtained from 8.4.3.9,

*J* = total number of carbon black aggregates on the spot; also represents the total amount of carbon black aggregates in the volume of the suspension that was delivered onto the filter paper and the grid (spot),

*L* = total chloroform volume used on sonication to remove the sample from the polyester/cotton ball, obtained from 8.4.3.2 and 8.4.3.3,

*V* = volume of the suspension delivered onto the filter paper and the grid (spot), obtained from 8.4.3.5 and 8.4.3.7,

*P* = total number of carbon black particles in the collected sample,

*S* = Surface area sampled, obtained from 6.3.2 and measured to ±5 mm<sup>2</sup>,

*T* = conversion factor that converts the area from nm<sup>2</sup> to cm<sup>2</sup>,  $T = 10^{-14}$ ,

*Q* = area occupied by one carbon black aggregate, available by carbon black manufacture, and

*R* = area occupied by total number of carbon black aggregates (*P*) over the sampled area (*S*), %.

To calculate the sensitivity of the analysis, repeat all calculation in 8.4.4 and use one for a number of carbon black aggregates counted (65 400 nm<sup>2</sup>).

8.4.5 *Assumptions for the Quantitative TEM Analysis:*

8.4.5.1 Uniform and complete collection of representative sample from 100 cm<sup>2</sup>.

8.4.5.2 Environmental conditions have not been detrimental to the sample.

8.4.5.3 Uniform deposition of sample in chloroform on grid.

8.4.5.4 Complete removal of acinoform carbon from sample medium.

8.4.5.5 The sensitivity of the test method is dependent on locating one aggregate in the total area examined and assuming a single aggregate area of 65 400 nm<sup>2</sup> (see Test Method D 3849, 11.1.6)

8.5 *X-ray Analysis:*

8.5.1 *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 or wavelength dispersive spectrometry to determine if an individual component in the sample has an appropriate sulfur to carbon ratio consistent with commercially produced carbon black. 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. 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 or a scanning 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. Determine if the specific particles have extraneous components not normally found in carbon black.

8.5.2 *Apparatus and Chemicals:*

8.5.2.1 *Transmission Electron Microscope (TEM) or Scanning Electron Microscope (SEM)*, equipped with energy or wavelength dispersive analysis equipment.

8.5.2.2 *TEM Grids* (see 20.3) or *SEM Sample Mounts*.

8.5.2.3 *Ultrasonic Bath* (TEM method).

8.5.2.4 *Scissors* (TEM).

8.5.2.5 *Glass Test Tubes* (TEM), 10 by 75-mm.

8.5.2.6 *Pipettes* (TEM), disposable.

8.5.2.7 *Chloroform*, spectrophotometric-grade (TEM).

8.5.2.8 *Polyester Balls or Glass Fiber Filter Pad* (TEM).

8.5.2.9 *Carbon Evaporator* (SEM).

8.5.2.10 *Carbon Black Standard(s)*, in accordance with Test Methods D 1619.

8.5.3 *Procedure*

8.5.3.1 *TEM Samples:*

(1) Follow the procedure in accordance with 7.3.1 to 7.3.8 for the sample as well as one or more of the carbon black standards from Test Methods D 1619.

(2) Isolate the specific particle in question and center the beam on the particle.

(3) Following the manufacturer's instructions for the energy dispersive equipment attached to the microscope, determine the elemental composition versus one or more of the carbon black standards from Test Methods D 1619 which have known sulfur contents. In addition, determine if other non-carbon components besides sulfur are present in significant amounts

8.5.3.2 *SEM Samples:*

(1) Attach the sticky tape sample collected to an SEM sample mount with double-sided sticky tape. Be careful not to damage the sample.

(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.

(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 analysis.

(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 non-carbon components besides sulfur are present in significant amounts.

8.6 *Thermogravimetric Analysis:*

8.6.1 *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.

8.6.2 *Apparatus:*

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

8.6.2.2 *Glass Fiber Filter Pad.*

8.6.2.3 *Tweezers.*

8.6.3 *Procedure:*

8.6.3.1 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<sup>3</sup>/min) and at 650°C under air (50 cm<sup>3</sup>/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<sup>3</sup>/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<sup>3</sup>/min. Heat from 350 to 650°C at 10°C/min and record.

8.6.3.2 Repeat 8.5.3.1 for the sample in question and record the mass loss of the sample in nitrogen and the mass loss of the sample in air.

8.6.3.3 Calculate the volatile content using the following equation:

$$\% \text{ volatiles} = \frac{(\text{mass loss of sample in nitrogen} - \text{mass loss of blank in nitrogen})}{(\text{mass loss of sample in air} - \text{mass loss of blank in air})} \times 100 \quad (7)$$

**9. Report**

9.1 Report the following information for each sample:

9.1.1 A Sampling and Meteorology Record (see Table 2).

9.1.2 A Chain of Custody Record (see Table 1).

9.1.3 Observation from the TEM analysis (Section 7).

9.1.3.1 Furnish necessary supporting photomicrographs.

9.2 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:

9.2.1 Light Microscopy (8.3).

9.2.2 Streak Test (8.2).

9.2.3 X-ray Analysis (8.5).

9.2.4 Thermogravimetric Analysis (8.6).

9.2.5 Quantitative TEM Analysis (8.4).

9.2.5.1 Record findings in Table 3.

9.2.5.2 Calculate in accordance with 8.4.4 and report results and sensitivity in Table 3.

9.2.5.3 If no carbon black aggregates are found, report less than 0.001 %.





**ANNEX**

**(Mandatory Information)**

**A1. ACINOFORM MORPHOLOGY OF SOOTS AND CARBON BLACK**

**A1.1 Scope**

A1.1.1 The acinoform morphology that appears like a cluster of grapes is the characteristic morphology of soots, carbon black, and several other materials. Several photomicrographs (Figs. A1.1-A1.14) taken on a transmission electron

microscope are attached for comparison purposes. The photomicrographs are to be taken as examples and comparisons in the laboratory and should be done against locally collected samples. The shape, size, and widely number of nodules per aggregate can vary widely.

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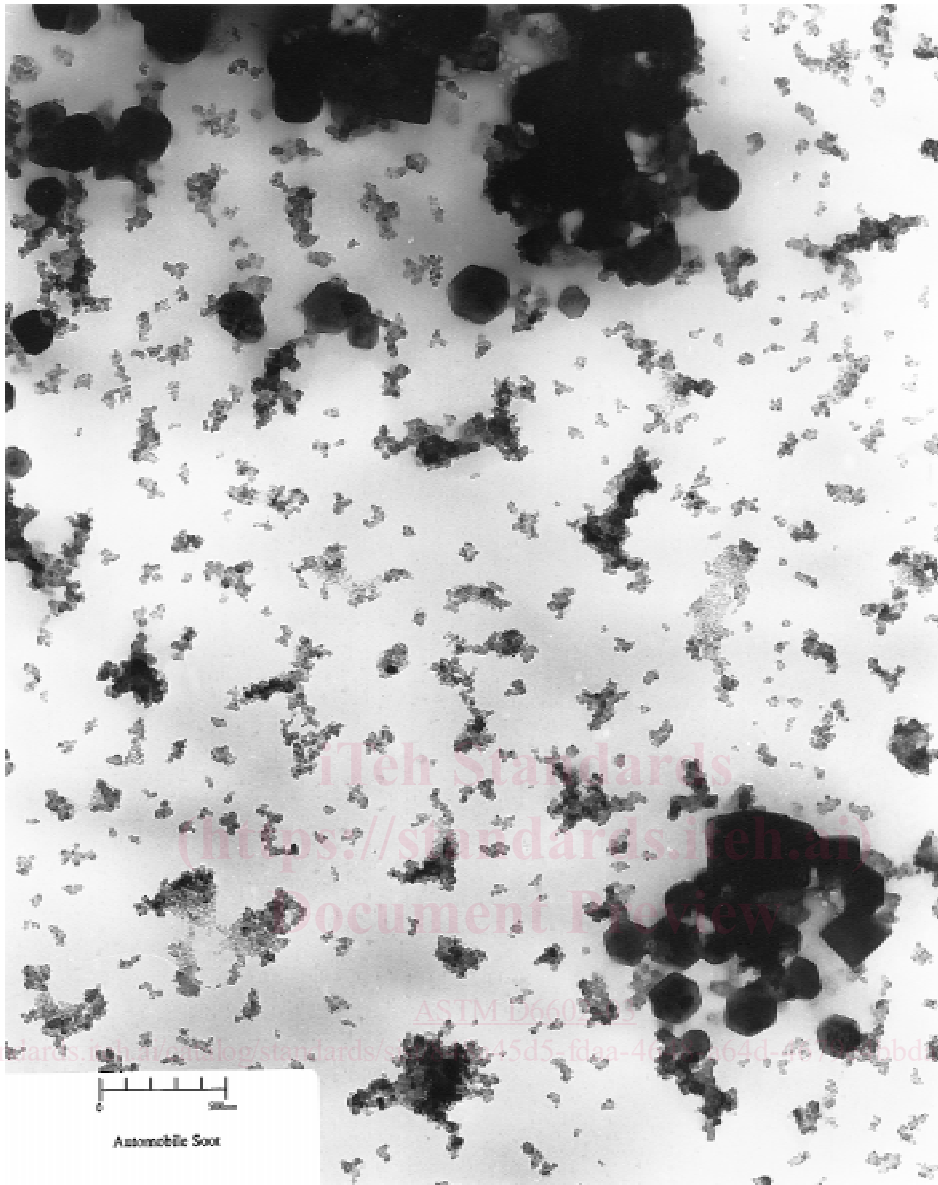


FIG. A1.1 Automobile Soot, Scale = 500 nm