



# Standard Test Method for Determining Concentration of Airborne Single-Crystal Ceramic Whiskers in the Workplace Environment by Scanning Electron Microscopy<sup>1</sup>

This standard is issued under the fixed designation D 6059; 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 test method covers the sampling methods and analysis techniques used to assess the airborne concentration and size distribution of single-crystal ceramic whiskers (SCCW), such as silicon carbide and silicon nitride, which may occur in and around the workplace where these materials are manufactured, processed, transported, or used. This test method is based on the collection of fibers by filtration of a known quantity of air through a filter. The filter is subsequently evaluated with a scanning electron microscope (SEM) for the number of fibers meeting appropriately selected morphological and compositional criteria. This test method has the ability to distinguish among many different types of fibers based on energy dispersive X-ray spectroscopy (EDS) analysis. This test method may be appropriate for other man-made mineral fibers (MMMMF).

1.2 This test method is applicable to the quantitation of fibers on a collection filter that are greater than 5  $\mu\text{m}$  in length, less than 3  $\mu\text{m}$  in width, and have an aspect ratio equal to or greater than 5:1. The data are directly convertible to a statement of concentration per unit volume of air sampled. This test method is limited by the diameter of the fibers visible by SEM (typically greater than 0.10 to 0.25  $\mu\text{m}$  in width as determined in 12.1.5) and the amount of coincident interference particles.

1.3 A more definitive analysis may be necessary to confirm the presence of fibers with diameters  $\leq 0.10$  to 0.25  $\mu\text{m}$  in width. For this purpose, a transmission electron microscope (TEM) is appropriate. The use of the TEM method for the identification and size measurement of SCCW is described in Practice D 6058 and Test Method D 6056.

1.4 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.5 *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 applica-*

*bility of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 1193 Specification for Reagent Water<sup>2</sup>

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres<sup>3</sup>

D 4532 Test Method for Respirable Dust in Workplace Atmospheres<sup>3</sup>

D 6056 Test Method for Determining Concentration of Airborne Single-Crystal Ceramic Whiskers in the Workplace Environment by Transmission Electron Microscopy<sup>3</sup>

D 6057 Test Method for Determining Concentration of Airborne Single-Crystal Ceramic Whiskers in the Workplace Environment by Phase Contrast Microscopy<sup>3</sup>

D 6058 Practice for Determining Concentration of Airborne Single-Crystal Ceramic Whiskers in the Workplace Environment<sup>3</sup>

E 691 Practice for Conducting Interlaboratory Study to Determine the Precision of a Test Method<sup>4</sup>

E 766 Practice for Calibrating the Magnification of SEM Using NBS SRM 484<sup>5</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 *analytical sensitivity, n*—airborne fiber concentration represented by a single fiber counted in the SEM.

3.1.1.1 *Discussion*—Although the terms *fiber* and *whisker* are, for convenience, used interchangeably in this test method, whisker is correctly applied only to single-crystal fibers whereas a "fiber" may be single- or poly-crystalline or may be noncrystalline.

3.1.2 *aspect ratio, n*—the ratio of the length of a fiber to its width.

3.1.3 *fiber, n*—for the purpose of this test method, an elongated particle having a length greater than 5  $\mu\text{m}$ , a width less than 3  $\mu\text{m}$ , and an aspect ratio equal to or greater than 5:1.

3.1.4 *fibrous, adj*—composed of parallel, radiating, or interlaced aggregates of fibers, from which the fibers are sometimes

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.03.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 03.01.

separable. That is, the aggregate may be referred to as fibrous even if it is not composed of separable fibers, but has that distinct appearance. The term fibrous is used in a general mineralogical way to describe aggregates.

3.1.5 *man-made mineral fiber, n*—any inorganic fibrous material produced by chemical or physical processes.

3.1.6 *single-crystal ceramic whiskers, n*— a man-made mineral fiber that has a single-crystal structure.

3.2 For definitions of other terms used in this test method, see Terminology D 1356.

#### 4. Summary of Test Method

4.1 The sample is collected on a mixed cellulose ester (MCE) filter by drawing air, using a sampling pump, through an open-face 25-mm electrically conductive sampling cassette assembly (1,2).<sup>6</sup> A section of the filter is transferred to an SEM stub and the fibers are identified, sized, and counted at a magnification of 2000× in the SEM using the criteria discussed in Section 11. Results are expressed as a fiber concentration per unit volume of air and a fiber loading per unit area of filter. The airborne concentration is expressed as fiber per millilitre (f/mL) and fiber loading is expressed as fibers per square millimetre (f/mm<sup>2</sup>).

#### 5. Significance and Use

5.1 The SCCW may be present in the workplace atmosphere where these materials are manufactured, processed, transported, or used. This test method can be used to monitor airborne concentrations of SCCW fibers in these environments. It may be employed as part of a personal or area monitoring strategy.

5.2 This test method is based on morphology and elemental composition. The analysis technique has the ability to identify SCCW.

NOTE 1—This test method assumes that the analyst is familiar with the operation of SEM/EDS instrumentation and the interpretation of data obtained using these techniques.

5.3 This test method is not appropriate for measurement of fibers with diameters  $\leq 0.10$  to  $0.25 \mu\text{m}$  due to visibility limitations associated with SEM. The TEM method may be used to provide additional size information of SCCW if needed (see Practice D 6058 for additional information on the use of this test method).

5.4 Results from the use of this test method shall be reported along with 95 % confidence limits for the samples being studied. Individual laboratories shall determine their intralaboratory coefficient of variation and use it for reporting 95 % confidence limits (1,3,4).

#### 6. Interferences

6.1 This test method has been designed to filter air for the determination of SCCW concentration. However, filtration of air also involves collection of extraneous particles and other fibers that may not be of interest. Extraneous particles may obscure the fibers by overlay or by overloading of the filter.

This situation can be managed by regulating the air volume sampled and thus the filter loading. Fibers should appear separated from other particles to ensure an adequate opportunity for their recognition as separate entities in the SEM and accurate counting. Some coincident particle agglomeration does occur even with these guidelines. Analyze an alternate filter with a reduced loading if the obscuring condition appears to exceed 15 % of the filter area (5). Redeposition of a portion of an overloaded filter is permitted only in circumstances where an alternate filter is not available and cannot be obtained through resampling (see 10.1.5).

#### 7. Apparatus and Reagents

7.1 *Sampling Cassette*—Use a 25-mm electrically conductive cassette assembly such as a three-piece cassette with an extension cowl or retainer ring containing a  $0.45\text{-}\mu\text{m}$  pore-size MCE filter and a support pad. Seal the cassette assembly with shrink tape. Reloading of used cassettes is not permitted.

7.2 *Personal Sampling Pump*—Use a portable battery-operated pump for personal sampling. Each pump must be capable of operating within the range from 0.5 to 4 L/min and continuously over the chosen sampling period (1). The flow must be free from pulsation. All pumps shall be calibrated prior to use (6).

7.3 *Area Sampling Pump*—Use a personal sampling pump or a non-portable high-volume pump for area sampling. Each pump shall be capable of operating within the range from 0.5 to 16 L/min and continuously over the chosen sampling period (1). The flow shall be free from pulsation. All pumps shall be calibrated prior to use (6).

7.4 *Vinyl tubing or equivalent.*

7.5 *Scanning Electron Microscope*, a SEM capable of operating using an accelerating voltage of at least 15 kV. The SEM must be capable of performing EDS analysis. A light element X-ray analyzer capable of detecting carbon, nitrogen, and oxygen is recommended.

7.6 *Vacuum Evaporator*—For vapor deposition of conductive layers of carbon.

NOTE 2—Sputter coaters and carbonaceous fiber coaters are not appropriate.

7.7 *SEM Sample Preparation Stubs*—Stubs made of carbon are suitable. (A carbon planchet disk glued to a metal holder is also acceptable.)

7.8 *Conducting DAG*, (colloidal graphite) type adhesive paint or double-sided conductive carbon tape.

7.9 *NIST SEM Magnification Standard, SRM 484* (see Practice E 766).

7.10 *Sample Preparation Area*, consisting of either a clean room facility or a room containing a laminar flow hood.

7.11 *Specification D 1193 Type II Water*, (particle-free).

7.12 *Tweezers.*

7.13 *Scalpel Blades.*

7.14 *MCE Filters*, 25 mm, 0.45 and 0.22- $\mu\text{m}$ .

7.15 *Funnel/Filter Assembly*, 25-mm.

7.16 *Miscellaneous Supplies.*

NOTE 3—If the alternate sample preparation method discussed in 10.4 is utilized, the following additional apparatus and reagents will be necessary:

<sup>6</sup> The boldface numbers in parentheses refer to a list of references at the end of this test method.

7.16.1 *Oven*, capable of operating at 65°C is required to collapse the filter. A hot plate capable of maintaining the required temperature is an acceptable alternative to the oven.

7.16.2 *Plasma Asher*, a low-temperature asher (LTA) is required to plasma-etch the collapsed MCE filter. A nominal 100-W unit is suitable.

7.16.3 *Oxygen*, used as a bleed gas in the plasma asher.

7.16.4 *Micro-syringe or Pipette*, a device capable of consistently delivering a solution volume of 100 µL is required.

7.16.5 *Dimethyl Formamide* (DMF).

7.16.6 *Glacial Acetic Acid*.

7.16.7 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>7,8</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

## 8. Sample Collection

8.1 Collect samples of airborne SCCW on MCE filters using sampling cassettes and pumps as noted in Section 7.

8.2 Remove the outlet plug from the sampling cassette and connect it to a sampling pump by means of flexible, constriction-proof tubing.

8.3 Perform a leak check of the sampling system by activating the pump with the closed cassette and rotameter (or other flow measurement device) in line. Any flow indicates a leak that must be eliminated before starting the sampling operation.

8.4 Remove the inlet plug from the sampling cassette to eliminate any vacuum that may have accumulated during the leak test, then remove the entire inlet cap.

8.5 Conduct personal and area sampling as follows:

8.5.1 For personal sampling, fasten the sampling cassette to the worker's lapel in the worker's breathing zone and orient it face down. Adjust the calibrated flow rate to a value between 0.5 and 4 L/min (1). Typically, a sampling rate between 0.5 and 2.5 L/min is selected (2-4,6,7). Also see Test Method D 4532.

8.5.2 Place area samples on an extension rod facing down at a 45° angle. Adjust the calibrated flow rate to a value between 0.5 and 16 L/min (1). Typically, a sampling rate between 1 and 10 L/min is selected (8).

8.5.3 Set the sampling flow rate and time to produce an optimum fiber loading between 100 to 1300 f/mm<sup>2</sup> (1,2). The time of sampling can be estimated by using the following equation:

$$t = \frac{(A_c)(F_L)}{(Q)(C_e)10^3} \quad (1)$$

<sup>7</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

<sup>8</sup> The effective collection area ( $A_c$ ) should be measured periodically, especially if different types of cassettes are used.

where:

$A_c$  = active filter collection area (~385 mm<sup>2</sup> for 25-mm filter),<sup>8</sup>

$t$  = time, min,

$F_L$  = fiber loading, f/mm<sup>2</sup>,

$Q$  = sampling flow rate, L/min,

$C_e$  = estimated concentration of SCCW, f/mL, and

$10^3$  = conversion factor.

8.5.4 At a minimum, check the flow rate before and after sampling. If the difference is greater than 10 % from the initial flow rate, the sample shall be rejected. Also see Test Method D 4532.

8.6 Carefully remove the cassette from the tubing at the end of the sampling period (ensure that the cassette is positioned upright before interrupting pump flow). Replace the inlet cap and inlet and outlet plugs, and store the cassette.

NOTE 4—Deactivate the sampling pump prior to disconnecting the cassette from the tubing.

8.7 Submit at least one field blank (or a number equal to 10 % of the total samples, whichever is greater) for each set of samples. Remove the cap of the field blank briefly (approximately 30 s) at the sampling site, then replace it. The field blank is used to monitor field sampling procedures. Field blanks shall be representative of filters used in sample collection (for example, same filter lot number).

8.8 Submit at least one unused and unopened sealed blank which is used to monitor the supplies purchased as well as procedures used in the laboratory. The sealed blank shall be representative of filters used in sample collection (for example, same filter lot number).

## 9. Transport of Samples

9.1 Ship the samples in a rigid container with sufficient packing material to prevent jostling or damage. Care shall be taken to minimize vibrations and cassette movement.<sup>9-96</sup>

NOTE 5—Do not use shipping material that may develop electrostatic forces or generate dust.

NOTE 6—Shipping containers for 25-mm sampling cassettes are commercially available and their use is recommended.

9.2 Include in the container a list of samples, their descriptions, and all other pertinent information.

## 10. Specimen Preparation

10.1 The objective of the specimen preparation technique is to produce a sample suitable for analysis in the SEM. Procedures as described as follows or other equivalent methods may be used to prepare samples.

10.1.1 Wipe the exterior of the sampling cassettes with a damp cloth to minimize the possibility of contamination before taking them into the clean preparation area.

10.1.2 Perform specimen preparation in a well-equipped, clean facility.

10.1.3 *Direct Sample Preparation*:

10.1.3.1 Carefully cut a wedge of the filter (for example, 25 %) with a curved, steel surgical blade using a rocking motion to prevent tearing.

NOTE 7—Use care not to disturb the particles on the filter surface.

10.1.3.2 Attach the filter section, particle side up, onto an

SEM stub using conducting DAG or double-sided, conductive carbon tape.

10.1.3.3 If DAG is used, wait until it is dried then place the SEM stub inside the bell jar of a vacuum evaporator. No waiting is necessary if double-sided, conductive tape is used. Evaporate a section of graphite rod (approximately 1-mm diameter by 8-mm length) onto the surface of the filter.

NOTE 8—Rotation of the sample at an angle ( $\sim 45^\circ$ ) is recommended during the coating process.

NOTE 9—Evaporation of gold (Au) or palladium (Pd), or both, on the sample may be used to improve visibility in the SEM.

10.1.3.4 Remove the sample and store in a clean, dry environment until analysis.

10.1.4 *Alternate Sample Preparation*—This test method is provided because it has been reported to give better contrast and visibility which may result in a better estimate of the fiber concentration. It is based on work that was originally reported by Burdett and Rood and it involves the use of a solvent mixture to partially collapse the filter matrix, thereby holding any collected particles in place (9). The collapsed filter is then lightly plasma etched to remove the top surface of the filter. This step is performed so as to expose any small fibers that might otherwise be hidden below the surface of the filter and yet not free any fibers from the collapsed matrix.

10.1.4.1 Prepare a mixture of 35 % DMF, 15 % acetic acid and 50 % distilled water.

NOTE 10—All percentages are volume percents.

10.1.4.2 Place 100  $\mu\text{L}$  of the preceding solution on the polished side of a high-density carbon planchet. Cut a wedge of the MCE filter (for example, 25 %) with a steel surgical blade, and then gently place it, particle side up, onto the solution. A shallow angle is used to minimize the possibility of entrapping air bubbles.

10.1.4.3 After a 5-min wait period, place the sample in an oven that has been preheated to  $65^\circ\text{C}$ . After an additional 15 min, remove the sample from the oven and allow to cool to room temperature. The sample should be covered to minimize contamination from other airborne particles.

10.1.4.4 Place the sample in the plasma asher and etch the filter.

NOTE 11—Because plasma ashers vary greatly in their performance, both from unit to unit and between different positions in the asher chamber, it is difficult to specify the conditions that shall be used. Insufficient etching will result in a failure to expose embedded fibers, and too much etching may result in loss of particles from the surface. It is recommended that the time for etching of a known weight of a collapsed filter be established and that the etching tare weight be calculated in terms of micrometres per second. The actual etching time used for a particular asher and operating conditions will then be set such that a  $\sim 1$  to 2- $\mu\text{m}$  layer (not more than 10 %) of collapsed surface will be removed.

10.1.4.5 Place the SEM stub inside the bell jar of a vacuum evaporator. Evaporate a section of graphite rod (approximately 1-mm diameter by 8-mm length) onto the surface of the filter.

NOTE 12—Rotation of the sample at an angle ( $\sim 45^\circ$ ) is recommended during the coating process.

NOTE 13—Evaporation of gold (Au) or palladium (Pd), or both, on the sample may be used to improve visibility in the SEM.

10.1.4.6 Remove the sample and store in a clean, dry

environment until analysis.

10.1.5 *Indirect Sample Preparation*—Resuspension of particulate matter collected on an overloaded filter and subsequent filtering onto another substrate may result in loss or breakup of the sample materials. Therefore, resuspension is permitted only in circumstances where an alternate filter is not available and cannot be obtained through resampling (for example, evaluation of a prototype procedure where the operational parameters cannot be duplicated). If indirect sample preparation procedures are employed, it must be clearly noted in the report. Furthermore, it must be clearly stated that results were obtained from the use of indirect sample preparation techniques and used only as an estimate of SCCW concentrations in the workplace environment. The following procedures are appropriate for this purpose.

10.1.5.1 Carefully remove the filter from the sampling cassette and cut a wedge (for example,  $\frac{1}{2}$  or  $\frac{1}{4}$  or the area of the original filter) as accurately as possible from the filter with a curved, steel surgical blade using a rocking motion to prevent tearing.

NOTE 14—Use care not to disturb the particles on the filter surface.

NOTE 15—The size of the wedge will depend on filter loading. If the sample is very heavily loaded, then a smaller wedge (for example,  $\frac{1}{8}$  or  $\frac{1}{16}$  the area of the original filter) may be more appropriate.

10.1.5.2 Place the section of filter into a 100-mL beaker.

10.1.5.3 Add approximately 80 mL of filtered ASTM Type II distilled water to the beaker.

10.1.5.4 Place the beaker into the ultrasonic bath. Sonicate for approximately 1 min.

10.1.5.5 Remove the section of filter and rinse it using filtered distilled water. The rinse shall be collected in the 100-mL beaker. Add enough distilled water to result in a 100-mL suspension.

10.1.5.6 Filter the suspension using a funnel through a 25-mm, 0.22- $\mu\text{m}$  MCE filter using vacuum filtration techniques. Rinse the interior of the beaker into the funnel using filtered distilled water.

NOTE 16—It is recommended that disposable funnels be used to reduce the potential for contamination.

NOTE 17—Use of a 47-mm funnel/filter assembly is permissible provided the active filter area is accounted for in the calculations in 13.3.

NOTE 18—If the resuspended filter is too heavily loaded with particles to permit analysis, then reprepare the sample using a smaller portion of the original filter in accordance with 10.1.5.1.

10.1.5.7 Remove the funnel from the vacuum system. Place the deposited filter in a desiccator for approximately 2 h to remove moisture.

10.1.5.8 Cut a wedge of the filter (for example, 25 %) with a curved, steel surgical blade and place onto a SEM stub and carbon coat in accordance with 10.1.3.2 and 10.1.3.3. If the alternate sample preparation approach is utilized, then follow the procedures in accordance with 10.1.4.

NOTE 19—Account for the area of the filter used in the resuspension process in the equations provided in 13.3 when calculating the estimated airborne concentration. For example, if 25 % of the original filter area was deposited onto a 25-mm filter, then a dilution factor of 4 is used in the calculations.