



Designation: D4856 – 99 (Reapproved 2004)

Standard Test Method for Determination of Sulfuric Acid Mist in the Workplace Atmosphere (Ion Chromatographic)¹

This standard is issued under the fixed designation D4856; 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 ion chromatographic test method describes the determination of sulfuric acid mist in air samples collected from workplace atmospheres in a three-piece cassette filter.

1.2 The lower detection limit of this test method is 0.017 mg/m³ of sulfuric acid (H₂SO₄) mist in 60 L of air sampled at 1 L/min.

1.3 This test method is relatively free from interference. The only known interference is soluble or partially soluble sulfate salts.

1.4 *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.* For specific precautionary statements, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*²

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

D1605 Practices for Sampling Atmospheres for Analysis of Gases and Vapors³

D1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres

D4327 Test Method for Anions in Water by Chemically Suppressed Ion Chromatography

¹ This test method is under the jurisdiction of ASTM Committee D22 on Sampling Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.04 on Workplace Atmospheres.

Current edition approved October 1, 2004. Published December 2004. Originally approved in 1988. Last previous edition approved in 1999 as D4856 - 99^{ε1}. DOI: 10.1520/D4856-99R04.

² 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³ Withdrawn.

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1356.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *eluent*—ionic mobile phase used to transport the sample through the exchange columns.

3.2.2 *resolution*—ability of a column to separate constituents under specified test conditions.

4. Summary of Test Method

4.1 A known volume of air is drawn through a cassette filter holder containing a 37-mm mixed cellulose ester membrane filter of 0.8- μ m pore size. The filter is held in a 3-piece cassette supported by a cellulose back-up pad.⁴

4.2 The filter is desorbed with Specification D1193 Type 1 water and an aliquot of the desorbed sample is injected into an ion chromatograph. The sample is pumped through two different ion exchange columns into a conductivity detector. Those columns are a precolumn and separator column which are packed with low-capacity anion exchanger. Ions are separated based on their affinity for the exchange sites of the resin. A method for anion suppression is used to reduce background conductivity of the eluent.

5. Significance and Use

5.1 Sulfuric acid is used in the manufacture of fertilizer, explosives, dyestuffs, other acids, parchment paper, glue, and the pickling of metal.

5.2 This test method has been found satisfactory for measuring sulfuric acid at levels required by federal occupational health regulations.

6. Interferences

6.1 Soluble or partially soluble sulfate salts, for example, sodium or calcium sulfate, will constitute a positive bias.

⁴ Precision ($CV_T = 0.082$) was obtained from NIOSH Contract No. CDC-99-74-45 on a range of 0.561 – 2.577 mg/M³ using cellulose ester filters.

7. Apparatus

7.1 Sampling Equipment:

7.1.1 A 3-piece 37-mm filter cassette constructed of styrene acrylonitrile is used to hold the filter that is supported by a cellulosic pad. The cassette has polyethylene end plugs that fit into an inlet and outlet sampling orifice.

7.1.2 The filter that is used in this procedure is a 37-mm diameter cellulose ester membrane filter of a 0.8- μ m pore size.

7.1.3 A portable sampling pump capable of a 1 L/min sampling rate with a filter cassette containing a backing pad and cellulose ester membrane filter previously described.

7.2 *Ion Chromatograph*—capable of delivering 2 to 5 mL of eluent per minute at a pressure of from 200 to 700 psi [1.3 to 4.8 MPa].

7.2.1 *Precolumn*—a column placed before the separator column to protect it from being fouled by particulate matter.

7.2.2 *Separator Column*—a column packed with pellicular anion exchange resin that is suitable for resolving the sulfate anion.

7.2.3 *Suppressor Column or Membrane*—a column packed with cation exchange resin that is capable of converting the eluent and separated anions to their respective acid forms or membrane that allows the selective removal of anions.

7.2.4 *Detector*—a low-volume, flow through, temperature-compensated, electrical conductivity cell equipped with a metre capable of reading from 0 to 1 000 μ S/cm on a linear scale.

7.2.5 *Recorder*—compatible with the detector output.

7.2.6 *Syringe*—minimum capacity of 2 mL and equipped with a male pressure fitting.

8. Reagents

8.1 Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other reagents may be used provided it can be demonstrated that they are of sufficiently high purity to permit the use without decreasing the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean ultra-pure, Type I water as described in Specification **D1193**.

8.3 *Eluent*—Dissolve 10.080 g of sodium bicarbonate (0.003 M NaHCO₃) and 1.0176 g sodium carbonate (0.0024 M Na₂CO₃) in water and dilute to 4 L with water. Some anion suppressor membranes use the effluent from the detector. See manufacturer's guidelines for appropriate use.

8.4 Stock Solutions:

8.4.1 *Sulfate Stock Solution* (1.00 mL = 1.00 mg SO₄²⁻) Dry sodium sulfate (Na₂SO₄) for 1 h at 105°C and cool in dessicator. Dissolve 1.4790 g of dried salt in water and dilute to 1 L with water.

8.5 *Suppressor Regenerant Solution (for use with suppressor columns)*—Cautiously add 111 mL of concentrated H₂SO₄

(sp gr 1.84) to 600 mL of water. Cool the solution and dilute to 4 L with water. Some anion suppressor membranes use the effluent from the detector. See manufacturer's guidance for appropriate use.

8.6 *Anion Working Solutions*—Prepare a blank and a minimum of three different working solutions containing the following concentrations of sulfate. The sulfate solutions are prepared by diluting the stock solution.

8.6.1 High sulfate stock concentration (100 mg/L) is prepared by the dilution of 100 mL of the sulfate stock solution to 1 000 mL in a volumetric flask with water.

8.6.2 Intermediate sulfate stock concentration (10 mg/L) is prepared by the dilution of 100 mL of the high stock sulfate concentration to 1 000 mL in a volumetric flask with water.

8.6.3 Low sulfate stock concentration (1 mg/L) is prepared by diluting 100 mL of the intermediate stock sulfate concentration to 1 000 mL in a volumetric flask with water.

9. Precautions

9.1 *Safety Precautions*—Extreme care must be taken when preparing solutions from concentrated sulfuric acid. The transfers should be performed in a fume hood with adequate ventilation while wearing the proper safety equipment.

9.2 *Technical Precautions*—All storage containers should be plastic such as polyethylene (or polypropylene) to prevent leaching of the analytes. All connections must be made with non-metallic materials suitable for use with ion chromatographs.

10. Sampling

10.1 For general information on sampling refer to Practices **D1357** and **D1605**.

10.2 Attach the cassette assembly containing the cellulose ester filter to a personal sampling pump using tubing of the proper size as to render a leak proof system and clip the cassette to the worker's lapel.

10.3 Collect air samples at 1 L/min until a minimum of 40 L has been collected.

10.4 The cellulose ester filter should be removed from the cassette filter holder within one hour of sampling and transferred to a screw cap, polyethylene (or polypropylene) bottle.

11. Calibration

11.1 *Determination of Retention Time*—The retention time for sulfate anion is determined by injecting a standard solution and noting the time required for a peak to appear on the chromatogram.

11.2 Concentrations of sulfate are analyzed that encompass the range of sulfate expected for the samples, (for example, 1 to 100 mg/L).

11.3 Prepare an analytical curve for sulfate on linear graph paper using peak height or area versus concentration. A least-squares plot of the data should be presented.

11.4 A blank should be analyzed of each prepared solution and used to correct detector response.