Standard Test Method for Determination of Sulfuric Acid Mist in Workplace Atmospheres Collected on Mixed Cellulose Ester Filters (Ion Chromatographic Analysis)[1]

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1. Scope

1.1 This ion chromatographic test method describes the determination of sulfuric acid mist in air samples collected from workplace atmospheres on a mixed cellulose ester (MCE) filter.

NOTE 1—Other filter types such as quartz fiber, polytetrafluoroethylene (PTFE), and polyvinyl chloride (PVC) filters are also suitable.

1.2 The lower detection limit of this test method is 0.001 mg/sample or 0.017 mg/m^3 of sulfuric acid (H_2SO_4) mist in 60 L of air sampled at 1 L/min.

1.3 This test method is subject to interference from soluble and partially soluble sulfate salts. Other sulfur-containing compounds can be oxidized to sulfate and also interfere.

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

1.5 No detailed instrument operating instructions are provided because of differences among various makes and models of ion chromatography (IC) systems. Instead, the analyst shall follow the instructions provided by the manufacturer of the particular instrument, analytical column, and suppressors used.

1.6 *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

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

D4327 Test Method for Anions in Water by Suppressed Ion Chromatography

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

2.2 *ISO and European Standards:*

ISO 648 Laboratory glassware—One Mark pipettes[3]

ISO 7708 Air quality—Particle size fraction definitions for health-related sampling[3]

ISO 1042 Laboratory glassware—One-mark volumetric flasks[3]

EN 482 Workplace atmospheres—General requirements for the performance of procedures for the measurement of chemical agents[4]

EN 1540 Workplace atmospheres—Terminology[4]

EN 13890 Workplace atmospheres—Procedures for measuring metals and metalloids in airborne particles—Requirements and test methods[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1356 and EN 1540.

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.

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[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality.

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[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] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[4] Available from European Committee for Standardization (CEN), Avenue Marnix 17, B-1000, Brussels, Belgium, http://www.cen.eu.

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4. Summary of Test Method

4.1 A known volume of air is drawn through mixed cellulose ester membrane filter-mounted in an appropriate air sampler. Examples are, but not limited to: inhalable samplers, 25-mm 3-piece, and 37-mm 3-piece cassettes supported by a back-up pad or screen.[5]

4.2 The sulfuric acid collected on the filter is desorbed with D1193 Type 1 water. An aliquot of the desorbed sample solution is injected into an ion chromatograph to determine the sulfate ion concentration.

5. Significance and Use

5.1 Sulfuric acid is used in the manufacture of fertilizer, explosives, dyestuffs, other acids, parchment paper, glue, lead acid batteries, textiles, etc., and in the pickling of metals.

5.2 This test method has been found to be satisfactory in the measurement of sulfuric acid for comparison with relevant occupational exposure limits.

6. Interferences

6.1 Soluble or partially soluble sulfate salts, for example, sodium or calcium sulfate, will be measured as sulfuric acid. Other sulfur-containing compounds can be oxidized to sulfate and also interfere.

7. Apparatus

7.1 *Sampling Equipment:*

7.1.1 Air sampler designed to collect the appropriate aerosol size fraction needed. Examples are: inhalable sampler, 3-piece 37-mm or 25-mm filter cassette constructed of styrene acrylonitrile to hold the filter that is supported by a cellulose pad.

7.1.2 A MCE filter.

NOTE 2—This method may also be used with other appropriate filters such PTFE, Glass Fiber, PVC, and others.

7.1.3 A personal sampling pump capable of maintaining the required sampling rate through the sampler throughout the sampling period.

7.2 *Ion Chromatograph:*

7.2.1 *Pump,* capable of delivering a constant flow of 0.1 to 5 mL of eluent per minute at a pressure of from 3.4 to 34 MPa (500 to 5000 psi).

7.2.2 *Injection Valve,* a low dead volume, non-metallic valve fitted with a sample loop having a volume of up to 500 µl, for injecting the samples into the eluent stream. An autosampler can be attached for automation.

7.2.3 *Guard Column,* a column placed before the separator column to protect it from being fouled by particulate matter.

7.2.4 *Separator Column,* a column packed with anion exchange resin that is suitable for resolving the sulfate anion.

7.2.5 *Suppressor Module,* a module to reduce the total conductivity of the eluent, suitable for use with the separator column and capable of converting the eluent and separated anions to their respective acid forms.

7.2.6 *Conductivity Detector,* a low-volume, flow-through, temperature-compensated, electrical conductivity cell.

7.2.7 *Recorder, Integrator, or Computer,* a device for the purpose of measuring peak height or area, compatible with the detector output, and capable of recording detector response as a function of time.

7.2.8 *Eluent Reservoir,* a container suitable for storing a prepared eluent solution.

7.2.9 *Eluent Generation System,* for continuous production of eluent, suitable for use with the selected separator column, as an alternative to using a manually-prepared eluent.

7.2.10 *Ultrasonic Bath,* preferably with a timer, suitable for use in the ultrasonic extraction.

7.3 *Laboratory Supplies:*

7.3.1 *One-mark Volumetric Flasks,* capacities between 10 mL and 2000 mL.

7.3.2 *One-mark Pipets,* complying with the requirements of ISO 648.

7.3.3 *Disposable Screw-cap Polyethylene Vessels,* of 15-mL capacity.

7.3.4 *Disposable Filters,* polytetrafluorethylene (PTFE), pore size 0.25 µm, for use in ion chromatography.

7.3.5 *Disposable 2-mL or 5-mL Syringes,* with Luer lock connector, for use with disposable filters, or for sample injections without an autosampler.

7.3.6 *Autosampler Vials,* suitable for the autosampler used.

7.3.7 *Pipet Tips,* plastic, disposable, of assorted sizes, as needed.

7.3.8 *Labware,* preferably plastic (beakers, flasks, graduated cylinders, etc.), of assorted sizes, as needed.

7.3.9 *Tweezers,* manufactured from plastic or tipped with PTFE, for loading and unloading filters into samplers.

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

8.3 *Stock Solutions*—1000 µg/mL (mg/L) sulfate in water. Use a commercial standard solution with a certified concentration traceable to national standards.

NOTE 3—The sodium carbonate/sodium bicarbonate eluent prescribed below is an example that can be used with separator column for the determination of sulfate by chemically suppressed ion chromatography. The manufacturer's literature will give information on the composition of eluent to be used with a specific column.

8.4 *Sodium Carbonate/Sodium Bicarbonate Eluent*—0.0031 Na_2CO_3 and 0.00035 M $NaHCO_3$. Dissolve 0.657 g of anhydrous Na_2CO_3 and 0.059 g of $NaHCO_3$ in a 2000-mL (2-L) volumetric flask with water and dilute to mark.

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[5] Precision ($CV_T = 0.082$) was obtained (NIOSH Contract No. CDC-99-74-45) over a range of 0.561 – 2.577 mg/M^3 using mixed cellulose ester filters.

8.5 *Eluent Generation Cartridge*—Potassium hydroxide or potassium carbonate cartridge for eluent generator, appropriate for column and suppressor used.

8.6 *Suppressor Regenerant Solution (for use with suppressor columns)*—Many suppressors currently use electrolysis of the eluent for chemical suppression. Refer to manufacturer's literature for the composition of the suppressor regeneration solution.

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 Attach the sampler containing the filter to a personal sampling pump using tubing of the appropriate size so as to render a leak-proof system and fasten it to the worker's lapel.

10.2 Collect air samples at the appropriate flow rate for the sampler until a minimum of 60 L has been collected.

10.3 Remove the filter from the sampler within one hour of sampling and transfer 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 *Preparation of Calibration Solutions*—Using the stock standard solution and water, prepare at least five working standards using appropriate pipettes and volumetric flasks. Standards shall encompass the range of sulfate concentrations expected for the samples, (for example, 1 to 100 µg/L).

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

11.4 At least one blank of each prepared solution shall be analyzed.

12. Procedures

12.1 Pipet 10 mL of water into the sample bottle containing the filter. Shake the sample bottle vigorously or sonicate it for 15 minutes, and allow to stand until the sample solution comes to room temperature.

12.2 Filter an aliquot of the sample solution through a disposable filter (7.3.4) using a disposable syringe (7.3.5).

12.3 Set up the IC system for the analysis of sulfate based on manufacturer's literature for the column, suppressor, and system used.

12.4 Transfer a portion of the filtered sample solution to an autosampler vial, or a syringe for manual injections, and inject an aliquot into the chromatograph (for example, 50 µL for a 4-mm column).

NOTE 4—Manual injections require 2 to 3 mL to ensure complete flushing of the injection loop.

12.5 Determine the amount of sulfate in each sample by comparing peak area or height to the response obtained from the calibration curve determined in 11.3. If sulfate is greater than the highest standard, dilute with water and rerun using the appropriate dilution factor.

13. Calculation

13.1 Calculate the concentration (mg/m^3) of sulfuric acid in air as follows:

$$\text{mg/m}^3\text{, H}_2\text{SO}_4 = \frac{\mu\text{g/mL SO}_4 \times 10 \times 1.02}{V_{\text{air}}} \quad (1)$$

where:

10 = millilitres of water added to filter,
1.02 = conversion factor for H_2SO_4, from SO_4
V_{air} = litres of air sampled.

14. Precision and Bias

14.1 The single-operator and overall precision of this test method, within its designated range for seven operators in seven different laboratories with a 10-mL volume, is expressed as follows:

Theoretical, µg	Observed Standard Deviation, µg
6.00	1.13
60.0	7.7
120	17.5

14.2 Recoveries and bias of known amounts of sulfate in seven different laboratories using the same manufacturer's instrumentation and operation conditions are expressed as follows:

Theoretical, (µg)	Observed, (µg)	Bias, (µg)	Bias, (%)	Statistically Significant 95 % Level
6.00	5.07	−0.93	−15.5	Yes
60.0	49.1	−10.9	−18.2	Yes
120	97.6	−22.4	−18.7	Yes

15. Keywords

15.1 air monitoring; ion chromatography; sampling and analysis; sulfuric acid mist; workplace atmosphere

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