

SULFURIC ACID IN WORKPLACE ATMOSPHERES



Method Number:	ID-113
Matrix:	Air
OSHA Standard:	1.0 mg/m ³
Collection Procedure:	A known volume of air is drawn through a mixed cellulose ester membrane filter (MCEF).
Recommended Air Volume:	480 liters
Recommended Sampling Rate:	2 liters per minute
Analytical Procedure:	Filters are desorbed and the sample is analyzed by ion chromatography.
Detection Limit:	0.5 µg/mL of solution
Precision:	(CV _r) = 0.090
Method Classification:	P

Methods Development Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
Salt Lake City, UT 84115-1802

1. Introduction

This method describes the collection and analysis of airborne sulfuric acid using ion chromatography.

1.1 History

Prior to the use of this method, air samples were collected on 5- μ m PVC filters and were analyzed by the barium titration method. Samples were desorbed with warm deionized water. The pH of the sample was adjusted with 1.8% perchloric acid. Isopropanol was added and the resulting solution was titrated with 0.005 M Ba(ClO₄)₂ using thurin as the indicator.

This method desorbs the MCEF with 10 mL of eluent solution (0.003 M CO₃⁼/0.0024 M HCO₃⁼). The samples are analyzed by ion chromatography with a conductivity detector. A regenerate solution was used for ion suppression but an ion suppressor may be substituted.

1.2 Uses (8.1)

Sulfuric acid is used in the fertilizer industry for production of superphosphates and ammonium sulfate.

The chemical industry consumes sulfuric acid in the manufacture of phosphoric acid by the wet process.

Sulfuric acid is used in the manufacture of paper, aluminum sulfate, and is used extensively for water purification.

The petroleum industry uses sulfuric acid in the alkylation process and in refining of petroleum distillates for removal of sulfur and gum-forming compounds.

Other important Industrial applications consuming large amounts of sulfuric acid include steel pickling and manufacture of titanium pigments, rayon, dyes, intermediates, and detergents.

1.3 Physical Properties (8.2)

Sulfuric acid is a dense oily liquid, colorless to dark brown (depending on purity). Commercial grades are approximately, 96% pure. Sulfuric acid is a strong oxidant, is toxic, a strong irritant to tissue, very corrosive, and has a great affinity for water.

Physical Constants:

Specific Gravity:	1.84
Melting Point:	10.4 °C
Boiling Point:	315 °C - 338 °C
Molecular Weight:	98.08

2. Working Range and Detection Limit

2.1 The working range for a 480 liter air sample is 0.01 to 10 mg/m³ SO₄⁼. This corresponds to 5 to 4800 μ g of sulfate.

2.2 The sensitivity at 30 μ mho full scale is 5 μ g of analyte (SO₄⁼) per sample per mm chart deflection.

2.3 The detection limit is approximately 0.5 μ g SO₄⁼/mL of solution injected, corresponding to 5 μ g of analyte per 10 mL of sample. The detection limit may be improved by using a larger injection volume (for auto sampler only) or by using a smaller volume than 10 mL to desorb the sample.

3. Precision and Accuracy (8.3)

- 3.1 The Relative Standard Deviation (RSD) of the analytical method is 5% or less in the range 50 to 1000 $\mu\text{g SO}_{4=}$ per sample, 3 corresponding to 0.10 to 2.1 mg/m^3 of analyte for a 480 liter air volume.
- 3.2 The coefficient of variation (CV_T) = 0.090. This value was calculated from tabulated Quality Control samples in the range of 100 to 200 μg of $\text{SO}_{4=}$ (N = 54). These samples were analyzed from September 1979 to March 1980.

4. Interferences (8.4)

- 4.1 Due to the method of collection (cellulose ester filters) and analysis (IC for $\text{SO}_{4=}$) any particulate sulfates will cause a positive interference.
- 4.2 Large quantities of nitrates will cause some masking of the sulfate peak.

5. Advantages and Disadvantages

- 5.1 Interferences may not easily be identified if identification is based on retention time.
- 5.2 The method can be automated and is quick and accurate compared to the previous methods using titrations with nebulous endpoints.
- 5.3 The sampling procedure employed uses filters as opposed to impingers which are used in other sampling methods for acid mist. Such a sampling procedure eliminates the inherent problems of using impingers.

6. Sampling Procedure

- 6.1 Apparatus - Filter holder, 2 or 3 piece cassette, polystyrene 37 mm in diameter. Mixed cellulose ester membrane filter, 0.8 micrometer pore size, 37 mm diameter, supported by a cellulose backup pad. Personal sampling pump with calibrated flow in line with a loaded filter holder to an accuracy of $\pm 10\%$ at the 95% confidence limit at the recommended flow rate. Stopwatch, tweezers, screw caps, 20 mL scintillation vials.
- 6.2 A mixed cellulose ester membrane filter, 0.8 micrometer pore size, 37 millimeter diameter is placed in a two or three piece cassette, supported by a cellulose backup pad.
- 6.3 The cassette is then attached to a personal sampling pump, that has been calibrated in line with a loaded-filter holder to an accuracy of $\pm 10\%$ at the 95% confidence limit at the recommended flow rate (2 liters/minute).
- 6.4 The cassette is placed in the sampling area or worker's breathing zone. Approximately 480 liters of air are drawn through the cassette using a calibrated sampling pump.
- 6.5 After sampling, the cellulose ester membrane filter is removed from the cassette and placed in a clean 20 mL scintillation vial to avoid low recovery of sulfuric acid. The filter is handled with tweezers to avoid contamination. The vial is sealed and identified with OSHA Form 21 and shipped to the laboratory for analysis.
- 6.6 With each batch of up to 20 samples, an appropriate blank filter is submitted for analysis.
- 6.7 When particulate sulfates are known to be present in the workplace atmosphere they should be listed as interferences.

7. Analytical Procedure

- 7.1 Apparatus - Ion chromatograph, equipped with conductivity detector and recorder, or integrator (an auto sampler helps automate the analysis), 10 mL pipette, 1 mL plastic syringe with male luer fitting, Anion Separator Column 3 × 250 mm with Concentrator Column, Anion Suppressor Column 10 × 100 mm, and appropriate volumetric glassware for dilutions and standard preparation. A typical analytical column is an AS4 analytical column from Dionex.
- 7.2 Reagents - All reagents used should be ACS analyzed reagent grade or better.
- 7.2.1 Deionized, filtered, conductivity grade water with a specific conductance of 8 $\mu\text{mho/cm}$ or less for preparation of eluents and other solutions which will be used in the ion chromatograph.
- 7.2.2 Sodium Carbonate, Na_2CO_3 .
- 7.2.3 Sodium Bicarbonate, NaHCO_3 .
- 7.2.4 Sulfate Stock Standard (1000 ppm SO_4^{2-}). Dissolve 1.479 g of Na_2SO_4 into 1 liter of deionized water. Sulfate working standards are made by diluting the stock solution with eluent.
- 7.2.5 Standard Eluent (0.003 M CO_3^{2-} / 0.0024 M HCO_3^-). Dissolve 5 g Na_2CO_3 and 5 g NaHCO_3 in 20 liter carboy with deionized water.
- 7.2.6 Regenerant Solution (1 N H_2SO_4). Dilute 111 mL of concentrated H_2SO_4 to 4 liters in deionized water.
- 7.3 Safety Precautions
- 7.3.1 Care should be used when handling reagents, especially the regenerant solution (1 N H_2SO_4) to avoid chemical burns.
- 7.3.2 Care should be exercised when using laboratory glassware. Chipped pipettes, volumetric flasks, beakers, or any glassware with sharp edges exposed should not be used to avoid the possibility of cuts, abrasions, and lost samples.
- 7.3.3 Pipetting should never be done by mouth - a bulb should always be used.
- 7.4 Standard Preparation
- 7.4.1 A 1000 $\mu\text{g/mL}$ standard stock solution is prepared by dissolving 1.479 g of Na_2SO_4 into one liter of deionized water.
- 7.4.2 Working standards are prepared in the analytical range of 0.2 $\mu\text{g/mL}$ to 100 $\mu\text{g/mL}$ SO_4^{2-} from dilutions of the 1000 $\mu\text{g/mL}$ stock solution. These standard solutions should be prepared fresh weekly.
- 7.4.3 If an auto sampler capable of variable injection is used, only a 50 $\mu\text{g/mL}$ SO_4^{2-} standard is necessary. This intermediate working standard should be prepared fresh monthly.

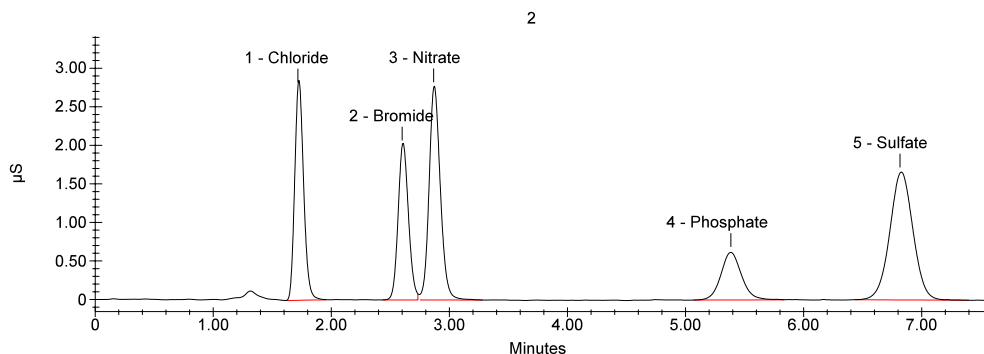
7.5 Sample Preparation

- 7.5.1 If the filter is not in a 20 mL scintillation vial, remove the filter from the cassette and place in a clean 20 mL vial.
- 7.5.2 If the air volume is adequate (greater than or equal to 480 liters) Pipette 10 mL of eluent (0.003 M $\text{CO}_3^{=}$ / 0.0024 M HCO_3^-) into each sample vial and cap (if the air volume is less than 100 liters, a smaller volume of eluent is used). Let stand, with occasional vigorous shaking, for 30 minutes. When particulate sulfates are listed as interferences, the filter should be extracted with appropriate amounts of eluent, to allow the determination of total acid content by titration. Sample solutions which are not clear should be filtered before analysis.
- 7.5.3 If using an auto sampler, transfer some of the sample into an appropriate sampling vial. The vial should be at least half full. Label each vial with the appropriate laboratory identification number.
- 7.5.4 For hand injection, use 1 mL of the eluent to flush the 0.1 mL injection loop thoroughly.

7.6 Analysis (8.5)

- 7.6.1 For general instrument set up refer to Section 7 of the Ion Chromatography Standard Operating Procedure.
- 7.6.2 The normal instrument parameters are:

instrument:	Dionex DX-500
guard column:	AG4
column:	HS4
eluent:	0.003 M Na_2CO_3 / 0.0024 M NaHCO_3
flow rate:	2 mL/min
suppressor column:	ASRS Ultra
injection volume:	50 μL
retention time:	7 min



- 7.6.3 With the instrument set up and stabilized, place the auto sampling vials into the sampling tray using tray positions one through five for standards.
- 7.6.4 Enter the proper parameters into the auto sampler (See Section 4 of the Ion Chromatography Standard Operating Procedure).
- 7.6.5 Start the auto sampler and observe the first few chromatograms to ensure proper operation. Periodically check the zero offset between samples to correct any baseline drift and to ensure proper sensitivity and retention time of the analyte ($\text{SO}_4^{=}$).
- 7.6.6 Use the timer to stop the run if the auto sampler is to be left unattended.

- 7.6.7 For hand injection, a 1 mL aliquot is taken up in a syringe from the 20 mL vial and injected into the injection port with the toggle switch in the load position. After the sample is loaded, switch the toggle to the inject position and start the integrator or push the PIP button if a strip chart recorder is being used.
- 7.6.8 For both hand and auto sample injections, record the sample number onto the chromatogram. A record of the sample identity and instrument conditions should be kept.
- 7.6.9 As the analysis proceeds, check the retention times of standards vs. samples to ensure uniformity. A typical chromatograph of a mixed standard of $\text{SO}_{4=}$, NO_{3-} , and PO_{4-3} , is shown in Figure 1.
- 7.6.10 If interfering substances are present, establish positive identity of the sulfate peak by spiking known amounts of standard solution and obtain better separation by changing the eluent concentration or by reducing the flow rate.

7.7 Calculations

7.7.1 Peak areas or heights of the standards are used to construct a standard curve using the Auto Colorimetric Program. The samples results are obtained from a plot of peak height or peak area vs. $\text{SO}_{4=}$ concentration. The blank corrected sample values are then calculated using the Auto Colorimetric Program.

7.7.2 Sample numbers and volumes are entered into the calculator in the following way:

Sample Number, Peak Area or Height, L - Air Volume, mL - Solution Volume, mL - Aliquot Volume.

7.7.3 Air Concentration values are calculated by the following equation:

$$\text{mg/m}^3 = \frac{(\text{mg calculated})(\text{mL sample vol})(1.03*)(\text{dilution factor})}{(\text{liters of air})(\text{mL aliquot})}$$

*Gravimetric Factor for H_2SO_4 .

8. References

- 8.1 Encyclopedia of Chemical Technology, Second Edition, Volume 19.
- 8.2 Merck Index, Ninth Edition, (1976), page 1163.
- 8.3 Tabulated data from Occupational Safety & Health Administration Quality Control Division.
- 8.4 OSHA Ion Chromatography Standard Operating Procedure, Prepared by the Ion Chromatography Committee, Occupational Safety & Health Administration Analytical Laboratory, Inorganic Division.
- 8.5 NIOSH Manual of Analytical Methods, Second Edition, Volume 5, Method Number P&CAM 268.