

# SULFUR DIOXIDE

6004

SO<sub>2</sub>

MW: 64.06

CAS: 7446-09-5

RTECS: WS4550000

METHOD: 6004, Issue 2

EVALUATION: PARTIAL

Issue 1: 15 May 1989

Issue 2: 15 August 1994

**OSHA :** 5 ppm  
**NIOSH:** 2 ppm; STEL 5 ppm; Group I Pesticide  
**ACGIH:** 2 ppm; STEL 5 ppm  
 (1 ppm = 2.62 mg/m<sup>3</sup> @ NTP)

**PROPERTIES:** gas; vapor density 2.26 (air = 1);  
 BP -10 °C; MP -72.7 °C;  
 nonflammable

**SYNONYMS:** none

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	FILTER + TREATED FILTER (cellulose + Na <sub>2</sub> CO <sub>3</sub> ; preceded by 0.8-µm cellulose ester membrane)	<b>TECHNIQUE:</b>	ION CHROMATOGRAPHY
<b>FLOW RATE:</b>	0.5 to 1.5 L/min	<b>ANALYTE:</b>	sulfite and sulfate ions
<b>VOL-MIN:</b>	4 L @ 5 ppm	<b>EXTRACTION:</b>	10 mL 1.75 mM NaHCO <sub>3</sub> /2.0 mM Na <sub>2</sub> CO <sub>3</sub>
<b>-MAX:</b>	200 L	<b>INJECTION LOOP VOLUME:</b>	50 µL
<b>SHIPMENT:</b>	routine	<b>ELUENT:</b>	1.75 mM NaHCO <sub>3</sub> /2.0 mM Na <sub>2</sub> CO <sub>3</sub> , 2 to 3 mL/min
<b>SAMPLE STABILITY:</b>	not determined	<b>COLUMNS:</b>	Ion Pac AS4A separator, Ion Pac AG4A guard; micromembrane suppressor [2]
<b>FIELD BLANKS:</b>	2 to 10 field blanks per set	<b>CONDUCTIVITY SETTING:</b>	10 µS full scale
ACCURACY		<b>CALIBRATION:</b>	standard solutions of SO <sub>3</sub> <sup>2-</sup> and SO <sub>4</sub> <sup>2-</sup> in eluent
<b>RANGE STUDIED:</b>	not studied	<b>RANGE:</b>	11 to 200 µg SO <sub>2</sub> per sample
<b>BIAS:</b>	not determined	<b>ESTIMATED LOD:</b>	3 µg SO <sub>2</sub> per sample [2]
<b>OVERALL PRECISION (<math>\hat{S}_{rT}</math>):</b>	not determined	<b>PRECISION (<math>\hat{S}_r</math>):</b>	0.042 [2]
<b>ACCURACY:</b>	not determined		

**APPLICABILITY:** The working range is 0.2 to 8 ppm (0.5 to 20 mg/m<sup>3</sup>) for a 100-L air sample. The method is applicable to STEL samples. SO<sub>2</sub> is collected on the back (treated) filter. Sulfuric acid, sulfate salts, and sulfite salts are collected on the front filter and may be quantitated as total particulate sulfate.

**INTERFERENCES:** Sulfur trioxide gas, if present in dry atmospheres, may give a positive interference for SO<sub>2</sub>.

**OTHER METHODS:** This revises P&CAM 268 [3]. P&CAM 146 [4], P&CAM 163 [5], and S308 [6] use 0.3 N H<sub>2</sub>O<sub>2</sub> for sampling, followed by titration with NaOH or barium perchlorate. P&CAM 160 [7] uses tetrachloromercurate solution and visible spectrophotometry. P&CAM 204 [8] uses a solid sorbent (molecular sieve 5A), thermal desorption, and mass spectrometry.

**REAGENTS:**

1. Water, deionized, filtered, specific conductance  $\leq 10 \mu\text{S/cm}$ .
2. Fixative solution. Dissolve 25 g  $\text{Na}_2\text{CO}_3$  in deionized water. Add 20 mL glycerol and dilute with deionized water to 1 L.
3. Eluent: 1.75 m  $\text{M}$   $\text{NaHCO}_3$ /2.0 m  $\text{M}$   $\text{Na}_2\text{CO}_3$ . Dissolve 0.588 g  $\text{NaHCO}_3$  and 0.848 g  $\text{Na}_2\text{CO}_3$  in 4 L filtered deionized water.
4. Calibration stock solutions, 1 mg/mL (as the anion). Prepare in duplicate.
  - a. **Sulfite:** dissolve 0.1575 g  $\text{Na}_2\text{SO}_3$  in water. Add 2 mL glycerol. Dilute to 100 mL. Prepare fresh daily.
  - b. **Sulfate:** dissolve 0.1479 g  $\text{Na}_2\text{SO}_4$  in deionized water. Dilute to 100 mL. Stable several weeks.

\* See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Sampler: two 37-mm diameter cassette filter holders (connected in series by a M-M Luer adapter, e.g., Millipore XX1102503, or a short piece of plastic tubing) containing:
  - a. (Front cassette) cellulose ester membrane filter, 0.8- $\mu\text{m}$  pore size, supported by a backup pad.
  - b. (Back cassette) cellulose filter (Whatman 40 or equivalent) which has been saturated with fixative solution and dried 20 to 30 min at 100 °C, supported by a porous plastic support pad.
2. Personal sampling pump, 0.5 to 1.5 L/min, with flexible connecting tubing.
3. Vials, glass, 20-mL, screw-cap, such as scintillation vials.\*\*
4. Ion chromatograph, HPIC-AS4A anion separator and HPIC-AG4A guard, anion micromembrane suppressor, conductivity detector, and strip chart recorder. (Optional: integrator.)
5. Syringes, 10-mL, polyethylene, with luer tip.\*\*
6. Filters, in-line, luer-tip holder with membrane filter, 13- or 25-mm, 0.45- $\mu\text{m}$  pore size.
7. Micropipets, 50- to 1000- $\mu\text{L}$ , with disposable tips.\*\*
8. Volumetric flasks, 50- and 100-mL.\*\*
9. Pipet, 10-mL.\*\*
10. Polyethylene bottles, 250-mL.\*\*

\*\* Clean by rinsing thoroughly with deionized water.

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**SPECIAL PRECAUTIONS:** None.

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**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove end caps of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 1.5 L/min for a total sample size of 40 to 200 L. Do not exceed a total particulate loading of 2 mg on the front filter.
4. Seal the sampler and pack securely for shipment.

NOTE: If determination of sulfuric acid is required, transfer the front (membrane) filter to a clean vial within 4 h to avoid low recovery of sulfate. Handle the filter with tweezers to avoid contamination.

**SAMPLE PREPARATION:**

5. Put the two filters from the sampler into separate, clean vials. Discard the backup pads. Add 10.0 mL eluent to each vial and let stand, with occasional vigorous shaking, for 30 min.

NOTE: The  $\text{SO}_2$  collected on the treated (back) filter is present as sulfite, which oxidizes in air slowly (over several weeks) to sulfate. The contributions of sulfite and sulfate found on the back filter must be summed, with appropriate stoichiometric factors applied, to give the  $\text{SO}_2$  concentration (step 11).

6. Pour each sample into a syringe fitted with an in-line filter.

#### CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards.
  - a. Add known aliquots of sulfate calibration stock solution to eluent in 50-mL volumetric flasks and dilute to the mark to produce solutions containing 1 to 20  $\mu\text{g/mL}$   $\text{SO}_4^{2-}$ .
  - b. Prepare sulfite standards in the same manner over the same range.
  - c. Store working standards in tightly-capped polyethylene bottles. Prepare fresh working standards daily.
  - d. Analyze working standards with samples and blanks (steps 8 through 10). Prepare a calibration graph for each anion [peak height (mm or  $\mu\text{S}$ ) vs.  $\mu\text{g}$  sulfite or sulfate].

#### MEASUREMENT:

8. Set ion chromatograph to conditions given on page 6004-1, according to manufacturer's instructions.
9. Inject sample aliquot. For manual operation, inject 2 mL of sample from syringe to ensure complete rinse of sample loop.

NOTE: All samples, eluents, and water flowing through the ion chromatograph must be filtered to avoid plugging system valves or columns.

10. Measure peak heights of sulfite and sulfate peaks.

NOTE: If peak height exceeds linear calibration range, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.

#### CALCULATIONS:

11. Determine the mass,  $\mu\text{g}$ , of sulfate equivalent found on the front ( $W_f$ ) and back ( $W_b$ ) filters and in the corresponding average media blanks ( $B_f$  and  $B_b$ ).

NOTE: The sulfate equivalent is the sum of the sulfate peak,  $\mu\text{g}$ , and 1.200 times the sulfite peak,  $\mu\text{g}$ , on the chromatogram ( $1.200 = \text{MW } \text{SO}_4^{2-} / \text{MW } \text{SO}_3^{2-}$ ):  $\mu\text{g}_{\text{sulfate equivalent}} = \mu\text{g}_{\text{sulfate}} + 1.200 \mu\text{g}_{\text{sulfite}}$ .

12. Calculate the concentration,  $C_{\text{SO}_2}$ , of sulfur dioxide, applying the factor 0.667 ( $\text{MW } \text{SO}_2 / \text{MW } \text{SO}_4^{2-}$ ):

$$C_{\text{SO}_2} = \frac{(W_b - B_b)}{V} \cdot 0.667, \text{ mg/m}^3.$$

13. Calculate the concentration,  $C_{\text{SO}_4}$ , of particulate sulfate (including sulfuric acid) in the air volume sampled,  $V$  (L):

$$C_{\text{SO}_4} = \frac{(W_f - B_f)}{V}, \text{ mg/m}^3.$$

**EVALUATION OF METHOD:**

The sampler was adapted from that of Pate, et al. [9]. In experiments in which  $\text{SO}_2$  was generated by permeation tube and collected in impingers containing  $\text{H}_2\text{O}_2$ , untreated 0.8- $\mu\text{m}$  cellulose ester membrane filters were shown to allow complete passage of  $\text{SO}_2$  [10]. In subsequent sampling of an atmosphere containing ca. 10 ppm  $\text{SO}_2$  at 1 L/min for 30 min, two treated filters were placed in series following a cellulose ester membrane filter. Recoveries were: 0.667 mg  $\text{SO}_2$  from the first treated filter, 0.02 mg  $\text{SO}_2$  from the second treated filter, and less than 0.003 mg  $\text{SO}_2$  in the backup impinger containing 0.3 N  $\text{H}_2\text{O}_2$  [11]. Cellulose ester filters spiked with 0.2 mg  $\text{H}_2\text{SO}_4$  gave the following recoveries: 83.5% using  $\text{H}_2\text{O}$  extraction, 98.5% using hot  $\text{H}_2\text{O}$  extraction, and 82.5% using 0.01 M HCl for extraction.

A study on filter impregnating solutions compared  $\text{NaHCO}_3$  and KOH. The chromatograms of samples from the KOH-treated filters had noticeably flattened and broadened peak shapes as well as retention times reduced by approximately 10% when compared to the chromatograms of  $\text{H}_2\text{SO}_4$  spiked on filters impregnated with  $\text{NaHCO}_3$  [1].

**REFERENCES:**

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**METHOD REVISED BY:**

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