

# HYDROGEN SULFIDE

6013

H<sub>2</sub>S

MW: 34.08

CAS: 7783-06-4

RTECS: MX1225000

**METHOD:** 6013, Issue 1

**EVALUATION:** FULL

**Issue 1: 15 August 1994**

**OSHA :** C 20 ppm; P 50 ppm/10 min  
**NIOSH:** C 10 ppm/10 min  
**ACGIH:** 10 ppm; STEL 15 ppm  
 (1 ppm = 1.39 mg/m<sup>3</sup> @ NTP)

**PROPERTIES:** gas; d (liq) 1.54 g/mL @ 0 °C;  
 BP - 60 °C; VP 20 atm @ 25 °C;  
 vapor density (air=1) 1.19;  
 explosive range 4.3 to 46% v/v in air

**SYNONYMS:** sulfuretted hydrogen; hydrosulfuric acid; hepatic gas; stink damp

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	FILTER + SOLID SORBENT TUBE (Zefluor, 0.5 µm; coconut shell charcoal, 400 mg/200 mg)	<b>TECHNIQUE:</b>	ION CHROMATOGRAPHY, CONDUCTIVITY
<b>FLOW RATE-RANGE:</b>	0.1 to 1.5 L/min	<b>ANALYTE:</b>	sulfate ion
<b>-RECOMMENDED:</b>	0.2 L/min	<b>DESORPTION:</b>	2 mL 0.2 M NH <sub>4</sub> OH + 5 mL 30% H <sub>2</sub> O <sub>2</sub>
<b>VOL-MIN:</b>	1.2 L @ 10 ppm	<b>INJECTION VOLUME:</b>	50 µL
<b>-MAX:</b>	40 L	<b>ELUENT:</b>	40 mM NaOH, 1.5 mL/min
<b>SHIPMENT:</b>	routine	<b>COLUMN:</b>	Ion-Pac AS4A separator, AG4A guard
<b>SAMPLE STABILITY:</b>	at least 30 days @ 25 °C [1]	<b>CALIBRATION:</b>	SO <sub>4</sub> <sup>2-</sup> in deionized water
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>RANGE:</b>	17 to 200 µg per sample
<b>ACCURACY</b>		<b>ESTIMATED LOD:</b>	11 µg per sample
<b>RANGE STUDIED:</b>	1.4 to 22.0 mg/m <sup>3</sup> [1] (20-L samples)	<b>PRECISION (S<sub>r</sub>):</b>	0.031 [1]
<b>BIAS:</b>	- 0.23% [1]		
<b>OVERALL PRECISION (S<sub>r,T</sub>):</b>	0.059 [1]		
<b>ACCURACY:</b>	± 11.8%		

**APPLICABILITY:** The working range is 0.6 to 14 ppm (0.9 to 20 mg/m<sup>3</sup>) for a 20-L air sample [1]. The method is applicable to 15-min samples taken at 1 L/min and 10-min samples taken at 1.5 L/min. The upper limit of loading depends on the concentrations of hydrogen sulfide and other substances in the air, including water vapor. High relative humidity (80%) increases the capacity of the sampler four-fold, relative to dry air. Some lots of charcoal have excessively high sulfur backgrounds and/or poor desorption efficiencies; therefore, screening of each lot should be done before field use.

**INTERFERENCES:** SO<sub>2</sub> is a positive interference, equivalent to H<sub>2</sub>S by approximately twice the SO<sub>2</sub> concentration by weight. Methyl and ethyl mercaptans do not interfere [1].

**OTHER METHODS:** Alternate methods are S4 [2] which uses impinger collection, and P&CAM 296 [3] which uses a molecular sieve sampler but has poor stability.

**REAGENTS:**

1. Ammonium hydroxide solution, 25%.
2. Hydrogen peroxide, 30%.\*
3. Sodium hydroxide, 50% (w/v).\*
4. Extraction soln: 0.2 M NH<sub>4</sub>OH.
5. Eluent: 40 m M NaOH. Dilute 4.16 mL of 50% NaOH to 2 L with deionized water (degassed).
6. Suppressor regenerant: 0.025 N H<sub>2</sub>SO<sub>4</sub>. Dilute 1.4 mL concentrated H<sub>2</sub>SO<sub>4</sub> to 2 L with deionized water.\*
7. Calibration Stock solution: 1 mg/mL (as anion). Dissolve 0.1814 g K<sub>2</sub>SO<sub>4</sub> in 100 mL deionized water.
8. H<sub>2</sub>S, calibration gas mixture, or permeation device.

\* See Special Precautions

**EQUIPMENT:**

1. Sampler: glass tube, 10 cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing 20/40 mesh activated (600 °C) coconut shell charcoal (front = 400 mg, back = 200 mg) separated by a 6-mm urethane foam plug. A silanized glass wool plug precedes the front section and a 6-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available. Zefluor PTFE prefilter, 0.45- $\mu$ m, 25-mm, with porous plastic support pad in 25-mm cassette.  
NOTE: Some lots of charcoal have excessively high sulfur backgrounds, and/or desorption efficiencies. Screen each lot before field use.
2. Personal sampling pump, 0.1 to 1.5 L/min, with flexible connecting tubing.
3. Ion chromatograph, conductivity detector, integrator and columns (page 6013-1).
4. Centrifuge tubes, 15-mL, plastic with screw caps.
5. Syringes, 10-mL, polyethylene with luer tip.
6. Syringe filters, 13-mm, 0.45- $\mu$ m pore size.
7. Vials, autosampler, 4-mL, PTFE-lined caps.
8. Micropipettes, disposable tips.
9. Pipettes, 2-, 3-, 5-mL.
10. Volumetric flasks, 10-, 25-mL.
11. Vortex mixer (optional).

**SPECIAL PRECAUTIONS:** Hydrogen peroxide is a strong oxidizer causing burns to skin and mucous membranes. Sulfuric acid and sodium hydroxide are extremely corrosive to all body tissue. Wear protective clothing and eye protection. All work should be performed in a fume hood.

**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler and attach prefilter with a small piece of flexible tubing immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.1 and 1.5 L/min for a total sample size of 15 to 40 L.
4. Cap the sorbent tubes with plastic caps and plug prefilter cassettes. Pack securely for shipment.  
**NOTE:** The prefilters may be discarded or analyzed for particulate sulfates by, e.g., Method 6004.

**SAMPLE PREPARATION:**

5. Place the front and back sorbent sections of the sampler tube in separate screw-top centrifuge tubes. Discard the glass wool and foam plugs.
6. Add 2.0 mL of 0.2 M NH<sub>4</sub>OH and 5.0 mL H<sub>2</sub>O<sub>2</sub> to each centrifuge tube. Attach screw cap and loosen 1/4 turn.
7. Allow to react at least 10 min. Tighten cap and shake for 30 s or vortex 10 s.

8. Dilute to 10 mL with 3 mL of deionized water. Cap and shake vigorously.
9. Transfer sample to 10-mL plastic syringe fitted with in-line filter.

**CALIBRATION AND QUALITY CONTROL:**

10. Calibrate daily with at least six working standards over the range 0.1 to 20 µg sulfate ion per mL of sample (1 to 200 µg per 10 mL).
  - a. Add known amounts of calibration stock solution to deionized water in 10- or 25-mL volumetric flasks and dilute to the mark. Prepare fresh working standards biweekly.
  - b. Analyze together with samples and blanks (steps 14 and 15).
  - c. Prepare calibration graph (peak height vs. µg SO<sub>4</sub><sup>2-</sup> per sample).
11. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 10). Prepare four tubes at each of three levels plus three media blanks.
  - a. Generate concentrations of H<sub>2</sub>S from a calibration gas mixture or a permeation device. Mix with dilution air as necessary.
  - b. Collect samples at a flow rate of 1 L/min for 30 min.
  - c. Cap the tubes and allow to stand overnight.
  - d. Desorb (steps 5 through 9) and analyze together with working standards (steps 14 and 15).
  - e. Prepare a graph of DE vs. µg sulfate recovered.
12. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph is in control.

**MEASUREMENT:**

13. Set ion chromatograph according to manufacturer's recommendations and to conditions given on page 6013-1.
14. Inject a 50-µL sample aliquot manually or with autosampler.
15. Measure peak height.

NOTE: If peak height is above the linear range of the working standards, dilute with deionized water, reanalyze, and apply the appropriate dilution factor in calculations.

**CALCULATIONS:**

16. Determine the mass, µg (corrected for DE) of sulfate ion found in the sample front (W<sub>f</sub>) and back (W<sub>b</sub>) sorbent sections, and in the average media blank front (B<sub>f</sub>) and back (B<sub>b</sub>) sorbent sections. NOTE: If W<sub>b</sub> > W<sub>f</sub>/10, report breakthrough and possible sample loss.
17. Calculate concentration, C, of hydrogen sulfide in the air volume sampled, V (L), applying the factor 0.3548 (MW H<sub>2</sub>S/MW SO<sub>4</sub><sup>2-</sup>) for the conversion of SO<sub>4</sub><sup>2-</sup> to H<sub>2</sub>S:

$$C = \frac{0.3548 (W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

**EVALUATION OF METHOD:**

The method was evaluated by sampling generated test atmospheres of H<sub>2</sub>S in air [1]. Time-weighted average samples were taken at four concentration levels over a range of 1.4 to 22 mg/m<sup>3</sup> (1 to 16 ppm). For ceiling concentrations or short-term exposure limits, 15-L samples were collected at 1 L/min. Breakthrough was determined for coconut charcoal from a generated atmosphere at a concentration of 20 ppm (2 x PEL) and at both low (~20%) and high (~80%) relative humidity (RH). Breakthrough volumes for low and high RH were 21 L and 84 L, respectively, corresponding to capacities of 588 µg of H<sub>2</sub>S (low RH) and 2352 µg of H<sub>2</sub>S (high RH). At 1 x PEL, the equivalent breakthrough volume is 42 L (low RH) and 164 L (high RH). Large coconut charcoal tubes have sufficient capacity to collect a 4-h sample at the PEL of 10 ppm, as well as STEL samples (15 ppm for 15 min). H<sub>2</sub>S samples are stable for at least

30 days. Recoveries, based on mass of H<sub>2</sub>S found on samples analyzed on day 1, were 97.2% for ambient storage and 98.9% for refrigerated storage. The overall method for H<sub>2</sub>S has a limit of detection of 11 µg per sample and a limit of quantitation of 17 µg per sample. A mean bias of -0.17% was determined from the recoveries of six samples generated at each of four concentration levels (0.1, 0.5, 1, and 2 x PEL) with a precision ( $\bar{S}_r$ ) of 0.031. The method had a total precision including pump error ( $\bar{S}_{rT}$ ) of 0.059, and an estimate of overall error of ±11.6%.

**REFERENCES:**

- [1] Cassinelli, ME, Backup Data Report, NMAM 6013, Hydrogen Sulfide. NIOSH/DPSE (1992).
- [2] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S4, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
- [3] NIOSH Manual of Analytical Methods, 2nd ed., V. 6, P&CAM 296, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).

**METHOD WRITTEN BY:**

Mary Ellen Cassinelli, NIOSH/DPSE.