

CARBON DISULFIDE

1600

CS₂

MW: 76.14

CAS: 75-15-0

RTECS: FF6650000

METHOD: 1600, Issue 2

EVALUATION: FULL

Issue 1: 15 May 1985

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OSHA : 20 ppm; C 30 ppm; P 100 ppm
NIOSH: 1 ppm; STEL 10 ppm (skin)
ACGIH: 10 ppm (skin)
 (1 ppm = 3.11 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.263 g/mL @ 20 °C
 BP 46.5 °C; MP -112 °C; VP 40 kPa
 (300 mm Hg; 40% v/v) @ 20 °C;
 explosive range 1 to 50% v/v in air

SYNONYMS: dithiocarbonic anhydride

SAMPLING	MEASUREMENT
<p>SAMPLER: SOLID SORBENT TUBE + DRYING TUBE (coconut shell charcoal, 100 mg/50 mg, and sodium sulfate, 270 mg)</p> <p>FLOW RATE: 0.01 to 0.2 L/min</p> <p>VOL-MIN: 2 L @ 10 ppm -MAX: 25 L</p> <p>SHIPMENT: dryer attached to charcoal, refrigerated</p> <p>SAMPLE STABILITY: 1 week @ 25 °C 6 weeks @ 0 °C</p> <p>BLANKS: 2 to 10 field blanks per set</p>	<p>TECHNIQUE: GAS CHROMATOGRAPHY, SULFUR FPD</p> <p>ANALYTE: sulfur</p> <p>DESORPTION: 1 mL toluene; stand 30 min</p> <p>INJECTION VOLUME: 5 µL</p> <p>TEMPERATURE-INJECTION: 150 °C -DETECTOR: 145 °C -COLUMN: 30 °C</p> <p>CARRIER GAS: N₂ or He, 20 mL/min</p> <p>COLUMN: glass, 2 m x 6-mm OD, 5% OV-17 on 80/100 mesh GasChrom Q or equivalent</p> <p>CALIBRATION: standard solutions of CS₂ in toluene</p> <p>RANGE: 0.05 to 0.5 mg per sample</p> <p>ESTIMATED LOD: 0.02 mg per sample [2]</p> <p>PRECISION (\hat{S}_r): 0.052 @ 0.28 to 1.1 mg per sample [1]</p>
ACCURACY	
<p>RANGE STUDIED: 46 to 183 mg/m³ [2] (6-L samples)</p> <p>BIAS: - 0.78%</p> <p>OVERALL PRECISION (\hat{S}_{rT}): 0.059 [1]</p> <p>ACCURACY: ± 12.9%</p>	

APPLICABILITY: The working range is 10 to 200 mg/m³ (3 to 64 ppm) for a 5-L air sample and is applicable to ceiling determinations. Better sensitivity may be obtained by using higher sampling rates if high humidity is not present [3,4]. This method has been used extensively in the viscose rayon industry and at carbon disulfide production facilities.

INTERFERENCES: No interference occurs from hydrogen sulfide [4]. Water vapor is a potential sampling interferant [4] which is removed by the drying tube. Alternate GC columns, e.g., 5% OV-210 on Chromosorb G-HP or DB-5 fused silica capillary, aid in resolution of chromatographic interferences.

OTHER METHODS: This revises Method S248 [5] and Method 1600 (dated 2/15/84). The criteria document method [3] uses a higher sampling rate. This method replaces P&CAM 179 which uses a similar collection method but extraction-atomic absorption for measurement [6].

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Toluene, chromatographic quality.
3. Calibration stock solution, 0.0253 mg/ μ L. Dilute 0.253 g CS₂ (0.200 mL at 20 °C) to 10 mL with toluene. Prepare in duplicate.
4. Oxygen, purified.
5. Nitrogen or helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
 - a. Drying tube: glass tube, 7 cm long, 6-mm OD, 4-mm ID; single 270-mg section of granular anhydrous sodium sulfate between two silylated glass wool plugs. This removes moisture equivalent to 6 L of air at 100% RH and 22 °C.
 - b. Sorbent tube: glass tube, 7 cm long, 6-mm OD, with flame-sealed ends and plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-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. Available commercially.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. PTFE tubing, 5-mm ID.
4. Refrigerant, bagged (0 °C).
5. Gas chromatograph, FPD with sulfur filter, integrator and column (see page 1600-1).
NOTE: A valve to vent the solvent peak when it elutes from the column is useful to protect the detector.
6. Vials, glass, 25-mL, PTFE-lined caps.
7. Volumetric flasks, 10-mL.
8. Syringe, 10- μ L, readable to 0.1 μ L.
9. Delivery pipets, 1- to 100- μ L and 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C) [3,7]; work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing. Connect the drying tube to the front section of the charcoal tube with a 20-mm section of PTFE tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 2 to 25 L.
NOTE: Samples may be taken up to 1 L/min if ambient humidity is low [3,4].
4. Keep the drying tube connected to the charcoal tube during shipping. Refrigerate (0 °C) to prevent CS₂ migration to the back section. Cap the open ends. Pack securely for shipment.
NOTE: Store samples away from any source of CS₂ to avoid contamination.

SAMPLE PREPARATION:

5. Detach and discard drying tube. Place front and back sorbent sections of sampler tube in separate vials. Discard glass wool and foam plugs.
 6. Pipet 1.0 mL toluene into each vial. Cap each vial.
 7. Allow to stand 60 min with occasional agitation.
- NOTE: Keep desorbed samples and standards away from sources of CS₂ to avoid contamination.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
 - a. Add known amounts of calibration stock solution to toluene in 10-mL volumetric flasks and dilute to the mark to prepare solutions in the range 0.02 to 0.5 mg CS₂/mL.
 - b. Analyze together with samples and blanks (steps 11 and 12).
 - c. Prepare calibration graph ([peak area]^{1/2} vs. mg CS₂).

NOTE: The FPD has a small linear range. Additional working standards may be required [9].
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
 - a. Remove and discard back sorbent section of a media blank sampler.
 - b. Inject a known amount (1 to 20 µL) of calibration stock solution directly onto front sorbent section with a microliter syringe.
 - c. Cap the tube. Allow to stand overnight.
 - d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
 - e. Prepare a graph of DE vs. mg CS₂ recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

NOTE: At low levels (<0.1 mg CS₂ per sample), DE may be low and variable.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1600-1. Inject sample aliquot manually using solvent flush technique or with autosampler.

NOTE 1: The retention time for toluene is ca. 30 min, which may be shortened by temperature programming.

NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of desorbed sample with toluene, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass (corrected for DE), mg, of CS₂ found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.

NOTE: If W_b > W_f/10, report breakthrough and possible sample loss.
14. Calculate concentration, C, of CS₂ in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method modifies S248, in that 1 mL toluene (instead of 10 mL benzene) is used to desorb samples, resulting in a better desorption efficiency at low levels and safer working conditions for the analyst [8]. Method S248 [5] was issued on January 30, 1976, and validated over the range 15 to 59 mg/m³ using a 6-L sample with spiked samplers and atmospheres generated by syringe pump/triple air dilution and verified by total hydrocarbon analyzer [1]. Overall precision, \hat{S}_{rT} , was 0.059 with "found" concentrations 0.8% lower than "true" concentrations for 18 samples tested, representing a non-significant bias. Breakthrough (with drying tube preceding charcoal tube) occurred at 162 min (100% RH, 40 ppm CS₂, 0.2 L/min sampling rate) = 32.4 L; DE (0.28 to 1.12 mg/sample) = 0.86; storage stability (0.56 mg/sample) = 85% recovery after one week at 25 °C. At a 1 L/min sampling rate, breakthrough occurred at 19 L at 100 mg/m³ [4]. A user check of this method gave an estimated LOD of 0.02 mg CS₂ per sample [2].

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, S248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
- [2] User check, UBTL, Inc., NIOSH Sequence #3990-L (unpublished, November 9, 1983).
- [3] Criteria for a Recommended Standard...Occupational Exposure to Carbon Disulfide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-156 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
- [4] McCammon, C.S., P.M. Quinn and R. Kupel. A Charcoal Sampling Method and a Gas Chromatographic Analytical Procedure for Carbon Disulfide, Am. Ind. Hyg. Assoc. J., **36**, 618-624 (1975).
- [5] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
- [6] Ibid., Vol. 1, P&CAM 179, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
- [7] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123, available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
- [8] Foley, G. D. NIOSH/DPSE (internal memo, April 17, 1985).
- [9] Quincoces, C.E. and M.G. Gonzaleg. Characterization of the Flame Photometric Detector in the Sulfur Mode, Chromatographia **20**:371 (1985).

METHOD REVISED BY:

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