DIMETHYL SULFATE 2524

$(CH_3O)_2SO_2$ MW: 126.13 CAS: 77-78-1 RTECS: WS8225000

METHOD: 2524, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
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OSHA : 0.1 ppm (skin)
NIOSH: 0.1 ppm/8 hours (skin); carcinogen
ACGIH: 0.1 ppm (skin); suspect carcinogen
(1 ppm = 5.16 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.332 g/mL @ 20 °C;
BP 188 °C with decomposition;
MP -31.8 °C; VP 0.07 kPa (0.5 mm Hg; 700 ppm) @ 20 °C

SYNONYMS: methyl sulfate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Poropak P, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.25 L @ 1 ppm
-MAX: 12 L

SAMPLE STABILITY: at least 1 week @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1.8 to 24.5 mg/m^3 [1] (1.2-L samples)

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): 0.073 [1]

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ELECTROLYTIC CONDUCTIVITY DETECTOR (SULFUR MODE)

ANALYTE: dimethyl sulfate

DESORPTION: 1 mL diethyl ether, 30 min

INJECTION VOLUME: 4 µL

TEMPERATURE-INJECTION: 180 °C
-COLUMN: 2 min @ 50 °C; then 30 °C/min to 120 °C; hold

CARRIER GAS: He, 20 mL/min

COLUMN: 1.8 m x 3.2-mm OD stainless steel, packed with 5% DEGS on 80/100 mesh Chromosorb WHP

CALIBRATION: dimethyl sulfate in diethyl ether

RANGE: 1 to 120 µg per sample

ESTIMATED LOD: 0.25 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.06 @ 1.1 to 39 µg per sample [1]

APPLICABILITY: The working range is 0.03 to 4 ppm (0.17 to 20 mg/m^3) for a 6-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This revises P&CAM 301 [2].

REAGENTS:

1. Dimethyl sulfate, 99%.*
2. Diethyl ether,* anhydrous, preserved with ethanol.
3. Calibration stock solution, 12 µg/µL. Add 120 mg (90 µL) dimethyl sulfate to a pre-weighed 10-mL volumetric flask. Re-weigh and dilute to the mark with diethyl ether.
4. Helium, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 50/80 mesh Porapak P (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 0.2 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
   NOTE: Some batches of Porapak P initially gave poor recovery. Good recoveries were obtained after the sorbent had been heated at 180 °C in a vacuum oven for 16 hrs.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, electrolytic conductivity detector (sulfur mode), integrator, and column (see page 2524-1).
   NOTE: A new column must be primed before attempting quantitative work by repeatedly injecting aliquots of calibration stock solution until the detector response to dimethyl sulfate reaches a plateau.
4. Vials, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10-µL and other convenient sizes for preparing standards, readable to 0.1-µL.
6. Volumetric flasks, 10-mL.
7. Pipets, 1-mL.

SPECIAL PRECAUTIONS: Dimethyl sulfate is a suspect carcinogen, and both the liquid and vapor are extremely severe irritants to skin, eyes, and mucous membranes. It is an insidious hazard -- warning properties are poor and symptoms are delayed up to 10 h or more [3,4]. All transfers involving dimethyl sulfate should be performed in a fume hood. Personal protective equipment should be used to prevent any bodily exposure even to the vapor.

Diethyl ether is an extreme fire (flash point = -45 °C) and explosion hazard (possible peroxide formation); 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.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.25 to 12 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the separating plugs.
6. Add 1.0 mL diethyl ether to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.25 to 120 µg dimethyl sulfate per sample (2.5 to 1200 µg/10 mL).
   a. Add known amounts of calibration stock solution to 10-mL volumetric flasks and dilute to the mark with diethyl ether.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. µg dimethyl sulfate).
9. Determine desorption efficiency (DE) at least once for each lot of Porapak P used for sampling in the calibration range (step 8). 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 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. µg dimethyl sulfate recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2524-1. Set electrolytic conductivity detector for operation in sulfur mode according to manufacturer's recommendations. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with diethyl ether, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak height.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of dimethyl sulfate 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 dimethyl sulfate in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

For the evaluation, a Tracor Model 310 Hall electrolytic conductivity detector was used [1]. It was operated with a furnace temperature of 950 °C, oxygen at 20 mL/min as the reactant gas, and filtered, deionized water at 1 mL/min as the conductivity solvent. The capacity of Porapak P for the collection of dimethyl sulfate was estimated from a log retention volume vs. reciprocal absolute temperature plot of data obtained by chromatographing 30-µg quantities of dimethyl sulfate on a 100-mg sorbent bed. Based on these data, the estimated volumetric capacity decreases from 39 L at 25 °C to 16 L at 35 °C. In a test of humidity and storage effects, six tubes were spiked with 0.6 µg dimethyl sulfate. After passing 12 L of humid air (80% RH) through each, they were stored for seven days. Upon analysis, these samples showed no significant loss of dimethyl sulfate.

This method was compared with an independent method based on collection of dimethyl sulfate on Tenax-GC, derivatization of p-nitrophenol with the collected dimethyl sulfate, and HPLC (UV detection) of the resulting p-nitroanisole. For three sets of six dynamically-generated samples, the concentrations and precisions (relative standard deviations) found using this method were 1.8 (0.061), 4.35 (0.074), and 24.5 (0.070) µg/L. The corresponding results found by the independent method for simultaneously-generated samples were 3.18 (0.153), 7.18 (0.090), and 20.4 (0.086) µg/L. Because of the inconsistency of the results and possible inaccuracy in the independent method, the accuracy of this method remains to be determined.

REFERENCES:

[1] Lunsford, R. A., and P. M. Fey. Backup Data Report for P&CAM 301 (NIOSH, unpublished, December 29, 1978).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 301, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] The Merck Index, 11th Ed., Merck & Co., Inc., Rahway, NJ (1989).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

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