n-BUTYL MERCAPTAN 2525

$CH_3CH_2CH_2CH_2SH$ MW: 90.19 CAS: 109-79-5 RTECS: EK6300000

METHOD: 2525, Issue 2 **EVALUATION: FULL** **Issue 1: 5 May 1989**
Issue 2: 15 May 1996

OSHA: 0.5 ppm
NIOSH: C 0.5 ppm
ACGIH: 0.5 ppm
(1 ppm = 3.69 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.842 g/mL @ 25 °C; BP 98 °C; VP 4.7 kPa (35 mm Hg; 4.6% v/v) @ 20 °C

SYNONYMS: butanethiol; 1-butanethiol; 1-mercaptobutane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Chromosorb 104, 150 mg/75 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L
-MAX: 4 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 17 to 74 mg/m^3 [1] (1.5-L samples)

BIAS: - 2% [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.062 [1]

ACCURACY: ± 14.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FPD SULFUR MODE

ANALYTE: *n*-butyl mercaptan

DESORPTION: 1 mL acetone; stand 15 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 150 °C
-DETECTOR: 200 °C
-COLUMN: 140 °C

COLUMN: glass, 1.2 m x 2-mm ID, packed with 60/80 mesh Chromosorb 104

CARRIER GAS: N_2, 50 mL/min

CALIBRATION: standard solutions of *n*-butylmercaptan in acetone

RANGE: 20 to 200 µg per sample [2]

ESTIMATED LOD: 3 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.015 @ 30 to 110 µg per sample [1]

APPLICABILITY: The working range is 5 to 50 mg/m^3 (1.4 to 14 ppm) maximum sample size is based on the capacity of the Chromosorb 104 to collect vapors of *n*-butyl mercaptan in air at high relative humidity (94%) [1]. Smaller concentrations may be determined if desorption efficiency is adequate.

INTERFERENCES: None identified.

OTHER METHODS: This revises NIOSH Method S350 [2].

REAGENTS:

1. Acetone, chromatographic quality.
2. *n*-Hexane, reagent grade.
3. *n*-Butyl mercaptan.*
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Oxygen, purified.
7. Air, filtered, compressed.
8. Calibration stock solution, 13.47 mg/mL. Add 160 µL of pure *n*-butyl mercaptan to acetone and dilute to 10 mL. Prepare in duplicate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 8.5 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps containing two sections of 60/80 mesh Chromosorb 104 (front = 150 mg; back = 75 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 0.025 L/min airflow must be less than 3.4 kPa (25 mm Hg). The sampling tubes are commercially available (SKC, Inc. Cat. # 226-109).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame photometric detector with sulfur filter, integrator, and column (page 2525-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10-µL (readable to 0.1 µL) and 50-µL.
6. Flasks, volumetric, 10-mL.
7. Pipet, 1.0-mL.
8. File, triangular.

SPECIAL PRECAUTIONS: Store *n*-butyl mercaptan away from oxidizing and flammable materials [3,4]. The analyte is highly flammable and irritating to the eyes and mucous membranes. Work 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 0.05 L/min for a total sample size of 1 to 4 L.
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL acetone to each vial. Attach cap to each vial.
7. Allow to stand 15 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range 0.3 to 20 µg/mL.
   a. Add known amounts of calibration stock solution to acetone in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area squared vs. µg *n*-butyl mercaptan).
9. Determine desorption efficiency (DE) at least once for the batch of Chromosorb 104 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 calibration stock solution (2 to 20 µL) containing a known amount of *n*-butyl mercaptan 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 *n*-butyl mercaptan 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 2525-1. Inject sample aliquot manually using solvent flush technique. Vent the acetone peak so that it will not extinguish the flame in the detector.
    NOTE: If peak area is above the linear range of the working standards, dilute with acetone, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of *n*-butyl mercaptan found in the sample front (W_f) and back (W_b) sorbent sections, and in the average 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 *n*-butyl mercaptan 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:

This method was validated over the range 17 to 74 mg/m^3 at 22 °C and 759 mm Hg using a 1.5-L sample [1]. Overall precision, $\hat{S}_{rT}$, was 0.062 with an average recovery of 0.98. The concentration of *n*-butyl mercaptan was independently determined from the syringe delivery rate and dilution flow rates. Desorption efficiency was 0.90 in the range 28 to 110 µg per sample. The breakthrough volume (effluent concentration = 5% of influent concentration) was 4.0 L; this was determined by sampling humid air (94% relative humidity), containing 74 mg/m^3 *n*-butyl mercaptan at 0.023 L/min.

REFERENCES:

[1] NIOSH [1977]. Backup data report for S350, prepared under NIOSH Contract 210-76-0123.
[2] NIOSH [1978]. *n*-Butyl mercaptan: Method S350. In: Taylor DG, Ed. NIOSH manual of analytical methods, 2nd. ed., V. 4. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No.78-175.
[3] General Electric [1982]. Material safety data sheet, #504 Butyl Mercaptan, General Electric Co., Schenectady, N.Y. 12305.
[4] NIOSH [1981]. NIOSH/OSHA Occupational health guidelines for occupational hazards. U.S. Department of Health and Human Services, DHHS (NIOSH) Publication No. 81-123, available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE. Method S350 was originally validated under NIOSH Contract 210-76-0123.