

MERCAPTANS, METHYL-, ETHYL-, and n-BUTYL-

2542

CH ₃ SH	MW: 48.11	CAS: 74-93-1	RTECS: PB4375000
CH ₃ CH ₂ SH	62.13	75-08-1	KI9625000
CH ₃ CH ₂ CH ₂ CH ₂ SH	90.19	109-79-5	EK6300000

METHOD: 2542, Issue 1

EVALUATION: PARTIAL

Issue 1: 15 August 1994

OSHA : Table 1

PROPERTIES: Table 1

NIOSH: Table 1

ACGIH: Table 1

SYNONYMS: Methyl mercaptan: methanethiol; mercaptomethane; methyl sulfhydryate

Ethyl mercaptan: ethanethiol; mercaptoethane; ethyl sulfhydryate

n-Butyl mercaptan: butanethiol; 1-mercaptobutane; 1-butanethiol

SAMPLING	MEASUREMENT
<p>SAMPLER: FILTER (glass fiber, 37-mm, impregnated with mercuric acetate)</p> <p>FLOW RATE: 0.1 to 0.2 L/min</p> <p>VOL-MIN: 10 L @ 0.5 ppm -MAX: 150 L</p> <p>SHIPMENT: protect samples from light [1,2]</p> <p>SAMPLE STABILITY: at least 3 weeks @ 25 °C</p> <p>BLANKS: 2 to 10 field blanks per set</p>	<p>TECHNIQUE: GAS CHROMATOGRAPHY, FPD SULFUR MODE</p> <p>ANALYTE: methyl, ethyl and n-butyl mercaptans</p> <p>EXTRACTION: 20 mL HCl (25% v/v) plus 5 mL 1,2-dichloroethane, 2 min</p> <p>INJECTION VOLUME: 1 µL</p> <p>TEMPERATURE-INJECTOR: 250 °C -DETECTOR: 250 °C -COLUMN: 30 °C 2 min, 15 °C/min, 200 °C</p> <p>COLUMN: narrow-bore, fused-silica capillary, 30 cm x 0.25-mm ID, 1 µm DB-1</p> <p>CARRIER GAS: He, 1.0 mL/min; makeup gas: N₂, 20 mL/min</p> <p>CALIBRATION: standard solutions of mixed mercaptans in 1,2-dichloroethane</p> <p>RANGE: Table 2</p> <p>ESTIMATED LOD: Table 2</p> <p>PRECISION (\hat{S}_r): Table 2</p>
ACCURACY	
<p>RANGE STUDIED: Table 2</p> <p>BIAS: not determined</p> <p>OVERALL PRECISION (\hat{S}_{rT}): Table 2</p> <p>ACCURACY: not determined</p>	

APPLICABILITY: The working ranges are 0.2 to 10 ppm for a 20-L air sample for all three mercaptans [1-4].

INTERFERENCES: Dimethyl disulfide, diethyl disulfide and dibutyl disulfide may interfere [2-4].

OTHER METHODS: This is a modification of OSHA Method 26 for methyl mercaptan with the addition of ethyl- and n-butyl mercaptan [2].

REAGENTS:

1. Methyl mercaptan*
gas, lecture bottle, 99.5+%.
2. Ethyl mercaptan,* 99+%.
3. n-Butyl mercaptan,* 99+%.
4. Mercuric acetate, ACS reagent grade.
5. Hydrochloric acid, ACS reagent grade.
6. 1,2-Dichloroethane, ACS reagent grade.
7. Methyl mercaptan calibration stock solution, 0.394 mg/mL. Pipet 5.0 mL methylene chloride into a vial and attach PTFE-lined cap. Add 1.0 mL pure methyl mercaptan gas (measured at 25 °C, 1 atm) to the liquid using gas-tight syringe.
8. Ethyl mercaptan calibration stock solution, 2.52 mg/mL. Dissolve 30 µL ethyl mercaptan in methylene chloride in a 10-mL volumetric flask and dilute to the mark.
9. n-Butyl mercaptan calibration stock solution, 3.34 mg/mL. Dissolve 40 µL n-butyl mercaptan in methylene chloride in a 10-mL volumetric flask and dilute to the mark.
10. Helium, purified.
11. Hydrogen, prepurified.
12. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass fiber filters impregnated with mercuric acetate. The filters are prepared by immersing 37-mm Gelman Metrigard (or equivalent) glass fiber filters with acrylic binder in 5% (w/v) aqueous solution of mercuric acetate, dried in the air, and then assembled in two-piece filter cassettes without backup pads. The filters exhibit yellowish color, but it does not affect their collection efficiency.
2. Personal sampling pump, 0.10 to 0.20 mL/min, with flexible polyethylene or PTFE tubing.
3. Gas chromatograph with a flame photometric detector, capillary column, integrator.
4. Vials, glass, 2-mL and 5-mL, PTFE-lined crimp caps.
5. Syringes, 10-, 50, and 250-µL.
6. Volumetric flasks, 10-mL.
7. Pipets, 5- and 20-mL glass, delivery, with pipet bulb.
8. Separatory funnel, 30-mL.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the plugs from the filter cassette immediately before sampling. Connect the cassette to the sampling pump with flexible tubing. Air being sampled should not pass through any hose or tubing before entering filter cassette.
3. Sample at an accurately known flow rate between 0.1 and to 0.2 L/min for a total sample size of 10 to 150 L.
4. Replace the plugs in the filter cassette immediately after sampling. Store protected from light.

SPECIAL PRECAUTIONS: Store methyl-, ethyl-, and n-butyl-mercaptans from flammable and oxidizing materials [5,6]. The analytes are highly flammable and irritating to the eyes. Work in a hood.

SAMPLE PREPARATION:

5. Add 20 mL of 25% (v/v) hydrochloric acid and 5 mL of 1,2-dichloroethane to a 30-mL separatory funnel. Fold sample filter and insert into the neck of a separatory funnel, without allowing the filter to become wet. While seating the stopper, push filter into funnel.
6. Shake funnel for 2 min without venting.
7. Let stand at least 5 min, until the phases completely separate. Then drain the 1,2-dichloroethane into a vial and seal with a PTFE-lined cap.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range of the samples:

- a. Add known amounts of calibration stock solution to 1,2-dichloroethane in 10-mL volumetric flasks and dilute to the mark.
 - b. Analyze together with samples and blanks (steps 10 and 11).
 - c. prepare calibration graphs: either quadratic curves, i.e., peak area vs. concentration of mercaptans, or linear curves, i.e., $\ln(\text{peak area})$ vs. $\ln(\text{concentration})^2$ can be used for calibration.
9. Determine recovery (R) for each lot of glass fiber filters impregnated with mercuric acetate in the concentration range of interest. Prepare four filters at each of three concentrations plus three media blanks.
- a. Apparatus for preparing and sampling gas spikes is shown in Figure 1. The apparatus is composed of glass and Teflon.
 - b. Sample at a rate of 0.2 L/min for 100 min.
NOTE: Protect the samples from light.
 - c. Extract the samples (steps 5 through 7) and analyze (steps 10 and 11).
 - d. Prepare separate recovery graphs for each mercaptan (R vs. μg analyte).

MEASUREMENT:

10. Set gas chromatograph to conditions given on page 2542-1. Set air and hydrogen flow rates on the flame photometric detector to manufacturer's specification. Inject 1- μL sample aliquot via the split injection mode. Retention times: methyl mercaptan, 2.4 min; ethyl mercaptan, 3.2 min; n-butyl mercaptan 6.9 min.
11. Measure peak area.

CALCULATIONS:

12. Determine the mass, μg , of methyl-, ethyl-, and n-butyl-mercaptans found in the samples (W) and in the average media blanks (B).
13. Calculate concentration, C, of the mercaptans in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method modifies OSHA Method 26, Methyl Mercaptan [2], and further develops and evaluates the procedure for ethyl- and n-butyl mercaptans, as well as methyl mercaptan [1]. The method was evaluated for recovery and extraction efficiency with gas spikes, 18 samples (6 at each level, 0.5, 1, and 2 x PEL)(Figure 1). Recoveries were 82.7% for methyl mercaptan, 89.3% for ethyl mercaptan, and 93.0% for n-butyl mercaptan. Test atmospheres of methyl- and ethyl mercaptans were generated with permeation tubes as the analyte source. Six samples at one level (1 x PEL) were collected and analyzed. Recoveries for generated samples, corrected for extraction efficiency, were $98.6 \pm 8.9\%$ for methyl mercaptan and $102 \pm 7.8\%$ for ethyl mercaptan. Samples of n-butyl mercaptan were not generated. Samples prepared by spiking impregnated filters with a solution of mixed mercaptans were found to be stable for at least three weeks at ambient temperatures when protected from light. The evaluation data are summarized in Table 2.

REFERENCES:

- [1] Xue, Zhi-Lun, Backup Data Report for Methyl, Ethyl, and n-Butyl Mercaptans (NIOSH/DPSE, unpublished, October, 1991).
- [2] OSHA Analytical Laboratory, Method 26, Methyl Mercaptan, February 1981.
- [3] Knarr, R. and Rapport, S.M., Determination of Methanethiol at Parts-per-Million Air Concentration by Gas Chromatography, *Anal. Chem.*, **52**, 733-736 (1980).
- [4] Knarr, R. and Rapport, S.M., Impregnated Filters for the Collection of Ethanethiol and Butanethiol in Air, *Am. Ind. Hyg. Assoc. J.*, **42**, 839-941 (1981).
- [5] Material Safety Data Sheet, #504 Butyl Mercaptan, General Electric, Schenectady, NY 12305 (1982).
- [6] NIOSH/OSHA Occupational Health Guidelines for Occupational 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.

METHOD REVISED BY:

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TABLE 1. GENERAL INFORMATION

Compound	Exposure Limits (ppm)			1 ppm = mg/m ³ @ NTP	Density @ 20 °C (g/mL)	BP (°C)	kPa (mm Hg)
	OSHA	NIOSH	ACGIH				
Methyl mercaptan	C 10	C 0.5/15 min	0.5 ppm	2.0	0.866	6.2	> 1 atm
Ethyl mercaptan	C 10	C 0.5/15 min	0.5 ppm	2.6	0.839	35	58.9 (442)
n-Butyl mercaptan	10 ppm	C 0.5/15 min	0.5 ppm	3.7	0.834	98.4	4.7 (35)

TABLE 2. EVALUATION DATA

Compound	Range Studied* (mg/m ³)	Measurement		LOD (µg/sample)	Overall Precision S _r
		Range (µg/sample)	Precision S _r		
Methyl mercaptan	1.0 to 4.0	10 to 50	0.055	4	0.091
Ethyl mercaptan	1.3 to 5.6	10 to 50	0.059	5	0.097
n-Butyl mercaptan	1.8 to 7.4	20 to 70	0.063	7	0.086

* 180-L samples

FIGURE 1. SAMPLE SPIKING AND COLLECTION SYSTEM