ACETALDEHYDE

MF: CH_3CHO MW: 44.05 CAS: 75-07-0 RTECS: AB1925000

METHOD: 2538, Issue 1 **EVALUATION: UNRATED** **Issue 1: 15 August 1993**

OSHA : 200 ppm
NIOSH: carcinogen; lowest feasible level
ACGIH: 100 ppm; STEL 150 ppm
(1 ppm = 1.80 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.78 g/mL @ 20 °C;
BP 20.4 °C; VP 750 mm Hg @ 20 °C;
explosive range 4 to 60% v/v in air

SYNONYMS: acetic aldehyde; ethanal.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
[2-(hydroxymethyl)piperidine (2-HMP)
on XAD-2, 450 mg/225 mg]

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 100 ppm
-MAX: 12 L

SHIPMENT: routine

SAMPLE STABILITY: 100% recovery after 21 days @ 0 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 180 to 720 mg/m^3 [2]
(3-L samples)

BIAS: 0.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.12 [2]

ACCURACY: ± 23.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: oxazolidine derivative of acetaldehyde

DESORPTION: 5 mL toluene, 60 min ultrasonic

INJECTION VOLUME: 1 µL, splitless

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 70 °C 1 min; 6 °C/min to 110 °C (hold 2 min) 30 °C/min to 260 °C (hold 1 min.)

CARRIER GAS: He, 1 mL/min; makeup 29 mL/min

COLUMN: wide-bore, fused-silica capillary, 15 m x 0.32-mm; 1-µm DB-1301 film

CALIBRATION: standard solutions of acetaldehyde on coated sorbent

RANGE: 4 to 2200 µg per sample [2]

ESTIMATED LOD: 2 µg per sample [1, 2]

PRECISION ($\hat{S}_r$): 0.090 @ 26 to 107 µg per sample [1]

APPLICABILITY: The working range is 0.74 to 407 ppm (1.3 to 730 mg/m^3) for a 3-L air sample.

INTERFERENCES: None identified. An alternative chromatographic column is a 2 m x 6-mm OD x 2-mm ID glass column containing 10% UCON 50-HB-5100 + 2% KOH on 80/100 Chromosorb W-AW.

OTHER METHODS: This is an adaptation of OSHA Method 68 [1], and is a convenient alternative to Method 3507.

REAGENTS:

1. Toluene, chromatographic quality, containing 0.02% (v/v) dimethylformamide or other suitable internal standard.
2. Acetaldehyde*, high-purity. Store in freezer at ca. -20 °C.
3. 2-(Hydroxymethyl)piperidine (2-HMP). Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
4. Calibration stock solution, 31.2 mg/mL. (APPENDIX A)
5. Helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 11 cm long, 8-mm OD, 6-mm ID, flame sealed ends with plastic caps, containing two sections of 40/60 mesh 2-(hydroxymethyl) piperidine coated on XAD-2 and separated by 2-mm glass-wool plug (front = 450 mg; back = 225 mg). Tubes are commercially available (Supelco, Inc. ORBO-25 or equivalent), or may be prepared (see APPENDIX B).
2. Personal sampling pump, 0.01 to 0.05 L/min. with flexible connecting tubing.
3. Gas chromatograph, capillary column, FID, integrator (page 2538-1).
4. Vials, 7-mL, glass, with PTFE-lined screw caps.
5. Ultrasonic bath or mechanical shaker.
6. Pipets, volumetric, 1- and 5-mL with pipet bulb.
7. Flasks, volumetric, 10- and 25-mL.
8. Syringe, 10 µL, readable to 0.1 µL.

SPECIAL PRECAUTIONS: Acetaldehyde is toxic if inhaled or if it comes in contact with the eyes or skin [3], and is an animal carcinogen [4]. Exercise appropriate precautions in handling this chemical.

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 12 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place front section and front glass-wool plug of the sampler in a vial. Place back section and center glass-wool plug in a separate vial. Discard rear glass-wool plug.
6. Add 5.0 mL to toluene to each vial. Cap each vial tightly.
7. Agitate in an ultrasonic batch for 60 min.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range of the samples.
   a. Place 450-mg portions of coated XAD-2 sorbent, from the same lot as used to collect the air samples, into vials.
   b. Inject known volumes of calibration stock solution or a serial dilution thereof onto the sorbent to obtain acetaldehyde working standards in the range 2 to 2200 µg. Cap vials.
      NOTE: Prepare working standards ca. 16 h before air samples are to be analyzed to ensure that the reaction between acetaldehyde and 2-HMP is complete.
   c. Prepare three media blanks.
   d. Desorb (steps 5 through 7) and analyze (steps 10 and 11) the working standards and media blanks along with the samples and field blanks.
   e. Prepare calibration graph, ratio of peak area of analyte/peak area of internal Standard vs.

µg acetaldehyde.

9. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.
   NOTE: A desorption efficiency study is not usually necessary since standards are prepared on the coated sorbent.

MEASUREMENT:

10. Set gas chromatograph to conditions given on page 2538-1. Set air and hydrogen flows on the flame ionization detector to manufacturer's specifications. Inject 1-µL sample aliquot via the splitless injection technique. Retention time = 6.8 min for acetaldehyde under these conditions.
11. Measure peak area. Divide the peak area of analyte by the peak area of the internal standard on the same chromatogram.

CALCULATIONS:

12. Determine the mass, µg, of acetaldehyde 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 1: If $W_b > W_f/10$, report breakthrough and possible sample loss.
    NOTE 2: Under these conditions, there is typically no detectable acetaldehyde blank level.
13. Calculate concentration, C, of acetaldehyde 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 originally developed and fully validated by OSHA [2} over the range 180 to 720 mg/m [3] per sample. A storage study was done by spiking commercially-available tubes with standard solutions of acetaldehyde [1]. Recovery (26.8 and 107 µg/sample) was 100% after 21 days of refrigerated storage. A migration study was also performed at the above concentrations. After 21 days refrigerated storage, no acetaldehyde was detected on the back sections of the samples. Additional evaluation information is available [2]. Field samples of acetaldehyde were also successfully analyzed by utilizing this method [1]. This method has not been evaluated by NIOSH, except for the storage and migration studies.

REFERENCES:

[1] Williams, Karen J. Analytical Report for Acetaldehyde Samples, NIOSH (MRSB) Sequence #6384, Unpubl. NIOSH (1988).

[2] "OSHA Analytical Methods Manual, " U.S. Dept. of Labor, Occupational Safety and Health Administration, OSHA Analytical Laboratory, Salt Lake City, UT, Method #68 (1988).

[3] 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.

[4] IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Allyl Compounds, Aldehyde, Epoxides and Peroxides, International Agency for Research on Cancer Vol 36:101-132 Lyon, France (1984).

METHOD REVISED BY:

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