ACETALDEHYDE by GC 2538

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

METHOD: 2538, Issue 1 **EVALUATION: UNRATED** **Issue 1: 15 August 1994**

OSHA : 200 ppm
NIOSH: carcinogen; lowest feasible level
ACGIH: C 25 ppm; suspect carcinogen
(1 ppm = 1.801 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.78 g/mL @ 20 °C; BP 20.4 °C; VP 100 kPa (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:

Karen J. Williams.

APPENDIX A: PREPARATION OF CALIBRATION STOCK SOLUTION

Prepare by diluting a known amount of acetaldehyde with toluene:

a. Determine the weight of a sealed 25-mL volumetric flask containing approximately 15 mL of toluene.
b. Place the sealed volumetric flask and a 1-mL pipet in the same freezer used to store the acetaldehyde.
c. After 30 minutes, remove the sealed volumetric flask, 1-mL pipet and the acetaldehyde.
d. Immediately pipet 1.0 mL of acetaldehyde into the cold flask, reseal the flask and allow it to warm to room temperature.
e. Reweigh the flask and subtract the tare weight from the weight of the reweighed flask to determine the weight of acetaldehyde added.
f. Dilute the contents of the flask to the mark with toluene.
g. Store the stock standards in a freezer. Prepare fresh stock standards every 10 days.

APPENDIX B: PREPARATION OF XAD-2 SORBENT COATED WITH 2-HMP

Weigh 125 g of crude XAD-2 adsorbent into a 1-L Erlenmeyer flask. Add about 200 mL of water to the flask and then swirl the mixture to wash the adsorbent. Discard any adsorbent that floats to the top of the water and then filter the mixture using a fritted Buchner funnel. Transfer the adsorbent back to the Erlenmeyer flask and repeat the water wash and the filtration. Air-dry the adsorbent for about 2 min. Transfer the adsorbent back to the Erlenmeyer flask and then add about 200 mL methanol to the flask. Swirl and filter the mixture as before. Transfer the washed adsorbent to a 1-L evaporative flask and remove the methanol using rotary evaporation. Cool the flask to room temperature and add 13 g of 2-HMP and 200 mL of toluene to the flask. Swirl the mixture and then allow it to stand for an hour. Remove the toluene using rotary evaporation. Seal the flask and allow the coated adsorbent to stand overnight at ambient temperature.

Transfer the coated adsorbent to a Soxhlet extractor. Extract the material with toluene for about 24 hours. Replace the contaminated toluene with fresh toluene and continue the extraction for an additional 24 hours. Replace the second aliquot of contaminated toluene with methanol and continue the Soxhlet extraction for 4 hours. Transfer the adsorbent to a weighed 1-L, round-bottomed, evaporative flask and remove the methanol using the rotary evaporation apparatus. Determine the weight of the adsorbent and then add an amount of 2-HMP, which is 10%, by weight, of the adsorbent. Add 200 mL toluene and swirl the mixture. Allow the flask to stand for 1 hour. Remove the toluene using rotary evaporation. If the last traces of toluene are difficult to remove, add about 100 mL of methanol to the flask, swirl the mixture and then remove the solvents using rotary evaporation.

XAD-2 adsorbent treated in this manner will often contain residual formaldehyde derivative levels of about 0.1 µg/150 mg of adsorbent. The formaldehyde blank level and potential acrolein and acetaldehyde chromatographic interferences should be determined at this time. If the formaldehyde blank and/or any interference is determined to be too high, return the lot to the Soxhlet extractor, extract with toluene again and recoat with 2-HMP. This process can be repeated until an acceptable blank and/or level of chromatographic interferences is attained.

The coated adsorbent is now ready to be packed into sampling tubes. The sampling tubes should be stored in the dark and separated by lot number. A sufficient amount of each lot of coated adsorbent should be retained to prepare analytical standards for use with air samples from that lot number.