$H_2C=CHCHO$ MW : 56.07 CAS: 107-02-8 RTECS: AS1050000

METHOD: 2501, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
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OSHA : 0.1 ppm
NIOSH: 0.1 ppm; STEL 0.3 ppm; Group I Pesticide
ACGIH: 0.1 ppm, STEL 0.3 ppm
(1 ppm = 2.29 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.8389 g/mL @ 20 °C; BP 52.5 °C; MP -88 °C; VP 28.5 kPa (214 mm Hg; 28% v/v) @ 20 °C; explosive range 2.8 to 31% v/v in air

SYNONYMS: 2-propenal; acrylicaldehyde; acrylaldehyde; allylaldehyde.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (2-(hydroxymethyl)piperidine on XAD-2, 120 mg/60 mg)

FLOW RATE: 0.01 to 0.1 L/min

VOL-MIN: 13 L @ 0.1 ppm
-MAX: 48 L

SHIPMENT: routine

SAMPLE STABILITY: at least 4 weeks @ 25 °C [1]

BLANKS: 2 to 10 field blanks and 10 media blanks per set

ACCURACY

RANGE STUDIED: 0.12 to 1.50 mg/m^3 (24-L samples)

BIAS: 7.0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.111 [1]

ACCURACY: ± 29%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, NITROGEN-SPECIFIC DETECTOR

ANALYTE: 9-vinyl-1-aza-8-oxabicyclo[4.3.0]nonane

DESORPTION: 2 mL toluene; ultrasonic bath for 30 min

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 230 °C
-DETECTOR: 250 °C
-COLUMN: 90 °C for 8 min; 20 °C/min; hold @ 200 °C for 11 min

CARRIER GAS: Helium, 30 mL/min

COLUMN: 2 m x 2-mm glass, 5% SP-2401-DB on Supelcoport (100-120 mesh)

CALIBRATION: acrolein spiked on coated sorbent

RANGE: 3 to 36 µg per sample

ESTIMATED LOD: 2 µg per sample

PRECISION ($\hat{S}_r$): not determined

APPLICABILITY: The working range is 0.05 to 0.2 ppm (0.13 to 0.5 mg/m^3) for a 24-L air sample. For STEL measurements, the limit of the method is 0.9 ppm for a 15-min sample at 0.1 L/min.

INTERFERENCES: None known. Peaks for acetaldehyde and formaldehyde oxazolidines may be observed in the chromatogram, but they are resolved from the acrolein peak. Capacity of the sampler is reduced if sampling in air containing acids [1] .

OTHER METHODS: This method was developed to give improved sample stability and to provide for ease of personal sampling compared to P&CAM 118 [2] and P&CAM 211 [2], which have not been revised.

REAGENTS:

1. Toluene, chromatography quality.
2. Acrolein,* freshly distilled under N_2 to remove stabilizer. Store at 0 °C.
3. 2-(Hydroxymethyl)piperidine. Recrystallize several times from isooctane until pure by GC analysis. Store in dessicator.
4. XAD-2 (Amberlite - Rohm and Haas) or equivalent. Extract 4 h in soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight.
5. Calibration stock solution, 1.0 µg/µL. Add 11.9 µL acrolein to a septum-capped 10-mL volume of toluene.

* See Special Precautions

EQUIPMENT:

1. Sampling tube: glass tube, 10 cm x 4-mm ID, containing a 120-mg front section and a 60-mg back-up section of the 2-(hydroxymethyl) piperidine-coated XAD-2 (see APPENDIX) with flame-sealed ends. Sorbent sections are retained and separated by small plugs of silanized glass wool. Pressure drop ca. 2.2 inches of water (756 Pa) at 0.10 L/min. Tubes are commercially available (Supelco ORBO 23 or equivalent).
2. Sampling pump, 0.01 to 0.1 L/min, with flexible connecting tubing.
3. Vials, 4-mL, with septum and plastic screw caps.
4. Ultrasonic bath.
5. Pipettes, volumetric, 1- and 2-mL, with pipet bulb.
6. Flasks, volumetric, 10-mL.
7. Pipettes, disposable, 2-mL.
8. Syringes, 10-µL (readable to 0.1 µL) and 25- and 50-µL.
9. Gas chromatograph, nitrogen-specific detector, integrator and column (page 2501-1).
10. File.

SPECIAL PRECAUTIONS: Acrolein is an acute irritant and a potential fire hazard (flash point = -17.8 °C); work with this compound only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Score with a file and 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 0.1 L/min for a total sample size of 1.5 to 48 L.
   NOTE: Sampling rate is limited by the speed of reaction of acrolein with the sorbent coating. Sampling at rates above 0.10 L/min could cause appreciable acrolein breakthrough, possibly invalidating the sample.

SAMPLE PREPARATION:

4. Score each sampler with a file in back of the rear sorbent section.
5. Break sampler at score line. Remove and place glass wool plug and rear sorbent section in a 4-mL vial.
6. Transfer front section with the remaining glass wool plugs to a second 4-mL vial.
7. Add 2.0 mL of toluene to each vial. Screw cap tightly onto each vial.
8. Agitate vials by placing them in an ultrasonic bath for 30 min.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six standards covering the range of the samples.
   a. Weigh ten 120-mg portions of the coated sorbent into 4-mL vials with septum caps. If the bulk coated sorbent is not available, remove the front section from 10 unused samplers (media blanks).
   b. Inject aliquots of the calibration stock solution into the vials at six different levels and allow to stand overnight at room temperature. Prepare two standards at each level.
   c. Desorb (steps 7 and 8) and analyze together with samples and blanks (steps 10 and 11).
   d. Prepare calibration graph (peak area or height vs. concentration of acrolein, µg/mL).
      NOTE: The calibration procedure used in this method does not require a desorption efficiency (DE) correction to be made. If DE is needed, see the APPENDIX.

MEASUREMENT:

10. Set gas chromatograph to conditions given on page 2501- 1. Set air and hydrogen flows on the nitrogen specific detector to manufacturer's specifications. Inject 1-µL sample aliquot.
11. Measure peak area or peak height. Acrolein derivative t_r = 3.6 min and t_r for 2-(hydroxymethyl)piperidine = 10.7 min for these conditions.

CALCULATIONS:

12. Read the µg/mL of acrolein found in the sample front (W_f) and back (W_b) sorbent sections from the calibration graph and multiply by the desorption volume, 2 (mL). Calculate concentration, C (mg/m^3), of acrolein in the air volume sampled, V (L):
    NOTE: Because the working standards are prepared on media blanks, no additional blank correction is necessary.

$$C = \frac{(W_f + W_b) \cdot 2}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

The method was evaluated over the range of 0.12 to 1.5 mg/m^3 using 24-L samples. Average desorption efficiencies were ca. 1.0 for all levels studied. Mean recovery was 107%, representing an insignificant bias in the method [1]. Concentration of the generated acrolein vapor was independently verified by a modification of P&CAM 211 by Shell Development Co. [3]. No breakthrough was observed for an 8-h sample at 0.10 L/min (48 L) of a 4.5 mg/m^3 of acrolein at 80% RH. The method has been used by three separate analysts at NIOSH and no intralaboratory bias was observed. Measurement precision ($\bar{S}_r$) was not determined. Overall accuracy was ± 29%; therefore, the method does not meet the ± 25% criterion for a valid method.

REFERENCES:

[1] Kennedy, E.R., O'Connor, P.F., Gagnon, Y.T. "Determination of Acrolein in Air as an Oxazolidine Derivative by Gas Chromatography," Anal. Chem. 56(12):2120-2123 (1984).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 1, P&CAM 118 and 211, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] Shell Development Company Analytical Department. Determination of Acrolein in Air, Bubbler/Colorimetric Method, SRC 11A11/79, Shell Development Company Westhollow Research Center.

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APPENDIX:

SORBENT PREPARATION

Add 1 g of the purified 2-(hydroxymethyl)piperidine in 50 mL of toluene for each 9 g of extracted XAD-2 sorbent . Allow this mixture to stand for 1 h with occasional swirling. Remove the solvent by rotary evaporation at 37 °C and dry at 130 Pa (1 mm Hg) at ambient temperature for approximately 1 h. To determine the amount of background for each batch, desorb several 120-mg portions of the coated sorbent with toluene and analyze using steps 6 through 11. No blank peak is expected for acrolein although a blank for formaldehyde and acetaldehyde may be observed.

DESORPTION EFFICIENCY

The determination of desorption efficiency (DE) is not necessary when using the calibration procedure outlined in this method. The following procedure can be used to determine DE, if necessary:

a. Using a 10-µL syringe and the calibration stock solution inject four sampling tubes at each of five levels. Open several blank tubes but add no acrolein to them. Cap all the tubes.
b. Using the 10-µL syringe, spike the calibration stock solution into 4-mL vials containing 2 mL of toluene and 10 mg of purified 2-(hydroxymethyl)piperidine. Prepare four replicate vials at each of the five concentrations used in step a.
c. Allow the spiked tubes, spiked standard solutions and blank tubes to stand overnight at ambient temperature to assure complete reaction. Desorb and analyze the spiked and blank tubes according to steps 4 through 11. Analyze the spiked solutions according to steps 10 and 11.
d. To calculate the recovery, compare the blank-corrected peak areas or heights of the acrolein peak found in the spiked tubes (Q_r - B) to the peak area or height of the acrolein peak found in the spiked solutions (Q_a).

$$DE = \frac{(Q_r - B)}{Q_a}.$$

e. Prepare a graph of DE vs. mg acrolein recovered.