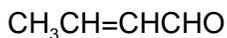


CROTONALDEHYDE

3516



MW: 70.09

CAS: 4170-30-3

RTECS: GP9499000

METHOD: 3516, Issue 1

EVALUATION: FULL

Issue 1: 15 August 1994

OSHA : 2 ppm
NIOSH: 2 ppm
ACGIH: 2 ppm; suspect carcinogen
 (1 ppm = 2.87 mg/m³ @ NTP)

PROPERTIES: liquid; pungent odor; BP 104 °C;
 d 0.85 g/mL @ 20 °C; VP 2.7 kPa
 (20 mm Hg, 2.6% v/v) @ 20 °C; explosive
 range 2.1 to 15.5% v/v in air

SYNONYMS: crotonic aldehyde; trans-2-butenal, crotonal

SAMPLING		MEASUREMENT	
SAMPLER:	MIDGET BUBBLER (hydroxylamine/formate buffer solution)	TECHNIQUE:	D I F F E R E N T I A L P U L S E POLAROGRAPHY
FLOW RATE:	0.1 to 0.2 L/min	ANALYTE:	crotonaldehyde oxime
VOL-MIN:	1 L @ 2 ppm	DROP TIME:	1 s
-MAX:	49 L	SCAN RATE:	5 mV/s
SHIPMENT:	refrigerate bubblers at 8 °C during shipment if samples cannot be analyzed within 4 h	SCAN RANGE:	-0.6 to -1.2 V (vs. SCE)
SAMPLE STABILITY:	4 h maximum @ 25 °C, 7 days minimum at 8 °C	CALIBRATION:	standard solutions of crotonaldehyde in hydroxylamine/formate buffer solution
BLANKS:	2 to 10 field blanks per set	RANGE:	35 to 139 µg per sample
		ESTIMATED LOD:	not determined
		PRECISION (\hat{S}_r):	0.024 [1]
ACCURACY			
RANGE STUDIED:	2.9 to 23.4 mg/m ³ (12-L samples)		
BIAS:	-2.8%		
OVERALL PRECISION (\hat{S}_{rT}):	0.061 (2.9 to 11.6 mg/m ³) [1]		
ACCURACY:	±14.8%		

APPLICABILITY: The working range is 1 to 10 ppm (2.9 to 29 mg/m³) for a 12-L air sample. The upper limit of the method is dependent on the concentration of hydroxylamine, which should be maintained at 50-fold molar excess over total amount of crotonaldehyde sampled. Collection efficiency outside the method range has not been evaluated.

INTERFERENCES: Other volatile aldehydes (e.g., acrolein, formaldehyde, benzaldehyde).

OTHER METHODS: This is Method P&CAM 285 [2] in a revised format. An aldehyde screening method [3] and a method for priority pollutants [4], both of which include crotonaldehyde, have been described.

REAGENTS:

1. Hydroxylamine hydrochloride, reagent grade.
2. Sodium hydroxide, 0.1 M, reagent grade.
3. Formic acid, reagent grade.
4. Sodium formate, reagent grade.
5. Hydroxylamine collection solution. Dissolve 0.68 g of hydroxylamine hydrochloride in 1 L deionized water. Adjust to pH 5 with 0.1 M sodium hydroxide.
6. Formic acid/sodium formate buffer. Add 3.4 g sodium formate and 2 mL formic acid to 500-mL volumetric flask. Bring to volume with deionized water.
7. Crotonaldehyde,* 85%.
8. Crotonaldehyde stock solution. Prepare solutions containing 17.19 and 1.179 mg/mL of crotonaldehyde in deionized water.
9. Nitrogen, prepurified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Glass midget bubblers.
2. Personal sampling pump, 0.1 to 0.2 L/min, and trap with flexible tubing. Trap is a midget bubbler or impinger with stem broke off.
3. Volumetric flasks, 1-L, 500-mL, and convenient sizes for preparing stock standard solutions.
4. Pipets, 10-mL, 5-mL, and other convenient sizes.
5. Syringes for preparing spiked standard samples.
6. Potentiostat with differential pulse polarographic capability.
7. China marker.
8. PTFE tubing 15 cm x 7-mm ID or PTFE plugs for sealing the inlet and outlet of the bubbler stem before shipment.

NOTE: Wash all glassware with detergent, rinse with deionized water and dry. Midget bubblers should be heated in an oxidizing atmosphere at about 580 °C to remove organic contaminants.

SPECIAL PRECAUTIONS: Crotonaldehyde is highly toxic, flammable liquid [5]. Prevent contact with skin, eyes, and clothing. Do not breathe vapors; crotonaldehyde vapors irritate the mucous membranes, nose and respiratory tract. Vapors can severely irritate the eyes, causing lacrimation. Contact with eyes can cause corneal burns. Contact with skin causes irritation and may cause burns. Wash thoroughly after handling.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler and trap in line.
 2. Rinse bubblers with 10 mL hydroxylamine solution. Pipet 10 mL of hydroxylamine solution buffered at pH 5 into each midget bubbler. Mark the liquid level on the bubbler with a china marker. Ensure that bubbler frit is covered.
3. Attach outlet of midget bubbler to inlet of trap used to protect pump during sampling. Attach trap to pump with metal holder. Connect outlet of trap to pump by flexible tubing.
 4. Sample at an accurately known flow rate between 0.1 and 0.2 L/min for a total sample size of 1 to 49 L.
NOTE: Sampled air should not pass through any tubing containing polyvinylchloride (PVC) before entering the bubbler; PVC tubing is known to give interferences in the method.
 5. Discard any material collected by the trap. If more than 1 mL of material is collected in the trap, the sample should be considered invalid.
 6. Seal the inlet and outlet of the bubbler stem by connecting a piece of PTFE tubing between them or by inserting PTFE plugs in the inlet and outlet. Pack securely for shipment. If samples cannot be analyzed within four hours, they must be refrigerated at 8 °C during shipping and until analysis time.
 7. Collect a bulk sample (ca. 1 g) in a glass vial with a PTFE-lined cap and ship separately.

SAMPLE PREPARATION:

8. Remove bubbler stem and drain contents into bubbler flask. If necessary, bring to 10-mL mark with distilled water. Add 5 mL formate buffer solution and swirl bubbler to mix contents well.

CALIBRATION AND QUALITY CONTROL:

9. Prepare at least six working standards having concentrations to cover the range of 6 to 280 µg per sample (corresponding to 0.1 to 4 times the OSHA standard).
 - a. Add appropriate aliquots ($\leq 100 \mu\text{L}$) of stock solution to 10 mL of hydroxylamine solution, followed by addition of 5 mL of formate buffer solution.
 - b. Analyze with samples and blanks (step 11).
 - c. Prepare calibration graph of peak current vs. mass (μg) of crotonaldehyde per 15 mL of sample.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

11. Transfer sample to electrochemical cell and purge with oxygen-free nitrogen for 3 min at 200 mL/min. Analyze by differential pulse polarography: 1 second drop time, 5 mV/second scan rate, and -0.6 V to -1.2 V scan range vs. a saturated calomel electrode (SCE). Analysis should be conducted in a relatively stable temperature environment. Measure peak current due to reduction of crotonaldehyde oxime. The half wave potential, $E_{1/2}$, of crotonaldehyde oxime is -1.03 V vs. SCE. Rinse electrodes before analyzing next sample.

CALCULATIONS:

12. Determine the mass, μg , for each sample (W) and for the average media blank (B) from the standard calibration graph.
13. Calculate concentration, C, of crotonaldehyde in the air volume sampled, V (L), applying a correction for the collection efficiency, which was determined to be 96%:

$$C = \frac{(W - B)}{V \cdot 0.96}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The average concentrations obtained from analysis of samples collected from test atmospheres at 0.5X, 1X, 2X, and 4X the OSHA standard were 10.0% lower, 2.1% lower, 3.7% higher, and 3% higher, respectively, than the "true" concentrations. The difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, the method has no uncorrected bias. Storage stability studies on samples collected in a test atmosphere at a concentration of 5.80 mg/m³ indicated that collected samples are stable for at least 7 days at 8 °C. Collection efficiency for the midjet bubbler was determined to be 0.96 for an average of 24 samples and a correction must be applied. Statistical information [6] and details of the test procedures [1] can be found elsewhere.

REFERENCES:

- [1] Backup Data Report for Crotonaldehyde, prepared under NIOSH Contract No. 210-76-0123.
- [2] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 285, U.S. Dept of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
- [3] Aldehydes Screening Method #2539, NIOSH Manual of Analytical Methods, 3rd Ed., Third Supplement, May 15, 1989.
- [4] Spingham, A. L. GC/MS Analytical Method for Priority Pollutants Including Crotonaldehyde, J. Chromatogr. Sci., 20(6), 286-288 (1982).
- [5] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.
- [6] Documentation of the NIOSH Validation Test, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

METHOD REVISED BY:

M. Eileen Birch, Ph.D., NIOSH/DPSE; data obtained under NIOSH Contract 210-76-0123.