ETHYLENIMINE

C_2H_5N MW: 43.07 CAS: 151-56-4 RTECS: KX5075000

METHOD: 3514, Issue 2 **EVALUATION: FULL** **Issue 1: 2 May 1979**
Issue 2: 15 August 1994

OSHA : carcinogen
NIOSH: carcinogen
ACGIH: 0.5 ppm (skin)
(1 ppm = 1.76 mg/m^3)

PROPERTIES: liquid; mp, -74.0 °C; bp, 56-57 °C; d 0.8321 g/mL @ 24 °C; VP 21 kPa (160 mm Hg) @ 20 °C

SYNONYMS: aziridine, azacyclopropane

SAMPLING

SAMPLER: BUBBLER
(Folin's reagent)

FLOW RATE: 0.2 L/min

VOL-MIN: 1 L @ 0.5 ppm
-MAX: 48 L

SHIPMENT: ship at 5 °C in dark

SAMPLE STABILITY: 14 days @ 5 °C in dark

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.16 to 21 mg/m^3
(2.6- to 39-L samples)

BIAS: - 2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.069

ACCURACY: ± 15.5%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 4-(1-aziridinyl)-1,2-naphthoquinone

EXTRACTION: 4 mL of $CHCl_3$, 15 sec. (twice)

FINAL VOLUME: 10 mL

INJECTION VOLUME: 10 µL

MOBILE PHASE: 59.5% hexane:40% chloroform (with 1% ethanol):0.5% 2-propanol

FLOW RATE: 1.3 mL/min

COLUMN: Lichrosorb DIOL 25 cm x 4.6-mm)

DETECTOR: UV @ 254 nm

CALIBRATION: 4-(1-aziridinyl)-1,2-naphthoquinone in $CHCl_3$

RANGE: 1 to 795 µg per sample

ESTIMATED LOD: 0.3 µg per sample

PRECISION ($\hat{S}_r$): 0.024

APPLICABILITY: The working range is 0.014 to 11 ppm (0.025 to 20 mg/m^3) for a 40-L air sample. A variation of this method has been used to measure ethylenimine in air at 0.02 to 0.10 mg/m^3 at a manufacturing plant [1,2]. The modifications of the method included use of a µBondapak-CN column in place of the Lichrosorb DIOL column and 50:48:2 hexane:dichloromethane:2 -propanol for the mobile phase.

INTERFERENCES: Propylenimine and 2-bromoethylamine interfere.

OTHER METHODS: This method replaces Method P&CAM 300 [3] and is a variation of the method of Evans et al. [4]. The product of ethylenimine and Folin's reagent can be measured spectrophotometrically [5,6].

REAGENTS:

1. Chloroform with 1% ethanol as a preservative, UV grade.
2. Hexane, UV grade.
3. 2-Propanol, UV grade.
4. Methanol, UV grade.
5. Ethylenimine.*
6. 1,2-Naphthoquinone-4-sulfonic acid, sodium salt.
7. Deionized water.
8. NaOH solution (0.1 M). Dissolve 1 g of NaOH in water to make 250 mL of solution.
9. KH_2PO_4 solution (0.1 M). Dissolve 3.40 g of KH_2PO_4 in water to make 250 mL of solution.
10. Buffer solution (pH = 7.7). Mix 100 mL of 0.1 M KH_2PO_4 with 93.4 mL of 0.1 M NaOH.
11. Folin's reagent. Dissolve 0.40 g of 1,2-naphthoquinone-4-sulfonic acid, sodium salt, in 100 mL of buffer solution. Dilute to 500 mL with water. Wrap flask with aluminum foil and refrigerate. Solution is stable for 5 days.
12. Na_3PO_4 solution (0.5 M). Dissolve 19 g of Na_3PO_4·12H2O in water to make 100 mL of solution.
13. 4-(1-Aziridinyl)-1,2-naphthoquinone. See Appendix.
14. Calibration stock solution, 500 µg/mL. Dissolve 125 mg of 4-(1-aziridinyl)-1,2-naphthoquinone in chloroform to make 250 mL of solution.
15. Recovery stock solution, 10 mg/mL. Dissolve 2.50 g of ethylenimine in chloroform to make 250 mL of solution.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: midget bubbler, with 15 mL of Folin's reagent.
2. Personal sampling pump, 0.2 L/min, with flexible, connecting tubing.
3. High performance liquid chromatograph with column (page 1) and UV detector.
4. Syringes, 1-mL, readable to 10 µL.
5. Syringes, 100-µL, readable to 1 µL.
6. Syringes, 10-µL, readable to 0.1 µL.
7. Volumetric flasks, low actinic glass, 500-, 250-, 100-, and 10-mL.
8. Graduated cylinders, 100- and 25-mL.
9. Separatory funnels with PTFE stopcocks.
10. Funnels, glass.
11. Beakers, 2-L and 50-mL.
12. Aluminum foil.
13. Filter paper.
14. pH paper.
15. Pipet bulb.

SPECIAL PRECAUTIONS: Ethylenimine is carcinogenic, very toxic, and extremely flammable [7]. This compound is strongly irritating to the eyes, skin, and mucous membranes. Handle only in a hood.

SAMPLING:

1. Calibrate the personal sampling pump with a representative sampler in line.
2. Sample at 0.2 L/min for a sample size of 1 to 48 L.
3. After sampling, use a pipet bulb to force air through the bubbler stem to dislodge ethylenimine derivative and recover sampling solution. Rinse the stem with 2 mL of chloroform, and add the wash to the bubbler. Seal the bubbler with a nonreactive stopper (PTFE or glass). Do not seal with rubber.
4. Protect the sample from light, and ship at 5 °C.

SAMPLE PREPARATION:

5. Transfer sample solution to a 60-mL separatory funnel.
6. Rinse bubbler with 4 mL of chloroform, and add rinse to separatory funnel.
7. Cap and shake funnel for 15 seconds. Allow the phases to separate.
8. Collect chloroform extract in a 10-mL volumetric flask.
9. Repeat steps 6 and 7, and collect chloroform extract in the same volumetric flask.
10. Dilute solution in the volumetric flask to 10 mL with chloroform.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with working standards over the range of 1.4 to 3681 µg of 4-(1-aziridinyl)-1,2-naphthoquinone per sample. Express the quantities of 4-(1-aziridinyl)-1,2-naphthoquinone in terms of the corresponding quantities of ethylenimine (1 µg of 4-(1-aziridinyl)-1,2-naphthoquinone corresponds to 0.216 µg of ethylenimine). The corresponding range is 0.3 to 795 µg of ethylenimine per sample.
    a. Dilute portions of the calibration stock solution to prepare a series of working standards in the range of 0.3 to 795 µg of ethylenimine per sample (0.03 to 79.5 µg/mL).
    b. Analyze according to steps 13 and 14.
    c. Prepare a calibration graph (peak area or peak height versus µg of ethylenimine per sample).
12. Determine recovery from bubblers.
    a. Dilute portions of recovery stock solution with chloroform to prepare a series of spiking solutions in the range of interest.
    b. Add known quantities of ethylenimine in spiking solutions to bubblers containing 15-mL quantities of Folin's reagent. Prepare five samples at each of three levels over the range of interest.
    c. Prepare sample solutions (steps 5 through 10) and analyze (steps 13 and 14).
    d. Calculate recovery, R (µg of ethylenimine found divided by µg of ethylenimine applied).
    e. Prepare a graph of recovery versus µg of ethylenimine found.

MEASUREMENT:

13. Set the liquid chromatograph according to manufacturer's instructions and to conditions on page 1.
14. Analyze sample solutions with standards.

CALCULATIONS:

15. Determine the quantities of ethylenimine in the sample corrected for Recovery, W (µg), and the average media blank, B (µg), from the calibration graph.
16. Calculate the concentration, C (mg/m ^{3}), of ethylenimine in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method is based on Method P&CAM 300, which was evaluated with controlled atmospheres of ethylenimine [3]. Overall precision ($\hat{S}_{rT}$) was 0.069 (52 samples, pooled) for 2.6- to 39-L samples at 0.16 to 21 mg/m ^{3}; $\hat{S}_{rT}$ includes an assumed pump error of 0.05. Independent concentrations of ethylenimine vapor in the controlled atmospheres (referred to as "taken" values) were calculated from the measured total air flow and the delivery rate of the syringe pump. Recoveries with controlled atmospheres

(recovery = average found concentration divided by the taken concentration) ranged from 91 to 105% for six sets of samples at 0.16 to 21 mg/m ^{3}; thus, bias for sampling and analysis was not significant. Collection efficiencies of samplers at 0.15 L/min were >99% at 21 and 204 mg/m ^{3}. Average recoveries from 15-mL quantities of Folin's reagent (fortified with ethylenimine in chloroform) were 0.93 and 0.95 at the 1.67- and 16.7-µg levels of ethylenimine, respectively; the precision ($\bar{S}_r$) was 0.024 (12 samples, pooled). Samples at the 1.67- and 16.7-µg levels were stable in Folin's reagent during storage for 14 days at 5 °C in the dark.

Methylamine, diethylamine, butylamine, ethanolamine, dihexylamine, dicyclohexylamine, benzylamine, dibenzylamine, and aniline do not interfere with measurement of ethylenimine. Propylenime and 2-bromoethylamine interfere.

REFERENCES:

[1] Analytical Report for Ethylenimine, Sequence #3680. Unpubl., NIOSH (1982)
[2] Ruhe, R.L., NIOSH Health Hazard Evaluation Report, HETA 82-287-1240, NIOSH, Cincinnati, Ohio (1982).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 300, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[4] Evans, D.J., R.J. Mayfield and I.M. Russell. J. Chromatogr., 115, 391-395 (1975).
[5] Rosenblatt, D.H., P. Hlinka and J. Epstein. Anal. Chem., 27, 1290-1293 (1955).
[6] Crompton, T.R. Analyst (London), 90, 107-111 (1965).
[7] 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.

METHOD WRITTEN BY:

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APPENDIX

SYNTHESIS OF 4-(1-AZIRIDINYL)-1,2-NAPHTHOQUINONE

Place 2 g of 1,2-naphthoquinone-4-sulfonic acid, sodium salt, and 250 mL of water into a 1-L separatory funnel which is wrapped with aluminum foil. Add 25 mL of 0.5 M trisodium phosphate, and shake the mixture. Ascertain that the pH is between 10.5 and 11.5. Add 0.3 mL of ethylenimine and shake at intervals over 10 min. Extract the 4-(1-aziridinyl)-1,2-naphthoquinone with six 200-mL portions of chloroform. Combine extracts in a 2-L beaker wrapped with aluminum foil. Cover the beaker with aluminum foil which is punctured with three holes, and evaporate chloroform with a nitrogen purge. Transfer the dry residue to a 50-mL beaker wrapped with aluminum foil. Add 35 mL of methanol and 1 mL of chloroform to the residue. A portion of the residue will remain undissolved. Filter and cool the solution to 0 °C. Wash the crystallized product with 4 mL of chilled methanol, and dry the product with a nitrogen purge. Melting point = 173 to 175 °C.