

ETHYLENEDIAMINE

2540



MW: 60.1

CAS: 107-15-3

RTECS: KH8575000

METHOD: 2540, Issue 2

EVALUATION: UNRATED

Issue 1: 15 May 1989

Issue 2: 15 August 1994

OSHA : 10 ppm
 NIOSH: 10 ppm
 ACGIH: 10 ppm (skin)
 (1 ppm = 2.46 mg/m³)

PROPERTIES: liquid; d 0.90 g/mL @ 20 °C;
 BP 116 - 117 °C; VP 1.43 kPa;
 (10.7 mm Hg); flash point 34 °C

SYNONYMS: ethylenediamine: EDA; 1,2-diaminoethane; 1,2-ethanediamine

| SAMPLING | | MEASUREMENT | |
|---|--|--|--|
| SAMPLER: | SOLID SORBENT TUBE (1-naphthylisothiocyanate-coated XAD-2, 80 mg/40 mg) | TECHNIQUE: | HPLC, UV DETECTION |
| FLOW RATE: | 0.01 to 0.1 L/min [1] | ANALYTE: | naphthylisothiourea derivative of analytes |
| VOL-MIN: | 1 L @ 10 ppm | DESORPTION: | 2 mL dimethylformamide (DMF), ultrasonic 30 min |
| -MAX: | 20 L | INJECTION VOLUME: | 10 µL |
| SHIPMENT: | routine | COLUMN: | 10-µm radial cyano, 10 cm x 8-mm ID in Waters RCM-100 radial compression mode |
| SAMPLE STABILITY: | >30 days @ 20 °C [2] | MOBILE PHASE: | EDA, 80/20 isooctane/isopropanol; DETA and TETA, 50/50 isooctane/isopropanol at 3 mL/min |
| BLANKS: | 2 to 10 field blanks per set | CALIBRATION: | standard solutions of derivatives in DMF |
| ACCURACY | | RANGE: | 5 to 465 µg per sample |
| RANGE STUDIED: | 0.016 to 8 mg/m ³ ; (10-L samples) | ESTIMATED LOD: | 0.9 µg per sample |
| OVERALL PRECISION (\hat{S}_{rT}): | 0.06 [1] | PRECISION ($\hat{S}_{\bar{S}}$): | 0.013 |
| BIAS: | -6.6% | | |
| ACCURACY: | ± 17.4% | | |

APPLICABILITY: The working range for EDA is 1 to 130 mg/m³ for a 10-L air sample. This method is the result of evaluation [2] of OSHA Method #60 for DETA, EDA, TETA [1]. The theoretical capacity of each front section is 1.3 mg of EDA.

INTERFERENCES: Other primary or secondary amines may react with the sampler coating reagent, and thereby reduce the sampler capacity.

OTHER METHODS: This replaces NIOSH Method P&CAM 276 [3]. The method of Anderson, et al., for EDA [4] is an alternate method using thiourea derivatization and HPLC analysis.

REAGENTS:

1. XAD-2 resin, reagent grade.
2. 1-Naphthylisothiocyanate (NTIC), reagent grade.
3. Methylene chloride, reagent grade.
4. Dimethylformamide (DMF), HPLC grade.
5. Isooctane, HPLC grade.
6. Isopropanol, HPLC grade.
7. Ethylenediamine (EDA),* high purity.
8. Diethylenediamine (DETA),* high purity.
9. Triethylenetetramine (TETA),* high purity.
10. Calibration stock solution, 4.8 mg/mL DETA, 4.50 mg/mL EDA, 4.9 mg/mL TETA. Dissolve 95.4 mg DETA, 90.0 mg EDA, and 98.2 mg TETA in 600 mg of NTIC, allow to react for at least 60 minutes, and dilute to 20 mL with DMF.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame sealed ends with plastic caps, containing 2 sections of 16/50 mesh XAD-2 resin coated with 10% 1-naphthylisocyanate (front = 80 mg; back = 40 mg) separated by a plug of PTFE wool (see APPENDIX). Tubes are commercially available.
2. Personal sampling pump calibrated to 0.01 to 0.1 L/min.
3. High performance liquid chromatograph (HPLC), UV, 254 nm, cyano column and integrator (page 2540-1).
4. Vials, 4-mL.
5. Syringes, microliter, readable to 0.1 μ L.
6. Pipets, 2-mL.
7. Flasks, volumetric, 25- and 50-mL.
8. Ultrasonic water bath.

SPECIAL PRECAUTIONS: The vapors of these amines are painful and irritating to the eyes, nose, throat, and respiratory system. The liquids can cause severe damage to the eye and serious burns to the skin [1,5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling.
3. Attach the sampler to personal sampling pump with flexible tubing.
4. Sample at an accurately known flow rate between 0.01 to 0.1 L/min for a total sample size of 1 to 20 L.
5. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

6. Transfer each sorbent section to separate sampling vials.
7. Add 2.0 mL DMF to each vial.
8. Agitate in an ultrasonic water bath for 30 minutes.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards in the range of the samples.
 - a. Prepare working standards by serial dilution of the stock standards with DMF.
 - b. Analyze together with samples, blanks, and QC samples (steps 12 and 13).
 - c. Prepare separate calibration graph (peak area vs. μ g per sample) for EDA, DETA, and TETA.
10. Determine the desorption efficiency (DE) at least once for each lot of XAD-2 resin used for sampling. Prepare three tubes at each of five levels plus 3 media blanks.
 - a. Inject a known amount of analyte onto the NTIC-coated resin.
 - b. Allow to stand overnight.

- c. Desorb and analyze together with the working standards.
- d. Prepare a graph of DE vs. μg amine recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration curve and DE graph are in control.

MEASUREMENT:

12. Set liquid chromatograph according to manufacturer's recommendations and conditions given on page 2540-1.
13. Inject sample aliquot manually or with autosampler. Measure peak area.
NOTE: If the peak response is above the range of the working standards, dilute the standards with DMF, reanalyze and apply the appropriate dilution factors in calculations.

CALCULATIONS:

14. Determine the mass, μg (corrected for DE) of each analyte found in the sample front sorbent (W_f) and the sample back sorbent (W_b) sections and in the average media blank front (B_f) and back (B_b) sections.
15. Calculate concentration, C, of each analyte in the air volume sampled, (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was developed by and subjected to the evaluation procedures of the OSHA Organics Methods Evaluation Branch [1]. NIOSH evaluated the method for recovery, storage stability, precision, and accuracy and found comparable results [2]. The detection limits obtained by OSHA [1] corresponded to air concentrations of 0.004 ppm, 0.15 ppm, and 0.004 ppm for DETA, EDA, and TETA respectively, for a 10-L air volume. The method was validated over the range of 0.8 to 80 $\mu\text{g}/\text{sample}$ for DETA, 4.6 to 465 $\mu\text{g}/\text{sample}$ for EDA, and 1.3 to 119 $\mu\text{g}/\text{sample}$ for TETA [1]. Desorption efficiency studies as performed by OSHA [1] using 6 samples at 3 levels gave a recovery of 99.0% for DETA, 99.2% for EDA, and 99.8% for TETA. The recovery of DETA, EDA, and TETA from samples used in a 15-day storage study was 89, 94, and 91%, respectively. These samples were generated by spiking the amines onto a glass wool plug in front of a sampling tube and drawing approximately 10 liters of air at 80% relative humidity through them. A 30-day storage study conducted by NIOSH [2] showed similar recoveries. Collection efficiency studies were done [1] by drawing 10-L of air at 80% relative humidity through Teflon wool plugs positioned ahead of the samplers and spiked with the pure amine. No DETA or TETA was found on the back section with a loading of 57.2 μg of DETA or 32.5 μg of TETA. At a loading of 414 μg of EDA, the back section was found to contain 12.2 μg of EDA.

REFERENCES:

- [1] Elskamp, Carl J. "OSHA Method #60, Ethylenediamine (EDA), Diethylenetriamine (DETA), Triethylenetetramine (TETA)." Organic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, Utah. September, 1986.
- [2] Neumeister, Charles. NIOSH/MRSB In-House Evaluation of OSHA Method #60, (NIOSH, Unpublished, June 17, 1988).
- [3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, P&CAM 276, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

- [4] Anderson, K., Hallgren, C., Levin, J., and Nilsson, C. "Determination of Ethylenediamine in Air Using Reagent-Coated Adsorbent Tubes and High-Performance Liquid Chromatography on the 1-Naphthylisothiurea Derivative, "Am. Ind. Hyg. Assoc. J., 46(4), 225-229 (1985).
- [5] 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 #17-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD WRITTEN BY:

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APPENDIX:

PREPARATION OF NTIC-COATED XAD-2 RESIN:

- a. Weigh sufficient XAD-2 resin (16/50 mesh 120 mg XAD resin per tube) to allow preparation of tubes for sampling, blanks, quality control, and recovery studies.
- b. Dissolve sufficient 1-naphthylisothiocyanate in methylene chloride to coat the XAD-2 resin at a 10% loading (w/w).
- c. Place the XAD-2 resin in the NTIC solution, mix, and remove methylene chloride using rotary evaporation.
- d. Load the coated XAD-2 resin into 7 cm long, 6-mm OD, 4-mm ID, glass tubes so that the front section contains 80 mg and the back section contains 40 mg. Use PTFE-wool plugs to separate and contain the two sections. Cap the finished tubes with plastic caps.