

AMINES, ALIPHATIC

2010

(1) Diethylamine: (C₂H₅)₂NH MW: 73.14 CAS: 109-89-7 RTECS: HZ8750000
 (2) Dimethylamine: (CH₃)₂NH 45.08 124-40-3 IP8750000

METHOD: 2010, Issue 2

EVALUATION: PARTIAL

Issue 1: 15 May 1989

Issue 2: 15 August 1994

OSHA : See Table 1
NIOSH: See Table 1
ACGIH: See Table 1

PROPERTIES: See Table 1

SYNONYMS: (1) DEA; N,N-diethamine; N-ethylethanamine;
 (2) N-methylmethanamine; DMA

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (silica gel, 150 mg / 75 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.01 to 1.0 L/min	ANALYTE:	amines listed above
VOL-MIN:	3 L @ OSHA standards (Table 1)	DESORPTION:	1 mL dilute H ₂ SO ₄ in 10% (v/v) aqueous methanol, 3 h ultrasonic
-MAX:	30 L	INJECTION VOLUME:	1 µL
SHIPMENT:	refrigerated	COLUMN:	1.8 m x 4-mm ID glass, 4% Carbowax 20M + 0.8% KOH on Carbosieve B (60/80 mesh)
SAMPLE STABILITY:	not determined	CARRIER GAS:	nitrogen, 30 mL/min
FIELD BLANKS:	2 to 10 field blanks per set	CALIBRATION:	standard solutions of analyte in dilute sulfuric acid
ACCURACY		RANGE:	(1) 0.5 to 11 mg per sample [1] (2) 0.15 to 2.6 mg per sample [1]
RANGE STUDIED:	see EVALUATION OF METHOD	ESTIMATED LOD:	0.02 mg per sample
BIAS:	(1) -5.0%; (2) 0.8%	PRECISION (\hat{S}_r):	see EVALUATION OF METHOD
OVERALL PRECISION (\hat{S}_{rt}):	see EVALUATION OF METHOD		
ACCURACY:	(1) ±16.0%; (2) ±12.5%		

APPLICABILITY: The working ranges for 20-L air samples are 8 to 183 ppm (25 to 550 mg/m³) for diethylamine and 4 to 71 ppm (7.5 to 130 mg/m³) for dimethylamine. A nitrogen-specific detector instead of an FID will greatly increase sensitivity. This alternative detector has been used for amines with a 30 m x 0.25-mm x 0.25-µm film DB-5 fused-silica capillary column, w ith column temperature 60 °C for 1 min, programmed to 300 °C at 10°/min; detector, 300 °C and injector, 250 °C.

INTERFERENCES: This method has been evaluated only in dry air [1]. Silica gel may have a reduced capacity at high humidity. The methanol peak could interfere in low-level analyses.

OTHER METHODS: This revises and combines Methods S139 and S142 [2]. The methods for other aliphatic amines are similar [3,4,5,6]. To avoid possible sample instability on silica gel, OSHA developed a method (OSHA 34) which employs XAD-7 coa ted with 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole for sampling followed by HPLC of the derivative [7].

REAGENTS:

1. Sulfuric acid, 0.1 M, in 10% (v/v) aqueous methanol (90% H₂O + 10% methanol).*
2. Potassium hydroxide (KOH) solution, 0.3 M.*
3. Amines, highest purity available.*
NOTE: Dimethylamine is commercially available as a 40% aqueous solution (Aldrich Co. or equivalent).
4. Calibration stock solution.* Dilute 1 mL of amine to 10 mL with deionized water. Check concentration by titrating with standard sulfuric acid.
5. Hydrogen, prepurified.
6. Nitrogen, purified.
7. Air, compressed and filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube flame-sealed ends, with plastic caps, 7 cm x 6-mm OD x 4-mm ID, containing two sections of 20/40 mesh silica gel (front = 150 mg; back = 75 mg). Silanized glass wool plug precedes front. Urethane foam plugs, separate and retain the back section. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Refrigerated, bagged ("Blue-Ice," or equivalent).
4. Gas chromatograph, FID, integrator, and column (page 2010-1).
5. Vials, glass, 2-mL, with PTFE-lined caps.
6. Ultrasonic bath.
7. Syringes, 20- μ L, 10- μ L, 1- μ L.
8. Pipets, 0.5-, 1-, 2-, and 10-mL.
9. Volumetric flasks, 10-mL.
10. File.
11. Tweezers.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the samplers immediately prior to sampling. Attach sampler to pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1.0 L/min for a total sample size of 3 to 30 L.
4. Cap the samplers and pack securely for shipment with bagged refrigerant.

SPECIAL PRECAUTIONS: The amines are highly flammable and have strong ammoniacal odors. They can cause severe eye damage and can easily be absorbed through the skin [8]. Sulfuric acid is highly corrosive, and potassium hydroxide is caustic. All work with these compounds should be performed in a hood. Use proper protective clothing including gloves, safety glasses, and laboratory coat.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Add the glass wool plug to the front sorbent section vial. Discard the foam plugs.
6. Add 1.0 mL 0.1 M H₂SO₄ in aqueous methanol. Tightly cap the vial.
7. Agitate the vials in ultrasonic water bath for 3 h.
NOTE: The water in the ultrasonic bath can get hot (ca. 50-60 °C) during the desorption period. Therefore, all vials must be tightly capped to minimize evaporation losses.
8. Neutralize the sample solution as follows: let silica gel particles settle for a few minutes. Transfer a 500- μ L aliquot of the supernatant liquid to a clean vial. Add 500 μ L 0.3 M KOH. (The pH of the solution should be greater than 10). Analyze the solutions immediately (steps 12 through 14).
NOTE: Ensure that no silica gel is present when adding KOH to prevent loss of analyte [1].

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards covering the range of interest.

- a. Add aliquots of the calibration stock solutions to 10-mL volumetric flasks and dilute to the mark with 0.1 M sulfuric acid in aqueous methanol.
- b. Neutralize the standards as in step 8.
- c. Analyze with samples and blanks (steps 12 through 14).
- d. Prepare a calibration graph (peak area or peak height vs. mg of amine per sample).
10. Determine desorption (DE) at least once for each lot of silica gel used for sampling in the concentration range of interest. Prepare four tubes at each of five levels plus media blanks.
 - a. Measure the amount of silica gel used in the front sorbent section into a vial.
 - b. Inject a known amount (1 to 20 μL) of calibration stock solution, or a dilution there of directly onto the silica gel.
 - c. Cap vial. Allow to stand overnight.
 - d. Desorb and neutralize as in steps 6 through 8.
 - e. Analyze together with working standards and blanks (steps 12 through 14).
 - f. Prepare a graph of DE vs. mg analyte recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2010-1. Use the following conditions as a guide.

<u>Compound</u>	<u>Temperature ($^{\circ}\text{C}$)</u>		
	<u>Injection</u>	<u>Column</u>	<u>Detector</u>
Diethylamine	160	70	200
Dimethylamine	155	60	200

NOTE: Use a removable glass liner at the inlet to the GC column. Remove the glass liner from the gas chromatograph and clean it with water and acetone rinses at the end of each day. In order to prevent salt buildup, the glass GC liner was soaked in a saturated KOH solution and packed with KOH-coated glass wool [9].

13. Inject sample aliquot manually using solvent flush technique or with autosampler.
14. Measure peak area or peak height.

CALCULATIONS:

15. Determine the mass, mg (corrected for DE), of analytes found in sample front (W_f) and back (W_b) sorbent sections and in the media blank front (B_f) and blank back (B_b) sorbent sections from the calibration graph.
16. Calculate concentration of analyte, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg}/\text{m}^3.$$

EVALUATION OF METHOD:

Precisions, biases, and recoveries listed below were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard [1,2,3]. Generated concentrations were independently verified. Breakthrough of the front section of the silica gel tube was not observed after sampling a dry test atmosphere. Sample stability was not determined.

Substance	SAMPLING			MEASUREMENT			OVERALL		
	BT ^a Vol. (L)	Conc. (mg/m ³)	Range (mg/m ³)	Range (mg/sample)	Precision (\hat{S}_r)	DE	Bias (%)	Precision (\hat{S}_{rT})	Accuracy ($\pm\%$)
Diethylamine	>46	160	36-165	1.8-7.1	0.02	0.82	5	0.07	18.7
Dimethylamine	>45.6	42.5	7.02-29.5	0.4-1.7	0.03	0.92	1.1	0.062	13.2

^aBreakthrough (BT) experiments performed at flow rate of 0.2 L/min.

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, S139 and S142, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.
- [2] NIOSH Manual of Analytical Methods, 2nd. ed., Vol. 3, S139 and S142, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
- [3] Ibid., Vol. 1, P&CAM 221, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
- [4] Ibid., S144, S146, and S150.
- [5] Campbell, Evan E., G.O. Wood, and R.G. Anderson. "Development of Air Sampling Techniques," Los Alamos Scientific Laboratory, Progress Reports (unpublished) LA-5634-PR (June 1974), LA-5973-PR (July 1975), and LA-6057-PR (September 1975).
- [6] Wood, G.O. and R.G. Anderson. "Development of Air Monitoring Techniques Using Solid Sorbents," Los Alamos Scientific Laboratory, Progress Reports (unpublished) LA-6216-PR (February 1976) and LA-6513-PR (September 1976).
- [7] OSHA Manual of Analytical Methods, USDOL OSHA Salt Lake City Technical Center, Salt Lake City, UT. Available from ACGIH, Cincinnati, OH (1991).
- [8] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981).
- [9] Andre, C.E. and A.R. Mosier. "Precolumn Inlet System for the Gas Chromatographic Analysis of Trace Quantities of Short-Chain Aliphatic Amines," *Anal. Chem.*, **45**. 1971 (1973).

METHOD REVISED BY:

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Table 1. Exposure Limits and Properties.

Compound	Exposure Limits, ppm			mg/m ³ /ppm @ NTP	Properties
	OSHA	NIOSH	ACGIH		
Diethylamine	25	10; STEL 25	5 (skin) STEL 15	2.99	Liquid; d 0.708 g/mL @ 20 °C; MP -50 °C; BP 55.5 °C; vapor density (air = 1) 2.5; VP 25.9 kPa (195 mm Hg) @ 20 °C; explosive limits in air 1.8 to 10.1% (v/v)
Dimethylamine	10	10	5; STEL 5	1.84	Gas; MP -92.2 °C; BP 6.88 °C; vapor density (air = 1) 1.6; VP 173.9 kPa (1307.2 mm Hg) @ 20 °C; explosive limits in air 2.8 to 14% (v/v)