(1) $HOCH_2CH_2NH_2$	MW: 61.10	CAS: 141-43-5	RTECS: KJ5775000
(2) $(HOCH_2CH_2)_2NH$	105.14	111-42-2	KL2975000
(3) $(HOCH_2CH_2)_3N$	149.19	102-71-6	KL9275000

METHOD: 3509, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

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

PROPERTIES: Table 1

SYNONYMS: (1) 2-aminoethanol; monoethanolamine; MEA
(2) 2,2'-iminodiethanol; diethanolamine; DEA
(3) 2,2',2"- nitrilotriethanol; triethanolamine; TEA

SAMPLING

SAMPLER: IMPINGER
(15 mL 2 mM hexanesulfonic acid)

FLOW RATE: 0.5 to 1 L/min

VOL-MIN: 5 L
-MAX: 300 L

SHIPMENT: routine

SAMPLE STABILITY: stable at least 3 weeks @ 20 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1] and Table 2

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, ion pairing [2,3]

ANALYTE: MEA, DEA, TEA

INJECTION LOOP VOLUME: 50 µL

ELUENT: 2 mM hexanesulfonic acid (HSA), 1 mL/min (2 mM HSA/0.5% v/v acetonitrile may also be used to reduce run time)

COLUMNS: Ion-pairing guard and cation separator, Dionex MPIC-NG1,MPIC-NS1, and cation suppressor

CONDUCTIVITY SETTING: 3 µS full scale

RANGE: see EVALUATION OF METHOD [1] and Table 2

ESTIMATED LOD: 7 to 20 µg per sample (Table 2)

PRECISION ($\bar{S}_r$): see EVALUATION OF METHOD [1] and Table 2

APPLICABILITY: The working ranges for MEA, DEA, and TEA are 0.08 to 12 ppm (0.2 to 30 mg/m ^{3}), 0.09 to 7 ppm (0.4 to 30 mg/m^3) and 0.1 to 5 ppm (0.6 to 30 mg/m ^{3}), respectively, for a 100-L air sample. The method is better suited to area sampling than personal sampling because it uses an impinger for sample collection.

INTERFERENCES: Larger amines such as cocomorpholine, triethylenediamine, 4-ethylmorpholine, 2-oxybis(N,N-dimethyl)ethylamine, n-cetyl- N,N-dimethylamine do not elute under these analytical conditions and do not interfere. Other low molecular weight amines may interfere. Sodium and ammonium ions can interfere with MEA.

OTHER METHODS: This is adapted from the method of Bouyoucos and Melcher [2,3]. There are no other NIOSH methods for DEA or TEA. MEA can be determined by method 2007, using silica gel collection and gas chromatographic analysis.

REAGENTS:

1. Hexanesulfonic acid (HSA), 2 m M (diluted from 0.1 M solution obtained from Dionex Corp.).
2. Acetonitrile, reagent grade.
3. Ethanolamine*, high purity.
4. Diethanolamine*, high purity.
5. Triethanolamine*, high purity.
6. Water, distilled.
7. Regenerant for IC suppressor. For fiber suppressor use 40 m M tetramethylammonium hydroxide (TMAOH) at 2 mL/min. For cation micromembrane suppressor use 2 m M TMAOH at 4 mL/min. Prepare fresh weekly and protect from atmospheric CO_2 (which can lead to high background).
8. Calibration stock solution, 1 µg/µL. Weigh 0.10 g of each amine into 100-mL volumetric flask and dilute to mark with 2 m M hexanesulfonic acid. Store in a polyethylene bottle.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: midget impinger containing 15 mL of 2 mM HSA.
2. Personal sampling pump, 0.5 to 1 L/min, with flexible connecting tubing and glass wool trap.
3. Ion chromatograph, with ion-pairing guard and separator columns, cation suppressor (fiber suppressor or micromembrane suppressor), integrator and strip chart recorder (page 3509-1).
4. Marker, China.
5. Vials, scintillation, plastic, 20-mL, for shipping and storage of samples.
6. Syringes, 10-mL, polypropylene, with luer tip.
7. Filters, luer tip, with membrane filter, 13- or 25-mm, 0.45-µm pore size.
8. Micropipets (or microliter syringes), 1- to 500-µL.
9. Flasks, volumetric, 50-, and 100-mL.
10. Bottles, polyethylene, 100-mL.
11. Pipet, 15-mL.

SPECIAL PRECAUTIONS: Ethanolamines can cause skin and eye irritation [4]. Usual laboratory safety procedures should be exercised.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Fill the impinger with 15 mL of 2 m M HSA. Mark the initial liquid level.
3. Attach impinger to sampling pump with flexible tubing. Insert a glass wool trap between the impinger and sampling pump to prevent splashover.
4. Sample at an accurately known flow rate between 0.5 and 1 L/min for a total sample size of 5 to 300 L.
5. Fill the sample solution in the impinger to the 15-mL mark with distilled water.
6. Transfer each impinger solution to a vial for shipment. Pack securely to avoid spillage during transit.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range of interest.
   a. Add known aliquots of calibration stock solution to 50-mL volumetric flasks and dilute to the mark with eluent.
   b. Store working standards in tightly-capped polyethylene bottles (glass may introduce sodium ions, a chromatographic interference). Prepare fresh weekly.
   c. Analyze working standards together with samples and blanks (steps 8 through 11).
   d. Prepare a calibration graph for each analyte (peak height vs. µg analyte).

MEASUREMENT:

8. Set the ion chromatograph to manufacturer's recommendations and to conditions given on page 3509-1. When using fiber or micromembrane suppression, if the background level is high, make several injections of acetonitrile through the sample loop to lower the background level.
   NOTE: Filter all samples, eluents, and water flowing through the ion chromatograph to avoid plugging system valves or columns.
9. Transfer a portion of sample solution to a syringe fitted with an inline membrane filter, for direct injection or for transfer to autosampler vials.
10. Inject 50-µL sample aliquot. For manual operation, inject 2 to 3 mL of sample from syringe (through inline filter) to ensure complete rinse of the sample loop.
11. Measure peak height. If sample peak height exceeds the linear calibration range, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

12. Determine the mass, µg, of analyte in the impinger (W) and in the average media blank (B) from the calibration graph.
13. Calculate the concentration, C, of analyte in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method was evaluated for DEA with generated air samples and for all three specified amines with liquid spiked samples [5]. Samples for DEA were generated from methanol solution delivered by a syringe pump to an ultrasonic nebulizer producing a mist which was mixed with dry, heated air in the initial mixing chamber to evaporate the methanol. The flow passed into a sampling manifold where it was mixed with humidified air to maintain a relative humidity of 73-78%. The system was monitored by measuring the level of methanol in the sampling manifold with a Miran 1A infrared analyzer. The recovery of DEA calculated from the methanol concentration varied from 70-95% in different generation runs. After studies were complete, the initial mixing chamber was rinsed with 2 m M HSA and was found to contain 52 mg DEA, and a rinse of the sampling chamber contained 23 mg DEA, indicating that DEA was lost in the generator during sample generation, and explaining the variation in recovery vs. that calculated from the methanol concentration. In the first run, four samples were generated to test the generation system. These samples were expected to contain 1305 µg DEA based on monitoring of the methanol concentration. They were found to have 1237 ± 56 µg DEA, giving a recovery of 94.8%. Next, twelve samples at each of two levels were generated for storage studies. All samples were collected at 0.75 L/min and stored at room temperature (20 °C). Finally, six samples including backup impingers were generated for breakthrough studies. The results of the storage and breakthrough studies are given below:

Storage studies:	2-Day Storage			21-Day Storage			Recovery
	N	Found, µg	RSD	N	Found, µg	RSD	after 21 days
Low level	5	226	4.9	5	215	13.4	95.1%
High level	6	885	3.3	4	865	3.0	97.7%

Breakthrough studies (stored 39 days at 20 °C):	N	Found, µg	RSD	Breakthrough (average)
Front section	6	4433	7.2	
Back section	6	137	N/A	2.68% (range 1.0-5.4%)
Total	6	4570	8.2	

The method was further evaluated by spiking 2 m M hexanesulfonic acid impinger solutions with all three ethanolamines, at 2, 10, and 20 times the estimated LOQ, six spikes per analyte at each level, and analyzing them after storage at room temperature (20 °C) either for 2 days or for 21 days. Recovery of all analytes and at all levels tested (42 to 409 µg MEA, 79 to 712 µg DEA, and 117 to 1161 µg TEA) was between 94 and 106% after 3 weeks storage.

REFERENCES:

[1] Bolyard, Michele and George Williamson, Method Development Efforts for Ethanolamine Compounds, NIOSH/MRSB, Unpubl. (NIOSH) 1988.
[2] Determination of Ethanolamines in Refinery Water, Application Note #39, Dionex Corporation, Sunnyvale, CA, (February, 1982).
[3] Bouyoucos, Spiros A. and Richard G. Melcher., Collection of ethanolamines in air and determination by mobile phase ion chromatography, Am. Ind. Hyg. Assoc. J. 47(3), 185-188 (1986).
[4] NIOSH Pocket Guide to Chemical Hazards, U.S. Dept. of Health and Human Services, Publ. (NIOSH) 90-117, National Institute for Occupational Safety and Health, Cincinnati, OH 45226 (1990).
[5] Foley, G. D., Bolyard, M. L. and L. Blade. Sampling and Determination of Six Specific Amines, presented at the American Industrial Hygiene Conference, San Francisco, CA (1988).

METHOD REVISED BY:

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TABLE 1. EXPOSURE LIMITS AND PROPERTIES.

Compounds	Exposure limits, ppm OSHA	NIOSH	ACGIH	Properties
Monoethanolamine (MEA)	3	3;* STEL 6	3; STEL 6	liquid; d 1.02 g/mL @ 20 °C; BP 170 5 °C; VP <0.13 kPa (<1 mm Hg); flash point 152 °C
Diethanolamine (DEA)	No PEL	3	3	crystals or liquid; d 1.088 g/mL @ 30 °C; MP 28 °C; BP 269 °C; VP <0.001 kPa (0.01 mm Hg); flash point 152 °C
Triethanolamine (TEA)	No PEL	No REL	5 mg/m^3	liquid; d 1.124 g/mL @ 20 °C; MP 21.2 °C; BP 335 °C (decomp.); VP 0.001 kPa (<0.01 mm Hg); flash point 191 °C

* Group III Pesticide

TABLE 2. RANGE, LOD, AND LOQ.

Measurement	Range Studied (mg/sample)	mg/m^3=1ppm @ NTP	LOD (µg/sample)	LOQ (µg/sample)	precision ($\bar{S}_r$)
Monoethanolamine (MEA)	0.04 to 0.4	2.50	7	20	0.028
Diethanolamine (DEA)	0.07 to 4.5	4.30	13	40	0.064
Triethanolamine (TEA)	0.12 to 1.16	6.10	20	60	0.079