Ethanolamine

Method no.:	PV2111
Matrix:	Air
Target concentration:	3 ppm (6 mg/m^3) OSHA TWA PEL
Procedure:	Samples are collected by drawing a known volume of air through sampling tubes containing XAD-2 resin coated with 10% 1-naphthylisothiocyanate (NITC) by weight. Samples are desorbed with dimethylformamide and the amine derivative is analyzed by high performance liquid chromatography (HPLC) using ultraviolet detection at 254 or 280 nm.
Air volume and sampling rate studied:	10 L at 0.1 L/min
Status of method:	Stopgap method. This method has been only partially evaluated and is presented for information and trial use.

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1. General Discussion

1.1 Background

1.1.1 History of procedure

The NIOSH Method 270 (Ref 5.1) is not convenient for the industrial hygienist in the field, as the ethanolamine is collected on silica gel tubes and the amine is stabilized by spiking the tubes with concentrated HCl after sampling. The sample is desorbed, neutralized, and then derivatized with benzaldehyde. Direct analysis of the ethanolamine is difficult for the chemist due to poor chromatography and carryover problems. A sampling tube containing XAD-2 resin coated with 10% NITC by weight to derivatize and stabilize the amine had good desorption, retention and storage efficiencies.

1.1.2 Potential workplace exposure (Ref 5.2)

Ethanolamine is used to remove CO_2 and H_2S from natural gas and other gases. Ethanolamine is used as an ingredient in many products: in the synthesis of surface active agents, in polishes, in hair waving solutions, in emulsifiers, as a softening agent for hides, and as a dispersing agent for agricultural chemicals.

1.1.3 Toxic Effects (This section is for information purposes and should not be taken as the basis for OSHA policy.)

The TLV of ethanolamine is based mainly on skin toxicity, causing redness, swelling, and lesions. Dogs, rats, and guinea pigs exposed to 100 ppm for 30 days were apathetic, had poor appetites, and had dermal effects ranging from ulceration to hair loss. Dogs exposed to 5 ppm for 90 days had skin irritation, weight loss, and a decrease in alertness and activity. (Ref. 5.3)

1.1.4 Physical properties (Ref 5.2):

Synonyms:	2-aminoethanol; 2-hydroxyethylamine; ethylolamine; colamine
Molecular weight:	61.08
Density:	1.0117
Freezing point:	10.30°C
Odor:	ammoniacal odor
Color:	light yellow liquid
Molecular formula:	C_2H_7NO
Flash point:	91°C (195°F)
CAS:	141-43-5
IMIS:	1030
RTECS:	KJ5775000
Structure:	

1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 8.09 ng per injection. This is the smallest amount which could be detected under normal operating conditions.

1.2.2 The overall detection limit is 0.06 ppm based on a 10-liter air volume, a desorption volume of 2 mL, and desorption efficiency of 100%. All ppm values stated in this method are based on a 10-L air volume and 2-mL desorption volume.

1.3 Advantages

1.3.1 The sampling procedure is convenient.

1.3.2 The analytical method is reproducible and sensitive.

1.3.3 Reanalysis of samples is possible.

1.3.4 It may be possible to analyze other compounds at the same time.

1.3.5 Interferences may be avoided by proper selection of column and LC parameters.

1.4 Disadvantages

Sampling tubes are not available commercially and must be prepared by the laboratory.

2. Sampling procedure

2.1 Apparatus

2.1.1 A calibrated personal sampling pump, the flow of which can be determined within ±5% at the recommended flow.

2.1.2 Sampling tubes containing XAD-2 resin coated with 10% NITC by weight. A sampling tube consists of two sections of coated XAD-2 resin separated by a glass wool plug. The front section contains 80-mg coated sorbent and the 40-mg backup section. The sections are held in place with glass wool plugs in a glass tube 4-mm ID × 70-mm length.

The adsorbent is prepared by coating commercially purified 16/50 mesh XAD-2 (Supelco) with 10% NITC by weight using methylene chloride as as a solvent. The solvent is removed by rotary evaporation (Ref 5.4)

2.1.3 Lengths of flexible tubing are needed to connect the sampling tubes to the sampling pumps.

2.1.4 Two plastic caps and an OSHA Form-21 are needed to seal each sampling tube after sampling.

2.2 Sampling technique

2.2.1 The ends of the sampling tube are opened immediately before sampling.

2.2.2 Connect the sampling tube to the sampling pump with flexible tubing with the smaller section towards the pump.

2.2.3 Tubes should be placed in a vertical position to minimize channeling.

2.2.4 Air being sampled should not pass through any hose or tubing before entering the sampling tube.

2.2.5 Seal the sampling tube with plastic caps immediately after sampling. Seal each sample lengthwise with OSHA Form-21.

2.2.6 With each batch of samples, submit at least one blank tube from the same lot used for air samples. This tube should be subjected to exactly the same handling as the samples (break ends, seal, & transport) except that no air is drawn through it.

2.2.7 Transport the samples (and corresponding paperwork) to the lab for analysis.

2.2.8 Bulks submitted for analysis must be shipped in a container separate from the samples.

2.3 Desorption efficiency

Sampling tubes were spiked with 0.65, 1.62, 3.24, and 6.48 ppm, ethanolamine. They were allowed to equilibrate at room temperature overnight. They were opened, each section placed into a 4-mL vial, and 2-mL dimethylformamide was added. They were allowed to desorb for 30 minutes with occasional shaking, and analyzed by HPLC. The desorption efficiency averaged 100% (Table 2.3).

Table 2.3
Desorption efficiency

Tube#	% Recovered 161.8 µg 6.48 ppm	% Recovered 80.9 µg 3.24 ppm	% Recovered 40.45 µg 1.62 ppm	% Recovered 16.18 µg 0.65 ppm
1	96.1	100	103	101
2	99.1	100	95.3	98.8
3	102	101	97.3	101
4	97.7	100	98.9	101
5	103	101	101	101
6	102	101	101	98.0
average	100	101	99.4	100
overall average		100		
standard deviation		±2.00		

2.4 Retention efficiency

Sampling tubes were spiked with 161.8 µg (6.48 ppm) ethanolamine, and 10 liters of humid air (93% RH) were drawn through them. They were desorbed and analyzed by HPLC. There was no ethanolamine found on the backup portions of the sampling tubes (Table 2.4).

Table 2.4
Retention Efficiency

Tube #	% Recovered 'A'	% Recovered 'B'	% Total
1	103	0	103
2	105	0	105
3	104	0	104
4	97	0	97
5	101	0	101
6	100	0	100
average			102

2.5 Storage

Sampling tubes were spiked with 80.9 µg (3.24 ppm) ethanolamine and stored at room temperature until they were desorbed and analyzed. The recoveries remained above 98.1% for the 16-day storage period (Table 2.5).

Table 2.5
Storage Study

Day	% Recovered
4	101
4	99.3
4	101
8	98.1
8	98.4
8	100
16	101
16	103
16	102

2.6 Precision

Precision was calculated using the area counts from six injections of each standard at concentrations of 0.405, 20.2, 40.5, and 80.9 µg/ml ethanolamine. (Table 2.6).

Table 2.6
Precision

Injection number	80.94 µg/mL 6.48 ppm	40.47 µg/mL 3.2 ppm	20.23 µg/mL 1.62 ppm	0.4047 µg/mL 0.32 ppm
1	4840660	2497430	1249926	266774
2	4843388	2450287	1251863	259756
3	4847381	2454235	1253753	259865
4	4854116	2457850	1249499	254630
5	4845563	2454948	1254341	250966
6	4839621	2447595	1256576	254752
average	4845122	2460391	1252660	257791
standard deviation	±5280	±18502	±2737	±5562
CV	0.00109	0.00752	0.00218	0.0216
Pooled CV		6.809		

$$\text{CV (Coefficient of Variation)} = \frac{\text{standard deviation}}{\text{average}}$$

$$\text{Pooled CV} = \sqrt{\frac{A1(CV1)^2 + A2(CV2)^2 + A3(CV3)^2 + A4(CV4)^2}{A1 + A2 + A3 + A4}}$$

A(1),A(2),A(3),A(4) = # of injections at each level

CV1,CV2,CV3,CV4 = Coefficients at each level

2.7 Air volume and sampling rate studied

2.7.1 The air volume studied was 10 liters.

2.7.2 The sampling rate studied was 0.1 liters per minute.

2.8 Interferences (sampling)

2.8.1 Compounds which react with the derivatizing reagent may decrease the capacity for the analyte.

2.8.2 Suspected interferences should be listed on sample data sheets.

2.9 Safety precautions

2.9.1 Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.9.2 Safety glasses should be worn at all times.

2.9.3 Follow all safety practices that apply to the workplace being sampled.

3. Analytical method

3.1 Apparatus

3.1.1 Liquid chromatograph equipped with an ultraviolet detector capable of monitoring 254 and 280 nm. The response is most sensitive at 254 nm. For this study a Waters M-6000A pump was used with a Waters 440 Absorbance Detector.

3.1.2 LC column capable of separating the analyte from any interferences. A l0-µm Zorbax CN, 25 cm × 4.6 mm ID, was used for this study.

3.1.3 An electronic integrator or some other suitable method of measuring peak areas.

3.1.4 Four milliliter vials with Teflon-lined caps for sample desorption.

3.1.5 A 20 µL syringe or other convenient size for sample injection, or an autosampler that can inject 15 µL. Injections were made with a Waters WISP 710 automatic sample injection module in this study.

3.1.6 A dispenser or pipet capable of delivering 2.0 mL dimethylformamide.

3.1.7 Volumetric flasks and pipets for preparing standards.

3.1.8 An analytical balance capable of weighing to the nearest 0.01 mg.

3.2 Reagents

3.2.1 Ethanolamine, reagent grade

3.2.2 Dimethylformamide (DMF), HPLC grade

3.2.3 1-Naphthylisothiocyanate (NITC), reagent grade

3.2.4 Isooctane, HPLC grade

3.2.5 Isopropanol, HPLC grade.

3.3 Sample preparation

3.3.1 Sample tubes are opened and the front and back section of each tube are placed in separate 4-mL vials.

3.3.2 Each section is desorbed with 2 mL DMF.

3.3.3 The vials are sealed immediately and allowed to desorb for 30 minutes with occasional shaking.

3.4 Standard preparation

3.4.1 Stock standards are prepared by diluting a known quantity of ethanolamine with a solution of NITC in DMF. The molecular weight of NITC is 185.25, and the molecular weight of ethanolamine is 61.08. One molecule of the derivative is formed from one molecule of ethanolamine and one molecule of NITC. An excess is added to insure that all of the ethanolamine is reacted. A derivatizing solution of 50 mg NITC in 100 mL DMF was prepared to make the analytical standards.

An analytical standard of 1 µL ethanolamine in 10 mL of this derivatizing solution would be equivalent to 8.1 ppm based on a 10-L air volume and 2 mL desorption. More concentrated standards can be prepared by weighing out the ethanolamine, then dry reacting with NITC by adding the molar quantity of NITC, and then diluting with the derivatizing solution. This ensures an excess of NITC. An analytical standard of approximately one drop of ethanolamine in 10 mL weighed 50 mg, then 152 mg NITC was weighed out in the same volumetric, and the derivatizing solution was added to obtain a stock standard of 5 mg/mL derivatized ethanolamine.

3.4.2 At least two separate stock standards should be made.

3.4.3 Dilutions of these stock standards are made over the range of the samples, down to the level of the detection limit. At least four working standards should be prepared, so that a curve of concentration versus response can be plotted. Sample concentrations should be bracketed with working standards.

3.4.4 Analytical standards and samples should not be placed in an ultrasonic bath, as this causes decomposition of the derivative.

3.5 Analysis

3.5.1 Liquid chromatograph conditions.

Column:	10-µm Zorbax CN, 25-cm × 4.6-mm ID
Mobile Phase:	80/20 isooctane/isopropanol at 1mL/min
Injection size:	10 µL
Detector:	UV at 254 nm or 280 nm

Chromatogram:

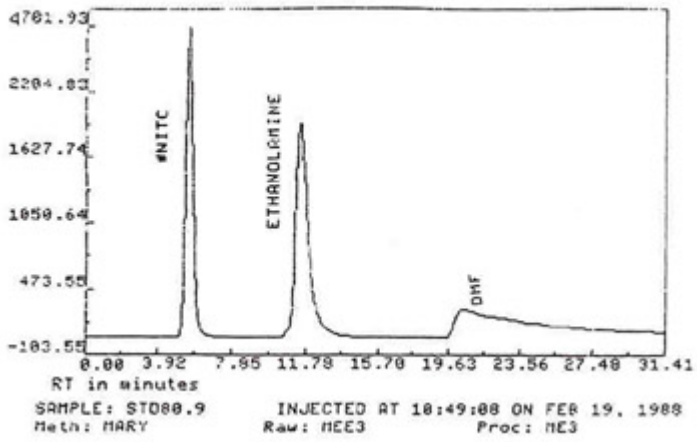

Figure 1. Standard of 80.9 ug/mL ethanolamine with NITC in DMF, analyzed by normal phase.

3.5.2 This analysis can also be run reverse phase, using the following conditions.

Column:	Whatman partisphere C_{18},10-cm × 7-mm
Mobile Phase:	30/70 acetonitrile/water at 1 mL/min
Injection size:	10 µL
Detector:	UV at 254 nm or 280 nm

Chromatogram:

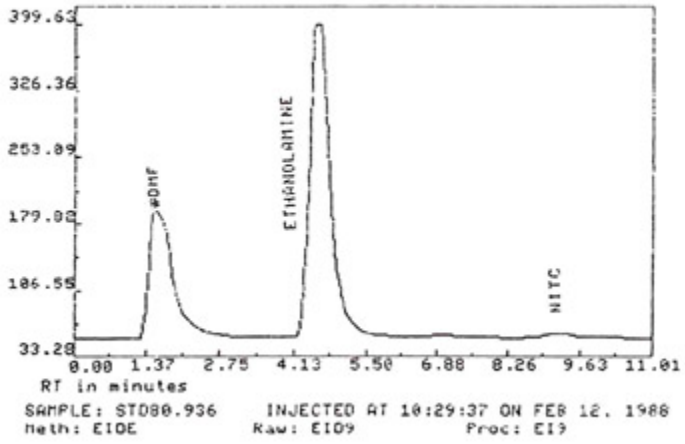

Figure 2. A standard of 80.9 ug/mL ethanolamine in DMF, analyzed by reversed phase.

3.5.3 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

3.6.1 Any compound having the general retention time of the analyte is an interference. Possible interferences should be listed on the sample data sheet. LC parameters should be adjusted if necessary so these interferences will pose no problems.

3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

3.7.1 A curve with area counts versus concentration is calculated from the calibration standards.

3.7.2 The area counts for samples are plotted with the calibration curve to obtain the concentration of triethylamine in solution.

3.7.3 To calculate the air concentration of analyte from the liquid concentration the following formulae are used:

$$\frac{(\mu g/mL)\ (\text{desorption volume})}{(\text{desorption efficiency})} = \text{mass of analyte in sample}$$

$$\frac{(\text{mass of analyte in sample})}{\text{molecular weight}} = \text{number of moles of analyte}$$

$$\begin{pmatrix}\text{number of moles}\\ \text{of analyte}\end{pmatrix}\begin{pmatrix}\text{molar volume at}\\ 25°C\ \&\ 760mmHg\end{pmatrix} = \begin{matrix}\text{volume the analyte will}\\ \text{occupy at } 25°C\ \&\ 760\ mmHg\end{matrix}$$

$$\frac{(\text{volume analyte occupies})(10^6)\ *}{(\text{air volume})} = ppm$$

* All units must cancel.

3.7.4 The above equations can be consolidated to form the following formula. To calculate the ppm of analyte in the sample based on a 5-liter air sample:

$$ppm = \frac{(\mu g/mL)(DV)(24.46)(10^6)(g)(mg)}{(5\ L)(DE)(MW)(1000\ mg)(1000\ mg)}$$

µg/mL	= concentration of analyte in sample or standard
24.46	= Molar volume (liters/mole) at 25°C and 760 mmHg.
MW	= Molecular weight (g/mole)
DV	= Desorption volume
5 L	= 5-liter air sample
DE	= Desorption efficiency

3.7.5 This calculation is done for each section of the sampling tube and the results added together.

3.8 Safety precautions

3.8.1. All handling of solvents should be done in a hood.

3.8.2. Avoid skin contact with all solvents. 3.8.3. Wear safety glasses at all times.

4. Recommendations for further study

Collection efficiencies need to be studied.

5. References

5.1 "NIOSH Manual of Analytical Methods", U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Second Edition, Vol. 4, Method 270.

5.2 Windholz, M., "The Merck Index", Tenth Edition, Merck & Co., Rahway N.J., 1983, p. 541.

5.3 "Documentation of the Threshold Limit Values and Biological Exposure Indices", Fifth Edition, American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 1986, p. 235.

5.4 Elskamp, C., Method 60, "Ethylenediamine, diethylenetriamine, and triethylenetetramine", Organic Methods Evaluation Branch, OSHA Analytical Laboratory, 1986.