DIETHANOLAMINE

Method number:	PV2018
Target concentration:	3 ppm (15 mg/cu m^3)
ACGIH TWA TLV:	2 mg/m^3
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 analyzed by desorbing the adsorbent with dimethylformamide and quantitating the amine derivative by high performance liquid chromatography (HPLC) using ultraviolet detection (UV).
Air volume and sampling rate:	100 minutes 0.1 L/min (10 L)
Status of method:	Partially validated 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 OSHA lab has been recommending the collection of diethanolamine with 0.1 N sulfuric acid bubblers. Direct analysis of the diethanolamine is difficult due to the peak shape and carryover problems. An adsorbent tube makes the collection easier for the industrial hygienist, and derivatization of the diethanolamine would improve the chromatography. Sampling tubes containing XAD-2 resin coated with 10% NITC by weight provided derivatization. The derivative desorbed well, was retained and showed no effects upon storage.

1.1.2 Potential workplace exposure (Ref 5.1)

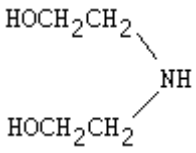
Diethanolamine is an adsorbent for acidic gases. It is used as an intermediate in the manufacture of resins and plasticizers. Diethanolamine acts as a detergent in paints, cutting oils, shampoos, and other cleaners.

1.1.3 Toxic Effects (This section is for information purposes only and should not be taken as the basis for OSHA policy.) (Ref. 5.1)

The recommended TLV for diethanolamine is the same as for ethanolamine due to similar skin effects, though diethanolamine has been shown to be less toxic in oral exposures. The LD_{50} in rats and guinea pigs for oral exposure is 2 g/kg. The skin exposure at 500 mg in a 24 hour period to the skin of rabbits resulted in mild damage. Exposure to the eye of rabbits at a level of 750 µg in a 24 hour caused severe damage.

1.1.4 Physical properties (Ref 5.2):

Compound:



CAS:	111-42-2
IMIS:	D129
RTECS:	KL2975000
Synonyms:	bis (2-hydroxyethyl) amine; diolamine; 2,2'-iminodiethanol; 2,2'-dihydroxydiethylamine
Molecular weight:	105.4
Density:	1.0966
Freezing point:	28 °C
Odor:	ammoniacal
Color:	clear liquid
Molecular formula:	$C_4H_{11}NO_2$

1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 1 ng, with a 15 µL injection volume. This is the smallest amount which could be detected under normal operating conditions.

1.2.2 The overall detection limit is 0.04 ppm based on a 10 liter air 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 amines 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 commercially available, and must be obtained from 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 with the sample tube attached.

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 backup section 40 mg. The sections are held in place with PTFE wool plugs in a glass tube 70-mm x 4-mm i.d..

The adsorbent is prepared by coating commercially purified 16/50 mesh XAD-2 (Supelco) with 10% NITC by weight using methylene chloride as a solvent. The solvent is removed by rotary evaporation (Ref 5.3)

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

2.2 Sampling technique

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

2.2.2 Connect the sample tube to the sampling pump with flexible tubing.

2.2.3 Tubes should be placed in a vertical position to minimize channeling, with the smaller section towards the pump.

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 end caps immediately after sampling. Seal each sample lengthwise with Form OSHA-21 seal.

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 separate container from the samples.

2.3 Desorption efficiency

2.3.1 A loading of 134.7 µg corresponds to 6.26 ppm based on a 10 liter air volume and a 2 mL desorption volume.

2.3.2 Sampling tubes were spiked with 269.4, 134.7, 67.35, and 13.47 µg diethanolamine. They were allowed to equilibrate at room temperature overnight. They were then opened, each section placed in a 4 mL vial, and 2 mL of dimethylformamide was added. They were allowed to desorb for 30 minutes with occasional shaking, then analyzed by HPLC. The desorption efficiency average was 100% (Table 1).

Table 1
Desorption Efficiency

Tube #	% recovery			
	269.4 µg	134.7 µg	67.35 µg	13.47 µg
1	103	104	102	99.8
2	101	104	96.3	99.8
3	103	104	94.3	97.5
4	104	104	95.9	98.9
5	101	104	95.2	97.6
6	100	105	98.9	97.0
average	102	104	97.1	98.4

overall average = 100%
standard deviation = ±3.33

2.4 Retention efficiency

2.4.1 Sampling tubes were spiked with 269.4 µg diethanolamine, and 10 liters of humid air (93% RH) was drawn through them. They were then desorbed and analyzed by HPLC. There was little or no diethanolamine found on the backup portions of the sampling tubes (Table 2).

Table 2
Retention Efficiency

Tube #	% recovery		
	'A'	'B'	total
1	99.9	0.0	99.9
2	101	0.0	101
3	92.6	0.4	92.6
4	101	0.4	101
5	97.7	0.3	98.0
6	99.4	0.6	100
average			98.8%

2.5 Storage

Sampling tubes were spiked with 134.7 µg diethanolamine and stored at room temperature until they were desorbed and analyzed. The recoveries remained above 92.5% for the 16-day storage period (Table 3).

Table 3
Storage Study

Days Stored	% recovered
4	99.6
4	105
4	104
8	99.6
8	101
8	98.0
16	101
16	97.3
16	92.5

2.6 Precision

Precision was calculated using the area counts from six injections of each standard at concentrations of 7.0, 70, and 140 µg/mL ethanolamine (based on a 10 liter air volume these concentrations correspond to 0.325, 3.25, and 6.5 ppm) (Table 4).

Table 4
Precision

Injection number	7.0 µg/mL 0.325 ppm	70.47 µg/mL 3.25 ppm	140 µg/mL 6.5 ppm
1	546480	5401085	12541460
2	528418	5650258	11950484
3	518930	5553324	11966070
4	510596	5251672	12048538
5	511803	5440720	11971644
6	517226	5233302	12164448
average	522242	5421727	12107107
standard deviation –	±13464	±164167	±227224
CV -	0.02578	0.03028	0.01877

pooled CV = 0.1077

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

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

A1, A2, A3, A4 = number of injections at each level
CV1, CV2, CV3, CV4 = Coefficients of variation 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 can 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 A High Performance Liquid chromatograph equipped with an ultraviolet detector capable of detecting 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 interference. A 10-cm × 8-mm i.d., 10-µm Radial CN 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 PTFE-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.

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

3.1.7 Volumetric flasks and pipettes for preparing standards.

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

3.2 Reagents

3.2.1 Diethanolamine, 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 diethanolamine with a solution of NITC in DMF. The molecular weight of NITC is 185.25, and the molecular weight of diethanolamine is 105.14. One molecule of the derivative is formed from one molecule of diethanolamine and one molecule of NITC. Excess NITC is added to insure that all of the diethanolamine is reacted. For example, a stock standard containing 2.694 mg/10 mL diethanolamine in DMF should contain at least 4.747 mg NITC, so 5 mg NITC was added to ensure that all the diethanolamine reacted.

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. Samples should be bracketed with working standards.

3.4.4 Standards and/or samples should not be placed in an ultrasonic, as it will decompose the derivative.

3.5 Analysis

3.5.1 Liquid chromatograph conditions.

Column:	10-cm × 8-mm i.d., 10 µm Radial CN,
Mobile Phase:	Isooctane:isopropanol, 80:20 at 1mL/min flow rate
Injection size:	15 µL
Detector:	UV at 254 nm
Retention time:	15.7 min
Chromatogram:	(See Figure 1)

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

3.5.3 A calibration curve is constructed by plotting detector response of standard injections versus µg of diethanolamine.

3.6 Interferences (analytical)

3.6.1 Any compound having the general retention time of the analyte is 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 To calculate the concentration of analyte in the air sample the following formulas are used:

$$mass\ of\ analyte,\ \mu g = \frac{(\mu g / mL)(desorption\ volume,\ mL)}{(desorption\ efficiency,\ decimal)}$$

$$moles\ of\ analyte = \frac{(mass\ of\ analyte,\ \mu g)(1\ g)}{(molecular\ weight)(10^6\ \mu g)}$$

$$volume\ of\ analyte = (moles\ of\ analyte)(molar\ volume)$$

$$ppm = \frac{(volume\ of\ analyte)(10^6)}{(air\ volume,\ L)}$$

* All units must cancel.

3.7.2 The above formulas can be consolidated to make the following formula that is used to calculate the ppm of analyte in the sample based on a 10-liter air sample, and a 1 mL desorbing solution:

$$ppm = \frac{(\mu g / mL)(DV)(24.46)}{(10\ L)(DE)(MW)}$$

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, mL
10 L = 10 liter air sample
DE = Desorption efficiency, decimal

3.7.3 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.

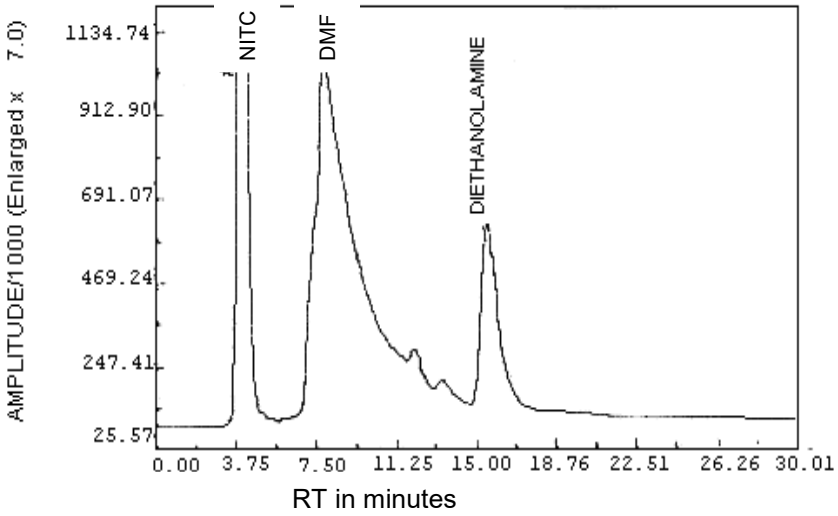


Figure 1. Standard of 134.7 µg/mL diethanolamine with NITC in DMF.

5 References

5.1 "Documentation of the Threshold Limit Values and Biological Exposure Indices," Fifth Edition, American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 1986, p.197.

5.2 Weast, R.C., "Handbook of Chemistry and Physics," 67th Edition, CRC Press Inc., Boca Raton FL, 1986, p. C244.

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