Method number:	PV2116
Target concentration:	5 ppm (20.7 mg/m^3)
Procedure:	Samples are collected by drawing a known volume of air through glass sampling tubes containing XAD-2 resin coated with 10% (w/w) 1-naphthylisothiocyanate (NITC). Samples are extracted with dimethylformamide and analyzed by LC using a UV detector.
Recommended sampling time and sampling rate:	100 min at 0.1 L/min (10 L)
Reliable quantitation limit:	140 ppb
Status of method:	Partially evaluated method. This method has been subjected to established evaluation procedures of the Methods Development Team and is presented for information and trial use.

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1. General Discussion

1.1 Background

1.1.1 History

Air samples collected on tubes containing XAD-2 resin coated with NITC were received at SLTC along with a request for analysis for aminoethylethanolamine (AEEA). This compound was collected on the same media used in OSHA Method 60[1], for diethylene triamine, so those extraction and analytical parameters were used as a starting point for AEEA. The AEEA was found to readily derivatize with the NITC to form a stable derivative. The mobile phase of 80:20 isooctane:isopropanol gave a separation for the AEEA peak from interferences from the NITC. The samples were extracted with dimethylformamide (DMF), with an extraction efficiency mean of 99.7% for the concentration range of 20.7 to 413 µg/tube. The retention efficiency study showed no AEEA on the back up section of the spiked tube or back up tube, for tubes spiked with 413.2 µg through which10-L humid air had been drawn. The storage study showed no loss for samples stored for up to 14 days under both refrigerated and ambient conditions.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.) [2,3]

AEEA is a moderate skin irritant, severe eye irritant, and moderate mucous membrane irritant. It is moderately toxic by ingestion, skin contact, and inhalation. It can cause skin sensitization and chemical asthma.

1.1.3 Workplace exposure[4,5]

AEEA is used in textile finishing compounds such as antifuming agents, dyestuffs, and cationic surfactants. It is used in resins, rubber products, insecticides, and medical formulations. AEEA is listed in EPA's HPV (high production volume) list of chemicals produced and/or imported into the United States.

1.1.4 Physical properties and other descriptive information[6,7]

CAS number:	111-41-1	IMIS[8]:	A120
molecular weight:	104.18	vapor density:	3.59
melting point:	<-18°C	boiling point:	243.7°C
appearance:	clear liquid	vapor pressure:	0.0013 kPa @ 20°C
odor:	mild ammoniacal	flash point:	135°C (275 °F)(cc)

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1 OSHA Sampling and Analytical Methods. http://www.osha.gov (accessed 5/21/2002).

2 Lewis, R., *Sax's Dangerous Properties of Industrial Materials,* Van Nostrand Reinhold: New York, 2002, p 176.

3 Pepys, J., Asthma due to Inhaled Chemical Fumes: Amino-ethyl ethanolamine in Aluminum Soldering Flux, *Clin Allergy*, 1972, 2(2), 197-204.

4 Lewis, R., Ed, *Hawley's Condensed Chemical Dictionary,* John Wiley & Sons: New York, 2001, p 592.

5 HPV Chemical List History. http://www.epa.gov/opptintr/chemtk/listhist.htm (accessed 5/21/2002).

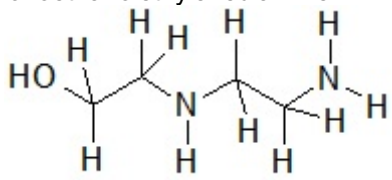
6 Lewis, R., *Sax's Dangerous Properties of Industrial Materials,* Van Nostrand Reinhold: New York, 2002, p 176.

7 Cheminfo http://ccohs.ca/products/databases/cheminfo.html (accessed 5/21/2002).

8 OSHA Chemical Sampling Information http://www.osha.gov (accessed 5/21/2002).

autoignition temperature:	368°C (695°F)	density:	1.0304
		molecular formula:	$C_4H_{12}N_2O$
solubility:	water, alcohol, acetone		
synonyms:	N-(2-aminoethyl)ethanolamine; 2-[(2-aminoethyl)amino] ethanol; N-hydroxyethyl-1,2-thanediamine; hydroxyethylethylenediamine; monoethanolethylenediamine		

structural formula:



This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[9]. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters.

1.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

The DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of analyte, such that the highest sampler loading was 10.34 µg of AEEA. This is the amount spiked on a sampler that would produce a peak at least 10 times the response for a sample blank. These spiked samplers were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate (SEE) and slope) for the calculation of the DLOP. The slope was 2418 and the SEE was 1440. The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The DLOP and RQL were 1.79 µg and 5.96 µg respectively. The recovery at the RQL was 97.2%.

Table 1.2
Detection Limit of the Overall Procedure for AEEA

mass per sample (µg)	area counts (µV·s)
0.00	0
1.03	1733
2.07	3890
3.10	5287
4.14	7345
5.17	9023
6.20	11528
7.24	15632
8.27	17639
9.31	22873
10.34	24876

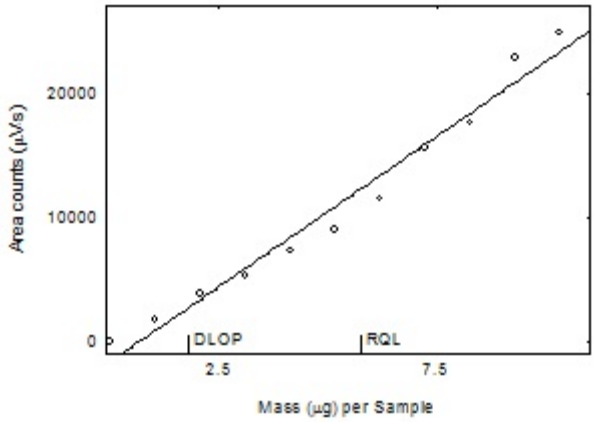


Figure 1.2.1 Plot of data to determine the DLOP/RQL for AEEA at 254 nm. (y = 2418 x - 1611; SEE = 1440)

[9] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

Below is the chromatogram of the RQL level.

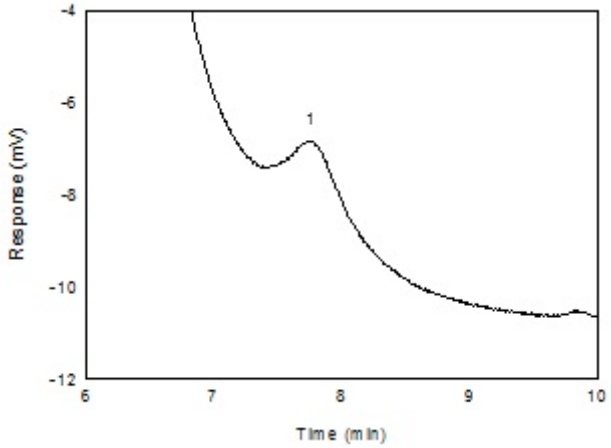


Figure 1.2.2 Chromatogram of the AEEA peak in a standard near the RQL at 254 nm. (1 = AEEA)

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to within ±5% of the recommended flow rate.

2.1.2 Samples are collected with 7-cm × 4-mm i.d. × 7-mm o.d. glass sampling tubes packed with two sections (80/40 mg) of XAD-2 resin coated with 10% by weight 1-naphthylisothiocyanate. The sections are held in place and separated with glass wool plugs. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (catalog no. 226-30-18).

2.2 Reagents

None required.

2.3 Technique

2.3.1 Immediately before sampling, break off the ends of the flame-sealed tube to provide an opening approximately half the internal diameter of the tube. Wear eye protection when breaking ends. Use tube holders to minimize the hazard of broken glass. All tubes should be from the same lot.

2.3.2 The smaller section of the adsorbent tube is used as a back-up and is positioned nearest the sampling pump. Attach the tube holder to the sampling pump so that the adsorbent tube is in an approximately vertical position with the inlet facing down during sampling. Position the sampling pump, tube holder and tubing so they do not impede work performance or safety.

2.3.3 Draw the air to be sampled directly into the inlet of the tube holder. The air being sampled is not to be passed through any hose or tubing before entering the sampling tube.

2.3.4 After sampling for the appropriate time, remove the adsorbent tube and seal it with plastic end caps. Seal each sample end-to-end with an OSHA-21 form as soon as possible.

2.3.5 Submit at least one blank sample with each set of samples. Handle the blank sample in the same manner as the other samples except draw no air through it.

2.3.6 Record sample air volumes (liters), sampling time (minutes) and sampling rate (L/min) for each sample, along with any potential interferences on the OSHA-91A form.

2.3.7 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples at refrigerator temperature. Ship any bulk samples separate from the air samples.

2.4 Extraction efficiency

The extraction efficiency was determined by spiking NITC-coated XAD-2 tubes with AEEA at 0.1 to 2 times the target concentration. These samples were stored overnight at ambient temperature. Samples were extracted with 2-mL DMF, shaken for 30 minutes, and analyzed. The mean extraction efficiency over the studied range was 99.7%. The wet extraction efficiency was determined at 1 times the target concentration by spiking the analyte onto NITC-coated XAD-2 tubes which had 10-L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) drawn through them immediately before spiking. The mean recovery for the wet samples was 98.7%.

Table 2.4
Extraction Efficiency (%) of AEEA

level		sample number						
× target concn	µg per sample	1	2	3	4	5	6	mean
0.1	20.7	99.2	98.5	99.8	98.8	100.1	100.4	99.5
0.25	51.7	99.8	98.7	100.1	98.5	100.4	100.3	99.6
0.5	103	98.3	98.2	99.3	99.8	101.0	100.4	99.5
1.0	207	100.8	100.9	98.7	99.9	98.4	100.3	99.8
1.5	310	99.5	100.1	100.3	98.9	99.7	100.1	99.8
2.0	413	99.8	101.2	98.5	99.6	100.5	100.3	100.0
1.0 (wet)	207	98.9	99.2	99.9	97.3	97.2	99.5	98.7

2.5 Retention efficiency

Six NITC-coated XAD-2 tubes were spiked with 413 µg (9.7 ppm) of AEEA and allowed to equilibrate for 4 h. Each spiked tube was placed in series with a second NITC-coated XAD-2 tube. Each sampling train had 10-L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) pulled through it at 0.1 L/min. The samples were extracted and analyzed. The mean recovery was 99.4%. There was no analyte found on the backup section of any of the spiked tubes or on the second tubes.

Table 2.5
Retention Efficiency (%) of AEEA

	sample number						
section	1	2	3	4	5	6	mean
front of spiked tube	98.8	97.7	99.7	100.6	100.2	99.6	99.4
rear of spiked tube	0.0	0.0	0.0	0.0	0.0	0.0	0.0
front of series tube	0.0	0.0	0.0	0.0	0.0	0.0	0.0
back of series tube	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	98.8	97.7	99.7	100.6	100.2	99.6	99.4

2.6 Sample storage

Fifteen NITC-coated XAD-2 tubes were each spiked with 207 µg (4.86 ppm) of AEEA. They were allowed to equilibrate for 4 h, then 10-L of air, with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 23 °C), was drawn through them. Three samples were analyzed immediately. The remaining tubes were sealed and six were stored at room temperature (23 °C), while the other six were stored at refrigerated temperature (4 °C). Three of the samples stored at room temperature and three of the samples stored at refrigerated temperature were analyzed after 7 days and the remaining three of each group after 14 days. The results indicate good storage stability for the time period studied.

Table 2.6
Storage Test for AEEA

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	99.8	100.5	98.5	99.8	100.5	98.5
7	99.7	98.5	99.1	98.6	98.9	99.1
14	99.6	97.8	99.5	99.4	98.7	99.3

2.7 Recommended air volume and sampling rate.

Based on the data collected in this evaluation, 10-L air samples should be collected at a sampling rate of 0.1 L/min for 100 minutes.

2.8 Interferences (sampling)

2.8.1 There are no known compounds which will severely interfere with the collection of AEEA. Other primary and secondary amines will collect on this medium, and form derivatives with the NITC, affecting the ability of the tube to collect AEEA, so sampling time should be adjusted if high concentrations of amines are expected.

2.8.2 Suspected interferences should be reported to the laboratory with submitted samples.

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan. Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs.

3.1 Apparatus

3.1.1 A liquid chromatograph equipped with a UV detector. For this evaluation, a Waters 600 Controller and pump were used, with a Waters 2487 Dual Wavelength Absorbance Detector, and a Waters 717 plus Autosampler was used.

3.1.2 An LC column capable of separating AEEA from the extraction solvent and any potential interferences. A 4.6 × 250 mm column packed with 5-µm Bakerbond cyanopropyl (JT Baker, Phillipsburg, NJ) was used in the evaluation.

3.1.3 An electronic integrator or some other suitable means of measuring peak areas. A Waters Millennium[32] Data System was used in this evaluation.

3.1.4 Glass vials with poly(tetrafluoroethylene)-lined caps. For this evaluation 4-mL vials were used.

3.1.5 A dispenser capable of delivering 2.0 mL of extracting solvent to prepare standards and samples. If a dispenser is not available, a 2.0-mL volumetric pipet may be used.

3.1.6 Volumetric flasks - 10-mL and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 Aminoethylethanolamine (AEEA), reagent grade. Acros 99% (lot 08515DS labeled 2-(2-aminoethyamine)ethanol) was used in this evaluation.

3.2.2 *N,N*-Dimethyl formamide (DMF), reagent grade. Fisher 99.5%+ (lot 933764) was used for this evaluation.

3.2.3 Isopropyl alcohol, HPLC grade. Fisher 99.9% (lot 0011554) was used in this evaluation.

3.2.4 Isooctane, HPLC grade. Fisher 99.0%+ (lot 024943) was used in this evaluation.

3.2.5 1-Naphthylisothiocyanate (NITC), reagent grade. Aldrich 95%+ (lot 09925MY) was used in this evaluation.

3.2.6 Mobile phase was 80:20 isooctane:isopropyl alcohol.

3.3 Standard preparation

3.3.1 Freshly prepare two stock standards. A stock standard of 2 mg/mL may be prepared by a) weighing out about 50 mg of NITC in a 10-mL flask, b) weigh out 20 mg AEEA by placing the drops on top of the NITC in the flask, and c) weigh out about 50 mg more NITC on top of the AEEA, making sure that the AEEA is covered on all sides by the NITC. Allow the AEEA to react with the NITC for at least 1 hour before adding the DMF. Partially fill the volumetric flask with DMF and allow to sit 30 minutes to begin dissolving the derivative, then swirl the contents until all of the solids are dissolved, and fill to the mark with DMF. Do not place the flask in a sonic bath to try to get the derivative to go into solution, as it will destroy the derivative. There must always be an excess of the NITC for the derivative to be completely formed. There are two amine groups which will react with the NITC, so this mole ratio must be used in calculating the amount of NITC to be added. For example, the amount of NITC needed for the above stock standard would be calculated:

20 mg AEEA × (NITC MW=185.25/AEEA MW=104.15) ×2 = 71 mg

In the above stock standard preparation a total of 100 mg NITC was weighed out so that an excess of NITC was present.

3.3.2 Diluted standards are prepared with a solution of 1 mg/mL NITC in DMF, so that an excess of NITC is always present. Bracket sample concentrations with working standard concentrations. If sample concentrations are higher than the concentration range of prepared standards, either analyze higher standards, or dilute the sample. The higher standards should be at least as high in concentration as the highest sample. Diluted samples should be prepared with a solution of 1 mg/mL NITC in the DMF. The range of standards used in this study was from 0.5 to 250 µg/mL. The instrument is calibrated on the amount of AEEA in each standard.

3.4 Sample preparation

3.4.1 Remove the plastic end caps from the sample tubes and carefully transfer the adsorbent sections to separate 4-mL vials. Discard the glass tube and glass wool plugs.

3.4.2 Add 2.0 mL of DMF to each vial.

3.4.3 Immediately seal the vials with poly(tetrafluoroethylene)-lined caps.

3.4.4 Agitate the vials on a shaker, or a rotator, for 30 minutes.

3.5 Analysis

3.5.1 HPLC conditions

column: Bakerbond cyanopropyl (CN) column 4.6 × 250 mm
injection size: 10 µL
mobile phase: 1 mL/min 80:20 isooctane:isopropyl alcohol
detector: UV at 254 and 280 nm
run time: 14 min
retention times: 1.7 min NITC
2.2 min DMF
6.8 min AEEA

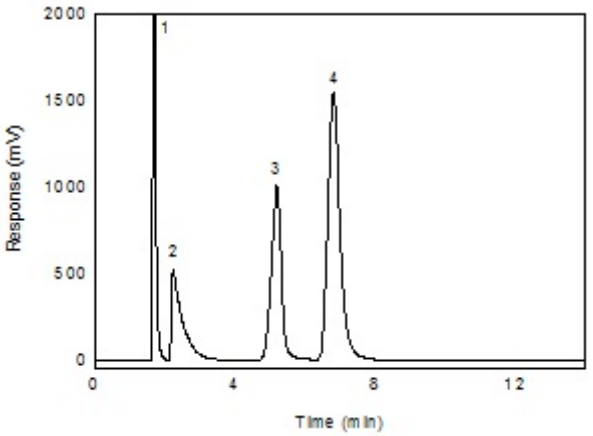


Figure 3.5.1. A chromatogram of 413 µg/mL AEEA in DMF with NITC at 254 nm. Key: (1) NITC; (2) DMF; (3) interference from NITC; (4) AEEA.

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

3.5.3 An external standard (ESTD) calibration method is used. A calibration curve can be constructed by plotting response of standard injections versus micrograms of analyte per sample. Bracket the samples with freshly prepared analytical standards over a range of concentrations.

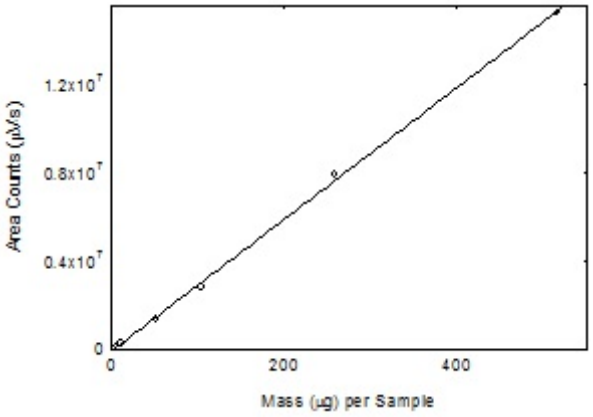


Figure 3.5.3. Calibration curve of AEEA at 254 nm. (Y = 2.96E4x - 9.52E4).

3.6 Interferences (analytical)

3.6.1 Any compound that produces a LC response and has a similar retention time as the analyte is a potential interference. If any potential interferences were reported, they should be considered before samples are extracted. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.2 When necessary, the identity or purity of an analyte peak may be confirmed by a photodiode array scan of the peak, by wavelength ratioing, or by LC/mass spec.

3.7 Calculations

The amount of analyte per sampler is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

$$C_M = \frac{M}{VE_E}$$

where C_M is concentration by weight (mg/m^3)
M is micrograms per sample
V is liters of air sampled
E_E is extraction efficiency, in decimal form

$$C_V = \frac{V_M C_M}{M_r}$$

where C_V is concentration by volume (ppm)
V_M is molar volume at 25 °C and 760 mm = 24.46
C_M is concentration by weight
M_r is molecular weight = 104.18

4. Recommendations for further study

   Collection, reproducibility, and other detection limit studies need to be performed to make this a validated method.