N,N-Dimethylethylamine

Method number:	PV2096
Control number:	T-PV2096-01-8711-CH
Target concentration:	25 ppm - There is no OSHA PEL or TLV for N,N-dimethylethylamine.
Procedure:	Samples are collected by drawing a known volume of air through a jumbo alumina tube, 400-mg reference section with a 200-mg backup section, lot 391. Samples are desorbed for 30 minutes with 2 mL deionized water, which has been neutralized to pH of 7 and then analyzed by gas chromatography with a nitrogen-phosphorous detector (GC-NPD).
Air volume and sampling rate studied:	40 minutes at 0.1 L/min (4 L)
Special requirements:	The capacity of the different lots of alumina tubes varied greatly. For each lot of alumina tubes used, the capacity should be checked.
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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Mary E. Eide

SOLVENTS BRANCH
OSHA Analytical Laboratory
Salt Lake City UT

1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA lab has been recommending collection of N,N-dimethylethylamine with a 0.1 N H_2SO_4 bubbler following the NIOSH method (S152) for collection of triethylamine (Ref 5.1). A paper by P.W. Langvardt and R.G. Melcher recommends collection and analysis of ethanolamines and isopropanolamines using alumina tubes (Ref 5.2). Adsorbent tubes are more convenient, so alumina tubes were tried as a collection media for N,N-dimethylethylamine. Different means of desorption and analysis were used than in the paper (Ref 5.2), since the analyte of interest was N,N-dimethylethylamine. Alumina tubes, in this study, were desorbed with either 0.1 N H_2SO_4 or deionized water. Analysis was by GC-NPD. Two different lots and sizes of alumina tubes were tried, because the capacity was different for the two lots. Lot 190 had a greater capacity, 6 liters with humid air (93% RH), but is no longer available, so alumina, lot 391 jumbo tubes, were evaluated. The desorption efficiency and the storage were good for both lots studied.

1.1.2 Potential workplace exposure (Ref 5.3)

N,N-dimethylethylamine is used in urea- and melamine-based enamels, as an antilivering agent. N,N-dimethylethylamine is used in foundries.

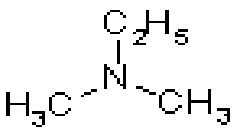
1.1.3 Toxic Effects (This section is for information purposes and should not be taken as the basis for OSHA policy.) (Ref 5.3)

N,N-dimethylethylamine has toxic effects similar to triethylamine, which causes corneal damage, pulmonary irritation, cellular necrosis of the liver and kidneys, and skin irritation.

1.1.4 Physical properties (Ref 5.4):

CAS:	598-56-1
IMIS:	0915
Molecular weight:	73.14
Density:	0.675
Boiling point:	37 °C
Melting point:	- 140 °C
Odor:	strong ammoniacal odor
Color:	clear liquid
Molecular formula:	$C_4H_{11}N$
Flash point:	- 36 °C

Structure:



1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 5 ng, with a 1-µL injection volume. This is the smallest amount which could be detected under normal operating conditions.

1.2.2 The overall detection limit is 0.3 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 compounds at the same time.

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

1.4 Disadvantages

None known.

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, is used.

2.1.2 Alumina tubes, lot 391, containing 400-mg adsorbing section with a 200 mg backup section separated by a 2-mm portion of urethane foam, with a silane treated glass wool plug before the adsorbing section and a 3-mm plug of urethane foam at the back of the backup section. The ends are flame sealed and the glass tube containing the adsorbent is 11-cm x 8-mm o.d. and 6-mm i.d., SKC tubes or equivalent.

2.2 Sampling technique

2.2.1 The ends of the alumina tubes are opened immediately before sampling.

2.2.2 Connect the alumina 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 alumina tube.

2.2.5 Seal the alumina tube with plastic caps immediately after sampling. Seal each sample lengthwise with a 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, and 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

A desorption efficiency of the 400/200 mg size alumina tube, lot 391, was performed by spiking six tubes each with 0.338, 0.675, and 1.35 mg of N,N-dimethylethylamine. The tubes were

stored at room temperature overnight. They were then opened, each section placed into a separate 4-mL vial, and desorbed with 2 mL deionized water. They were allowed to desorb for 30 minutes with occasional shaking, and then analyzed by GC-NPD (Table 2.3). The overall average desorption was 97.9%. Table 2.3

Table 2.3
Desorption Study Lot 391

tube #	% recovered		
	0.338 mg	0.675 mg	1.35 mg
1	97.3	97.2	93.1
2	100	103	93.7
3	99.8	98.4	96.6
4	102	101	95.8
5	97.4	97.5	98.6
6	99.5	07.9	93.3
average	99.3	99.2	95.2

overall average = 97.9%
standard deviation = ±2.80

2.4 Retention efficiency

Retention efficiency of lot 391 jumbo alumina tubes was performed by spiking six tubes with 0.675 mg N,N-dimethylethylamine and then drawing 4 liters of humid air, 94 % RH, through them. They were opened, each section placed into a separate 4-mL vial, and desorbed with 2 mL deionized water. They were allowed to desorb for 30 minutes with occasional shaking, and then analyzed by GC-NPD. While there was N,N-dimethylethylamine found on the backup portion of the alumina tubes, the amount recovered averaged 96.3% (Table 2.4). The recoveries were corrected for desorption efficiency.

Table 2.4
Retention Efficiency Lot 391

tube #	% recovered		
	'A'	'B'	total
1	89.5	9.3	98.8
2	79.9	18.5	98.2
3	78.1	16.6	94.7
4	83.7	12.3	96.0
5	88.9	4.8	93.7
6	lost	lost	lost

average = 97.7%

2.5 Storage

Storage stability for lot 391 jumbo alumina tubes was performed by spiking 0.675 mg N,N-dimethylethylamine on the tubes, and storing them at room temperature. The tubes were opened, each section placed into separate 4-mL vials, and desorbed with 2 mL deionized water. They were allowed to desorb for 30 minutes with occasional shaking, and then analyzed by GC-NPD. The storage stability remained above 95% for the 14 days studied (Table 2.5). The values in the table were corrected for desorption efficiency.

Table 2.5
Storage Study Alumina
Tube Lot 391

day	% recovered
5	99.6
5	97.1
5	96.2
14	96.4
14	95.9
14	101
average	97.7

2.6 Air volume and sampling rate studied

2.6.1 The air volume studied was 4 liters.

2.6.2 The sampling rate studied was 0.1 liter per minute.

2.7 Interferences

Suspected interferences should be listed on sample data sheets.

2.8 Safety precautions

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

2.8.2 Safety glasses should be worn at all times.

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

3 Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph equipped with a nitrogen-phosphorous detector.

3.1.2 GC column capable of separating the analyte from any interference. A 6-ft glass column packed with 4% Carbowax 20M, 0.8% KOH on Carbopack B 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 1-µL syringe or other convenient size for sample injection.

3.1.6 Pipettes for dispensing the desorbing solution.

3.1.7 Volumetric flasks, 5-mL and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 Purified GC grade nitrogen, hydrogen, and air.

3.2.2 Deionized water.

3.2.3 Reagent grade N,N-dimethylethylamine.

3.3 Sample preparation

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

3.3.2 Each section of the tube is desorbed with 2 mL deionized water.

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 Standards are prepared by diluting a known quantity of N,N-dimethylethylamine with deionized water.

3.4.2 At least four separate standards should be made from at least two separate stock standards. A curve is plotted, since the response can be non-linear on a NPD.

3.4.3 A standard of 337.5 µg/mL (0.5 µL/mL) N,N-dimethylethylamine in water corresponds to 57.62 ppm based on a 4 liter air volume, 2 mL desorption volume, and a 97.9% desorption efficiency for lot 391 jumbo tubes.

3.5 Analysis

3.5.1 As chromatograph conditions.

Column 6-ft glass packed with 4% Carbowax 20M, 0.8% KOH on Carbopack B

Flow rates	**(mL/min)**	**Temperature**	**(°C)**
Nitrogen:	24	Injector:	200
Hydrogen:	3	Detector:	220
Air:	50	Column:	120

Injection size: 1 µL
Elution time: 3.12 min

Chromatogram:

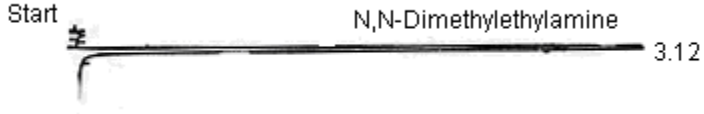


Figure 1. Standard of 675 µg/mL N,N-dimethylethylamine in water.

3.5.2 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 interference. Possible interferences should be listed on the sample data sheet. GC 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 Standards are plotted on a curve and the micrograms/milliliter of the samples are taken from the curve.

3.7.2 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.

3.7.3 The above formulas can be consolidated to obtain the following formula. To calculate the ppm of analyte in the sample based on a 4-liter air sample:

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

Where:

µg/mL = concentration of analyte in sample
24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg
MW = Molecular weight (g/mole)
DV = Desorption volume, mL
4 L = Air volume, L
DE = Desorption efficiency, decimal

3.7.4 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, gloves, and a lab coat at all times in laboratory areas.

4 Recommendations for further study

Collection efficiencies should be performed. Any lot of alumina tubes other than the ones in this study should be checked for retention efficiency before used in the field. Method needs to be fully validated.

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. 3., Method S152.

5.2 Langvardt, P.W., Melcher, R.G., Anal. Chem., 1980, vol. 52, p. 669.

5.3 Proctor, N.H., Hughes, J.P., "Chemical Hazards of the Workplace," J.B. Lippincott Co., Philadelphia PA, 1978, p. 497.

5.4 Weast, R.C., "Handbook of Chemistry and Physics," 67th Edition, CRC Press Inc., Boca Raton FL, 1986, p. C247.