Method no.:	PV2064
Matrix:	Air
Target concentration:	5 ppm (25 mg/m³) (OSHA PEL)
Procedure:	Samples are collected by drawing a known volume of air through a phosphoric acid coated XAD-7 tube.
Recommended air volume and sampling rate:	30 liters (L) at 0.2 L/min
Reliable quantitation limit:	0.02 ppm (0.09 mg/m^3)
Status of method:	Partially Evaluated Method. This method has been subjected to established evaluation procedures, and is presented for information and trial use.

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1. General Discussion

1.1 Background

1.1.1 History

Information had been received from the National Institute of Occupational Safety and Health (NIOSH) that there were some deficiencies in the NIOSH method for N,N-dimethylaniline. (Ref. 5.1) It was noted that desorption efficiencies and stability had not been tested on silica gel tubes. Because of these concerns, the desorption, retention and stability of N,N-dimethylaniline on silica gel tubes was tested.

A desorption study was done on silica gel tubes by spiking tubes at 0.5, 1.0, and 2.0 times the PEL. These were allowed to equilibrate overnight and the next day desorbed and analyzed. The recoveries over the range was 95%. This was followed by a retention study where tubes were spiked at 2.0 x the PEL, allowed to equilibrate overnight, 30 L of humid air drawn through each tube and then analyzed. The average recovery was 12%. This indicated that silica gel tubes had a poor retention of N,N-dimethylaniline under humid conditions. The interference effects of water vapor on the collection of N,N-dimethylaniline on silica gel tubes has been addressed previously. (Ref. 5.2)

Since the silica gel tube was not adequate, the sulfuric acid (H_2SO_4) coated glass fiber filter was tested because the method for toluidine uses acid coated filters. A desorption study at 0.1, 0.5, 1.0 and 2.0 times the PEL was done. The average recovery over the range was 99%. This was followed by a retention study where the acid coated filters were spiked at 2.0 x the PEL and allowed to equilibrate overnight. The next day 100 L of humid air was drawn through each filter and then analyzed. The average recovery was 4.2%. The acid coated glass fiber filter yielded a poor retention efficiency.

A sampling media that has been tested for some of the more volatile amines was tried next. This media is a 10% phosphoric acid (H_3PO_4) coated XAD-7 tube which gave good preliminary results. This report describes the analytical method developed for the sampling and analysis of N,N-dimethylaniline.

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

N,N-Dimethylaniline is toxic and can be absorbed through the skin and by inhalation. The severity of N,N-dimethylaniline toxicity varies. It has been reported that N,N-dimethylaniline does cause methemoglobin to form like aniline but at a less toxic level. Other reports point out the depressant effect of N,N-dimethylaniline which is greater than that of aniline. Also, there are few reports of industrial experience available to form accurate appraisals of health hazards. (Ref.5.3)

1.1.3 Workplace exposure

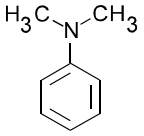
N,N-Dimethylaniline is used in the manufacture of vanillin, Michler's ketone, methyl violet and other dyes; as a solvent; and as a reagent. No information was available on the number of workers exposed to N,N-dimethylaniline. (Ref.5.3.)

1.1.4 Physical properties and other descriptive information (Ref. 5.4 unless otherwise indicated)

Synonyms:	N,N-dimethylbenzeneamine; dimethylphenylamine; N,N-dimethylphenylamine; benzenamine, N,N-dimethyl; (dimethylamino)benzene; dimethylaniline (Ref. 5.5)
CAS number:	121-69-7 (Ref. 5.5)
IMIS:	0931
RTECS:	BX4725000 (Ref. 5.5)

DOT:	UN 2253 (Ref. 5.5)
Molecular weight:	121.18
Flash point:	62.78°C closed cup; 76.67°C open cup (Ref. 5.3)
Boiling point:	192 to 194°C
Melting point:	2°C
Form:	oily liquid
Density:	0.956 at 20°C
Solubility:	insoluble in water; soluble in alcohol, chloroform, ether
Molecular formula:	$C_8H_{11}N$

Structural formula:



The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters of 30 liters and a desorption volume of one mL. Air concentrations listed in ppm are referenced to 25°C and 101.3 kPa (760 mmHg).

1.2 Limit defining parameters

1.2.1 Detection limit of the overall procedure (DLOP)

The detection limit of the overall procedure is 0.84 µg per sample (0.006 ppm or 0.028 mg/m³). This is the amount of analyte spiked on the sampler that will give a response that is significantly different from the background response of a sampler blank.

The DLOP is defined as the concentration of analyte that gives a response (Y_{DLOP}) that is significantly different (three standard deviations (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DLOP} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{BR} in chromatographic methods is typically inconvenient, and difficult because Y_{BR} is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SD_{BR} and the precision of data about the curve are similar, the standard error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for the DLOP:

$$SEE = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

Y_{obs} = observed response
Y_{est} = estimated response from regression curve
n = total no. of data points
k = 2 for a linear regression curve

At point Y_{DLOP} on the regression curve

$$Y_{DLOP} = A(DLOP) + Y_{BR}$$

A = analytical sensitivity (slope)

therefore

$$DLOP = \frac{(Y_{DLOP} - Y_{BR})}{A}$$

Substituting 3(SEE) + Y_{BR} for Y_{DLOP} gives

$$DLOP = \frac{3(SEE)}{A}$$

The DLOP is the amount of aniline spiked on the adsorbing section of the acid coated XAD-7 tubes that will give a response that is significantly different from the background response. Several tubes were spiked with various amounts of aniline from approximately 0.5 to 8 µg. These were stored overnight at ambient temperature. The next day these samples were desorbed and analyzed. The data obtained was used to calculate the required parameters (A = 799 and SEE = 224) for the calculation of the DLOP.

Table 1.2.1
Detection Limit of the Overall Procedure

mass per sample (µg)	area counts (µV-s)	recovery (decimal)
0	0	
0.50	1091	1.32
0.50	456	0.89
1.00	967	0.88
1.00	927	0.92
2.00	1937	0.98
2.00	1774	0.89
3.01	2730	0.95
3.01	2683	0.94
4.01	3357	0.91
4.01	3683	0.94
5.01	4367	0.95
5.01	3682	0.80
6.01	5281	0.93
6.01	5027	0.94
7.01	5734	0.92
7.01	5858	0.92
8.02	6608	0.92

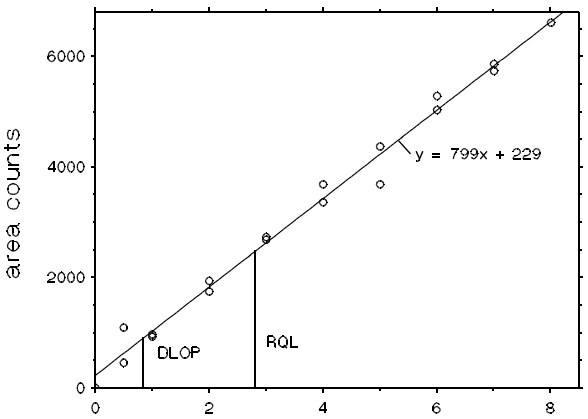


Figure 1.2.1. Plot of data to determine the DLOP/RQL.

1.2.2 Reliable quantitation limit (RQL)

The reliable quantitation limit is 2.8 µg per sample (0.02 ppm or 0.09 mg/m³). This is the amount of analyte spiked on a sampler that will give a signal that is considered the lower limit for precise quantitative measurements.

The RQL is considered the lower limit for precise quantitative measurements. It is determined from in the regression line data obtained for the calculation of the DLOP (Section 1.2.1), providing at least 75% of the analyte is recovered. The RQL is defined as the concentration of analyte that gives a response (Y_{RQL}) such that

$$Y_{RQL} - Y_{BR} = 10(SD_{BR})$$

therefore

$$RQL = \frac{10(SEE)}{A}$$

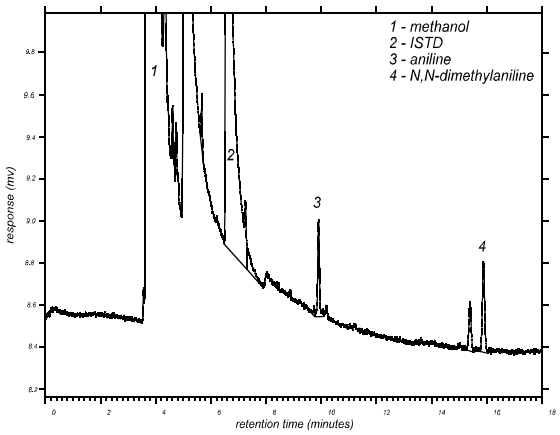


Figure 1.2.2. Reliable Quantitation Limit Chromatogram.

2. Sampling Procedure

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 on 10% phosphoric acid coated XAD-7 tubes, lot 540, containing 80 mg adsorbing section with 40 mg backup section. The sections are separated by a 2 mm urethane foam plug, with a silanized glass wool plug before the adsorbing section and a 3 mm urethane foam plug at the back of the backup section. The ends of the glass tube are flame sealed and the tube containing the adsorbent is 7 cm long with a 6 mm outside diameter. SKC tubes (catalog number 226-98, Fullerton, CA) or equivalent tubes may be used.

2.2 Technique

2.2.1 Immediately before sampling, break off the ends of the sampling tube. All tubes should be from the same lot.

2.2.2 Attach the sampling tube to the sampling pump with flexible tubing. It is desirable to utilize sampling tube holders which have a protective cover to shield the employee from the sharp, jagged end of the sampling tube. Position the tube so that sampled air passes through the sampling, larger, section of the tube first.

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

2.2.4 Attach the sampler vertically with the sampling, larger, section downward, in the worker's breathing zone, and positioned so it does not impede work performance or safety.

2.2.5 After sampling for the appropriate time, remove the sample and seal the tube with plastic end caps. Wrap each sample end-to-end with a Form OSHA-21 seal.

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

2.2.7 Record sample volumes (in liters of air) for each sample, along with any potential interferences.

2.2.8 Ship bulk samples in separate containers from the air samples.

2.3 Desorption efficiency

The desorption efficiencies (DE) of N,N-dimethylaniline were determined by liquid-spiking the sampling tubes with N,N-dimethylaniline at 0.1 to 2 times the PEL. These samples were stored overnight at ambient temperature. The next day the samples were desorbed and analyzed. The average desorption efficiency over the studied range was 92.9% with a standard deviation of 2.187.

Table 2.3.1 Desorption Efficiency of N,N-Dimethylaniline at 0.1 x the PEL

sample i.d.	µg spiked	µg recovered	recovery (decimal)
1	75.14	71.71	.954
2	75.14	71.80	.955
3	75.14	69.97	.931
4	75.14	71.68	.954
5	75.14	69.76	.928
6	75.14	73.03	.972

Table 2.3.2 Desorption Efficiency of N,N-Dimethylanilinem at 0.5 x the PEL

sample i.d.	µg spiked	µg recovered	recovery (decimal)
7	376	350	.932
8	376	352	.936
9	376	348	.925
10	376	341	.908
11	376	353	.940
12	387	349	.929

Table 2.3.3 Desorption Efficiency of N,N-Dimethylaniline at 1.0 x the PEL

sample i.d.	µg spiked	µg recovered	recovery (decimal)
13	751	693	.922
14	751	684	.911
15	751	687	.914
16	751	658	.876
17	751	667	.888
18	751	724	.964

Table 2.3.4 Desorption Efficiency of N,N-Dimethylaniline at 2.0 x the PEL

sample i.d.	µg spiked	µg recovered	recovery (decimal)
19	1503	1390	.925
20	1503	1389	.924
21	1503	1382	.920
22	1503	1408	.937
23	1503	1383	.920
24	1503	1391	.926

2.4 Retention efficiency

The acid coated XAD-7 tubes were spiked with 1503 µg (10 ppm or 50 mg/m³) of N,N-dimethylaniline, allowed to equilibrate overnight in a drawer at ambient temperature and then had 30 L humid air (80% RH at 25°C) pulled through them. They were opened, desorbed, and analyzed by GC-FID. The retention efficiency averaged 92%. There was no N,N-dimethylaniline found on the backup portions of the tubes.

Table 2.4
Retention Efficiency of N,N-Dimethylaniline at 2.0 x the PEL

sample i.d.	µg spiked	µg recovered	recovery (decimal)
R1	1503	1401	.932
R2	1503	1387	.923
R3	1503	1359	.904
R4	1503	1353	.900
R5	1503	1399	.931
R6	1503	1382	.919

2.5 Sample storage

The front sections of 12 acid coated XAD-7 sampling tubes were each spiked with 751 µg (5 ppm) of N,N-dimethylaniline. They were sealed and stored overnight at ambient temperature. The next day 30 L of humid air (80% RH at 25°C)was drawn through each tube at 0.2 L/min. Half of the tubes were stored in a drawer at ambient temperature and the other half were stored in a refrigerator at 0°C. After 7 days of storage three samples from the tubes stored under refrigeration and three samples from ambient storage were analyzed. The remaining samples were analyzed after 14 days of storage. The amounts recovered, which are not corrected for desorption efficiency, indicate good storage stability for the time period studied.

Table 2.5
Sample Storage

Ambient Storage				Refrigerator Storage			
days	µg theory	µg found	recovery (decimal)	days	µg theory	µg found	recovery (decimal)
7	751	596	.793	7	751	625	.832
7	751	651	.866	7	751	648	.862
7	751	628	.836	7	751	643	.856
14	751	737	.980	14	751	728	.969
14	751	727	.967	14	751	748	.995
14	751	736	.979	14	751	763	1.015

2.6 Recommended air volume and sampling rate.

2.6.1 The recommended air volume is 30 L.

2.6.2 The recommended sampling rate is 0.2 L/min.

2.7 Interferences

2.7.1 It is not known if any compounds will interfere with the collection of N,N-dimethylaniline on 10% phosphoric acid coated XAD-7 tubes. In general, the presence of other contaminant vapors in the air will reduce the capacity of adsorbent tubes to collect N,N-dimethylaniline.

2.7.2 Any suspected interferences should be reported to the laboratory.

2.8 Safety precautions (sampling)

2.8.1 Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.

2.8.2 Follow all safety practices that apply to the work area being sampled.

2.8.3 Wear eye protection when breaking the ends of the glass sampling tubes.

3. Analytical Procedure

3.1 Apparatus

3.1.1 A gas chromatograph (GC) equipped with a flame ionization detector (FID). A Hewlett Packard (HP) model 5890 was used in this evaluation.

3.1.2 A GC column capable of separating the analyte and an internal standard from any interferences. The column used in this study was a 60 m RTX-5, 1.0 µ film thickness, 0.32 mm i.d.

3.1.3 An electronic integrator or some suitable method of measuring peak areas. A Waters 860 data system was used in this evaluation.

3.1.4 Two milliliter vials with Teflon-lined caps.

3.1.5 A 10 µL syringe or other convenient size for standard preparation.

3.1.6 Pipets for dispensing the desorbing solution. A dispenser may be used.

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 N,N-Dimethylaniline, Reagent grade

3.2.3 Methanol, reagent grade.

3.2.4 1-Hexanol, reagent grade. This was used as an internal standard (ISTD).

3.2.5 Ammonium hydroxide, reagent grade.

3.2.6 Desorbing solution. The desorbing solvent was prepared by adding 1-hexanol and ammonium hydroxide to methanol at 25 µL/mL and 0.2N concentrations respectively.

3.3 Standard preparation

3.3.1 Stock standards are prepared by diluting a known quantity of N,N-dimethylaniline with the desorbing solution.

3.3.2 Dilutions of the stock standards with desorbing solution were made to obtain lower working range standards of 0.7 µg/mL to 1600 µg/mL.

3.4 Sample preparation

3.4.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2 mL vials.

3.4.2 Each section is desorbed with 1 mL of the desorbing solution.

3.4.3 The vials are sealed immediately and allowed to desorb for 30 minutes on a mechanical shaker.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

Injection size:	1 µL
<u>Flow rates (mL/min)</u>	
Nitrogen (make-up):	30
Hydrogen(carrier):	1.5
Hydrogen(detector):	60
Air:	450
<u>Temperatures (°C)</u>	
Injector:	200
Detector:	250
Oven:	120
<u>Retention times (min)</u>	
ISTD	6.9
Aniline	10.9
N,N-Dimethylaniline	18.1

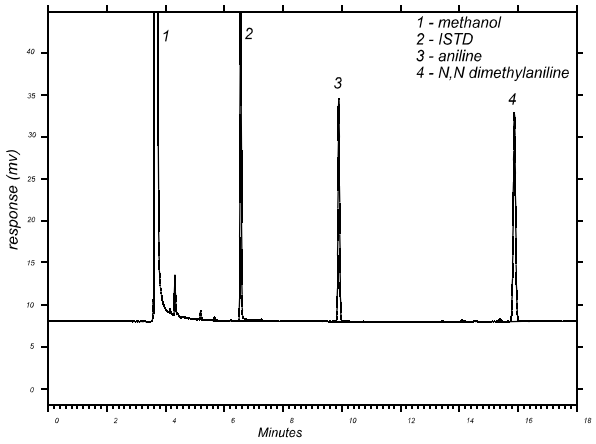


Figure 3.5.1. Chromatogram at the PEL.

3.5.2 Peak areas are measured with a data system or other suitable means.

3.6 Interferences (analytical)

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

3.6.2 When necessary, the identity of an analyte peak may be confirmed by GC-Mass spectrometry or by another analytical procedure.

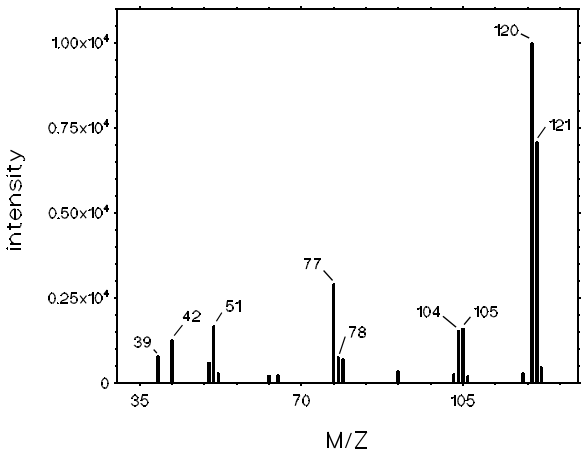


Figure 3.6.2. Mass Spectrum of N,N-Dimethylaniline (Ref. 5.6)

3.7 Calculations

3.7.1 Construct a calibration curve by plotting detector response versus concentration (µg/mL) of N,N-dimethylaniline.

3.7.2 Determine the µg/mL of N,N-dimethylaniline in each section of the samples and blank from the calibration curve.

3.7.3 Blank correct each sample by subtracting the µg/mL found in each section of the blank from the µg/mL found in the corresponding sections of the samples and then add the results together for the total µg/mL for each sample.

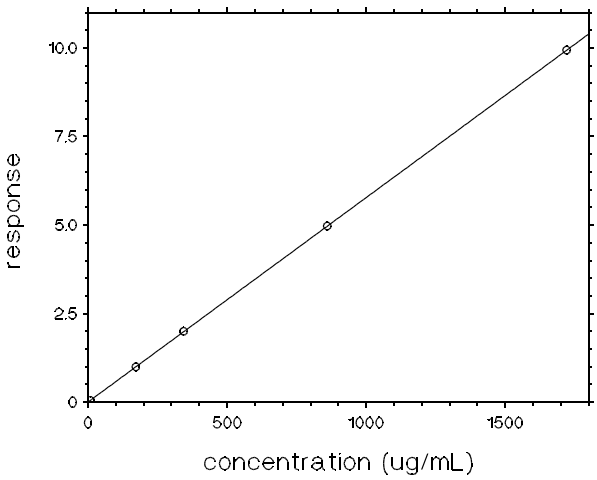


Figure 3.7.1. Calibration Curve.

3.7.4 Determine the air concentration using the following formula.

$$mg/m^3 = \frac{(\mu g/mL,\ blank\ corrected)x(desorption\ volume,\ mL)}{(air\ volume,\ L)x(desorption\ efficiency,\ decimal)}$$

$$ppm = \frac{(mg/m^3)x(24.46)}{MW}$$

where:
24.46 = molar volume (liters/mole) at 101.3 kPa (760 mm Hg) and 25°C
MW = molecular weight (g/mole) of N,N-dimethylaniline

3.8 Safety precautions

3.8.1 Adhere to the rules set down in your chemical hygiene plan when working with chemicals.

3.8.2 Avoid skin contact and inhalation of all chemicals.

3.8.3 Wear safety glasses, gloves and a lab coat at all times while in the laboratory areas.

4. Recommendations for Further Study

Collection studies need to be performed from a dynamically generated test atmosphere.

5. References

5.1 Eller, P. M., Ed.; *NIOSH Manual of Analytical Methods,* 3rd. ed; U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering: Cincinnati, DHHS (NIOSH) Publication No. 84-100, 1984, Method 2002.

5.2 Wood, G. and Anderson, R., *Am. Ind. Hyg. Assoc. J*, 1975, 36(7), 538-548.

5.3 *Documentation of the Threshold Limit Values and Biological Exposure Indices,* 5th. ed.; American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, 1986; p 207.

5.4 Budavari, S. ED.; *Merck Index*, 11th ed.; Merck: Rahway, NJ, 1989; p 510.

5.5 *Registry of Toxic Effects of Chemical Substances 1985-86 Edition*; DHHS(NIOSH) Publication No. 87-114, U.S. Department of Health and Human Services: Cincinnati, OH, 1987; p 487.

5.6 *EPA/NIH Mass Spectral Data Base,* Vol. 1, 1980,p 58.