Aniline

Method no.:	PV2079
Matrix:	Air
Target concentration:	5 ppm (19 mg/m³) (OSHA PEL)
Procedure:	Samples are collected by drawing a known volume of air through an acid coated XAD-7 tube. Samples are desorbed with of methanol containing 0.2 N ammonium hydroxide (NH_4OH) and analyzed by gas chromatography (GC) using a flame ionization detector.
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 aniline. (Ref. 5.1) It was noted that desoption efficiencies at low levels had not been tested and that the stability of samples for longer that 1 week was not known. Because of these concerns, the desorption, retenton and stability of aniline 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 96%. This was followed by a retention study where tubes were spiked at 2.0 times the PEL, allowed to equilibrate overnight, 30 L of humid air drawn through each tube and then analyzed. The average recovery was 3.9%. This did not indicate that silica gel tubes had a good retention of aniline under humid conditions. The interference effects of water vapor on the collection of aniline on silica gel tubes has been addressed previously. (Ref. 5.2)

            Since collection on silica gel was not adequate, the sulfuric acid (H_2SO_4) coated glass fiber filters were tested because the method for toluidine uses these 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 97%. 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 were drawn through each filter and then analyzed. The average recovery was 82%. Silica gel did not yield a satisfactory retention efficiency.

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

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

            Aniline is toxic and can be absorbed through the skin and by inhalation. At one time, the over-exposure resulting in aniline poisoning was common. The poisoning is due to the conversion of hemoglobin to methemoglobin which does not release oxygen to the tissues and results in cyanosis and possible death from asphyxiation. (Ref. 5.3 and 5.4)

            The acute oral LD_{50} of 0.44 g/kg has been reported for rats. (Ref. 5.4)
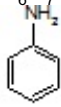
            Studies have been done on animals for evidence of carcinogenicity. The results of the studies are limited and most results are negative. (Ref. 5.5)

            Studies have been done on workers in the aniline-dye industry. The results from these studies attribute cancer deaths to chemicals other than aniline. (Ref. 5.6)

        1.1.3 Workplace exposure

            Aniline is used as a parent substance in the manufacture of several chemical products and intermdiates. The major uses are in the production of polymers (isocyanates), rubber chemicals, dyes, hydroquinone, drugs, acgriculture and miscellaneous applications. (Ref. 5.3) In 1979, the total production of eight companies in the United States amounted to 313 million kilograms and imports totaled 19,657 kilograms. (Ref. 5.5) There was no information available on the number of workers exposed to aniline.

1.1.4   Physical properties and other descriptive information (Ref. 5.3 unless otherwise indicated)

Synonyms: Benzenamine
CAS number: 62-53-3
IMIS: 0220
RTECS: BW6650000; 8036 (Ref. 5.7)
DOT: UN1547
Vapor pressure: 6.67 kPa (50 mmHg) at 102°C
Molecular weight: 93.1
Flash point: 76°C (169°F) (closed-cup)
Boiling point: 184.4°C
Melting point: -6.15°C
Color: colorless when fresh, darkens on exposure to air and light
Density: 1.022
Molecular formula: C_6H_7N
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 0.8 µg per sample (0.008 ppm or 0.03 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 aresponse that is signficantly different from the background response. Several tubes were spiked with various amounts of aniline from approximately 0.4 to 6 µg. These were stored overnignt at ambient temperature. The next day these samples were desorbed and analyzed. The data obtained was used to calculate the required parameters (A = 784 and SEE = 208) for the calculation of the DLOP.

Table 1.2.1
Detection Limit of the Overall Procedure

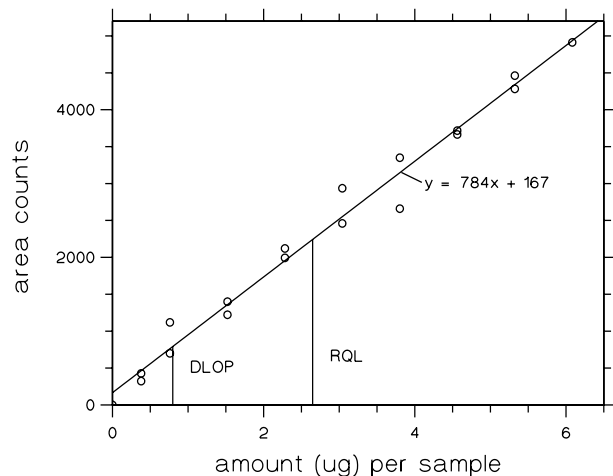| mass per sample (µg)	area counts (µV-s)
0	0
0.38	428
0.38	323
0.76	1119
0.76	699
1.52	1400
1.52	1222
2.28	1993
2.28	2121
3.04	2936
3.04	2459
3.80	3350
3.80	2660
4.56	3665
4.56	3717
5.32	4282
5.32	4462
6.08	4912

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

1.2.2   The reliable quantitation limit (RQL) is 2.7 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

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

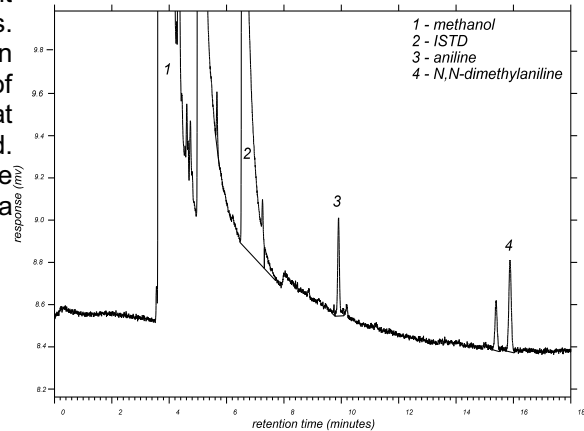Figure 1.2.2. Reliable quantitation limit chromatogram.

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 bacckup 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 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 aniline were determined by liquid-spiking the sampling tubes with aniline at 0.1 to 2 times the PEL. These samples were stored overnight in a drawer at ambient temperature. The next day the samples were desorbed and analyzed. The average desorption efficiency over the studied range was 91.4%.

Table 2.3.1
Desorption Efficiency of Aniline at 0.1 × the PEL

sample	µg spiked	µg recovered	recovery (decimal)
1	57.03	53.77	0.943
2	57.03	53.29	0.934
3	57.03	51.85	0.909
4	57.03	53.89	0.945
5	57.03	51.08	0.896
6	57.03	54.23	0.951

Table 2.3.2
Desorption Efficiency of Aniline at 0.5 × the PEL

sample	µg spiked	µg recovered	recovery (decimal)
7	285	261	0.917
8	285	259	0.907
9	285	259	0.909
10	285	254	0.893
11	285	264	0.925
12	285	261	0.915

Table 2.3.3
Desorption Efficiency of Aniline at 1.0 × the PEL

sample	µg spiked	µg recovered	recovery (decimal)
13	570	520	0.912
14	570	511	0.895
15	570	518	0.908
16	570	494	0.867
17	570	501	0.879
18	570	545	0.956

Table 2.3.4
Desorption Efficiency of aniline at 2.0 × the PEL

sample	µg spiked	µg recovered	recovery (decimal)
19	1141	1040	0.912
20	1141	1042	0.913
21	1141	1033	0.906
22	1141	1051	0.922
23	1141	1034	0.906
24	1141	1040	0.912

2.4   Retention efficiency

The acid coated XAD-7 tubes were spiked with 1141 µg (10 ppm or 38 mg/m³) of aniline, 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 aniline found on the backup portions of the tubes.

Table 2.4.1
Retention Efficiency of Aniline
at 2.0 × the PEL

sample	µg spiked	µg recovered	recovery (decimal)
R1	1141	1055	0.925
R2	1141	1045	0.916
R3	1141	1025	0.899
R4	1141	1047	0.918
R5	1141	1062	0.931
R6	1141	1047	0.918

2.5   Sample storage

The front sections of 12 acid coated XAD-7 sampling tubes were each spiked with 570 µg (5 ppm) of aniline. 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	570	460	0.807	7	570	478	0.838
7	570	493	0.865	7	570	495	0.868
7	570	478	0.838	7	570	490	0.86
14	570	559	0.98	14	570	551	0.966
14	570	545	0.956	14	570	564	0.99
14	570	554	0.972	14	570	578	1.01

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 aniline 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 aniline.

　　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　Folllow 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 µm 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   Aniline, Reagent grade

    3.2.3   Methanol, reagent grade.

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

    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 aniline with the desorbing solution.

    3.3.2   Dilutions of the stock standards with desorbing solution were made to obtain lower working range standards.

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

Figure 3.5.1.   Chromatogram at the PEL
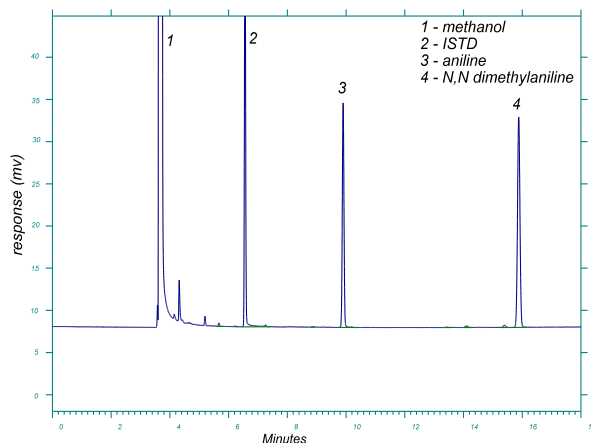
3.5.2 Peak areas are measured with a data system or other suitable means.

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.
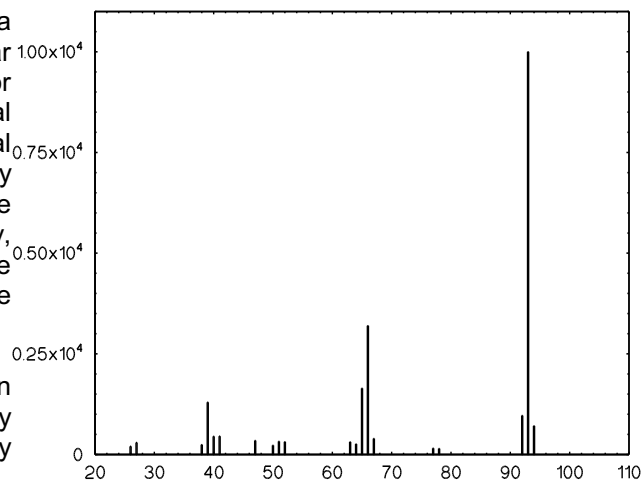
Figure 3.6.2. Mass Spectrum of Aniline (Ref. 5.8)

3.7 Calculations

3.7.1 Construct a calibration curve by plotting detector response versus concentration (µg/mL) of aniline.

3.7.2 Determine the µg/mL of aniline 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.

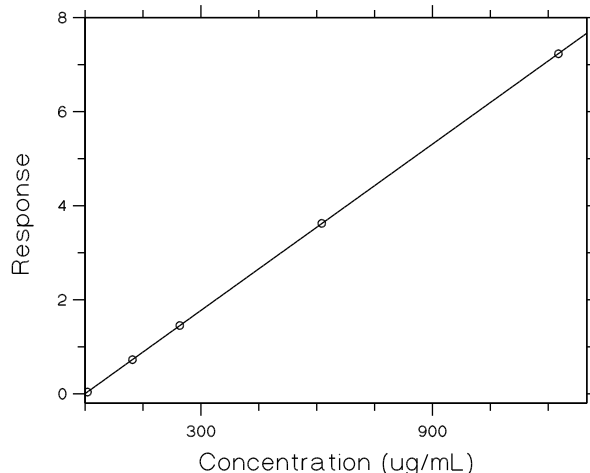Figure 3.7.1.   Calibration Curve

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3.7.4 Determine the air concentration using the following formula.

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

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

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

3.8 Safety precautions

3.8.1 Adhere to the rules set down in your chemical hygiene plan (which is mandated by the OSHA laboratory standard).

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 *NIOSH Manual of Analytical Methods,* 3rd. ed; Eller, P. M., 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, Gerry and Anderson, Robert *Am. Ind. Hyg. Assoc. J*, 1975, 36(7), 538-548.

5.3 *Kirk-Othmer Encyclopedia of Chemical Technology,* 3rd ed.; Grayson, M. Ed.; John Wiley & Sons: New York, 1980, Vol. 2; pp 309-316.

5.4 *Documentation of the Treshold Limit Values and Biological Exposure Indices,* 5th. ed.; American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, 1986; p 30.

5.5 *IRAC Monographs on the Evaluation of Carcinogenic Risks of Chemicals to Humans, Some Aromatic Amines, Anthraquinones and Nitroso Compounds, and Inorganic Fluorides Used in Drinking-water and Dental Preparations*; Volume 27; International Agency for Research on Cancer, Secretariat of the World Health Organization: UK, 1982, ISBN 92 8 321227 4.

5.6 *IRAC Monographs on the Evaluation of Carcinogenic Risks to Humans, Overall Evaluations of Carcinogenicity: An Updating of IRAC Monographs Volumes 1 to 42, Supplement 7*; International Agency for Research on Cancer, Secretariat of the Wold Health Organization: UK, 1987, ISBN 92 832 1411 0, ISSN 0250-9555.

5.7 *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 478.

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

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