Diphenylamine
N-Isopropylaniline

Method no.:	78
Matrix:	Air
Procedure:	Samples are collected closed-face by drawing known volumes of air through sampling devices consisting of three-piece cassettes, each containing two sulfuric acid-treated glass fiber filters separated by a spacer. Analysis is performed by extracting the filters with methyl alcohol and analyzing the free amines by high-performance liquid chromatography using an ultraviolet detector.
Recommended air volume and sampling rate:	100 L at 1 L/min

	N-isopropylaniline	diphenylamine
Target concentration:	2 ppm (11 mg/m^3)	10 mg/m^3
Reliable quantitation limit: (based on a 100-L air volume)	1.8 ppb (10 µg/m^3)	10 µg/m^3
Standard error of estimate at the target concentration: (Section 4.7.)	6.4%	6.3%

Special requirements:	Diphenylamine samples should be refrigerated until analyzed to help minimize loss of analyte during storage.
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: July 1989 Chemist: Carl J. Elskamp

Organic Methods Evaluation Branch
OSHA Analytical Laboratory
Salt Lake City, Utah

1. General Discussion

1.1. Background

1.1.1. History

The previous OSHA-evaluated method to determine diphenylamine in air involved collection in bubblers containing isopropyl alcohol with analysis by HPLC. (Ref. 5.1.) No method was found for *N*-isopropylaniline. Because it is inconvenient and at times unsafe to sample with bubbler solutions, and because *N*-isopropylaniline has recently been added to OSHA's PEL list, the acid-treated filter method which had been successfully evaluated for other aromatic amines (Refs. 5.2.-5.5.) was evaluated for these two amines. In the previously evaluated acid-treated filter methods for the other aromatic amines, a heptafluorobutyric acid anhydride derivative of the amines was prepared to obtain better sensitivities. Both *N*-isopropylaniline and diphenylamine have PELs (*N*-isopropylaniline = 2 ppm (10 mg/m^3), diphenylamine = 10 mg/m^3) which are considerably higher than the target concentrations of the other amines. Thus the enhanced sensitivity from derivatives was not needed. It was found that the filters could be efficiently extracted with methyl alcohol and the free amines analyzed by paired-ion HPLC.

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

The following is taken directly from the Trade Names Database of the Canadian Centre for Occupational Health and Safety. (Ref. 5.6.)

N-Isopropylaniline: Dermal contact and inhalation are expected to be the primary routes of occupational exposure to *N*-isopropylaniline. Although *N*-isopropylaniline is considered only slightly toxic on the basis of animal tests, human experience has shown that man is much more sensitive to methemoglobinemia following exposure to aromatic nitro (and amino) compounds than the rat or the rabbit. Methemoglobiriemia is a condition caused by changes in the blood cells which decrease the oxygen-carrying capacity of the blood. This oxygen deficiency may lead to cyanosis. As oxygen deficiency increases, the cyanosis may be associated with headache, weakness, irritability, drowsiness, shortness of breath and unconsciousness. Lethargy and stupor may be delayed 6 to 12 hours after exposure. Because of the high potential for this material to cause methemoglobin formation, *N*-isopropylaniline should be considered hazardous by all routes of exposure and exposures should be tightly controlled to prevent toxicity.

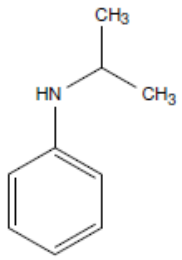
Diphenylamine: Diphenylamine dust can irritate the nose and throat. Absorption of large amounts of diphenylamine into the body by any route can affect the heart and blood. An increased pulse rate and increased blood pressure may occur. Some breakdown of the oxygen-carrying components of the blood may occur (methemoglobinemia).

1.1.3. Workplace exposure

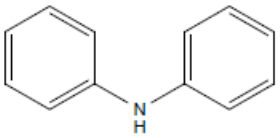
N-Isopropylaniline is used in the dyeing of acrylic fibers and as a chemical intermediate. Diphenylamine is used as a stabilizer for nitrocellulose explosives and celluloids, and in the manufacture of dyes. (Ref. 5.7.)

1.1.4. Physical properties and other descriptive information (Ref. 5.6.)

	N-isopropylaniline	diphenylamine
CAS no.:	768-52-5	122-39-4
molecular weight:	135.21	169.22
boiling point:	202 °C	302 °C
melting point:		52-55 °C
description:	clear straw-colored liquid with sweet aromatic odor	white to light tan to brown crystals with floral odor
solubility:	insoluble in water soluble in acetone, ethanol, benzene, carbon tetrachloride	300 mg/L in water at 25 °C. Freely soluble in ether, benzene, glacial acetic acid and carbon disulfide. Very soluble in ethyl alcohol, propyl alcohol, ethyl acetate, carbon tetrachloride, acetone and pyridine.
specific gravity:	0.9330 at 25/15.6 °C	1.159 at 20 °C
vapor pressure:	4.0 Pa (0.03 mm Hg) at 25 °C, 2933 Pa (22 mm Hg) at 100 °C	133 Pa (1 mm Hg) at 108.3°C
vapor density:		5.82 (air = 1)
flash point:	212 °F (Cleveland open cup)	302 °F (150 °C)
auto ignition temperature:		1173 °F (634 °C)
synonyms and trade names:	NIPA	anilinobenzene; Big Dipper; biphenylamine; DFA; DPA; C.I. 10355; difenylamin; *N*,*N*-diphenylamine; *N*-fenylanilin; No Scald; *N*-phenylaniline; phenyl aniline; *N*-phenylbenzeneamine; Scaldip
structural formula:		



N-isopropylaniline



diphenylamine

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm and ppb are referenced to 25 °C and 760 mm Hg.

1.2. Limit defining parameters

1.2.1. Detection limit of the analytical procedure

The detection limit of the analytical procedure is 1.7 ng per injection for both *N*-isopropylaniline and diphenylamine. This is the amount of analyte which will produce a peak with a height that is approximately 5 times the baseline noise. (Section 4.1.)

1.2.2. Detection limit of the overall procedure

The detection limit of the overall procedure is 1.0 µg per sample for both *N*-isopropylaniline and diphenylamine. This is the amount of analyte spiked on sample filters which allows recovery of an amount of analyte equivalent to the detection limit of the analytical procedure. These detection limits correspond to air concentrations of 1.8 ppb (10 µg/m^3) and 10 µg/m^3 for *N*-isopropylaniline and diphenylamine respectively. (Section 4.2.)

1.2.3. Reliable quantitation limit

The reliable quantitation limit is 1.0 µg per sample for both *N*-isopropylaniline and diphenylamine. This is the smallest amount of analyte which can be quantitated within the requirements of a recovery of at least 75% and a precision (±1.96 SD) of ±25% or better. These reliable quantitation limits correspond to air concentrations of 1.8 ppb (10 µg/m^3) and 10 µg/m^3 for *N*-isopropylaniline and diphenylamine respectively. (Section 4.3.)

The reliable quantitation limits and detection limits reported in this method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of an analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

1.2.4. Instrument response to the analyte

The instrument response over concentration ranges representing 0.5 to 2 times the target concentrations is linear for both analytes. (Section 4.4.)

1.2.5. Recovery

The recoveries of *N*-isopropylaniline and diphenylamine from samples used in 15-day storage tests remained above 91 and 76% respectively. The sample filters were stored in cassettes in a closed drawer at approximately 21 °C. (Section 4.5.) The recovery of analyte from the collection medium during storage must be 75% or greater.

1.2.6. Precision (analytical method only)

The pooled coefficient of variation obtained from replicate injections of analytical standards at 0.5, 1, and 2 times the target concentrations is 0.002 and 0.007 for *N*-isopropylaniline and diphenylamine respectively. (Section 4.6.)

1.2.7. Precision (overall procedure)

The precisions at the 95% confidence level for the 15-day storage tests are ±12.5 and ±12.3% for *N*-isopropylaniline and diphenylamine respectively. These include an additional ±5% for sampling error. The sample filters were stored in cassettes in a closed drawer at approximately 21 °C. (Section 4.7.) The overall procedure must provide results at the target concentration that are ±25% or better at the 95% confidence level.

1.2.8. Reproducibility

Six samples, spiked by liquid injection, and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The samples were analyzed after 2 days of storage at approximately 23 °C. No individual sample result deviated from its theoretical value by more than the precision of the overall procedure as reported in Section 1.2.7. (Section 4.8.)

1.3. Advantages

1.3.1. The acid-treated filter provides a convenient method of sampling for a number of aromatic amines.

1.3.2. The analysis is rapid, sensitive, and precise.

1.4. Disadvantages

None

2. Sampling Procedure

2.1. Apparatus

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

2.1.2. Samples are collected closed-face using a sampling device consisting of two sulfuric-acid treated 37-mm Gelman type A/E glass fiber filters contained in a three-piece cassette. The filters are prepared by soaking each filter with 0.5 mL of 0.26 N sulfuric acid. (0.26 N Sulfuric acid can be prepared by diluting 1.5 mL of 36 N sulfuric acid to 200 mL with deionized water.) The filters are dried in an oven at 100 °C for 1 h and then assembled into three-piece 37-mm polystyrene cassettes without support pads. The front filter is separated from the back filter by a polystyrene spacer. The cassettes are sealed with shrink bands and the ends are plugged with plastic plugs.

2.2. Reagents

None required

2.3. Sampling technique

2.3.1. Remove the plastic plugs from the sampling device immediately before sampling.

2.3.2. Attach the sampling device to the sampling pump with flexible tubing and place the device in the employee's breathing zone.

2.3.3. Seal the sampling device with the plastic plugs immediately after sampling.

2.3.4. Seal and identify each sampling device with an OSHA Form 21.

2.3.5. Submit at least one blank sampling device with each sample set. Handle the blanks in the same manner as the air samples, but draw no air through them.

2.3.6. Record the volume of air sampled (in liters) for each sample, along with any potential interferences.

2.4. Collection efficiency

2.4.1. Generation apparatus

Collection efficiency studies were conducted by drawing air through sampling devices that were attached to empty impingers. Microliter amounts of amine standards (in methyl alcohol) were injected into the impingers before sampling commenced. The inlets of the impingers were attached to a humid air generator so air at approximately 80% relative humidity could be drawn through the generation apparatus. The *N*-isopropylaniline sample generations were done at room temperature, while the impingers were heated to approximately 60 °C with a heat tape for the diphenylamine samples.

2.4.2. Collection efficiency at 2 times the target concentration

Three individual collection efficiencies were determined at 2 times the target concentration for each analyte. This was done by adding an amount of amine of interest, which was equivalent to 20 mg/m^3 for a 100-L air sample (approximately 2 mg), to each impinger before sampling at 1 L/min for 100 min. There was no analyte found on the back filter of any of the samples, while essentially all of the amine which was spiked into the impingers was recovered from the front filters.

2.5. Extraction efficiency

2.5.1. The average extraction efficiencies from six filters for each amine spiked at the target concentration are 100.5 and 100.4% for *N*-isopropylaniline and diphenylamine respectively. (Section 4.9.)

2.5.2. The stability of extracted samples was verified by reanalyzing the above samples 24 h later using fresh standards. The average extraction efficiencies for the reanalyzed samples were 99.2 and 99.1% for *N*-isopropylaniline and diphenylamine respectively. (Section 4.9.)

2.6. Recommended air volume and sampling rate

2.6.1. The recommended air volume is 100 L.

2.6.2. The recommended sampling rate is 1 L/min.

2.6.3. If a smaller air volume is desired, the reliable quantitation limits will be larger. For example, the reliable quantitation limit for *N*-isopropylaniline for a 15-L air sample would be 12 ppb.

2.7. Interferences (sampling)

2.7.1. Any compound in the sampled air that will react with the sulfuric acid on the treated filters or with the collected analyte is a potential sampling interference.

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

2.8. Safety precautions (sampling)

2.8.1. Attach the sampling equipment to the employees so that it will not interfere with work performance or safety.

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

3. Analytical Procedure

3.1. Apparatus

3.1.1. An HPLC equipped with an ultraviolet detector. A Waters HPLC consisting of a 600E pumping system, 990 photodiode array detector and 712 WISP auto-sampler was used in this evaluation.

3.1.2. An HPLC column capable of separating the analyte from the solvent and interferences. A Waters Radial-Pak 100-mm × 8-mm i.d. cartridge containing Nova-Pak C_{18} (end-capped 4-µm spherical particles) was used in conjunction with a Waters RCM-100 radial compression module.

3.1.3. An electronic integrator or some other suitable means of measuring peak areas or heights. A Hewlett-Packard 18652A A/D converter interfaced to a Hewlett-Packard 3357 Lab Automation Data System was used in this evaluation.

3.1.4. Small resalable glass vials with Teflon-lined caps capable of holding 4-mL. WISP-type auto-sampler vials were used in this evaluation.

3.1.5. A dispenser for methyl alcohol capable of delivering 3.0 mL.

3.1.6. 3A filtering apparatus to filter the extracted samples before they are injected into the HPLC. Disposable Cameo HPLC syringe filters (3-mm Magna Nylon 66 membrane filters, 5.0-µm pore size) manufactured by Micron Separations Inc. (available through Fisher Scientific) were used with a 10-mL Multi-fit glass syringe.

3.1.7. A pH meter with a combination electrode is used in the preparation of the HPLC mobile phase.

3.2. Reagents

3.2.1. *N*-Isopropylaniline and diphenylamine, reagent grade. The *N*-isopropylaniline used in this evaluation was purchased from Chem Service (West Chester, PA) and the diphenylamine was Lot 706921 from Fisher Scientific (Fair Lawn, NJ).

3.2.2. HPLC grade methyl alcohol and water. The methyl alcohol used in this evaluation was "b&j brand High Purity Solvent" manufactured by American Burdick and Jackson. The water was from an in-house Millipore Milli-Q water purification system.

3.2.3. Di-*n*-butylamine and phosphoric acid, reagent grade.

3.3. Standard preparation

3.3.1. Restrict the use of pure compounds and concentrated standards to regulated areas. Prepare concentrated stock standards by diluting the pure amines with methyl alcohol. Stock standards appear to be stable for at least three months when refrigerated.

3.3.2. Prepare analytical standards by injecting microliter amounts of stock standards into 4-mL vials containing 3.0 mL of methyl alcohol.

3.3.3. Bracket sample concentrations with analytical standard concentrations. If sample concentrations are higher than the upper range of prepared standards, prepare additional standards to ascertain detector response or dilute the methyl alcohol extract of the high samples.

3.4. Sample preparation

3.4.1. Transfer the sample filters to individual 4-mL vials.

3.4.2. Add 3.0 mL of methyl alcohol to each vial.

3.4.3. Recap and shake the vials end-to-end for 15 min.

3.4.4. Filter each sample extract with disposable filtration units prior to injection into the HPLC.

3.5. Analysis

3.5.1. HPLC conditions and information

mobile phase:	75/25, methyl alcohol/water containing 1.7 mL of di-*n*-butylamine per liter and buffered to pH 7.0 with phosphoric acid (paired-ion chromatography). To prepare 1 L of mobile phase, add 1.7 mL of di-*n*-butylamine to 250 mL of water, adjust the pH to 7.0 with phosphoric acid, and then add 750 mL of methyl alcohol. Degas prior to use.
flow rate:	2 mL/min
UV detector wavelength:	*N*-isopropylaniline, 245 nm diphenylamine, 285 nm
injection volume:	5 µL
column:	Waters Radial-Pak 100-mm × 8-mm i.d. cartridge containing Nova-Pak C_{18}
retention times:	*N*-isopropylaniline, 3.1 min diphenylamine, 4.1 min
chromatograms:	Section 4.10.

3.5.2. Measure peak areas or heights by use of an integrator or by other suitable means.

3.5.3. Construct a calibration curve by plotting response (peak areas or heights) of standard injections versus micrograms of analyte per sample. Bracket sample concentrations with standards.

3.6. Interferences (analytical)

3.6.1. Any compound that elutes in the same general time as the amine of interest is a potential interference. Suspected interferences reported to the laboratory with submitted samples by the industrial hygienist must be considered before samples are extracted.

3.6.2. HPLC parameters may be changed to possibly circumvent interferences.

3.6.3. Retention time on a single column is not considered proof of chemical identity. Analyte identity should be confirmed by mass spectrometry if possible.

3.7. Calculations

The analyte concentration for samples is obtained from the calibration curve in micrograms of analyte per sample. If any analyte is found on any back filter, that amount is added to the amount found on the corresponding front filter. If any analyte is found on the blank filters, the combined amount is subtracted from the combined sample amounts. The air concentrations are calculated using the following formulae:

$$\frac{mg}{m^3} = \frac{(ug\ of\ analyte\ per\ sample)}{(liters\ of\ air\ sampled)}$$

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

where

24.46 = the molar volume (liters) at 25 °C and 760 mm Hg

MW = 135.21 for *N*-isopropylaniline and 169.22 for diphenylamine

3.8. Safety precautions (analytical)

3.8.1. Restrict the use of pure compounds and concentrated standards to regulated areas. Avoid skin contact and inhalation of all chemicals.

3.8.2. Restrict the use of all chemicals to a fume hood if possible.

3.8.3. Wear safety glasses and a lab coat at all times while in the lab area.

4. Backup Data

4.1. Detection limit of the analytical procedure

The injection volume (5 µL) listed in Section 3.5.1. was used in the determination of the detection limit of the analytical procedure. The detection limit of 1.7 ng per injection for both *N*-isopropylaniline and diphenylamine was determined by analyzing dilute standards equivalent to 1.0 µg each of *N*-isopropylaniline and diphenylamine per sample. These amounts were judged to give peaks with heights approximately 5 times the baseline noise. Chromatograms are shown in Figures 4.1.1. and 4.1.2.

4.2. Detection limit of the overall procedure

The detection limits of the overall procedure were determined by analyzing filters spiked with loadings equivalent to the detection limits of the analytical procedure. Samples were prepared by injecting 1.0 µg each of *N*-isopropylaniline and diphenylamine onto acid-treated filters. These amounts are equivalent to 1.8 ppb (10 µg/m^3) and 10 µg/m^3 for *N*-isopropylaniline and diphenylamine respectively. The results are given in Tables 4.2.1. and 4.2.2.

Table 4.2.1.
Detection Limit of the Overall Procedure for *N*-Isopropylaniline

sample no.	µg spiked	µg recovered
1	1.0	0.971
2	1.0	0.928
3	1.0	0.942
4	1.0	0.985
5	1.0	1.00
6	1.0	0.971

Table 4.2.2.
Detection Limit of the Overall Procedure for Diphenylamine

sample no.	µg spiked	µg recovered
1	1.0	0.880
2	1.0	1.04
3	1.0	0.987
4	1.0	1.04
5	1.0	0.933
6	1.0	0.853

4.3. Reliable quantitation limit

The reliable quantitation limits were determined by analyzing filters spiked with loadings equivalent to the detection limits of the analytical procedure. Samples were prepared by injecting 1.0 µg each of *N*-isopropylaniline and diphenylamine onto acid-treated filters. These amounts are equivalent to 1.8 ppb (10 µg/m^3) and 10 µg/m^3 for *N*-isopropylaniline and diphenylamine respectively. The results are given in Tables 4.3.1. and 4.3.2.

Table 4.3.1.
Reliable Quantitation Limit for *N*-Isopropylaniline
(Based on samples and data of Table 4.2.1.)

sample no.	percent recovered	statistics
1	97.1	$\bar{x}$ = 96.6
2	92.8	
3	94.2	
4	98.5	SD = 2.7
5	100.0	Precision = ±(1.96)(2.7)
6	97.1	= ±5.3

Table 4.3.2.
Reliable Quantitation Limit for Diphenylamine
(Based on samples and data of Table 4.2.2.)

sample no.	percent recovered	statistics
1	88.0	$\bar{x}$ = 95.6
2	104.0	
3	98.7	
4	104.0	SD = 8.0
5	93.3	Precision = ±(1.96)(8.0)
6	85.3	= ±15.7

4.4. Instrument response to the analyte

The instrument response to the analytes over the range of 0.5 to 2 times the target concentrations was determined from multiple injections of analytical standards. These data are given in Tables 4.4.1. and 4.4.2. and Figure 4.4. The response is linear for both analytes with slopes (in area counts per micrograms of analyte per sample) of 1537 and 2614 for *N*-isopropylaniline and diphenylamine respectively.

Table 4.4.1.
Instrument Response to *N*-Isopropylaniline

× target conc.	0.5×	1×	2×
µg/sample	506.2	1012	2025
ppm	0.916	1.83	3.66
area counts	784080	1554040	3109350
	785996	1555610	3111450
	787603	1556630	3115480
	785875	1554250	3109950
	788350	1550440	3110050
	786308	1549730	3118030
$\bar{x}$ =	786369	1553450	3112385

Table 4.4.2.
Instrument Response to Diphenylamine

× target conc.	0.5×	1×	2×
µg/sample	501.8	1004	2007
mg/m^3	5.02	10.0	20.1
area counts	1349730	2684350	5274850
	1350460	2613570	5211220
	1354350	2616890	5220870
	1347210	2617630	5207250
	1347510	2628680	5233970
	1348040	2619460	5251500
$\bar{x}$ =	1349550	2630100	5233280

4.5. Storage test

Storage samples were generated by spiking sulfuric acid-treated glass fiber filters with amounts of analyte equal to the target concentrations (1012.5 µg of *N*-isopropylaniline, 1003.5 µg of diphenylamine). The filters were then assembled in three-piece cassettes with back filters. Thirty-six samples were prepared. One hundred liters of air at 82% relative humidity and 22.5 °C were then drawn through each sampling device. Six samples were analyzed immediately, fifteen were stored in a refrigerator at 0 °C, and fifteen were stored in a closed drawer at approximately 21 °C. Six samples, three from refrigerated and three from ambient storage, were analyzed at intervals over a period of fifteen days. The results are given in Tables 4.5.1. and 4.5.2. and shown graphically in Figures 4.5.1.1., 4.5.1.2., 4.5.2.1. and 4.5.2.2. The standard errors of estimate are 6.4 and 6.3% and the 95% confidence limits (±1.96 SD) are ±12.5 and ±12.3% for *N*-isopropylaniline and diphenylamine respectively. These values were obtained from Figures 4.5.1.2. and 4.5.2.2. for the ambient storage samples.

Table 4.5.1.
Storage Test for *N*-Isopropylaniline

storage time	% recovery					
(days)	(refrigerated)			(ambient)		
0	90.1	84.6	89.4	90.1	84.6	89.4
0	96.4	96.8	87.3	96.4	96.8	87.3
4	86.3	91.2	93.5	92.7	87.3	89.9
6	84.0	90.8	88.8	95.0	95.9	93.4
9	95.9	89.7	93.4	92.3	99.1	92.5
10	89.0	82.9	87.9	89.3	89.5	89.9
15	91.5	89.5	93.2	88.8	90.4	98.7

Table 4.5.2.
Storage Test for Diphenylamine

storage time	% recovery					
(days)	(refrigerated)			(ambient)		
0	93.7	95.0	95.8	93.7	95.0	95.8
0	95.8	95.4	97.8	95.8	95.4	97.8
4	92.4	90.6	89.6	79.4	87.2	93.9
6	97.4	94.1	95.2	94.7	81.4	89.3
9	88.3	95.1	91.6	84.9	80.8	82.1
10	90.6	89.0	90.5	86.2	83.0	81.3
15	85.0	83.3	86.7	75.9	73.8	76.9

4.6. Precision (analytical method only)

The precision of the analytical method for each analyte is the pooled coefficient of variation determined from replicate injections of standards. The precision of the analytical method for each analyte is given in Tables 4.6.1. and 4.6.2. These tables are based on the data presented in Section 4.4.

Table 4.6.1.
Precision of the Analytical Method for *N*-Isopropylaniline

× target conc.	0.5×	1×	2×
µg/sample	506.2	1012	2025
ppm	0.916	1.83	3.66
SD (area counts)	1488	2781	3547
CV	0.0019	0.0018	0.0011
$\overline{CV}$ = 0.0016			

Table 4.6.2.
Precision of the Analytical Method for Diphenylamine

× target conc.	0.5×	1×	2×
µg/sample	506.2	1012	2025
ppm	0.916	1.83	3.66
SD (area counts)	2676	27061	25995
CV	0.0020	0.0103	0.0050
$\overline{CV}$ = 0.0067			

4.7. Precision (overall procedure)

The precision of the overall procedure is determined from the storage data. The determination of the standard error of estimate (SEE) for a regression line plotted through the graphed storage data allows the inclusion of storage time as one of the factors affecting overall precision. The SEE is similar to the standard deviation, except it is a measure of dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

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

where

n = total no. of data points

k = 2 for a linear regression

k = 3 for a quadratic regression

Y_{obs} = observed % recovery at a given time

Y_{est} = estimated % recovery from the regression line at the same given time

An additional 5% for pump error is added to the SEE by the addition of variances. The precision at the 95% confidence level is obtained by multiplying the SEE (with pump error included) by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). The 95% confidence intervals are drawn about their respective regression lines in the storage graphs. The precisions of the overall procedure of ±12.5% for *N*-isopropylaniline and ±12.3% for diphenylamine were obtained from Figures 4.5.1.2. and 4.5.2.2. respectively.

4.8. Reproducibility

Six samples were prepared by injecting microliter quantities of standards onto acid-treated filters. The samples were stored at approximately 23 °C for 2 days. The samples were analyzed by a chemist unassociated with this evaluation. The results are given in Tables 4.8.1. and 4.8.2. The precision of the overall procedure is ±12.5% for *N*-isopropylaniline and ±12.3% for diphenylamine.

Table 4.8.1.
Reproducibility for *N*-Isopropylaniline

sample no.	µg expected	µg found	% found	% deviation
1	1086	1085	99.9	-0.1
2	723.8	715.6	98.9	-1.1
3	1086	1066	98.2	-1.8
4	361.9	364.8	100.8	+0.8
5	723.8	713.4	98.6	-1.4
6	361.9	352.0	97.3	-2.7

Table 4.8.2.
Reproducibility for Diphenylamine

sample no.	µg expected	µg found	% found	% deviation
1	770.3	759.3	98.6	-1.4
2	385.1	368.7	95.7	-4.3
3	770.3	746.6	96.9	-3.1
4	1155	1130	97.8	-2.2
5	1155	1117	96.7	-3.3
6	385.1	364.2	94.6	-5.4

4.9. Extraction efficiency

Six sample filters for each amine were spiked with the target concentration amounts by liquid injection (1012 µg of *N*-isopropylaniline and 1004 µg of diphenylamine). These samples were analyzed to determine the extraction efficiencies. To determine the stability of extracted samples, these samples were allowed to remain at room temperature for 24 h after extraction and were reanalyzed using fresh standards. The results are given in Tables 4.9.1. and 4.9.2.

Table 4.9.1.
Extraction Efficiency for *N*-Isopropylaniline

sample no.	% extracted	% extracted (reanalyzed after 24 h)
1	99.2	98.0
2	100.7	99.6
3	100.6	99.6
4	101.0	99.7
5	100.8	99.5
6	100.5	98.9
$\bar{x}$	100.5	99.2

Table 4.9.2.
Extraction Efficiency for Diphenylamine

sample no.	% extracted	% extracted (reanalyzed after 24 h)
1	99.1	97.9
2	100.4	99.7
3	100.9	99.4
4	100.9	99.5
5	100.5	99.1
6	100.5	98.8
$\bar{x}$	100.4	99.1

4.10. Chromatograms

Chromatograms of an analytical standard are shown in Figure 4.10. The chromatograms are from a 5-µL injection of a standard approximately equal to the target concentration for each analyte (1012 and 1004 µg of *N*-isopropylaniline and diphenylamine per sample respectively) for a 100-L sample.

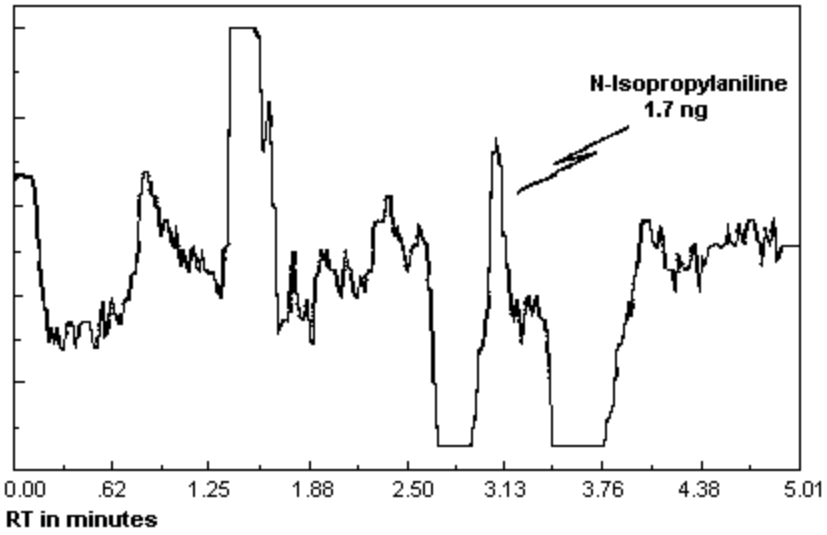


Figure 4.1.1. Detection limit chromatogram for *N*-isopropylaniline.

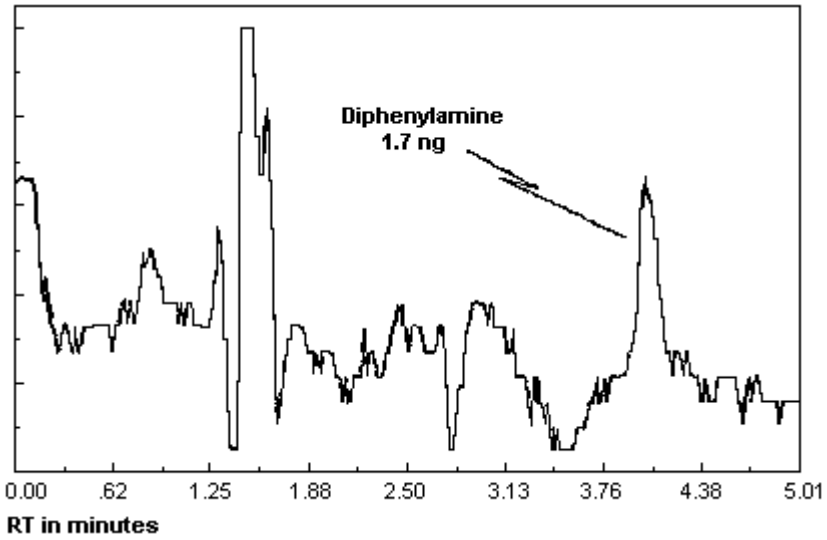


Figure 4.1.2. Detection limit chromatogram for diphenylamine.

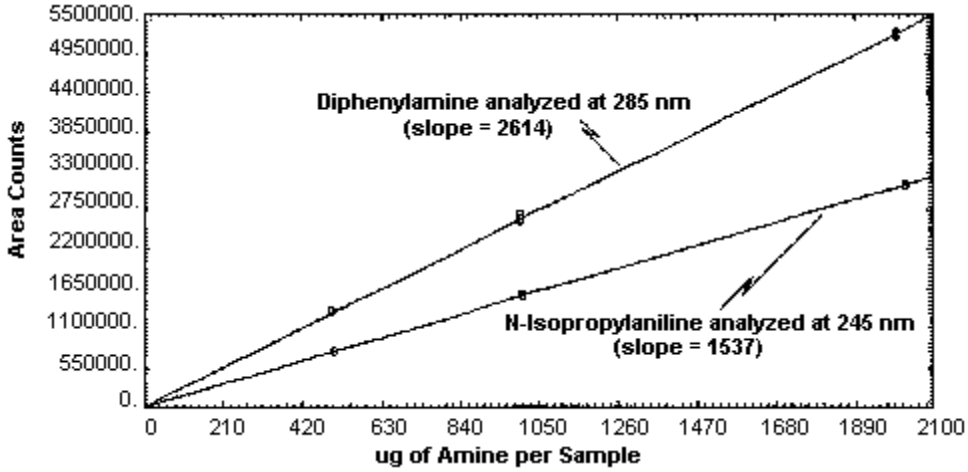


Figure 4.4. Instrument response to *N*-isopropylaniline and diphenylamine.

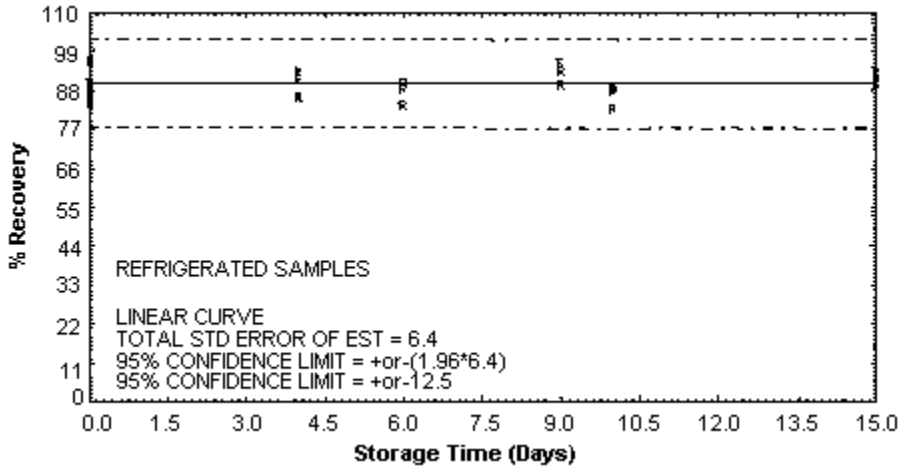


Figure 4.5.1.1. Refrigerated *N*-isopropylaniline storage samples.

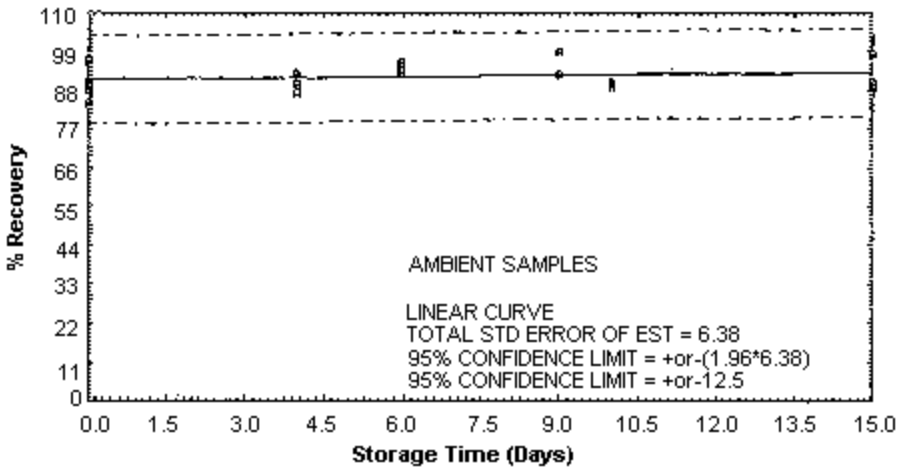


Figure 4.5.1.2. Ambient *N*-isopropylaniline storage samples.

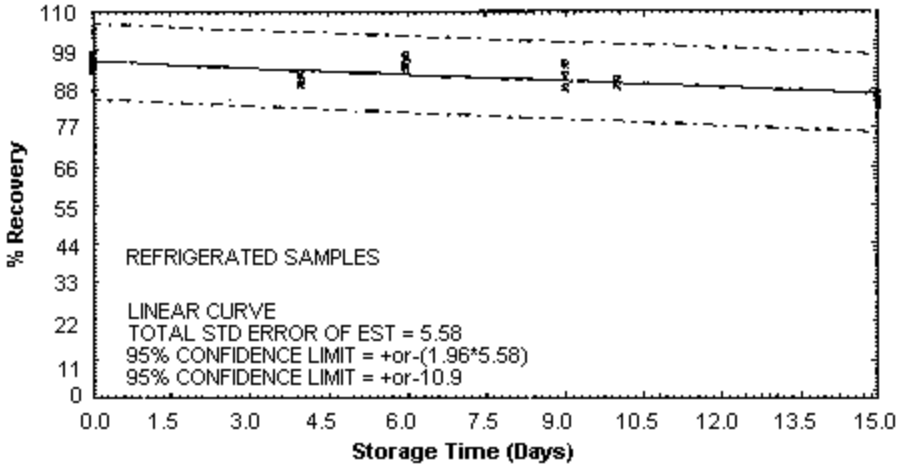


Figure 4.5.2.1. Refrigerated diphenylamine storage samples.

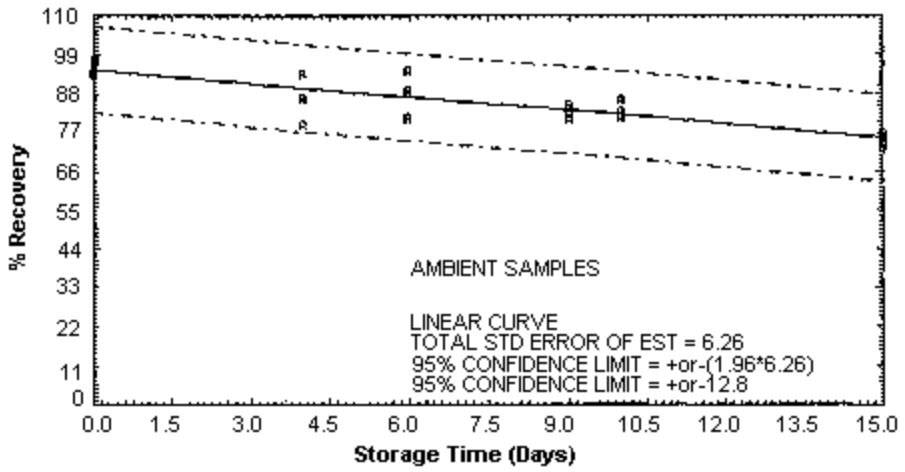


Figure 4.5.2.2. Ambient diphenylamine storage samples.

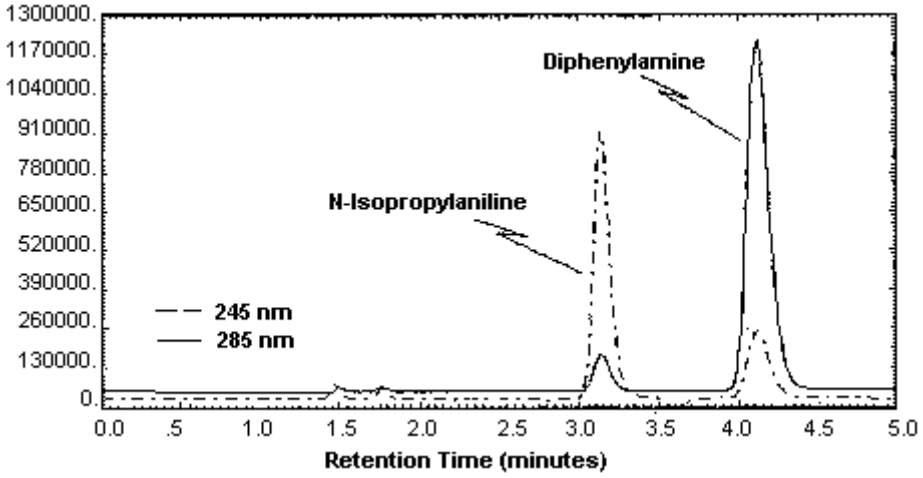


Figure 4.10. Chromatograms of a standard at the target concentrations.

5. References

5.1. "OSHA Analytical Methods Manual" U.S. Department of Labor, Occupational Safety and Health Administration; OSHA Analytical Laboratory: Salt Lake City, UT, 1985; Method 22; American Conference of Governmental Industrial Hygienists (ACGIH): Cincinnati, OH, ISBN: 0-936712-66-X.

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