4-AMINODIPHENYL (4-AMINOBIPHENYL)
α-NAPHTHYLAMINE (1-NAPHTHYLAMINE)
β-NAPHTHYLAMINE (2-NAPHTHYLAMINE)

Method number: 93

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 the ring section. The sample filters are transferred to separate glass vials containing 2 mL of deionized water within 10 h after sampling. Quantitation is performed by analyzing the heptafluorobutyric acid anhydride derivatives of the amines by gas chromatography using an electron capture detector.

Recommended air volume and sampling rate: 100 L at 1 L/min

	4-Aminobiphenyl	1-Naphthylamine	2-Naphthylamine
Target concentration:	1 ppb (6.9 µg/m^3)	1 ppb (5.9 µg/m^3)	1 ppb (5.9 µg/m^3)
Reliable quantitation limit:	1 ppt (6.9 ng/m^3)	1 ppt (5.9 ng/m^3)	1 ppt (5.9 ng/m^3)
Standard error of estimate at the target concentration:	5.3%	5.5%	5.3%

Status of method: Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: January 1992

Chemist: Carl J. Elskamp

Organic Methods Evaluation Branch
OSHA Salt Lake Technical Center
Salt Lake City, UT 84165-0200

1. General Discussion

1.1 Background

1.1.1 History

4-Aminobiphenyl, 1-naphthylamine and 2-naphthylamine are considered by OSHA to be carcinogens and the manufacture and use of all three are covered by special regulations published in the Code of Federal Regulations. (Refs. 5.1-5.3) There is no mention of permissible air concentrations in any of the regulations, so arbitrary target concentrations of 1 ppb were selected for this evaluation. Previously, the methodology recommended by OSHA for the determination of air concentrations of 4-aminobiphenyl involved collection with an impinger containing isopropanol. This practice is not only inconvenient and possibly dangerous for sampling and shipment of samples, it also has not been fully validated. The recommended collection of 1-naphthylamine and 2-naphthylamine utilized glass fiber filters backed up with silica gel tubes, which was based on NIOSH Method 5518. (Ref. 5.4) The obvious disadvantage with this method is that the collected samples are unstable at ambient temperature and must therefore be kept at freezer temperatures until analyzed.

Methodology based on collection with sulfuric acid-treated glass fiber filters has previously been validated at the OSHA Salt Lake Technical Center to determine a number of other aromatic amines. (Refs. 5.5-5.10) Depending on the target concentration of the particular amine, the analysis is performed by direct analysis by HPLC or by reacting the amine with heptafluorobutyric acid anhydride (HFAA) and analyzing the resulting derivative by GC. The latter procedure was chosen for these three amines to achieve the necessary sensitivity for the 1 ppb target concentrations. As was the case with some of the other amines, the sample filters must be transferred to vials containing deionized water within 10 h after sampling to enhance sample stability. This time constraint was chosen to be consistent with other methods having this requirement.

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

All three of these amines are listed as being carcinogens by OSHA and are covered by special regulations to minimize worker exposure by any route. (Refs. 5.1-5.3) 2-Naphthylamine and 4-aminobiphenyl are categorized as A1-Confirmed Human Carcinogens, without a TLV by the American Conference of Governmental Industrial Hygienists (ACGIH), whereas it is recommended that workers should be properly equipped to eliminate to the fullest extent possible all exposures to these two amines. (Ref. 5.11)

Exposure to 4-aminobiphenyl has been associated with a high incidence of bladder cancer in humans, thus the International Agency for Research on Cancer (IARC) states that there is sufficient evidence that it is carcinogenic to humans. (Ref. 5.12)

It has not been established whether 1-naphthylamine is a human carcinogen per se or is associated with an excess of bladder cancer due to its 2-naphthylamine content. Occupational exposure to commercial 1-naphthylamine containing 4-10% of 2-naphthylamine is strongly associated with bladder cancer. IARC states there is inadequate evidence that 1-naphthylamine is a human carcinogen. (Ref. 5.13)

2-Naphthylamine is a known human bladder carcinogen. There is also evidence that several metabolites of 2-naphthylamine are animal carcinogens. (Ref. 5.14)

1.1.3 Workplace exposure

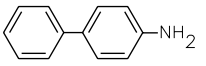
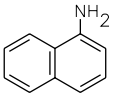
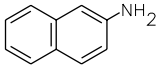
4-Aminobiphenyl is no longer manufactured commercially and is used only for research purposes. It had formerly been used as a highly efficient rubber antioxidant and as a dye

intermediate. It was reportedly an impurity in pre-1900 samples of aniline and is present in some samples of diphenylamine. (Ref. 5.12)

1-Naphthylamine is used in the manufacture of dyes, condensation colors, and rubber and in the synthesis of a large number of chemicals such as naphthionic acid (1-naphthylamine-4-sulphonic acid), N-1-naphthylphthalamic acid (an herbicide), N-phenyl-1-naphthylamine and 1-naphthol. 1-Naphthylamine does not occur as such in nature, but has been reported to be found in coal tar. Most commercial 1-naphthylamine, which is prepared by nitration of naphthalene and reduction of the products, contains 4-10% of 2-naphthylamine if synthesized by methods used in previous decades. Modern techniques have lowered this content to a maximum of 0.5%. (Ref. 5.13)

2-Naphthylamine is presently used only for research purposes. It had been used extensively as an intermediate in the manufacture of dyes and as an antioxidant for rubber. It is present as an impurity in 1-naphthylamine. It does not occur in nature as such, but can be formed in the pyrolysis of nitrogen-containing organic matter. It has been found in coal-tar and in cigarette smoke. (Ref. 5.14)

1.1.4 Physical properties and other descriptive information (Ref. 5.12-5.14)

	4-aminobiphenyl	1-naphthylamine	2-naphthylamine
CAS number:	92-67-1	134-32-7	91-59-8
molecular weight:	169.22	143.2	143.2
melting point:	53°C	50°C	111-113°C
boiling point:	191°C (2 kPa)	301°C	306°C
description:	colorless crystals turning dark upon oxidation	colorless crystals which darken in air to a reddish-purple color; unpleasant odor	colorless crystals which darken in air to a reddish-purple color
solubility:	very slightly soluble in cold water; soluble in hot water and non-polar solvents; soluble in lipids	0.16% dissolves in water at 25°C; freely soluble in alcohol, ether and many other organic solvents	soluble in hot water, alcohol, ether and many other organic solvents
structural formula:			

Physical properties and other descriptive information (continued)

	4-aminobiphenyl	1-naphthylamine	2-naphthylamine
synonyms:	4-biphenylamine; *p*-aminobiphenyl; *p*-aminodiphenyl; 4-aminodiphenyl; *p*-biphenylamine; *p*-phenylaniline; xenylamine	α-naphthylamine; 1-aminonaphthalene; C.I. Azoic Diazo Component 114 (Colour Index); Fast Garnet B Base; Fast Garnet Base B; naphthalidam; naphthalidine	β-naphthylamine; 2-aminonaphthalene; BNA; Fast Scarlet Base B

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppb and ppt are referenced to 25°C and 101.3 kPa (760 mmHg). Although the derivatives of the amines are analyzed, the equivalent masses of the amines are listed throughout the method.

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limits of the analytical procedure are 10.5, 8.9, and 8.9 fg per injection for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively. These are the amounts of each analyte that will produce peaks with heights that are approximately five times the baseline noise. (Section 4.1)

1.2.2 Detection limit of the overall procedure

The detection limits of the overall procedure are 0.677, 0.583, and 0.598 ng per sample for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively. These are the amounts of each analyte spiked on filters that, upon analysis, produce a peak similar in size to that of the respective detection limit of the analytical procedure. These detection limits correspond to air concentrations of 1 ppt (6.9 ng/m^3), 1 ppt (5.9 ng/m^3), and 1 ppt (5.9 ng/m^3) for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively. (Section 4.2)

1.2.3 Reliable quantitation limit

The reliable quantitation limits are 0.677, 0.583, and 0.598 ng per sample for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively. These are the smallest amounts of each analyte spiked on sample filters that 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 ppt (6.9 ng/m^3), 1 ppt (5.9 ng/m^3), and 1 ppt (5.9 ng/m^3) for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine 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 the three analytes. (Section 4.4)

1.2.5 Recovery

The recoveries of 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine from samples used in 15-day storage tests remained above 98%, 83%, and 97% respectively. The sample filters were stored in vials containing 2 mL of deionized water in a closed drawer at approximately 21°C. (Section 4.5)

1.2.6 Precision (analytical method only)

The pooled coefficients of variation obtained from replicate injections of analytical standards at 0.5, 1, and 2 times the target concentrations are 0.014, 0.013, and 0.014 for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively. (Section 4.6)

1.2.7 Precision (overall procedure)

The precisions at the 95% confidence level for the 15-day storage tests are ±10.5, ±10.8, and ±10.3% for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively.

These include an additional ±5% for sampling error. The sample filters were stored in vials containing 2 mL of deionized water in a closed drawer at approximately 21°C. (Section 4.7)

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 0°C. No individual sample result deviated from its theoretical value by more than the corresponding 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.

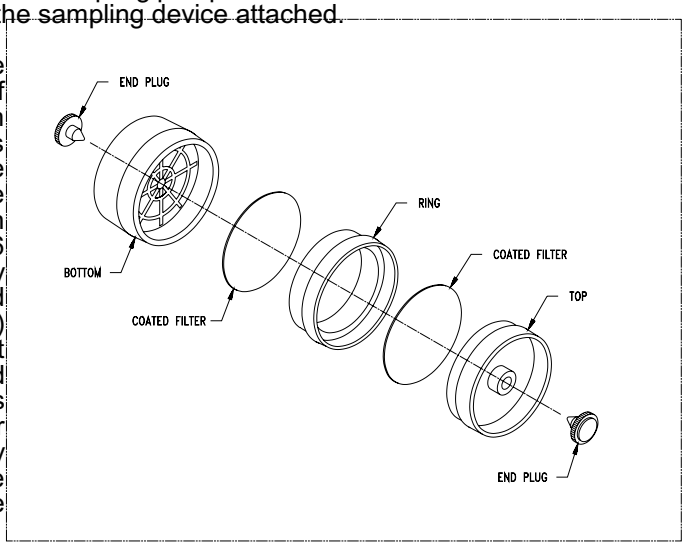
1.3.2 The analysis is rapid, sensitive, and precise.

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 polystyrene 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 cassettes without support pads. The front filter is separated from the back filter by the ring section. The cassettes are sealed with shrink bands and the ends are plugged with plastic plugs.



2.1.3 Small sealable vials with volumes of at least 7 mL are needed for sample shipment and storage. Glass scintillation vials with caps containing Teflon liners are recommended.

2.2 Reagents

Deionized water is needed for addition to the vials described in Section 2.1.3.

2.3 Sampling technique

2.3.1 Remove the plastic end 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 Immediately after sampling, seal the sampling device with plastic end plugs until the filters are transferred to vials containing deionized water.

2.3.4 At some convenient time within 10 h of sampling, carefully remove the filters from the cassettes and individually transfer them to separate vials. Add approximately 2 mL of deionized water to each vial. The water can be added before or after the filters are transferred.

2.3.5 Seal and identify each vial with an OSHA Form 21.

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

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

2.4 Collection efficiency

Collection efficiency studies were conducted by drawing humid air through a sampling device that was attached to a glass U-tube which was immersed in an oil bath heated to 70° C. Microliter amounts of stock standards were injected into the U-tube. Tests were done by adding amounts of amines approximately equal to two times the target concentrations for a 100-L sample (1.35 µg of 4-aminobiphenyl, 1.17 µg of 1-naphthylamine, and 1.20 µg of 2-naphthylamine). Similar tests were done by adding amounts approximately equal to ten times the target concentrations (6.77 µg of 4-aminobiphenyl, 5.83 µg of 1-naphthylamine, and 5.98 µg of 2-naphthylamine). The inlet of the U-tube was attached to a humid air generator so air at approximately 80% relative humidity could be drawn through it. After sampling for 100 min at 1 L/min, the filters were analyzed. None of the amines were found on any of the back filters for any of the tests.

2.5 Extraction efficiency

2.5.1 The average extraction efficiencies from six filters for each amine spiked at the target concentration are 99.6%, 99.5%, and 100.0% for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively. (Section 4.9)

2.5.2 The stability of extracted and derivatized samples was verified by reanalyzing the extraction efficiency samples 24 h later using fresh standards. The average recoveries for the reanalyzed samples are 100.9%, 99.5%, and 101.0% for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine 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 When short-term samples are required, the reliable quantitation limits will be larger. For example, the reliable quantitation limit for 4-aminobiphenyl for a 15-L air sample would be 6.7 ppt (46 ng/m^3).

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 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 A GC equipped with an electron capture detector. A Hewlett-Packard 5890A Gas Chromatograph equipped with a Nickel 63 electron capture detector and a 7673A autosampler was used in this evaluation.

3.1.2. A GC column capable of separating the amine derivatives from the solvent and interferences. A 15-m × 0.32-mm i.d., 1.0-µm film thickness, SPB-5 fused silica column (Cat. no. 2-4100M, Supelco, Inc., Bellefonte, PA) was used in this evaluation.

3.1.3 An electronic integrator or some other suitable means of measuring peak areas or heights. A Waters 860 Networking Computer System was used in this evaluation.

3.1.4 Small resealable vials with Teflon-lined caps capable of holding 4 mL.

3.1.5 A dispenser or pipet for toluene capable of delivering 2.0 mL.

3.1.6 Pipets (or repetitive pipets with plastic or Teflon tips) capable of delivering 1 mL for dispensing the sodium hydroxide and buffer solutions.

3.1.7 A repetitive pipet to deliver 25 µL of heptafluorobutyric acid anhydride (HFAA).

3.1.8 Disposable pipets to transfer the toluene layers after the samples are extracted.

3.1.9 A laboratory centrifuge.

3.2 Reagents

3.2.1 Saturated and 0.5 N NaOH solutions, prepared from reagent grade NaOH.

3.2.2 Toluene. American Burdick and Jackson "High Purity Solvent" brand toluene was used.

3.2.3 Heptafluorobutyric acid anhydride (HFAA). HFAA from Aldrich Chemical Company was used.

3.2.4 Phosphate buffer, prepared by dissolving 136 g of reagent grade potassium dihydrogen phosphate in approximately 900 mL of deionized water, adjusting the pH to 7.0 with saturated sodium hydroxide solution, and diluting to 1 L with deionized water.

3.2.5 4-Aminobiphenyl, 1-naphthylamine and 2-naphthylamine reagent grade. The amines used in this evaluation were purchased from Aldrich Chemical Company, Inc., Milwaukee, WI.

3.3 Standard preparation

3.3.1 ***CAUTION. THESE AROMATIC AMINES ARE CARCINOGENIC***. Restrict use of pure compounds and concentrated standards to regulated areas. Prepare concentrated stock standards by diluting the pure amines with toluene. Prepare analytical standards by injecting microliter amounts of diluted stock standards into vials that contain 2.0 mL of toluene. For example, prepare a 1.204 µg/µL stock standard of 4-aminobiphenyl by dissolving 30.10 mg into 25.00 mL of toluene. Dilute 3.00 mL of this stock to 25.00 mL to give a concentration of 0.1445 µg/µL. Prepare an analytical standard of 0.694 µg/sample by adding 4.80 µL of this solution to 2.0 mL of toluene.

3.3.2 Add 25 µL of HFAA to each vial. Recap and shake the vials for 10 s.

3.3.3 After allowing 10 min for the derivatives to form, add 1 mL of buffer to each vial to destroy the excess HFAA and to extract the heptafluorobutyric acid that is formed.

3.3.4 Recap and shake the vials for 10 s.

3.3.5 After allowing the two layers to separate, analyze the toluene (upper) layer of each standard by GC.

3.3.6 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.

3.4 Sample preparation

3.4.1 The sample filters are received in vials containing deionized water.

3.4.2 Add 1 mL of 0.5 N NaOH and 2.0 mL of toluene to each vial.

3.4.3 Recap and shake the vials for 10 min.

3.4.4 Centrifuge the vials at 2500 rpm for 10 min.

3.4.5 Transfer approximately 1 mL of the toluene (upper) layer of each sample to separate vials with clean disposable pipets.

3.4.6 Add 25 µL of HFAA to each vial containing the transferred toluene layer. Recap and shake the vials for 10 s.

3.4.7 After allowing 10 min for the derivatives to form, add 1 mL of buffer to each vial to destroy the excess HFAA and to extract the heptafluorobutyric acid that is formed.

3.4.8 Recap and shake the vials for 10 s.

3.4.9 After allowing the two layers to separate, analyze the toluene (upper) layer of each sample by GC.

3.5 Analysis

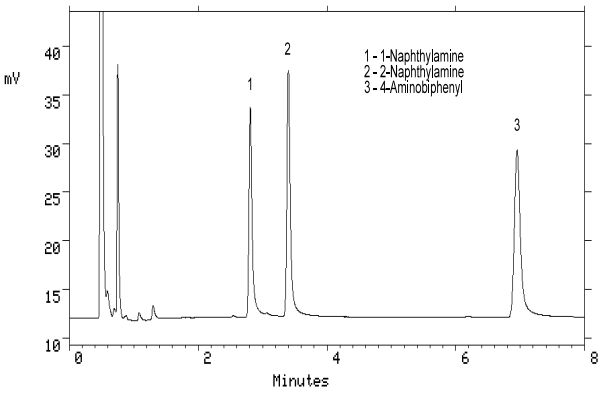
3.5.1 GC conditions and information

zone temperatures:	column, 180°C injector, 250°C detector, 300°C
gas flows:	column, 1.6 mL/min hydrogen (32 kPa head pressure) make up, 67 mL/min nitrogen

GC conditions and information (continued)

injection volume:	1.0 µL
split ratio:	33:1
column:	SPB-5, 1.0-µm df, 15-m × 0.32-mm i.d. fused silica (Supelco, Inc.)
retention times of derivatives:	1-naphthylamine, 2.8 min 2-naphthylamine, 3.4 min 4-aminobiphenyl, 7.0 min

chromatogram at 1×
the target concentrations:



3.5.2 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 HFAA derivative of 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 derivatized.

3.6.2 GC 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 GC/MS if possible.

3.7 Calculations

The analyte concentration for samples is obtained from the calibration curve in micrograms of analyte per sample. The back filter is analyzed to determine if there was any breakthrough from the front filter during sampling. If any analyte is found on any back filter, that amount is added to the amount found on the corresponding front filter. The combined amount is then corrected by subtracting the total amount (if any) found on the corresponding blank filters. The air concentrations are calculated using the following formulae. Extraction efficiency corrections are not necessary because the extraction efficiencies are essentially 100% for all three analytes.

$$\mu g/m^3 = \frac{(\mu g \text{ analyte per sample})(1000)}{(L \text{ of air sampled})}$$

$$ppb = (\mu g/m^3)(24.46)/(\text{molecular weight of analyte})$$

where 24.46 is the molar volume at 25°C and 101.3 kPa (760 mmHg)
and molecular weights are:

4-aminobiphenyl	169.22
1-naphthylamine	143.2
2-naphthylamine	143.2

3.8 Safety precautions (analytical)

3.8.1 ***CAUTION. THESE AROMATIC AMINES ARE CARCINOGENIC***. Restrict 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 (1 µL with a 33:1 split ratio) listed in Section 3.5.1. was used in the determination of the detection limits of the analytical procedure. The detection limits of 10.5, 8.9, and 8.9 fg per injection were determined by analyzing dilute standards equivalent to 0.677, 0.583, and 0.598 ng per sample for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively. These amounts were judged to give peaks with heights approximately five times the baseline noise.

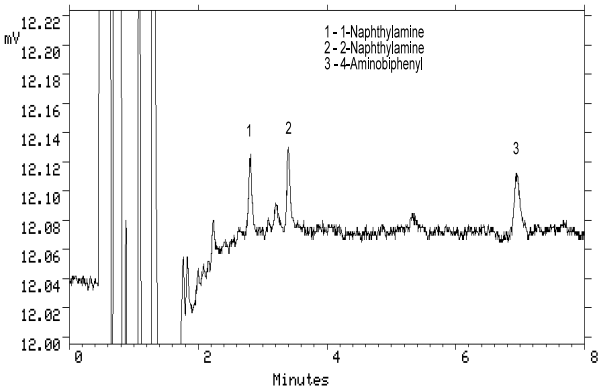


Figure 4.1. Detection limit chromatogram.

4.2 Detection limit of the overall procedure

The detection limits of the overall procedure were determined by analyzing filters spiked with 0.677, 0.583, and 0.598 ng of 4-aminobiphenyl, 1-naphthyl-amine and 2-naphthylamine respectively. These amounts correspond to air concen-trations of 1 ppt (6.9 ng/m^3), 1 ppt (5.9 ng/m^3), and 1 ppt (5.9 ng/m^3) for 4-amino-biphenyl, 1-naphthylamine and 2-naphthyl-amine respectively.

Table 4.2.1
Detection Limit of the Overall Procedure for 4-Aminobiphenyl

sample no.	ng spiked	ng recovered
1	0.677	0.679
2	0.677	0.711
3	0.677	0.737
4	0.677	0.692
5	0.677	0.729
6	0.677	0.672

Table 4.2.2
Detection Limit of the Overall Procedure for 1-Naphthylamine

sample no.	ng spiked	ng recovered
1	0.583	0.538
2	0.583	0.602
3	0.583	0.530
4	0.583	0.634
5	0.583	0.556
6	0.583	0.643

Table 4.2.3
Detection Limit of the Overall Procedure for 2-Naphthylamine

sample no.	ng spiked	ng recovered
1	0.598	0.583
2	0.598	0.533
3	0.598	0.548
4	0.598	0.544
5	0.598	0.563
6	0.598	0.541

4.3 Reliable quantitation limit

The reliable quantitation limits were determined by analyzing filters spiked with 0.677, 0.583, and 0.598 ng of 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively. These amounts correspond to air concentrations of 1 ppt (6.9 ng/m^3), 1 ppt (5.9 ng/m^3), and 1 ppt (5.9 ng/m^3) for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively.

Table 4.3.1
Reliable Quantitation Limit for 4-Aminobiphenyl
(Based on samples and data of Table 4.2.1)

percent recovered	statistics
100.3	
105.0	mean = 103.9
108.9	SD = 3.9
102.2	Precision = (1.96)(±3.9)
107.7	= ±7.6
99.3	

Table 4.3.2
Reliable Quantitation Limit for 1-Naphthylamine
(Based on samples and data of Table 4.2.2)

percent recovered	statistics
92.3	
103.3	mean = 100.2
90.9	SD = 8.4
108.7	Precision = (1.96)(±8.4)
95.4	= ±16.5
110.3	

Table 4.3.3
Reliable Quantitation Limit for 2-Naphthylamine
(Based on samples and data of Table 4.2.3)

percent recovered	statistics
97.5	
89.1	mean = 92.3
91.6	SD = 3.0
91.0	Precision = (1.96)(±3.0)
94.1	= ±5.9
90.5	

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. The response is linear for the three analytes with slopes (in area counts per micrograms of analyte per sample) of 190400, 123200, and 172400 for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively.

Table 4.4.1
Instrument Response to 4-Aminobiphenyl

× target concn	0.5×	1×	2×
µg/sample	0.339	0.677	1.355
ppb	0.49	0.98	1.96
area counts	64841	128816	257703
	63055	132970	261767
	63620	133544	255652
	63151	131985	257136
	64492	134002	257652
	65873	130839	260021
mean	64172	132026	258322

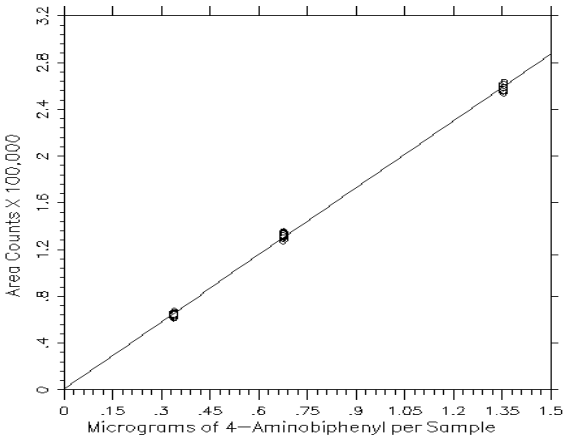


Figure 4.4.1. Instrument response to 4-aminobiphenyl

Table 4.4.2
Instrument Response to 1-Naphthylamine

× target concn	0.5×	1×	2×
µg/sample	0.291	0.583	1.165
ppb	0.50	1.00	1.99
area counts	42400	80354	151193
	41258	82766	152475
	41927	82878	148871
	41581	82221	149651
	41957	83052	149624
	43062	80568	151190
mean	42031	81973	150501

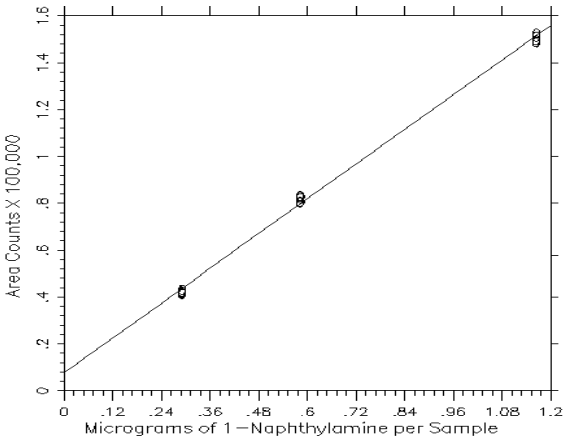


Figure 4.4.2. Instrument response to 1-naphthylamine.

Table 4.4.3
Instrument Response to 2-Naphthylamine

× target concn	0.5×	1×	2×
µg/sample	0.299	0.598	1.196
ppb	0.51	1.02	2.02
area counts	53264	105343	208686
	51596	108522	210998
	52491	108774	205566
	51609	107742	206601
	52797	108949	206832
	53743	105887	208931
mean	52583	107536	207936

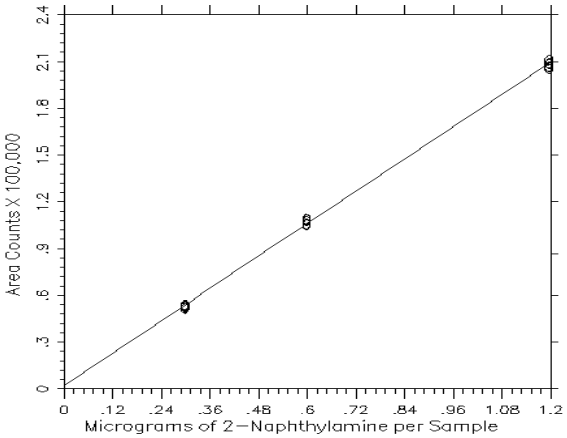


Figure 4.4.3. Instrument response to 2-naphthylamine.

4.5 Storage test

Thirty-six storage samples were generated by spiking sulfuric acid-treated glass fiber filters with amounts of analyte equal to the target concentrations (0.677, 0.583, and 0.598 µg of 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively). The filters were then assembled in cassettes and 100 L of air at approximately 80% relative humidity and 21 °C were then drawn through each sampling device. Within 1 h after the completion of drawing air through the devices, the filters were transferred to scintillation vials, each containing 2 mL of deionized water. 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 recoveries of 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine from samples stored at ambient temperature remained above 98%, 83%, and 97% respectively.

Table 4.5.1
Storage Test for 4-Aminobiphenyl

days of storage	% recovery (refrigerated)			% recovery (ambient)		
0	97.3	94.5	96.9	97.3	94.5	96.9
0	96.4	99.6	100.4	96.4	99.6	100.4
3	95.4	100.1	96.6	98.7	97.3	100.7
6	98.8	93.2	99.5	98.2	99.2	99.8
9	100.8	85.5	101.6	100.3	97.7	102.6
12	95.7	97.9	97.3	98.9	98.6	98.2
15	101.9	99.7	100.8	102.5	97.3	98.2

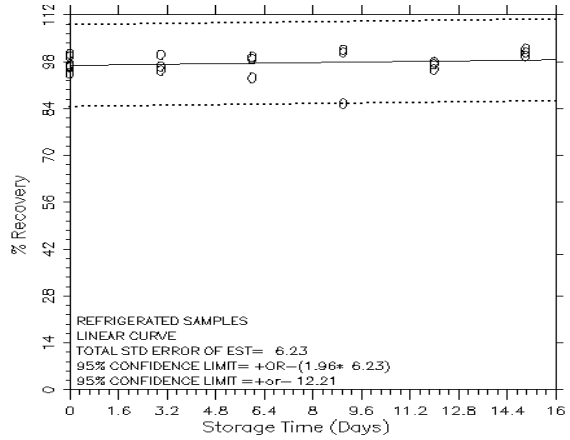


Figure 4.5.1.1. Refrigerated 4-aminobiphenyl storage samples.

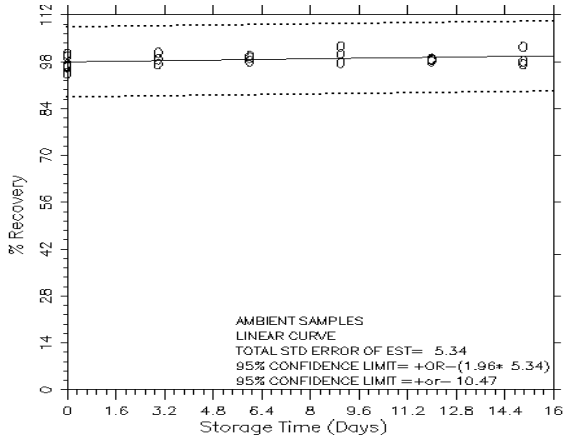


Figure 4.5.1.2. Ambient 4-aminobiphenyl storage samples.

Table 4.5.2
Storage Test for 1-Naphthylamine

days of storage	% recovery (refrigerated)			% recovery (ambient)		
0	96.4	95.1	97.1	96.4	95.1	97.1
0	98.1	100.7	100.5	98.1	100.7	100.5
3	92.5	98.8	93.5	89.6	90.6	93.5
6	99.5	94.2	100.0	91.6	92.3	91.1
9	97.0	83.4	98.3	88.6	87.7	90.3
12	95.2	95.9	97.0	89.6	87.0	88.9
15	100.0	99.2	98.3	83.2	82.7	80.8

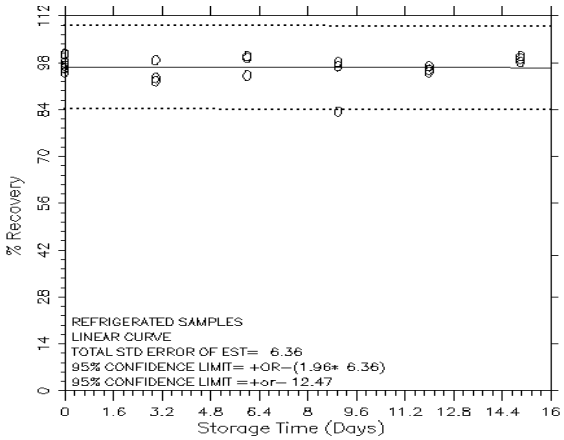


Figure 4.5.2.1. Refrigerated 1-naphthylamine storage samples.

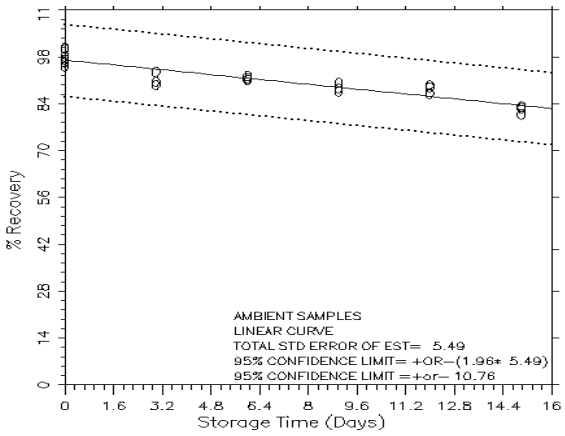


Figure 4.5.2.2. Ambient 1-naphthylamine storage samples.

Table 4.5.3
Storage Test for 2-Naphthylamine

days of storage	% recovery (refrigerated)			% recovery (ambient)		
0	96.8	95.0	95.8	96.8	95.0	95.8
0	97.3	100.3	99.8	97.3	100.3	99.8
3	93.8	99.5	94.7	96.5	95.7	99.2
6	98.8	92.6	99.3	98.0	98.0	98.6
9	96.6	84.6	100.2	97.3	96.5	99.6
12	96.5	97.3	98.1	98.3	97.0	97.0
15	99.8	98.8	98.1	97.6	95.6	94.0

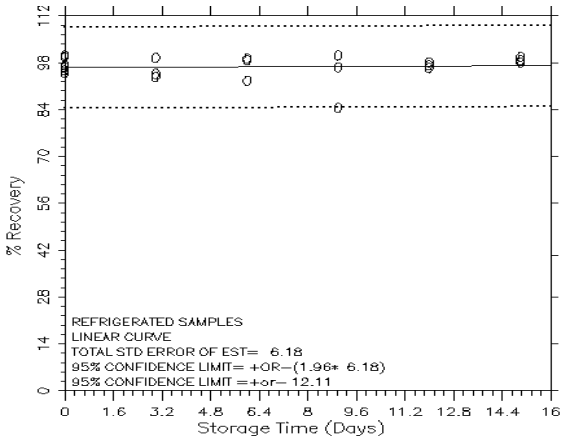


Figure 4.5.3.1. Refrigerated 2-naphthylamine storage samples.

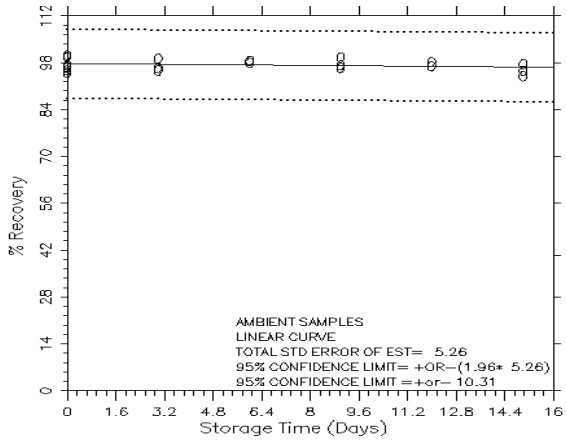


Figure 4.5.3.2. Ambient 2-naphthylamine storage samples.

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 coefficients of variation (CV) are calculated from the data from Tables 4.4.1.-4.4.3. The pooled coefficients of

Table 4.6.1
Precision of the Analytical Method
for 4-Aminobiphenyl
(Based on the Data of Table 4.4.1)

× target concn	0.5×	1×	2×
µg/sample	0.339	0.677	1.355
ppb	0.49	0.98	1.96
mean	64172	132026	258322
CV	0.0171	0.0147	0.0085

variation are 0.014, 0.013, and 0.014 for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively.

Table 4.6.2
Precision of the Analytical Method
for 1-Naphthylamine
(Based on the Data of Table 4.4.2)

× target concn	0.5×	1×	2×
µg/sample	0.291	0.583	1.165
ppb	0.50	1.00	1.99
mean	42031	81973	150501
CV	0.0151	0.0147	0.0089

Table 4.6.3
Precision of the Analytical Method
for 2-Naphthylamine
(Based on the Data of Table 4.4.3)

× target concn	0.5×	1×	2×
µg/sample	0.299	0.598	1.196
ppb	0.51	1.02	2.04
mean	52583	107536	207936
CV	0.0165	0.0145	0.0095

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 number of data points
k = 2 for linear regression
k = 3 for quadratic regression
Y_{obs} = observed percent recovery at a given time
Y_{est} = estimated percent 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 line in the storage graph as shown in Figure 4.5.1.1. The data for Figures 4.5.1.2, 4.5.2.2, and 4.5.3.2 were used to determine the SEEs of ±5.3%, ±5.5%, and ±5.3% and the precisions of the overall procedure of ±10.5%, ±10.8%, and ±10.3% for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively.

4.8 Reproducibility

Samples were prepared by injecting microliter quantities of standards onto acid-treated filters, assembling the filters into cassettes, and drawing 100 L of 80% relative humidity air through the samplers at 1 L/min. The filters were then transferred to separate vials containing 2 mL of deionized water and stored for 2 days at 0°C before being analyzed by another chemist. No individual sample result deviated from its theoretical value by more than the corresponding precision of the overall procedure. The precisions of the overall procedure are ±10.5%, ±10.8%, and ±10.3% for 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively.

Table 4.8.1
Reproducibility Data for 4-Aminobiphenyl

µg spiked	µg found	% found	% difference
0.677	0.679	100.3	+0.3
0.677	0.674	99.6	-0.4
0.677	0.640	94.5	-5.5
0.677	0.631	93.2	-6.8
0.677	0.630	93.1	-6.9
0.677	0.633	93.5	-6.5

Table 4.8.2
Reproducibility Data for 1-Naphthylamine

µg spiked	µg found	% found	% difference
0.583	0.628	107.7	+7.7
0.583	0.613	105.1	+5.1
0.583	0.592	101.5	+1.5
0.583	0.604	103.6	+3.6
0.583	0.602	103.3	+3.3
0.583	0.581	99.7	-0.3

Table 4.8.3
Reproducibility Data for 2-Naphthylamine

µg spiked	µg found	% found	% difference
0.598	0.583	97.5	-2.5
0.598	0.609	101.8	+1.8
0.598	0.560	93.6	-6.4
0.598	0.560	93.6	-6.4
0.598	0.561	93.8	-6.2
0.598	0.559	93.5	-6.5

4.9 Extraction efficiency

Six sample filters were spiked with the target concentration amounts by liquid injection (0.677, 0.583, and 0.598 µg of 4-aminobiphenyl, 1-naphthylamine and 2-naphthylamine respectively). These samples were analyzed to determine the extraction efficiencies. To determine the stability of extracted and derivatized samples, these same samples were allowed to remain at room temperature for 24 h and reanalyzed using fresh standards.

Table 4.9.1
Extraction Efficiency
for 4-Aminobiphenyl

sample number	% extraction (initial)	% extraction (24 h later)
1	97.9	100.6
2	98.2	101.2
3	101.0	99.6
4	99.0	100.7
5	99.7	100.3
6	101.6	103.2
mean	99.6	100.9

Table 4.9.2
Extraction Efficiency
for 1-Naphthylamine

sample number	% extraction (initial)	% extraction (24 h later)
1	97.6	98.3
2	99.7	99.3
3	101.2	98.6
4	99.0	99.8
5	99.0	99.3
6	100.5	101.7
mean	99.5	99.5

Table 4.9.3
Extraction Efficiency
for 2-Naphthylamine

sample number	% extraction (initial)	% extraction (24 h later)
1	97.3	99.3
2	99.8	100.2
3	101.7	100.7
4	100.0	101.7
5	100.0	100.8
6	101.3	103.2
mean	100.0	101.0

5. References

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