Method no.:	87
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 extracted with an aqueous EDTA solution and the extracts are analyzed for the free amines by HPLC using a UV detector.
Recommended air volume and sampling rate:	100 L at 1 L/min

	phenylenediamine		
	meta-	ortho-	para-
Target concentration:	0.10 mg/m^3	0.10 mg/m^3	0.10 mg/m^3
Reliable quantitation limit: (based on a 100-L air volume)	0.56 µg/m^3	2.1 µg/m^3	0.44 µg/m^3
Standard error of estimate at the target concentration: (Section 4.7.)	5.3%	7.9%	5.7%

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

Date: February 1991

Chemist: Carl J. Elskamp

Organic Methods Evaluation Branch
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Salt Lake City, Utah

1. General Discussion

1.1. Background

1.1.1. History

Phenylenediamines are particularly difficult to determine in air because they are very susceptible to oxidation reactions, which create sample stability and analytical problems. There are a number of methods in the literature which utilize various bubbler or impinger solutions for collection of air samples. (Refs. 5.1.- 5.5.) Sampling in this manner is very inconvenient and can potentially be unsafe because some of the collection solutions are toxic. There are also special shipping regulations which complicate the transport of samples to the laboratory for analysis. There is a published method for collection of *o*-phenylenediamine vapors using glass tubes packed with Tenax-GC. (Ref. 5.6.) Sample stability problems may exist with this method because the sampler is wrapped with aluminum foil during sampling to protect it from light. No storage tests were reported in the method. Also, this methodology does not address collection of aerosols or dusts, which may not be effectively collected with a solid sorbent tube.

Air sampling and analytical procedures have previously been evaluated by the OSHA Salt Lake Analytical Laboratory for a number of other aromatic amines which utilize a sampling device containing glass fiber filters coated with dilute sulfuric acid. (Refs. 5.7.-5.11.) With this sampling device, the amines are converted to amine salts on the filter. Not only does this provide for good collection efficiencies, it also eliminates stability problems because the salts are very stable compared to the free amines. With the exception of diphenylamine and *N*-isopropylaniline, which are analyzed by HPLC, the analysis scheme involves converting the amine salts to the free amines using excess sodium hydroxide and extracting the amines into toluene. The amines are then derivatized with heptafluorobutyric acid anhydride and the derivatives are analyzed by gas chromatography. This procedure is more sensitive than direct HPLC analysis of the free amines and was evaluated for the analysis of phenylenediamines because the target concentrations are fairly low. However, stability problems arose, especially for *p*-phenylenediamine, when the amine salts were converted to the free amines with sodium hydroxide. The instability was most likely due to oxidation of the free amines. It became apparent that the free phenylenediamines are too unstable and the extracted samples must be kept acidic until analyzed. The acidic extract is analyzed directly by HPLC. The amine salts are converted to the free amines upon injection by utilizing a mobile phase buffered to pH 7. A phosphate buffer was chosen because it has a high buffer capacity at this pH. Although all three isomers were sufficiently stable on the acid-treated filters, the ortho isomer was somewhat unstable in the acidic extract when deionized water was used to extract the filters. The stability of extracted samples for this isomer was greatly improved by using an aqueous EDTA solution instead. The stability of the other two isomers appeared to be the same for both water and EDTA solution extractions.

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

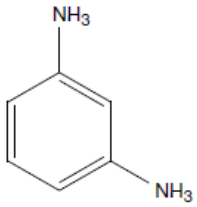
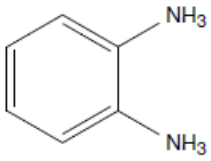
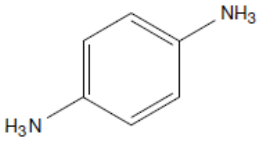
Exposure to phenylenediamines has been reported to affect the kidney, liver, and blood. Inhalation causes respiratory problems and asthma, but the most common toxic effect is dermatitis. (Ref. 5.12.) The current OSHA PEL and ACGIH TLV are 0.1 mg/m^3 for *p*-

phenylenediamine with skin notations. ACGIH is now considering the same TLV for *m*- and *o*-phenylenediamine and is also considering adding *o*-phenylenediamine to its suspected human carcinogen list. Currently there are no OSHA exposure limits for *m*- or *o*-phenylenediamine.

1.1.3. Workplace exposure

The major uses for phenylenediamines are in the manufacture of dyes. They are also used to dye hair and fur, as photographic development agents, curing agents for epoxy resins, vulcanization accelerators, and as components of gasoline antioxidants. (Ref. 5.13.)

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

	phenylenediamine		
	meta-	ortho-	para-
CAS no.:	108-45-2	95-54-5	106-50-3
molecular weight:	108.14	108.14	108.14
melting point:	62-63 °C	103-104 °C	145-147 °C
boiling point:	284-287 °C	256-258 °C	267 °C
description:	white crystals turning red on exposure of air	brownish-yellow crystals	white to slightly red crystals; darkens on exposure to air
solubility:	soluble in water, methanol, ethanol, chloroform, acetone, DMF, MEK, dioxane	slightly soluble in water; freely soluble in alcohol, chloroform, ether	soluble in 100 parts cold water; soluble in alcohol, chloroform, ether
structural formula:			
	meta	ortho	para

synonyms: (Ref. 5.13.)

***m*-phenylenediamine**: 1,3-diaminobenzene; 1,3-phenylenediamine; 3-aminoaniline; benzene, 1,3-diamino; *m*-aminoaniline; *m*-benzenediamine; *m*-diaminobenzene; *m*-fenylendiamin (Czech.); meta-aminoaniline; meta-benzenediamine; meta-diaminobenzene; metaphenylenediamine; phenylenediamine, meta, solid; CI 76025; CI Developer 11; Developer 11; Developer C; Developer H; Developer M; Direct Brown BR; Direct Brown GG

***o*-phenylenediamine**: 1,2-benzenediamine; 1,2-diaminobenzene; 1,2-phenylenediamine; 2-aminoaniline; *o*-benzenediamine; *o*-diaminobenzene; orthamine; CI 76010; CI Oxidation Base

***p*-phenylenediamine**: 1,4-diaminobenzene; 1,4-phenylenediamine; 4-amino-aniline; p-aminoaniline; *p*-benzenediamine; *p*-diaminobenzene; Para; paraphenylenediamine; phenylenediamine, para, solid; Pelagol D; Pelagol DR; Pelagol Grey D; Peltol D; PPD; Renal PF; Santoflex LC; Tertral D; Ursol D; USAF EK-394; Z0BA Black D; BASF Ursol D; Benzofur D; CI 76060; CI Developer 13; CI Oxidation Base 10; Developer 13; Developer PF; Durafur Black R; fenylenodwuamina (Polish); Fouramine D; Fourine 1; Fur Black 41866; Fur Black 41867; Fur Yellow; Furro D; Futramine D; Nako D; Orsin; Oxidation Base 10

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters.

1.2. Limit defining parameters

1.2.1. Detection limit of the analytical procedure

The detection limits of the analytical procedure are 0.14, 0.53, and 0.11 ng per injection for *m*-, *o*-, and *p*-phenylenediamine 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 56, 211, and 44 ng per sample for *m*-, *o*-,and *p*-phenylenediamine respectively. These are the amounts of each analyte spiked on sample filters that allow recovery of analytes equivalent to the respective detection limits of the analytical procedure. These detection limits correspond to air concentrations of 0.56, 2.1, and 0.44 µg/m^3 for *m*-, *o*-, and *p*-phenylenediamine respectively. (Section 4.2.)

1.2.3. Reliable quantitation limit

The reliable quantitation limits are 56, 211, and 44 ng per sample for *m*-, *o*-, and *p*-phenylenediamine 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 0.56, 2.1, and 0.44 µg/m^3 for *m*-, *o*-, and *p*-phenylenediamine 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 *m*-, *o*-, and *p*-phenylenediamine from samples used in 15-day storage tests remained above 98%, 84%, and 98% respectively. The sample filters were stored in cassettes 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 0.0063, 0.0095, and 0.0090 for *m*-, *o*-, and *p*-phenylenediamine respectively. (Section 4.6.)

1.2.7. Precision (overall procedure)

The precisions at the 95% confidence level for the 15-day storage tests are ±10.3, ±15.4 and ±11.1% for *m*-, *o*-, and *p*-phenylenediamine 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.)

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 48 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.

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 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. An unassembled sampling device is shown in Figure 2.1.2.

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

A collection efficiency study was conducted by drawing humid air through a sampling device that was attached to an impinger containing milligram amounts of the pure amines. The inlet of the impinger was attached to a humid air generator so air at approximately 80% relative humidity could be drawn through it. The impinger was heated to approximately 60 °C with a heat tape. After sampling for 4 h at 1 L/min, the filters were analyzed. None of the amines were found on the back filter and approximately 230, 670, and 130 µg of *m*-, *o*-, and *p*-phenylenediamine respectively were found on the front filter. This corresponds to air concentrations of 0.96, 2.8, and 0.54 mg/m^3 for *m*-, *o*-, and *p*-phenylenediamine respectively. Although this test demonstrates that the sampler has more than adequate capacity to collect larger air volumes at concentrations much higher than the target concentrations of 0.10 mg/m^3, a recommended air volume of 100 L was chosen to assure a sufficient safety margin and to maintain consistency with previously evaluated methods for aromatic amines.

2.5. Extraction efficiency

2.5.1. The average extraction efficiencies from six filters for each amine spiked at the target concentration are 100.8%, 97.6%, and 101.0% for *m*-, *o*-, and *p*-phenylenediamine respectively. (Section 4.9.)

2.5.2. The stability of extracted samples was verified by reanalyzing the extraction efficiency samples 24 h later using fresh standards. The average recoveries for the reanalyzed samples were 99.2%, 93.5%, and 98.4% for *m*-, *o*-, and *p*-phenylenediamine 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 *p*-phenylenediamine for a 15-L air sample would be 2.9 µg/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 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 system equipped with an ultraviolet detector. A Hewlett-Packard 1050 Series HPLC consisting of a pumping system, programmable variable wavelength detector and an 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 C18 (end-capped 5-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 capable of delivering 2.0 mL of the EDTA extraction solution.

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

3.2. Reagents

3.2.1. *m*-, *o*-, and *p*-Phenylenediamine, reagent grade. The amines used in this evaluation were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI).

3.2.2. HPLC grade acetonitrile and water. The acetonitrile used in this evaluation was "Optima" brand from Fisher Chemical (Fair Lawn, NJ) and the water was from an in-house Millipore Milli-Q water purification system.

3.2.3. Ethylenediaminetetraacetic acid (EDTA), reagent grade. A 0.1 g/L EDTA aqueous solution is used to extract the sample filters.

3.2.4. Phosphoric acid, 10 N sulfuric acid, and dibasic sodium phosphate (Na_2HPO_4), 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 accurately weighing approximately 50 mg of each amine into a 25-mL volumetric flask. Initially dissolve the amines with about 20 mL of 10 N sulfuric acid. *m*-Phenylenediamine is readily soluble. Sonication can be used to expedite dissolution of the *o*- and *p*-phenylenediamine. After the amines are totally dissolved, dilute to the mark with additional 10 N sulfuric acid and thoroughly mix the solution. Stock standards are stable for at least six months when stored in brown bottles in a refrigerator.

3.3.2. Prepare analytical standards by injecting microliter amounts of stock standards into 4-mL vials containing 2.0 mL of the EDTA extraction solution using a 10-µL syringe. Immediately rinse the syringe with water after the standards are prepared. If 5.00 µL of a 2.00 µg/µL (50.00 mg of amine to 25.00 mL with 10 N sulfuric acid) stock solution is injected into 2.0 mL of the EDTA extraction solution, the analytical standard would be equivalent to 10.0 µg of amine per sample, or 0.10 mg/m^3 for a 100-L air sample.

3.3.3. Bracket sample concentrations with analytical standard concentrations. If sample concentrations are higher than the upper range of prepared standards, prepare higher standards to ascertain detector response or dilute the extract of the samples using the EDTA extraction solution.

3.4. Sample preparation

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

3.4.2. Add 2.0 mL of the aqueous EDTA extraction solution to each vial.

3.4.3. Recap and periodically invert the vials over a period of 10 min.

3.4.4. Analyze by making direct injections of the extracts.

3.5. Analysis

3.5.1. HPLC conditions and information

mobile phase:	0.05 M sodium phosphate in 95/5, water/acetonitrile at pH 7.0. Prepare by adding 7.1 g of dibasic sodium phosphate per 1 L of the final total volume of mobile phase to the water. After the sodium phosphate has dissolved (expedited using sonication) adjust the pH of this aqueous solution to 7.0 with phosphoric acid. Add the acetonitrile to the pH-adjusted aqueous solution and mix thoroughly.
flow rate:	2 mL/min
UV detector wavelength:	240 nm
injection volume:	5 µL
column:	Waters Radial-Pak 100-mm × 8-mm i.d. cartridge containing Nova Pak C18
retention times:	*p*-phenylenediamine, 2.4 min; *m*-phenylenediamine, 3.8 min; o-phenylenediamine, 7.0 min
chromatogram:	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 formula.

$$\text{Ā}\bar{\text{A}}\,/\bar{\text{A}}^{3} = \frac{\bar{\text{A}}\,\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\,\bar{\text{A}}\,\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\,\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\,\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}}{(\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\,\bar{\text{A}}\bar{\text{A}}\,\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\,\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}})(\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\,\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}}\bar{\text{A}})}$$

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 limits of the analytical procedure. The detection limits of 0.14, 0.53, and 0.11 ng per injection were determined by analyzing dilute standards equivalent to 56, 211, and 44 ng per sample for *m*-, *o*-, and *p*-phenylenediamine respectively. These amounts were judged to give peaks with heights approximately five times the baseline noise. A chromatogram is shown in Figure 4.1.

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 56, 211, and 44 ng of *m*-, *o*-, and *p*-phenylenediamine respectively onto acid-treated filters. These amounts are equivalent to 0.56, 2.1, and 0.44 µg/m^3 for *m*-, *o*-, and *p*-phenylenediamine respectively.

Table 4.2.1.
Detection Limit of the Overall Procedure for
m-Phenylenediamine

sample no.	ng spiked	ng recovered
1	56	56.6
2	56	56.3
3	56	63.0
4	56	53.3
5	56	47.5
6	56	53.6

Table 4.2.2.
Detection Limit of the Overall Procedure for
o-Phenylenediamine

sample no.	ng spiked	ng recovered
1	211	204
2	211	213
3	211	200
4	211	197
5	211	195
6	211	193

Table 4.2.3.
Detection Limit of the Overall Procedure
p-Phenylenediamine

sample no.	ng spiked	ng recovered
1	44	39.3
2	44	42.3
3	44	47.2
4	44	45.6
5	44	42.4
6	44	44.2

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 56, 211, and 44 ng of *m*-, *o*-, and *p*-phenylenediamine respectively onto acid-treated filters. These amounts are equivalent to 0.56, 2.1, and 0.44 µg/m^3 for *m*-, *o*-, and *p*-phenylenediamine respectively.

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

sample no.	percent recovered	
1	101.1	
2	100.5	$\bar{A}$ = 98.3
3	112.5	SD = 9.1
4	95.2	Precision = (1.96)(±9.1)
5	84.8	= ±17.8
6	95.7	

Table 4.3.2.
Reliable Quantitation Limit for *o*-Phenylenediamine
(Based on samples and data of Table 4.2.2.)

sample no.	percent recovered	
1	96.7	$\bar{A}$ = 95.0
2	100.9	SD = 3.4
3	94.8	Precision = (1.96)(±3.4)
4	93.4	= ±6.7
5	92.4	
6	91.5	

Table 4.3.3.
Reliable Quantitation Limit for *p*-Phenylenediamine
(Based on samples and data of Table 4.2.3.)

sample no.	percent recovered	
1	89.3	$\bar{A}$ = 98.9
2	86.1	SD = 6.3
3	107.3	Precision = (1.96)(±6.3)
4	103.6	= ±12.3
5	96.4	
6	100.5	

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 2120, 1663, and 2805 for *m*-, *o*-, and *p*-phenylenediamine respectively. The instrument response is shown graphically in Figure 4.4.

Table 4.4.1.
Instrument Response to *m*-Phenylenediamine

× target concn	0.5×	1×	2×
µg/sample	4.918	9.837	19.67
mg/m^3	0.0492	0.0984	0.197
area counts	10260	20563	41330
	10096	20615	41218
	10037	20471	41425
	10143	20608	41385
	10146	20362	41399
	9992	20615	41581
Ā=	10112	20539	41390

Table 4.4.2.
Instrument Response to *o*-Phenylenediamine

× target concn	0.5×	1×	2×
µg/sample	5.203	10.41	20.81
mg/m^3	0.0520	0.104	0.208
area counts	7838	16545	33874
	7741	16644	33549
	7832	16472	33612
	7678	16438	33810
	7686	16634	33763
	7634	16121	33637
Ā =	7735	16476	33708

Table 4.4.3.
Instrument Response to *p*-Phenylenediamine

× target concn	0.5×	1×	2×
µg/sample	4.879	9.757	19.51
mg/m^3	0.0488	0.0976	0.195
area counts	13088	26947	54204
	13079	26891	53772
	13182	26703	54331
	12781	26439	53866
	13212	26538	53945
	12901	26866	54348
Ā =	13040	26731	54078

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 (9.837, 10.41, and 9.757 µg of *m*, *o*-, and *p*-phenylenediamine respectively). The filters were then assembled in three-piece cassettes with back filters. Thirty-six samples were prepared. One hundred liters of air at approximately 80% relative humidity and 21 °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 shown graphically in Figures 4.5.1.1., 4.5.1.2., 4.5.2.1., 4.5.2.2., 4.5.3.1., and 4.5.3.2. The recoveries of *m*-, *o*-, and *p*-phenylenediamine from samples stored at ambient temperature remained above 98%, 84%, and 98% respectively.

Table 4.5.1
Storage Test of *m*-Phenylenediamine

days of storage	% recovery					
	refrigerated			ambient		
0	100.5	98.8	98.7	100.5	98.8	98.7
0	95.5	96.6	98.0	95.5	96.6	98.0
3	97.7	97.1	98.8	96.7	103.4	97.2
6	99.2	97.4	98.4	100.2	98.6	99.9
9	98.0	98.7	99.4	99.9	99.9	100.1
12	98.5	100.1	99.8	100.9	100.1	100.3
15	93.4	96.7	95.3	99.8	98.9	100.5

Table 4.5.2
Storage Test of *o*-Phenylenediamine

days of storage	% recovery					
	refrigerated			ambient		
0	94.8	96.8	102.1	94.8	96.8	102.1
0	92.3	92.3	95.6	92.3	92.3	95.6
3	95.3	92.7	100.6	103.0	104.1	92.9
6	88.1	90.6	90.7	79.7	86.2	85.0
9	97.0	92.0	95.6	89.7	89.2	91.0
12	90.7	96.2	89.3	87.6	82.6	75.9
15	92.0	94.6	91.5	92.6	85.7	89.5

Table 4.5.3
Storage Test of *p*-Phenylenediamine

days of storage	% recovery					
	refrigerated			ambient		
0	99.3	101.1	100.4	99.3	101.1	100.4
0	95.4	96.1	100.5	95.4	96.1	100.5
3	95.5	92.2	94.4	93.1	99.5	101.2
6	97.1	96.4	97.9	91.8	98.8	97.7
9	98.0	97.0	98.9	97.3	97.6	95.9
12	95.6	100.5	100.0	100.1	101.3	98.3
15	94.5	98.0	94.2	98.6	98.7	101.0

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 precisions are based on the data from Section 4.4.

Table 4.6.1.
Precision of the Analytical Method for *m*-Phenylenediamine

× target concn	0.5×	1×	2×
µg/sample	4.918	9.837	19.67
mg/m^3	0.0492	0.0984	0.197
SD (area counts)	94.1	102.8	119.2
CV	0.0093	0.0050	0.0029
$\overline{CV}$ = 0.0063			

Table 4.6.2.
Precision of the Analytical Method for *o*-Phenylenediamine

× target concn	0.5×	1×	2×
µg/sample	5.203	10.41	20.81
mg/m^3	0.0520	0.104	0.208
SD (area counts)	84.7	192.6	126.9
CV	0.0110	0.0117	0.0038
$\overline{CV}$ = 0.0095			

Table 4.6.3.
Precision of the Analytical Method for *p*-Phenylenediamine

× target concn	0.5×	1×	2×
µg/sample	4.879	9.757	19.51
mg/m^3	0.0488	0.0976	0.195
SD (area counts)	167.3	206.8	248.6
CV	0.0128	0.0077	0.0046
$\overline{CV}$ = 0.0090			

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 linear regression
k = 3 for 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 standard errors of estimate are 5.3%, 7.9%, and 5.7% and the precisions of the overall procedure (95% confidence intervals) are ±10.3%, ±15.4%, and ±11.1% for *m*, *o*-, and *p*-phenylenediamine respectively. These values were obtained from Figures 4.5.1.2., 4.5.2.2., and 4.5.3.2. for the ambient storage samples.

4.8. Reproducibility

Six samples were prepared by injecting microliter quantities of standards onto acid-treated filters. The samples were stored at approximately 0 °C for 48 days. The samples were analyzed by a chemist unassociated with this evaluation. 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 ±10.3%, ±15.4%, and ±11.1% for *m*-, *o*-, and *p*-phenylenediamine respectively.

Table 4.8.1.
Reproducibility for *m*-Phenylenediamine

sample no.	µg found	µg expected	% found	% deviation
1	17.70	19.67	90.0	-10.0
2	9.692	9.837	98.5	-1.5
3	4.661	4.918	94.8	-5.2
4	9.224	9.837	93.8	-6.2
5	18.99	19.67	96.5	-3.5
6	5.130	4.918	104.3	+4.3

Table 4.8.2.
Reproducibility for *o*-Phenylenediamine

sample no.	µg found	µg expected	% found	% deviation
1	18.34	20.81	88.1	-11.9
2	9.768	10.41	93.8	-6.2
3	4.605	5.203	88.5	-11.5
4	9.502	10.41	91.3	-8.7
5	19.93	20.81	95.8	-4.2
6	4.703	5.203	90.4	-9.6

Table 4.8.3.
Reproducibility for *p*-Phenylenediamine

sample no.	µg found	µg expected	% found	% deviation
1	17.63	19.51	90.4	-9.6
2	9.523	9.757	97.6	-2.4
3	4.601	4.879	94.3	-5.7
4	9.256	9.757	94.9	-5.1
5	18.83	19.51	96.5	-3.5
6	4.990	4.879	102.3	+2.3

4.9. Extraction efficiency

Six sample filters for each amine were spiked with the target concentration amounts by liquid injection (9.837, 10.41, and 9.757 µg of *m*-, *o*-, and *p*-phenylenediamine respectively). These samples were analyzed to determine the extraction efficiencies. To determine the stability of extracted samples, these same samples were allowed to remain at room temperature for 24 h after extraction and were reanalyzed using fresh standards.

Table 4.9.1.
Extraction Efficiency for *m*-Phenylenediamine

sample no.	% extracted	% extracted (reanalyzed after 24 h)
1	99.6	98.1
2	99.2	99.8
3	100.3	100.1
4	101.9	98.4
5	100.7	98.0
6	103.2	100.9
Ã	100.8	99.2

Table 4.9.2.
Extraction Efficiency for *o*-Phenylenediamine

sample no.	% extracted	% extracted (reanalyzed after 24 h)
1	96.9	88.8
2	98.0	95.5
3	95.9	93.7
4	96.0	92.7
5	96.4	94.1
6	102.5	96.2
Ã	97.6	93.5

Table 4.9.3.
Extraction Efficiency for *p*-Phenylenediamine

sample no.	% extracted	% extracted (reanalyzed after 24 h)
1	99.9	97.0
2	100.2	98.3
3	99.3	99.4
4	101.7	97.7
5	101.6	98.7
6	103.2	99.6
Ã	101.0	98.4

4.10. Chromatogram

A chromatogram of an analytical standard is shown in Figure 4.10. The chromatogram is from a 5-µL injection of a standard approximately equal to the target concentration for each analyte (9.837, 10.41, and 9.757 µg of *m*-, *o*-, and *p*-phenylenediamine per sample respectively) for a 100-L sample.

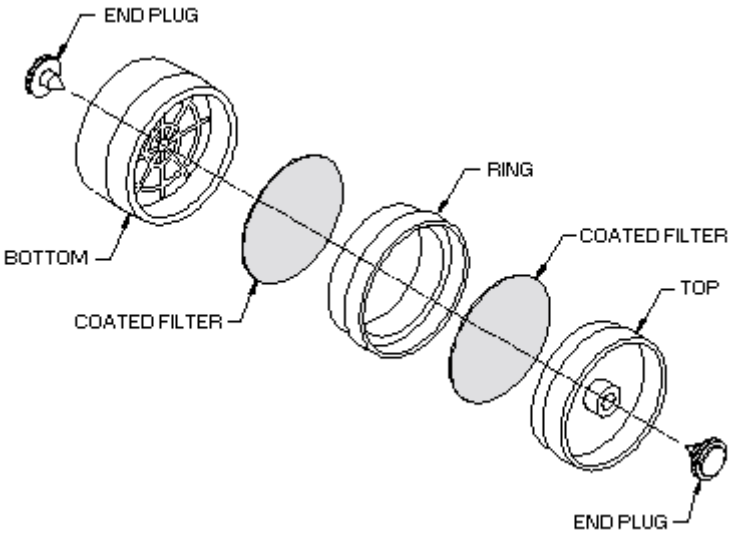


Figure 2.1.2. Unassembled sampling device for phenyldenediamines.

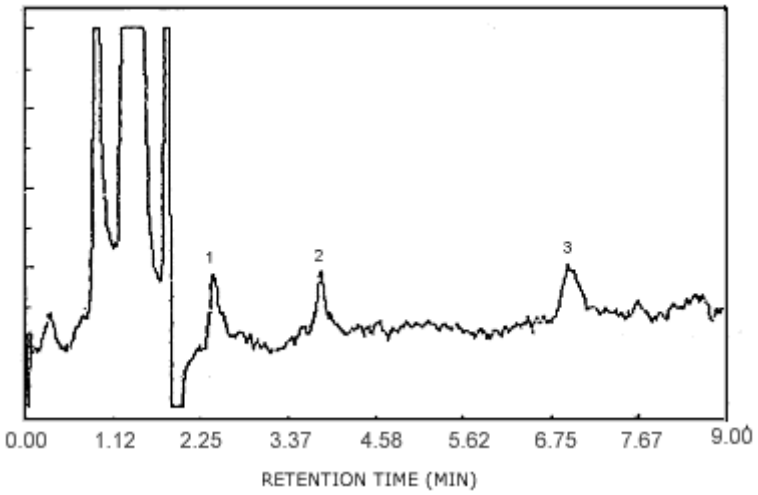


Figure 4.1. Detection limit chromatogram. Key: 1 = *p*-phenylenediamine, 2 = *m*-phenylenediamine, 3 = *o*-phenylenediamine.

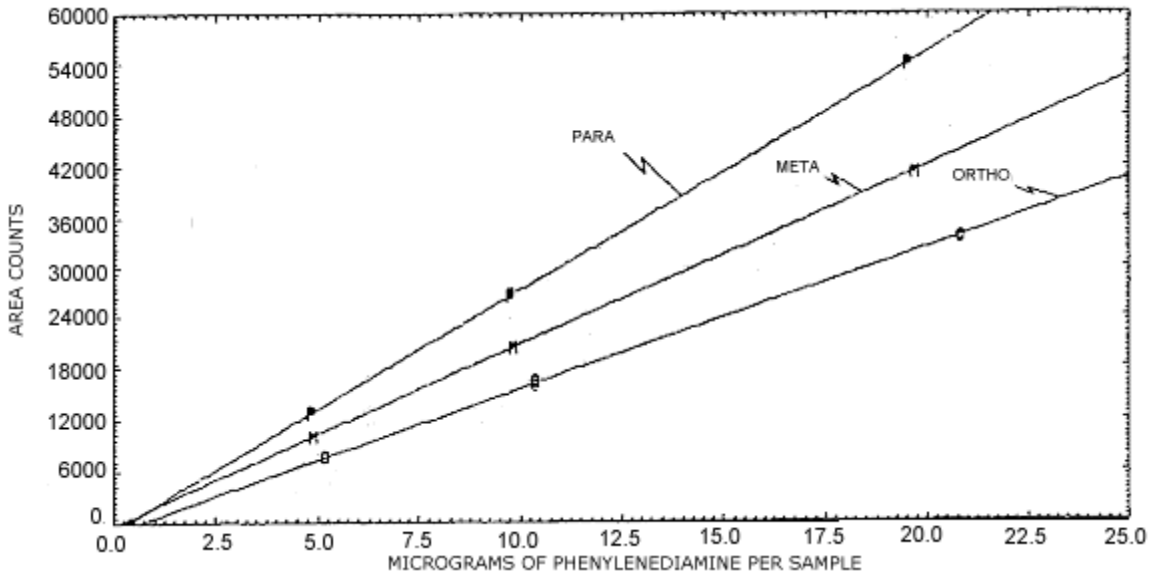


Figure 4.4. Instrument response.

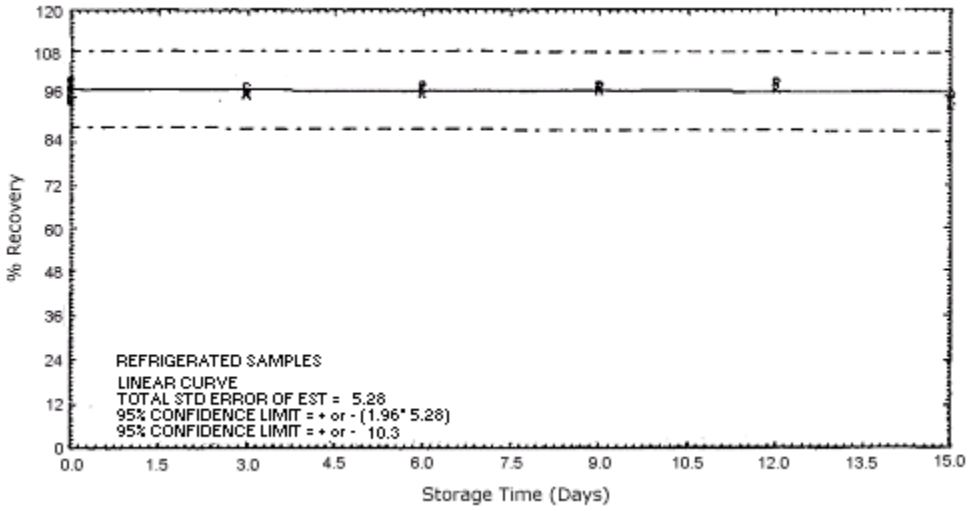


Figure 4.5.1.1. Refrigerated *m*-phenylenediamine storage samples.

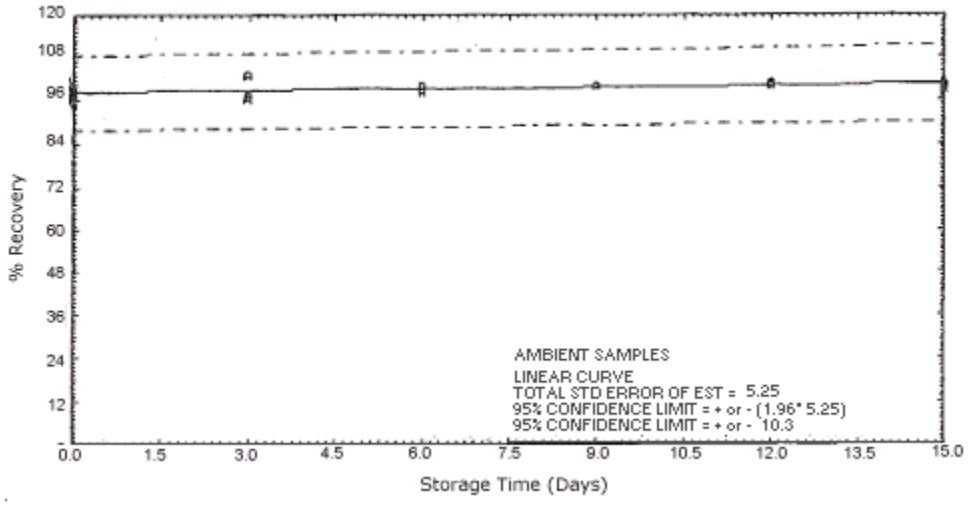


Figure 4.5.1.2. Ambient *m*-phenylenediamine storage samples.

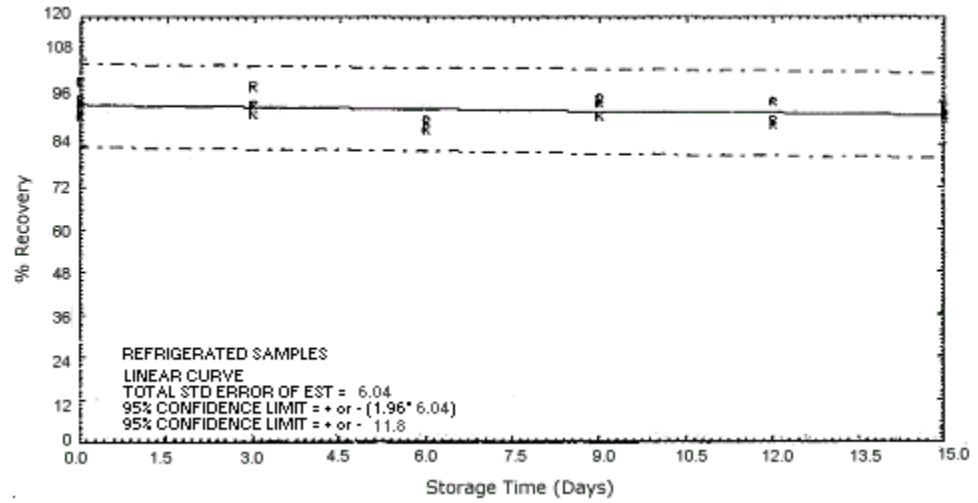


Figure 4.5.2.1. Refrigerated *o*-phenylenediamine storage samples.

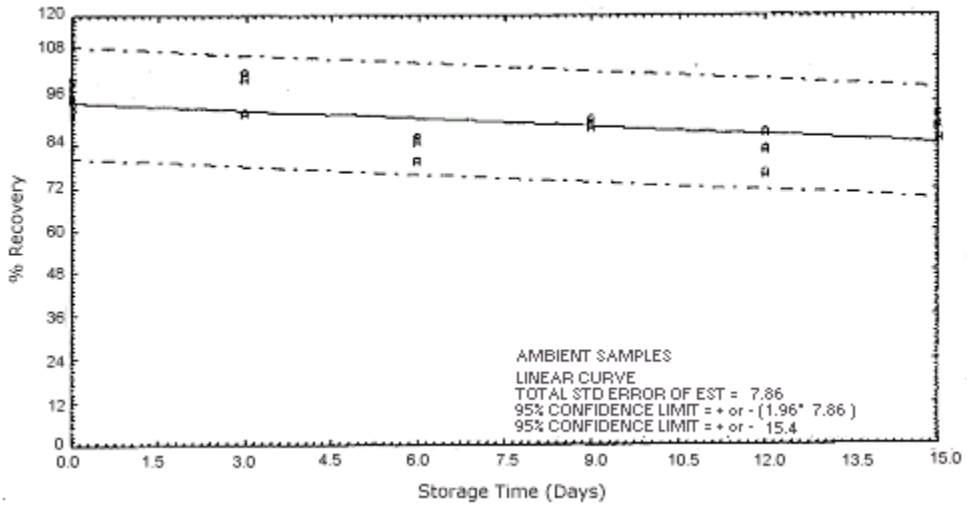


Figure 4.5.2.2. Ambient *o*-phenylenediamine storage samples.

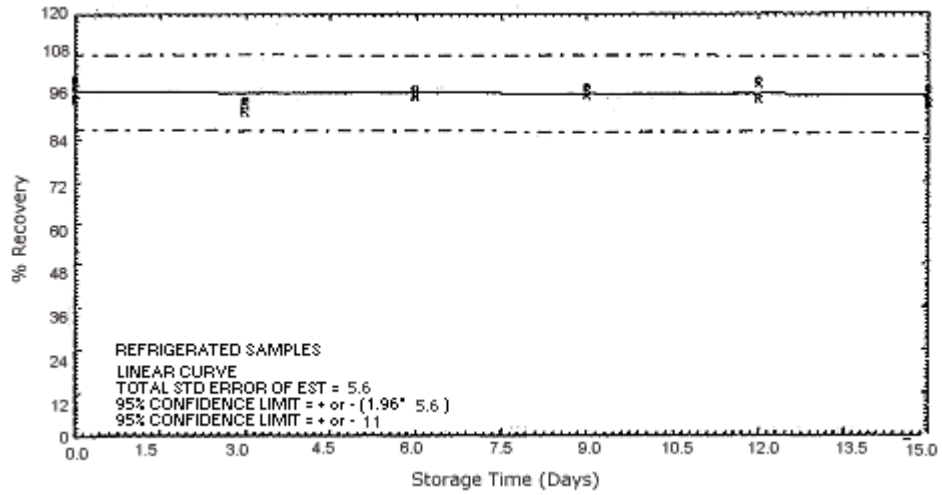


Figure 4.5.3.1. Refrigerated *p*-phenylenediamine storage samples.

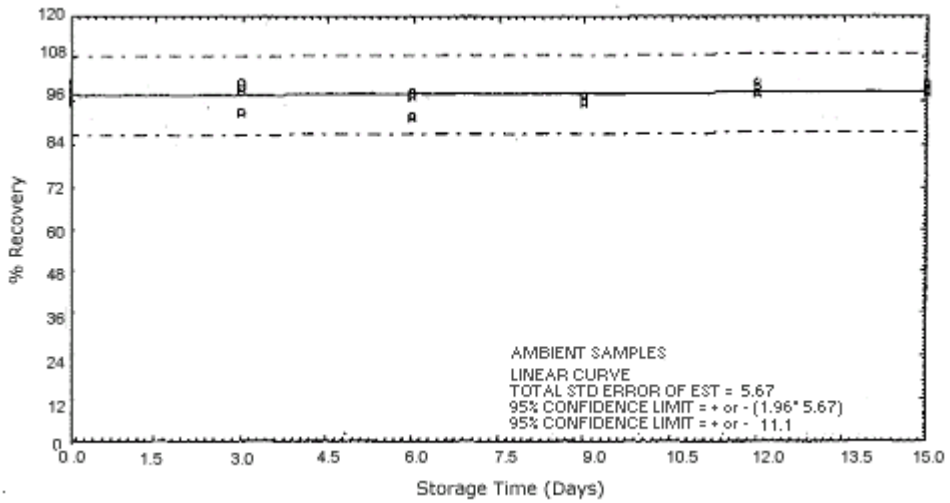


Figure 4.5.3.2. Ambient *p*-phenylenediamine storage samples.

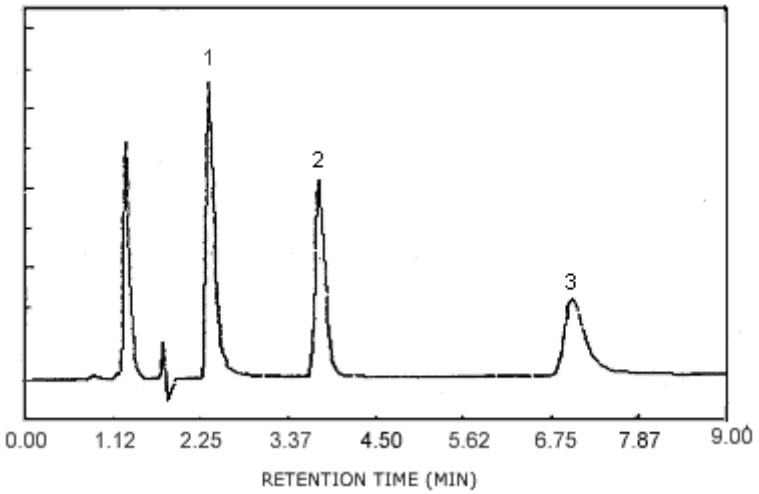


Figure 4.10. Chromatogram of a standard at the target concentrations. Key: 1 = *p*-phenylenediamine, 2 = *m*-phenylenediamine, 3 = *o*-phenylenediamine.

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