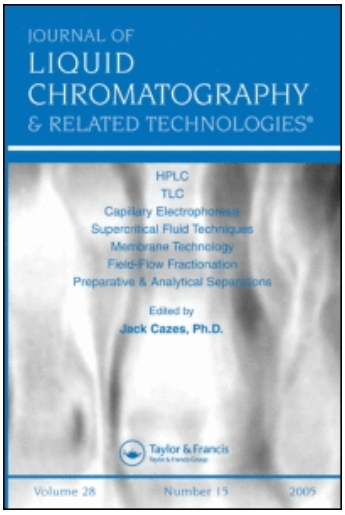

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

High Performance Liquid Chromatographic Determination of Phenylenediamines in Aqueous Environmental Samples

R. M. Riggin[a]; C. C. Howard[a]
[a] Battelle, Columbus Laboratories, Columbus, Ohio

To cite this Article Riggin, R. M. and Howard, C. C.(1983) 'High Performance Liquid Chromatographic Determination of Phenylenediamines in Aqueous Environmental Samples', Journal of Liquid Chromatography & Related Technologies, 6: 10, 1897 — 1905
To link to this Article: DOI: 10.1080/01483918308064898
URL: http://dx.doi.org/10.1080/01483918308064898

JOURNAL OF LIQUID CHROMATOGRAPHY, 6(10), 1897-1905 (1983)

HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC DETERMINATION OF PHENYLENEDIAMINES IN AQUEOUS ENVIRONMENTAL SAMPLES

R. M. Riggin and C. C. Howard

Battelle, Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

ABSTRACT

The use of high performance liquid chromatography (HPLC) for the determination of phenylenediamines has been studied. Detection limits using both ultraviolet (UV) and electrochemical (EC) detectors have been determined and EC is superior in most cases. Chromatographic conditions and sample preparation procedures are described for many phenylenediamines of environmental significance.

INTRODUCTION

Diaminobenzenes (herein the term "phenylenediamines" will be used) are of considerable environmental significance because of the carcinogenic properties of many of these compounds (1). These compounds are currently in widespread use as industrial chemicals for the production of dyes and pigments as well as polyurethane resins. Consequently there is a great need for routine methods for determining these compounds in environmental media.

Unfortunately the highly reactive and nonvolatile nature of the phenylenediamines makes gas chromatographic (GC) determination difficult, although a few studies have used GC for the

 0148-3919/83/0610-1897$3.50/0

determination of relatively high levels of certain phenylenediamines (2). HPLC is therefore the most suitable method for determining phenylenediamines and several studies have been reported (3-5). However, none of these studies have examined the separation, detection, and sample preparation parameters for determining a large number of phenylenediamines.

The objective of the study described herein was to establish suitable separation and detection parameters for the determination of as many phenylenediamines in commercial use as possible.

EQUIPMENT

All HPLC studies were performed using a modular system consisting of an Altex 100A pump, a Spherisorb ODS, 5 μm particle diameter, 250 x 4.6 mm stainless steel column, and a Rheodyne 7120 injector valve. Two detection systems were used; (1) an LDC Model 1203 fixed wavelength (254 nm) UV detector and (2) a Bioanalytical Systems Model LC-2A electrochemical detector with a glassy carbon working electrode.

MATERIALS

All reagents were "analytical reagent" grade conforming with ACS specifications unless otherwise stated. Solvents were "distilled-in-glass" quality from Burdick and Jackson Laboratories. Analytical standards were the highest purity available and were checked for purity using HPLC.

Reagent water was obtained from a Mill-Q water purification system consisting of reverse osmosis, ion-exchange, and activated carbon treatment modules. HPLC mobile phases were filtered through a Nucleopore 0.22 μm polyester membrane filter and degassed by heating in a loosely covered erlenmeyer flask before use. Strong cation exchange resin (AG 50W-x8) was purchased from Biorad Laboratories.

Sample Preparation Procedures

Two sample preparation approaches were employed for the determination of the full range of phenylenediamines. The first procedure involved solvent extraction of the water sample and was found to be suitable for most of the compounds of interest. However, the unsubstituted phenylenediamines (i.e. o-, m-, p-phenylenediamine) were not efficiently extracted and an alternate scheme involving ion-exchange isolation of the compounds was developed.

The solvent extraction scheme involved the following steps. An aliquot (500 mL) of the water sample was adjusted to pH 7 with 0.4 M Na_3PO_4 or 0.4 M phosphoric acid. The sample was then extracted serially with 100 mL, 50 mL, and 50 mL portions of methylene chloride. The extracts were combined and concentrated to ∿1 mL on a Kuderna-Danish (K-D) evaporator. Four milliliters of acetonitrile was added to the extract followed by reconcentration to ∿0.5 mL. The extract was then placed in a 25 mL volumetric flask, diluted to the mark with HPLC mobile phase, and analyzed by HPLC.

The ion-exchange sample preparation procedure was conducted as follows. One gram of AG 50-X8 (sodium form) was hydrated with 3 mL of reagent water. The resin was then transferred to a disposable plastic column and eluted with 15 mL of 0.05 M, pH 3, NaH_2PO_4. The sample was adjusted to pH 3 with 2 M phosphoric acid and a 10 mL aliquot eluted through the ion-exchange column. The column was then rinsed with 5 mL of 0.05 M, pH 3, NaH_2PO_4. Finally the compounds of interest were eluted using 10 mL of 30/70 methanol/pH 5.5, 0.5 M sodium acetate buffer. The eluate was then analyzed using HPLC.

RESULTS AND DISCUSSION

Comparison of UV and EC detection limits immediately demonstrated the superiority of EC for this application. Figure 1

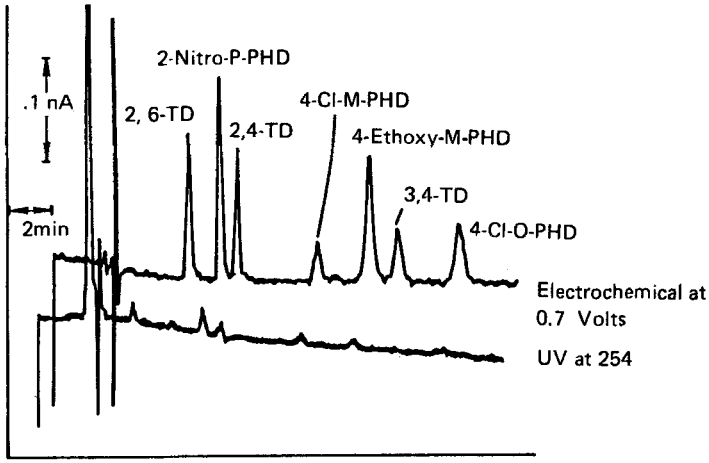

FIGURE 1. HPLC Separation of Various Phenylenediamines

Represents 0.8 ng on column for each PHD with the exception of 4-Cl-m-PHD 0.9 ng and 4-ethoxy-m-PHD (30 ng). See Table 1 for HPLC conditions.

graphically illustrates the 10-50 fold lower detection limit for EC compared to UV. Obviously the EC detector has the additional advantage of greater selectivity. The EC selectivity can be improved for selected compounds by reducing the detection potentials below that chosen for this study (700 mV). However, the nitro- and halogen-substituted compounds are not detected at lower potentials. Table 1 lists the retention and detection parameters for the various phenylenediamines of interest in this study. In general detection limits on the order of 0.2 nanograms injected were obtained for the various compounds. Most of the compounds of interest were chromatographically resolved although, as shown in Table 1, a few compound pairs (e.g. 2,5- and 2,6-toluenediamine) were not adequately resolved for simultaneous determination.

Recovery data for the groups of compounds determined by the two sample preparation procedures are shown in Tables 2 and 3.

TABLE 1

HPLC Retention Times and Detection Limits for Phenylenediamines

Compound	Retention Time (Min.)(a)	Estimated Detection Limit (Nanograms Injected)(b)
p-Phenylenediamine	4.8	0.2
m-Phenylenediamine	5.6	0.2
2,5-Toluenediamine	6.0	0.2
2,6-Toluenediamine	6.2	0.2
2-Methoxy-p-phenylenediamine	6.4	0.6
2-Nitro-p-phenylenediamine	7.8	0.2
2-Chloro-p-phenylenediamine	7.9	0.2
o-Phenylenediamine	8.2	0.2
4-Nitro-o-phenylenediamine	8.4	0.2
2,4-Toluenediamine	8.8	0.2
4-Methoxy-m-phenylenediamine	8.9	0.2
4-Chloro-m-phenylenediamine	12.1	0.7
4-Ethoxy-m-phenylenediamine	15.9	1.2
3,4-Toluenediamine	17.1	0.7
4-Chloro-o-phenylenediamine	18.4	0.6

(a) HPLC conditions as follows: Column-Spherisorb ODS, 5 μm particle diameter, 250 x 4.6 mm; Mobile phase - 30/70 methanol/0.1 M, pH 3.5, potassium phosphate with 0.01 M heptane sulfuric acid and 0.02 mM EDTA; Flow rate - 1 mL/min.; Injection Volume 20 μL; Detector potential - +700 mV vs. Ag/AgCl.

(b) Using electrochemical detection at 0.7 volts, and a signal to noise ratio of 5.

TABLE 2

Recovery of Various Phenylenediamines from Aqueous Media Using Methylene Chloride Extraction[a]

	2,4-TD	2,5-TD	2,6-TD	3,4-TD	4-Cl-M-PHD	4-Cl-O-PHD	2-NITRO-P-PHD	4-NITRO-O-PHD
Reagent H_2O (% recovery)	71[b]	29	65	68	79	87	89	64
Process Blank (ppb)	<3	<3	<2	<6	<5	<5	<2	<2
Wastewater (% recovery)	71	29	50	56	83	NA	NA	NA
Process Blank (ppb)	<2	<2	<1	<3	<2	--	--	--

(a) Aqueous media spiked at the 50 µg/L level.

(b) Average of duplicate analyses.

NA = Not analyzed

TD = Toluenediamine

PHD = Phenylenediamine

TABLE 3

Recovery of m,o,p-Phenylenediamine Spiked at the 50 µg/L Level from Aqueous Media Using Ion Exchange Chromatography

	m-PHD	o-PHD	p-PHD
D. I. H_2O (% Recovery)	73 ± 7.8[(a)]	73 ± 6.7	62 ± 1.6
Process Blank (ppb)	<3	<3	<2
Wastewater (% Recovery)	45 ± 8.3	55 ± 1.7	46 ± 3.2
Process Blank (ppb)	<2	<2	2

(a) Data for triplicate analyses.

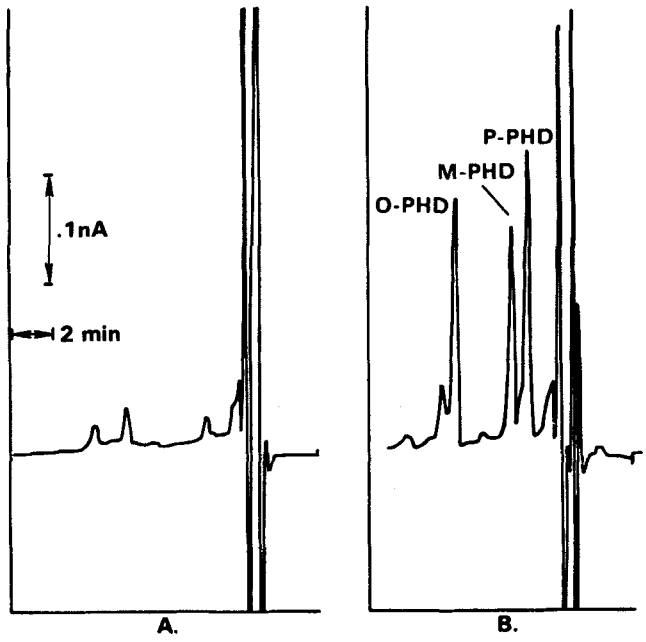

FIGURE 2. Chromatogram of Extracts of Wastewater (A) and of Wastewater Spiked at the 50 ppb Level With o, m, and p-Phenylenediamine (PHD)

As shown in these tables, recoveries were quite good for many of the compounds. However poor recovery (~30 percent) was obtained for 2,5-toluenediamine and only ~50 percent recoveries were obtained for the unsubstituted phenylenediamines from authenic wastewater samples. Figure 2 shows the HPLC separation of the three unsubstituted phenylenediamine isomers spiked into an authentic wastewater sample at the 50 µg/L level. The wastewater referred to in Tables 2 and 3 and Figure 2 is an industrial effluent, after secondary treatment, from a plant producing a variety of substituted aromatic amines.

CONCLUSIONS

While much work needs to be done to improve recoveries for some of the phenylenediamines, this study has demonstrated the clear advantage of using EC detection in conjunction with reversed phase, ion-pair HPLC for this application. Detection limits of a few µg/L were achieved for most of the phenylenediamines studied. This level of detectability is adequate for most environmental applications.

REFERENCES

1. Weisburger, E. K., Russfield, A. B., Homburger, F., Weisburger, J. H., Boger, E., Dougen, C., and Chu, K., Testing of Twenty-one Environmental Aromatic Amines or Derivatives for Long-Term Toxicity or Carcinogenicity. J. Env. Path. Toxicol. 2, 325, 1978.

2. Krasuska, E. and Celler, W., Gas Chromatographic Separation of Chloronitrobenzenes, Nitroanilines, and Phenylenediamines. J. Chrom. 147, 470, 1978.

3. Unger, P. D. and Friedman, M. A., High Performance Liquid Chromatography of 2,6- and 2,4-Diaminotoluene and its Application to the Determination of 2,4-Diaminotoluene in Urine and Plasma. J. Chrom. 174, 379, 1979.

4. Uchoytil, B., Thin-Layer and High Speed Liquid Chromatography of the Derivatives of 1,4-Phenylenediamine. J. Chrom. 93, 447, 1974.

5. Young, P. R. and McNair, H. M., High-Pressure Liquid Chromatography of Aromatic Amines. J. Chrom. 119, 569, 1976.