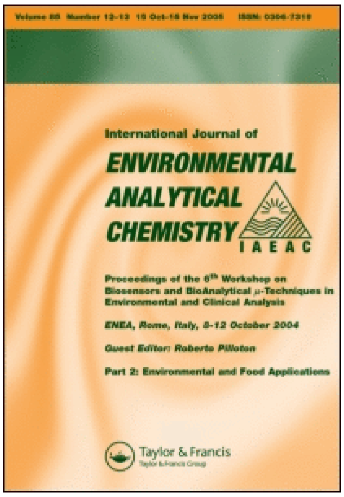

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The Gas-Chromatographic Determination of Aromatic Amines after Bromination in Surface Waters

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In this paper an analytical method is presented for the gas chromatographic determination of aniline, toluidines, monochloroanilines and dichloroanilines and their derivatives in surface water.

After a combined alkaline hydrolysis and extraction with iso-octane of the water sample in a Bleidner apparatus, the aromatic amines in the iso-octane extract are brominated and determined with a gas chromatograph equipped with a capillary column with OV-330 and a electron capture detector. The minimum detectable amounts in surface water samples were in the 5–15 ng l^{-1} range.

In the river Rhine aniline, 2-, 3- and 4-monochloroaniline and 3, 4-dichloroaniline were frequently detected. In 1979 mean values respectively 3.0, 0.52, 0.15, 0.22 and 0.40 $\mu g\, l^{-1}$.

KEY WORDS: Aromatic amines, gas chromatography, water, derivatization.

INTRODUCTION

Aromatic amines are introduced into the environment in several ways, viz. directly as industrial effluent and indirectly as transformation products from herbicides as the phenylcarbamates (e.g. propham, chlorpropham), phenylureas (e.g. monuron, diuron, linuron) and also from other compounds like paints and drugs. Aromatic amines are often toxic, carcinogenic and/or mutagenic.

Since 1971 samples from surface waters of the Netherlands were screened for the presence of herbicides and their aromatic moieties in a monitoring program (refs. 1 and 2). The sums of aromatic amines and their derivatives were determined colorimetrically. The practical lower limit of detectability was $0.5\,\mu g \cdot l^{-1}$. In 1971 several aromatic amines were also determined gas chromatographically after a derivatization which was based on the Sandmeyer reaction. After hydrolysis and diazotation of the aniline and subsequent treatment of the diazonium salts with a solution of potassium iodide, the corresponding phenyliodides are formed. The phenyliodides were determined in low concentrations with a gas chromatograph equipped with an electron-capture detector. The practical lower limit of detectability was $0.1\,\mu g \cdot l^{-1}$ for the individual aromatic amines. The yields were however often poor, e.g. for the toluidines 10–30%, for aniline 20–50%; however, for the monochloroanilines 75–88% and for 3,4-dichloroaniline even 82–95%.

Another derivatization reaction which gives compounds with good electron-capturing properties is bromination of the aromatic ring (ref. 3). In this reaction the nucleus of the aromatic amine is substituted at the 2, 4 and 6 position with bromine if these positions are not occupied by other groups. For the determination of several aromatic amines in a single step-capillary gas chromatography seems to be useful. In this study after hydrolysis the aromatic amines are brominated and determined with capillary gas chromatography.

EXPERIMENTAL

Materials

For extraction purposes, iso-octane (Nanograde, Baker) and petroleum ether (boiling range 40–60°C) were used.

Extraction and hydrolysis

25 ml of a 16 M solution of sodium hydroxide were added to a water sample of 500 ml in a round-bottomed flask. To another flask 100 ml of iso-octane were added. Both flasks were connected with the head of a Bleidner distillation/extraction apparatus and refluxed for 4 h.

Derivatization procedure

The iso-octane phase was cooled and extracted with 2 × 50 ml of a 2 M solution of hydrobromic acid for 5 min. To the combined aqueous extract 1 ml of a saturated solution of bromine was added and allowed to react for 60 min at 25°C. The excess bromine was removed by addition of a few drops of a saturated solution of sodium sulfite and to the extract a 16 M solution of sodium hydroxide was added until the pH was 10–11. The water phase was extracted with 2 × 10 ml petroleum ether for 5 min. The combined petroleum ether extracts were dried with anhydrous sodium sulfate. 2 μl of the petroleum ether phase were injected into the gas chromatograph.

Gas chromatography

apparatus:	Tracor Model 550 equipped with ^{63}Ni electron-capture detector	
column:	Pyrex, capillary (50 m × 0.25 mm ID) dynamically coated with OV 330	
temperatures:	injection port	:220°C
	oven	:isotherm at 120°C for 13.3 min, linear programming from 120°C to 210°C at $4°C \cdot min^{-1}$
	detector	:250°C
gas (nitrogen):	carrier gas	:$2\,ml \cdot min^{-1}$
	splitting gas	: $10\,ml \cdot min^{-1}$
	purge gas	:$50\,ml \cdot min^{-1}$

Macro syntheses of bromo derivatives

3 g of aromatic amine were added to a 5 M solution of hydrochloric acid; if necessary this solution was heated and acetic acid was added to dissolve the aromatic amines. 20 g of potassium bromide were added to the solution; a solution of potassium bromate ($25\,g \cdot l^{-1}$) was added dropwise until the solution was yellow. The bromo derivatives were purified by recrystallization from ethanol (100 %).

RESULTS AND DISCUSSION

As an illustration a gas chromatogram of 14 brominated aromatic amines (13 peaks) is shown in Figure 1.

Table I gives the melting points, relative retention times and relative sensitivities of the bromo derivatives of several aromatic amines compared with 2,6-dibromo-3,4-dichloroaniline and the recovery data obtained by spiking river water samples with the aromatic amines and carrying them through the entire analytical procedure.

Table II gives the recoveries of several pesticides obtained by spiking river water samples with the pesticides and carrying them through the entire analytical procedure.

TABLE I

Melting points, relative retention times and relative sensitivities of bromo derivatives of aromatic amines, and their overall-recovery from surface water ($\mu g \cdot l^{-1}$ range)

Aromatic amine	Bromo derivative	Melting point (°C)	Relative† retention time	Relative† sensitivity	Recovery (%)
aniline	2,4,6-tribromoaniline	119	0.83	0.83	100 ± 13
2-methylaniline	4,6-dibromo-2-methylaniline	41	0.75	0.32	71 ± 2
3-methylaniline	3-methyl-2,4,6-tribromoaniline	100	1.04	0.95	95 ± 5
4-methylaniline	2,6-dibromo-4-methylaniline	73	0.49	0.29	96 ± 9
2-chloroaniline	2-chloro-4,6-dibromoaniline	99	0.67	0.63	93 ± 11
3-chloroaniline	3-chloro-2,4,6-tribromoaniline	125	1.14	0.87	88 ± 7
4-chloroaniline	4-chloro-2,6-dibromoaniline	94	0.65	0.80	99 ± 2
2,3-dichloroaniline	4,6-dibromo-2,3-dichloroaniline	102	1.02	0.87	77 ± 11
2,4-dichloroaniline	6-bromo-2,4-dichloroaniline	73	0.47	0.50	102 ± 9
2,5-dichloroaniline	4,6-dibromo-2,5-dichloroaniline	106	1.02	0.87	80 ± 9
2,6-dichloroaniline	4-bromo-2,6-dichloroaniline	85	0.50	0.45	18 ± 2
3,4-dichloroaniline	2,6-dibromo-3,4-dichloroaniline	112	1.00	1.00	97 ± 7
3,5-dichloroaniline	3,5-dichloro-2,4,6-tribromoaniline	216	1.42	0.41	93 ± 11
2-nitroaniline	4,6-dibromo-2-nitroaniline	119	1.07	0.32	13 ± 3
4-nitroaniline	2,6-dibromo-4-nitroaniline	199	1.25	0.31	0 ± 0

†Retention times and sensitivities relative to 2,6-dibromo-3,4-dichloroaniline; retention time of 2,6-dibromo-3,4-dichloroaniline was 28.8 min; minimum detectable quantity of 2,6-dibromo-3,4-dichloroaniline was 1 pg.

Table III gives the limits of detection of several aromatic amines and the mean concentrations in the river Rhine at Lobith in 1979.

From the results presented in Table I:III it can be concluded that the proposed method is useful for the determination of aniline, methylanilines,

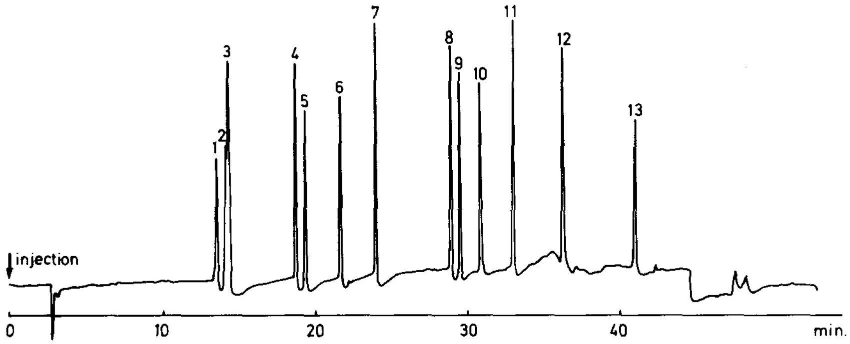

FIGURE 1 Separation of bromo derivatives of aromatic amines with a capillary column coated with OV-330.

Peaks: 1 = 6-bromo-2,4-dichloroaniline; 2 = 2,6-dibromo-4-methylaniline; 3 = 4-bromo-2,6-dichloroaniline; 4 = 4-chloro-2,6-dibromoaniline; 5 = 2-chloro-4,6-dibromoaniline; 6 = 4,6-dibromo-2-methylaniline; 7 = 2,4,6-tribromoaniline; 8 = 2,6-dibromo – 3,4-dichloroaniline; 9 = 4,6-dibromo-2,3-dichloroaniline/4,6-dibromo-2,5-dichloroaniline; 10 = 4,6-dibromo-2-nitroaniline; 11 = 3-chloro-2,4,6-tribromoaniline; 12 = 2,6-dibromo-4-nitroaniline; 13 = 3,5-dichloro-2,4,6-tribromo-aniline.

TABLE II
Recoveries of several pesticides

Pesticide	Aromatic amine after hydrolysis	Recovery (%)
propham	aniline	95
chlorpropham	3-chloroaniline	95
monuron	4-chloroaniline	91
monolinuron	4-chloroaniline	87
chloraniformethane	3,4-dichloroaniline	97
diuron	3,4-dichloroaniline	95
linuron	3,4-dichloroaniline	95
phenmedipham	3-methylaniline	95

monochloroanilines and dichloroanilines with the exception of 2,6-dichloroaniline and their derivatives like pesticides in surface water in very low concentrations (0.005–0.015 $\mu g \cdot l^{-1}$).

The method can be expanded with the determination of compounds like chlorotoluidines, bromoanilines and trichloroanilines.

TABLE III
Detection limit of several aromatic amines and the mean concentration found in the river Rhine at Lobith (1979)

Compound	Detection limit ($\mu g \cdot l^{-1}$)	Mean† concentration† ($\mu g \cdot l^{-1}$)
aniline	0.005	2.97
2-chloroaniline	0.005	0.54
3-chloroaniline	0.005	0.14
4-chloroaniline	0.005	0.22
2,3-and 2,5-dichloroaniline	0.005	0.04
2,4-dichloroaniline	0.010	0.02
2,6-dichloroaniline	0.05	<0.05
3,4-dichloroaniline	0.005	0.39
3,5-dichloroaniline	0.010	0.02
2-methylaniline	0.015	0.03
4-methylaniline	0.015	0.17

†Number of samples: 46

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