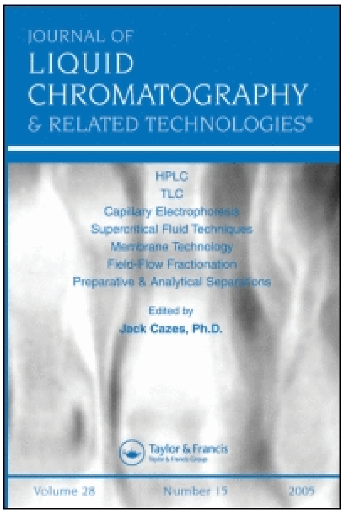

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HPLC DETERMINATION OF TRACE LEVELS OF BENZYLCHLORIDE, CHLOROBENZENE, NAPHTHALENE, AND BIPHENYL IN ENVIRONMENTAL SAMPLES

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ABSTRACT

A simple HPLC method with on-line preconcentration has been developed for the separation and the determination of trace levels of benzylchloride, chlorobenzene, naphthalene, and biphenyl in tap and surface water. The separation was achieved on the column 150 x 3.2 mm filled with Separon SGX C_{18}, d_p=5μm with the spectrophotometric detection at 220 and 250 nm. To enhance the selectivity of separation a water - methanol gradient was used. The method permits the measurement of benzylchloride, chlorobenzene, naphthalene, and biphenyl in environmental samples, with the detection limits of 10 ppt of naphthalene, 55 ppt of biphenyl, 90 ppt of benzylchloride, and 185 ppt of chlorobenzene (sample volume was 100 ml of water samples).

The assayed procedure has been applied for the quantitative determination of benzylchloride, chlorobenzene, naphthalene and biphenyl in tap water and river water.

INTRODUCTION

In the past few years, there has been growing concern about the quality of our environment. Fortunately, at the same time, there have been great strides made for the trace level determination of a wide variety of organic pollutants in surface and drinking water. Water from polluted rivers is used to feed buffer reservoirs as a first step in the production of drinking water. As the quality of river water is not constant, continuous monitoring is necessary.

Benzylchloride, chlorobenzene, naphthalene, and biphenyl are important pollutants of the atmosphere being a product of many industrial processes (pharmaceutical industry, manufacturing of colours, organic synthesis, ...). In most cases, they can be emitted separately, depending on the technological processes. The emissions influence the quality of water. These substances represent a group of noxious organic compounds, therefore, legal requirements of many countries are increasing, making it necessary to determine them at very low level. Concern about environmental pollution and occupational hazards due to the presence of these toxic compounds in water lead to the development of an HPLC method after on-line preconcentration.

Numerous studies have been published about single determination of benzylchloride, chlorobenzene, naphthalene, and biphenyl in environmental samples including gas chromatography[1-7] and RP high pressure liquid chromatography.[8-10]

A more fundamental study on the determination of naphthalene and other PAH's in environmental samples by RP HPLC with on-line preconcentration, were presented in references.[9,11-12] A work of Rigly and al.[13] summarised the influence of different factors on the recovery of extraction of naphthalene on the membrane. The GC and HPLC methods were used for analysis of extracts. The HPLC method (C_{18} column, methanol/water or acetonitrile/water mobile phase) was used to study biphenyl in environmental water samples.[14-16] The method for the determination of chlorobenzene and other toxic compounds was described in reference.[17] The separation was made using Al_2O_3 column and UV detector was used for detection. Benzylchloride can be determined using a column containing macroporous polystyrene.[18]

In the present paper the method for separation and determination of benzylchloride, chlorobenzene, naphthalene, and biphenyl in surface and tap water is discussed. To improve the limits of determination, on-line preconcentration has been developed.

Table 1

Gradient of the Mobile Phase

t/min	% A	%B
0	35	65
18	15	85

EXPERIMENTAL

Chemicals

Standards of benzylchloride (Merck), chlorobenzene, naphthalene (Accu US Standard) and biphenyl (Supelco) were analytical grade. Methanol was supplied by Merck and was HPLC grade.

Prior the use, the water samples were filtered over a 0.45 μm membrane filter.

Apparatus

An HPLC system (Hewlett Packard, Series 1100) consisted of a quaternary pump, a injection valve Rheodyne, and a diode array detector.

A Separon SGX C_{18} column (150 x 3.2 mm I. D., 5 μm particle size) was used for the HPLC assay. A Separon SGX C_{18} precolumn (30 x 3.2 mm I. D., 5 μm particle size) was used for the on-line preconcentration. Before use, the precolumn was washed by methanol (to remove memory effect) and then by water. The volume of injected spiked water samples was 50 cm^3 in the case of river water and 100 cm^3 for redestilled and tap water. The desorption of compounds under study was by gradient of mobile phase according to Table 1 in back-flash mode.

Chromatographic Conditions

The gradient elution has been recommended for HPLC procedure. Eluent A was water. Methanol was used as eluent B. The linear gradient of the mobile phase is shown in Table 1.

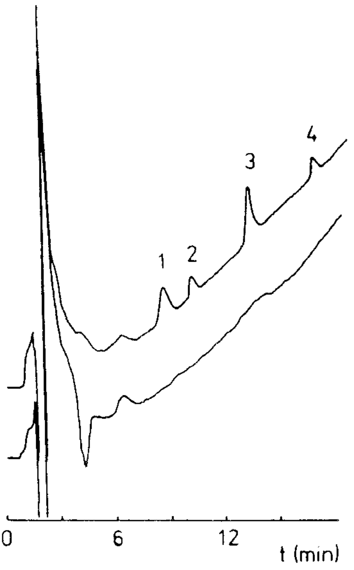

Figure 1. The chromatograms of the blank and the spiked redestilled water after on-line preconcentration (500 ppt of benzylchloride (1) and chlorobenzene (2), 100 ppt of naphthalene (3) and biphenyl(4)). Column: Separon SGX C_{18}, mobile phase: linear gradient of methanol in water from 65% to 85% during 18 min after injection of the sample, flow rate: 0.5 cm^3/min, detection: UV 220 nm. Precolumn: Separon SGX C_{18}, sample volume: 100 cm^3, flow rate: 2 cm^3/min.

The flow rate of the mobile phase was 0.5 cm^3/min and the flow rate of water samples into the precolumn was 2 cm^3/min. All experiments were done at the temperature of 25°C. A detection at 220 nm and 250 nm using the diode array detector was applied.

RESULTS AND DISCUSSION

In the experimental conditions described above, excellent and rapid separation has been achieved for all study compounds. Example of the HPLC separation of benzylchloride, chlorobenzene, naphthalene, and biphenyl using linear gradient elution is given in Figure 1. The advantage of the gradient elution was to not only decrease the time of analysis (great differences in the polarity of the quantified compounds), but also lowering of the limits of the detection (Table 2).

Table 2

The Limits of the Determination and Capacity Factors of Benzylchloride, Chlorobenzene, Naphthalene, and Biphenyl at Gradient and Isocratic Conditions

		Benzylchloride	Chlorobenzene	Naphthalene	Biphenyl
Gradient Elution					
	LD	190 ppb	285 ppb	20 ppb	190 ppb
	k	4.38	5.35	7.35	9.94
Isocratic Elution					
System A					
	LD	1.3ppm	2.5 ppm	n.d.	n.d.
	k	3.49	4.55	13.50	25.00
System B					
	LD	n.d.*)	n.d.*)	0.1 ppm	0.65 ppm
	k	2.65	3.25	4.01	6.13

LD = the limit of determination
system A = methanol/water (65/35 v/v)
system B = methanol/water (75/35 v/v)
n.d. = not determined
*) = low value of resolution between benzylchloride and chlorobenzene

When the isocratic elution is used the two chromatographic systems must be used for the separation. The first, for the separation of benzylchloride and chlorobenzene, includes the mixture of methanol in water 65 % / 35 % (v/v) as the mobile phase. The second system uses the mixture 75 % methanol in water (v/v) as mobile phase for the separation of naphthalene and biphenyl.

Whereas, all the study compounds can absorb the light of UV area the spectrophotometric detection is suitable. The wavelength 220 nm was used for the detection of benzylchloride, chlorobenzene, and naphthalene; and the wavelength 250 nm for the detection of biphenyl. At these wavelengths the maxima of absorption were founded.

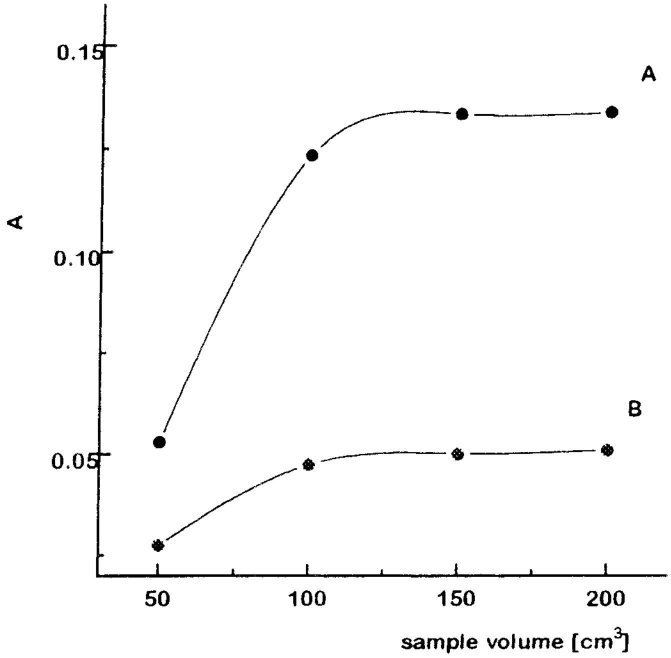

Figure 2. The breakthrough curves for benzylchloride (A) and chlorobenzene (B) at the concentration level 10 ppb. Precolumn: Separon SGX C_{18}, flow rate: 2 cm^3/min, A: area of the peak.

The most important criteria for on-line preconcentration is the breakthrough volume - the maximum sample volume that can be passed through the column without sample components breaking through. The properties of the packing material of the precolumn, physical and chemical parameters of the sample solution, flushing mode of mobile phase, the flow rate into the precolumn, and the temperature influence the retention of analytes. A reversed phase C_{18} packing material for the enrichment column was chosen to conform with the stationary phase used in the analytical column. A high capacity is required for the precolumn, whereas, selectivity and efficiency are important for the analytical column. The relationship of sample volume to the sorbent amount is determined by the substance with lowest retention.

The type and amount of packing material in the precolumn determines the maximum sample volume - the breakthrough volume. On-line trace experiment (and clean-up) by means of solid phase extraction, with short

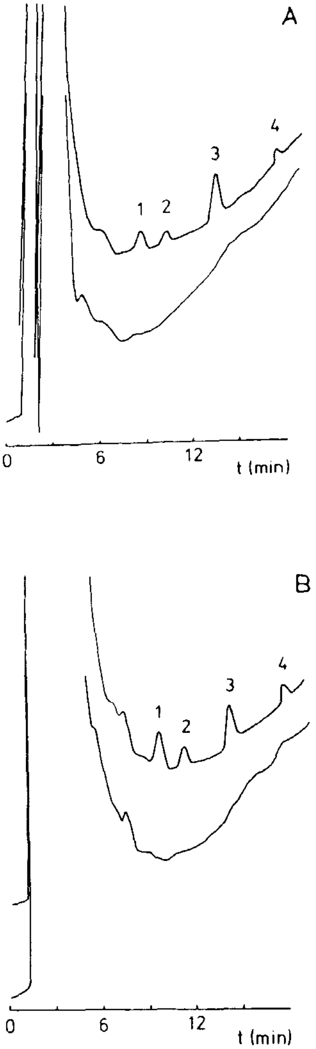

Figure 3. (A) The chromatograms of the blank and the spiked tap water after on-line preconcentration (500 ppt of benzylchloride (1) and chlorobenzene (2), 100 ppt of naphthalene (3) and biphenyl (4)). Sample volume: 100 cm^3. (B) The chromatograms of the blank and the spiked river (Danube) water after on-line preconcentration (1 ppb of benzylchloride (1) and chlorobenzene (2), 200 ppt of naphthalene (3) and biphenyl(4)). Sample volume: 50 cm^3. For the chromatographic conditions see Figure 1.

Table 3

The Limits of the Determination

Compounds	Redistilled Water/SV = 100 cm^3 With On-Line [ppt]	Redistilled Water/SV = 100 cm^3 Without On-Line [ppb]	Tap Water SV=100 cm^3 [ppt]	River Water SV=100 cm^3 [ppt]
Benzylchloride	90	190	145	145
Chlorobenzene	185	285	240	240
Naphthalene	10	20	15	30
Biphenyl	55	190	65	65

SV = sample volume

precolumns, is a popular column switching technique in liquid chromatography. In on-line experiments 3.2 mm diameter and 30 mm long precolumn was used. In this instance, the breakthrough studies were performed with the spiked redestilled water at the concentration level 10 ppb for all compounds. It was found that the capacity of the C_{18} precolumn was 105 cm^3 for benzylchloride and chlorobenzene, and in the case of naphthalene and biphenyl the breakthrough was more than 600 cm^3. The typical breakthrough curves for the spiked redestilled water (10 ppb of benzylchloride and chlorobenzene) with the breakthrough after 105 cm^3 are shown in Figure 2. The volume 100 cm^3 was used for the analysis of the redestilled and tap water. In the case of the surface (river) water, which contain many organic compounds, the sample volume containing 50 cm^3 was used for analysis.

As examples of real samples analyses, the chromatograms of the blank and the spiked tap water (500 ppt of benzylchloride and chlorobenzene, 100 ppt of naphthalene and biphenyl) are shown in Figure 3 (A) and chromatograms of the spiked river - Danube water (1 ppb of and chlorobenzene, 200 ppt of naphthalene and biphenyl) are shown in Figure 3 (B).

The determination of benzylchloride, chlorobenzene, naphthalene, and biphenyl was performed on the basis of measurement of absorbance at the wavelength of 220 nm (benzylchloride, chlorobenzene, naphthalene) and 250 nm (biphenyl) using calibration solutions containing known amounts of the compounds. In the range of concentrations from the limits of the determination (Table 3) to 10 ppb for all compounds the dependence of peak area on concentration was linear (correlation coefficients were over 0.999).

The limits of the determination afforded by HPLC method without preconcentration are in the range ppb and with on-line preconcentration in the range ppt. The lowest limits have been determined using a signal which gives 3 standard deviations above the mean blank signal. The results of the determination of the compounds under study in water are summarised in Table 3. In practice, it is obviously extremely difficult to eliminate all impurities in the reagent at levels corresponding to these very low limits of the determination.

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