Determination of chlorobenzenes in water by solid-phase extraction and gas chromatography–mass spectrometry

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Abstract

A method is described which permits the trace analysis of 10 chlorobenzenes in aqueous samples. Chlorobenzenes were extracted from water samples by solid-phase extraction with a C_{18} cartridge and analysis was carried out by gas chromatography–mass spectrometry in the selected-ion monitoring mode. The recovery and precision of the method were evaluated by extraction of spiked reagent-grade water at concentration levels of 0.1, 1.0 and 10.0 µg/l. This method was applied to the determination of chlorobenzenes in tap, ground and river water. By preparing 200 ml of environmental water samples, the detection limits of the compounds studied were in the range of 0.010–0.042 µg/l.   © 1998 Elsevier Science B.V.

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1. Introduction

Chlorobenzenes have been used as raw materials and intermediates in the manufacture of pesticides and chlorinated phenols and as process solvents. They can enter the aquatic environment through solid and liquid effluents and atmospheric discharges. These compounds have high octanol–water partition coefficients [1], so biological accumulation can be expected in the aquatic ecosystem. Because of their acute toxicity [2] and potential harmfulness to the aqueous environment [3], it is very important to monitor low levels of these compounds in the latter.

Trace analysis of chlorobenzenes in water is usually performed by gas chromatography combined with a previous concentration step including traditionally used liquid–liquid extraction (LLE) [1,4],

and the more recently developed microwave extraction [5] and microextraction [6]. Solid-phase extraction (SPE) as a sample preparation technique has been in use for a number of years [7,8], and has shown to be a suitable alternative to LLE because it can avoid or minimize the disadvantages of LLE [9–11]. Although there have been many reports about its application to the analysis of environmental pollutants in water, such as phenols [12], pesticides [13], polycyclic aromatic hydrocarbons [14] and other types of pollutants [15,16], the application of this technique to the analysis of chlorobenzene congeners in water is limited. Deans et al. [17] developed a SPE method for semi-volatile organic pollutants in spiked effluent and analyte recoveries of between 63 and 97% were obtained with a C_{18} cartridge for chlorobenzene, 1,4-dichlorobenzene and 1,2,4-trichlorobenzene. In their study, preconcentration factors of up to 100-fold were achieved and the

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GC method detection limits (without preconcentration) ranged from 0.18 to 0.28 μg/ml.

In this work we present a simple and reproducible method which involves SPE with a C_{18} cartridge for extracting 10 chlorobenzene isomers from water samples. Coupled with GC–MS in the selected-ion monitoring mode (SIM) for quantitative determination, good sensitivity and selectivity were achieved when the method was applied to the analysis of tap, ground and river water samples.

2. Experimental

2.1. Reagents and materials

The 10 chlorobenzenes (at least 98% purity) and internal standard 1,4-dibromobenzene (99% purity) were supplied by Aldrich (Milwaukee, WI, USA). Stock standard solutions (1 mg/ml) were prepared in ethyl acetate separately. The working standard solutions for calibration curves were obtained by dilution from stock solutions with ethyl acetate. The standard solution used to spike water samples was prepared by mixing the 10 chlorobenzenes in methanol at individual concentrations of 0.001 mg/ml. Pesticide-grade methanol and ethyl acetate were purchased from J.T. Baker (Phillipsburg, NJ, USA). Reagent-grade water was obtained from a Milli-Q System (Millipore, Milford, MA, USA).

In the SPE process, Bakerbond C_{18} cartridges containing 200 mg sorbent, purchased from J.T. Baker, and a Supelco (Bellefonte, PA, USA) vacuum manifold were used.

2.2. Apparatus, equipment and procedures

Before use, SPE cartridges were washed with ethyl acetate (5 ml) then conditioned with methanol (4 ml) followed by reagent-grade water (4 ml). Water samples (reagent-grade, tap, ground and river water) were fortified with the 10 chlorobenzenes by adding known volumes of standard solutions to give different spiked concentrations as required. 1,4-Dibromobenzene, used as internal standard was added to each sample at a concentration of 1.0 μg/l before extraction. Ground water and river water samples were prefiltered through 0.45-μm PTFE filters (Millipore, Bedford, MA, USA) to eliminate particulate matter before spiking. Methanol (0.5%, v/v) was added to each of the water samples before they were loaded onto the SPE columns to prevent deactivation of the silica sorbent [17]. The spiked samples were passed through the preconditioned cartridges at a flow-rate of 4 ml/min. After extraction the SPE cartridges were washed with 3 ml of reagent-grade water to remove soluble impurities and then dried by application of the sample vacuum for 8 min. The absorbed analytes were eluted with 2×1.5 ml of ethyl acetate. Each portion of the solvent was left to equilibrate in contact with the sorbent for 2 min. The combined eluates were filtered through anhydrous sodium sulphate and evaporated under a gentle nitrogen stream to 1 ml. A 1 μl aliquot was injected into the GC–MS system.

The GC–MS analysis of chlorobenzenes was performed on a Shimadzu (Tokyo, Japan) QP5000 GC–MS system. The GC system was fitted with a DB-1 30 m×0.32 mm I.D. (0.25 μm film thickness) fused-silica capillary column (J&W Scientific, Folsom, CA, USA). Helium was employed as carrier gas at 2 ml/min. The GC oven was held at 30°C for 1 min and then programmed to 220°C at 8°C/min. The injector temperature was 200°C and all injections were made in splitless mode. The GC–MS interface was maintained at 240°C and the mass spectrometer was scanned from m/z 40–350 to confirm the retention times of the compounds studied and to select the ions for identification and quantification. For quantitative determination by means of SIM, the analytes were identified by three or four selected ions for each compound and quantified by one selected ion as underlined in Table 1. A typical total ion chromatogram (TIC) as well as the mass fragmentograms of the corresponding molecular ions for quantification of the 10 chlorobenzenes and the internal standard is shown in Fig. 1. Quantification was performed by calculating peak areas relative to the internal standard, 1,4-dibromobenzene. Calibration curves constructed with standard solutions at concentrations between 0.010 and 2.0 μg/ml, with 0.20 μg/ml internal standard in each solution, showed good linearity for all chlorobenzenes studied with correlation coefficients (r^2) ranging from 0.9969 to 0.9999.

Table 1
Characteristics of GC–MS analysis

No.	Compound	t_R (min)	Selected ions (m/z)	Ion set	Time window (min)	Calibration curves		
						Slope	Intercept	r^2
1	1,3-Dichlorobenzene	8.31	146,148,111	I	5.5–9.2	3.2318	0.0599	0.9973
2	1,4-Dichlorobenzene	8.44	146,148,111			3.2674	0.0944	0.9969
3	1,2-Dichlorobenzene	8.86	146,148,111			3.0188	0.1155	0.9969
4	1,3,5-Trichlorobenzene	10.95	180,182,145	II	9.2–11.3	2.4178	0.0360	0.9994
5	1,2,4-Trichlorobenzene	11.72	180,182,145	III	11.3–12.1	1.4025	−0.0421	0.9998
6	1,4-Dibromobenzene[a]	11.89	236,234,157					
7	1,2,3-Trichlorobenzene	12.35	180,182,145	IV	12.1–12.7	2.4984	−0.0396	0.9999
8	1,2,4,5-Tetrachlorobenzene	14.58	216,214,218,181	V	12.7–15.7	2.4183	−0.0633	0.9999
9	1,2,3,4-Tetrachlorobenzene	15.32	216,214,218,181			2.1197	−0.0140	0.9998
10	Pentachlorobenzene	17.75	250,248,252,215	VI	15.7–18.2	1.9750	0.0149	0.9998
11	Hexachlorobenzene	20.62	284,286,282,288	VII	18.2–21.0	1.1113	0.0717	0.9975

[a] Internal standard.

3. Results and discussion

3.1. Method recoveries and precision

In order to assess the efficiency of the method, recovery and precision studies at relatively high, medium and relatively low concentration levels of the 10 chlorobenzenes in reagent-grade water were performed. Aliquots (200 ml) of reagent-grade water were spiked with different known volumes of the stock solution to obtain individual concentrations of the analytes at 0.1, 1.0, 10.0 µg/l. After 200 ml of sample was loaded onto SPE cartridge, 3 ml of ethyl acetate was used for recovering the analytes. The
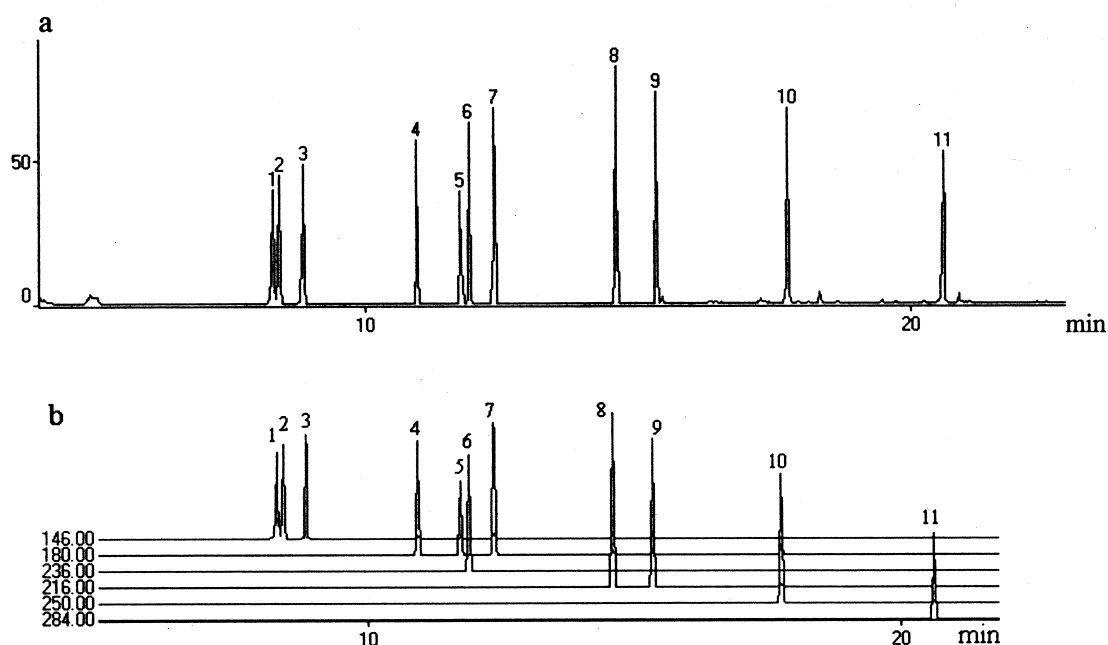

Fig. 1. (a) Total ion chromatogram (scanning from m/z 40 to 350) obtained from direct injection of 5 ng of each of the 10 chlorobenzenes and the internal standard; (b) the mass fragmentograms of the corresponding molecular ions of the chlorobenzenes and the internal standard for quantitation. Peak identifications and retention times are shown in Table 1.

Table 2
Summary of recovery and R.S.D. results at different individual concentrations of chlorobenzenes in 200 ml of reagent-grade water and limits of detection

Compound	%Recovery[a] (R.S.D.)			LOD (μg/l)
	0.1 μg/l	1.0 μg/l	10.0 μg/l	
1,3-Dichlorobenzene	67.9 (9.1)	69.0 (5.6)	73.4 (6.6)	0.010
1,4-Ddichlorobenzene	NA	74.4 (8.0)	76.2 (10.6)	NA
1,2-Dichlorobenzene	85.3 (4.7)	88.3 (4.7)	92.1 (5.2)	0.012
1,3,5-Trichlorobenzene	62.3 (6.8)	62.7 (6.1)	75.3 (2.3)	0.019
1,2,4-Trichlorobenzene	86.0 (9.0)	85.4 (4.1)	88.5 (1.6)	0.031
1,2,3-Trichlorobenzene	94.9 (4.2)	93.2 (6.4)	98.4 (2.4)	0.013
1,2,4,5-Tetrachlorobenzene	81.6 (9.9)	82.0 (5.4)	83.8 (1.9)	0.020
1,2,3,4-Tetrachlorobenzene	96.6 (8.7)	94.5 (4.0)	92.6 (4.1)	0.028
Pentachlorobenzene	88.5 (7.0)	90.2 (6.1)	88.0 (2.5)	0.028
Hexachlorobenzene	90.6 (13.3)	89.7 (5.9)	87.0 (8.7)	0.045

NA, not available.

[a] Mean values from four determinations.

experiment was repeated four times with four separate SPE cartridges. The recovery, relative standard deviation (R.S.D.) data are reported in Table 2. As can be seen, the recoveries for most chlorobenzenes (seven out of 10) are higher than 80% under the chosen experimental conditions and the R.S.D. values are below 10% in most cases. In our preliminary study, the elution efficiency of several solvents was compared. Among the solvents tested, hexane and methanol produced approximately 50–70% elution strength for most compounds relative to ethyl acetate. Dichloromethane did not show reproducible elution efficiency. Although toluene has a similar structure to chlorobenzenes, and thus shows stronger elution ability, the peak shapes of several chlorobenzenes, including 1,2,4-trichlorobenzene, 1,2,3-trichlorobenzene and 1,2,4,5-tetrachlorobenzene, in this solvent were very poor and made accurate quantification difficult. Furthermore, its relatively higher boiling point (110°C) suggests there would be more losses of the analytes during the concentration step due to the longer evaporation period needed. With 3 ml ethyl acetate as elution solvent good recoveries and reproducibilities could be obtained as shown in Table 2. This could be due to its moderate polarity and good wettability for the SPE sorbents [18]. Larger volumes of the elution solvent did not produce significant increase in response and recovery for each compound. The recoveries of 1,3-dichlorobenzene, 1,4-dichlorobenzene and 1,3,5-trichloroben-

zene were relatively lower than the higher chlorinated benzenes. Breakthrough tests were performed by using two cartridges in tandem and no target compound was found when checking the eluate from the second cartridge under the same conditions. Determinations before and after the solvent evaporation showed that the losses during the solvent evaporation step were about 11% for 1,3-dichlorobenzene and no more than 6% for all the other compounds. So partial losses for these three compounds might occur during the drying or other steps. Some losses on recoveries of 1,3-dichlorobenzene, 1,2-dichlorobenzene and 1,3,5-trichlorobenzene could be observed when reducing the spiking concentration from 10.0 to 1.0 μg/l, but no further serious losses occurred at the 0.1 μg/l level. For other compounds studied, the recoveries were independent of concentrations. R.S.D. values at lower concentration were slightly higher than those at higher concentration. Irreversible adsorption, losses during drying and evaporation, and spiking and determination errors could account for larger effects on these results when the concentration was lower. However, the losses were not significant, and the results were considered acceptable for trace analysis at low ppb levels.

3.2. Detection limits

Table 2 shows the limit of detection (LOD) data

which were obtained on the basis of the extraction of the water samples with spiking concentrations near the estimated detection limit and at a signal-to-noise (S/N) ratio of 3. These LOD values range from 0.010 to 0.045 µg/l when using 200-ml reagent grade samples, and are below the corresponding LOD values that are available in US Environmental Protection Agency (EPA) Method 524.2 [19], in which the detection limits for 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzenes are reported to be 0.12, 0.03, 0.03 and 0.04 µg/l, respectively (as determined by GC–MS).

3.3. Application to real environmental water samples

To assess the applicability of this method, real environmental water samples, as well as these samples fortified with the 10 chlorobenzenes, were analyzed. No target compound was found in genuine Singapore tap, ground water samples and Singapore River water samples. Results of recovery, R.S.D. and detection limits of environmental water samples spiked at the 1.0 µg/l level are tabulated in Table 3. For all these three water types, the mean relative recoveries and R.S.D. values for all chlorobenzenes studied were close to those obtained using reagent-grade water. Limits of detection in tap, ground and river waters were also similar to those obtained using

reagent-grade water, ranging from 0.010 to 0.042 µg/l (with extraction of 200 ml of water sample). These data illustrate that the matrix in real samples has little effect on the determinations under our method. Fig. 2 shows the TIC and mass fragmentograms obtained by extracting 200 ml of Singapore River water sample; as mentioned above, no chlorobenzenes were detected. The figure also shows possible interferences from the river matrix. However, in our experiments, the use of SIM precluded interferences from the sample matrix, thus providing high sensitivity and selectivity. Fig. 3 shows the mass fragmentograms of an extract of 200 ml of river water sample spiked with 1.0 µg/l chlorobenzenes. The method described in this work, which addressed the analysis of a more comprehensive series of chlorobenzenes than previous studies, may thus be used to determine trace levels of chlorobenzene congeners in environmental waters.

4. Conclusion

The results of this study demonstrate that the proposed analytical method involving SPE and GC–MS-SIM give acceptable recoveries and reproducibilities for 10 chlorobenzenes from tap, ground and river water samples. Detection limits at the ng/l level were achieved with a sample volume of only

Table 3
Summary of results from analysis of chlorobenzenes in fortified tap, ground and river water samples[a]

Compound	Tap water		Ground water		River water	
	Recovery[b] (R.S.D.) (%)	LOD (µg/l)	Recovery[b] (R.S.D) (%)	LOD (µg/l)	Recovery[b] (R.S.D) (%)	LOD (µg/l)
1,3-Dichlorobenzene	66.4 (7.7)	0.010	66.6 (8.4)	0.013	70.0 (7.2)	0.018
1,4-Dichlorobenzene	72.0 (8.6)	NA	73.8 (4.0)	NA	73.4 (8.5)	NA
1,2-Dichlorobenzene	87.2 (5.2)	0.011	84.3 (5.6)	0.011	85.1 (7.4)	0.013
1,3,5-Trichlorobenzene	61.2 (5.5)	0.022	59.1 (8.3)	0.021	64.5 (6.2)	0.024
1,2,4-Trichlorobenzene	78.6 (3.3)	0.032	85.5 (7.3)	0.031	87.5 (5.1)	0.042
1,2,3-Trichlorobenzene	92.1 (5.6)	0.015	93.5 (6.9)	0.013	96.1 (5.5)	0.014
1,2,4,5-Tetrachlorobenzene	80.8 (4.6)	0.023	82.7 (3.3)	0.017	81.8 (6.7)	0.020
1,2,3,4-Tetrachlorobenzene	91.4 (4.3)	0.030	96.0 (4.5)	0.022	94.5 (3.1)	0.025
Pentachlorobenzene	88.8 (5.8)	0.030	89.0 (6.7)	0.023	89.1 (7.3)	0.032
Hexachlorobenzene	88.2 (8.9)	0.041	90.9 (12.2)	0.036	88.1 (10.1)	0.041

[a] Water samples (200 ml) containing 1.0 µg/l of each chlorobenzene.
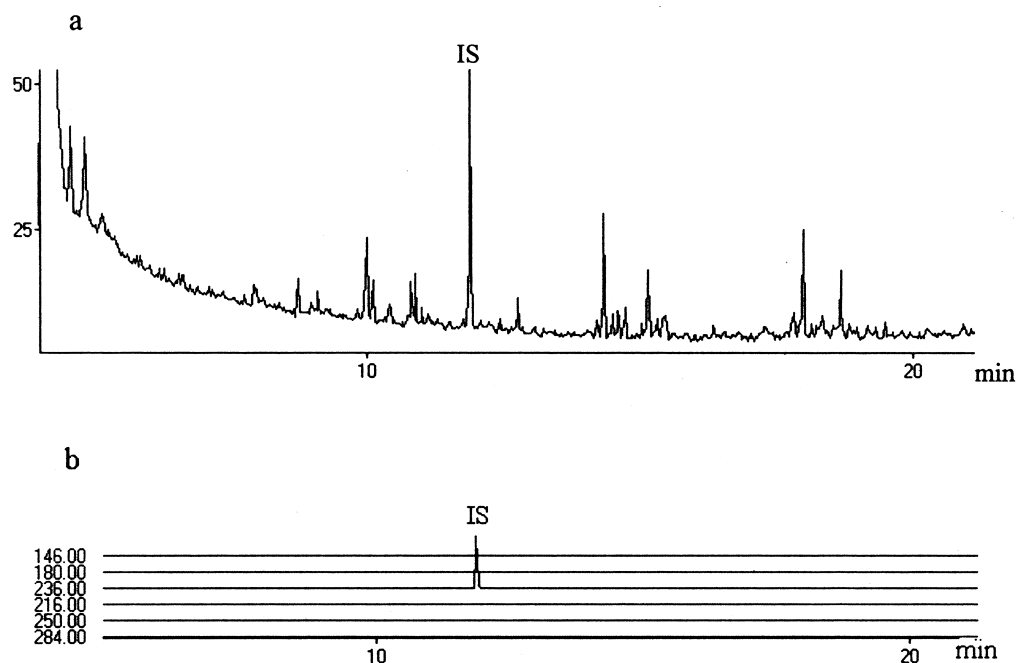[b] Mean values from four determinations.

Fig. 2. (a) Total ion chromatogram (scanning from m/z 40 to 350) obtained after SPE of 200 ml of Singapore River water sample; (b) mass fragmentograms of the same sample.
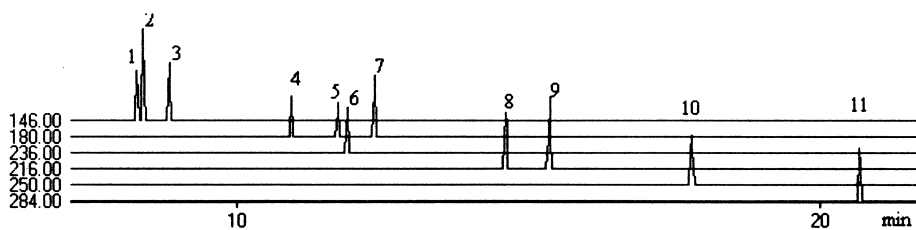

Fig. 3. Mass fragmentograms of the corresponding ions of chlorobenzenes by GC–MS-SIM obtained after SPE of 200 ml of Singapore River water spiked with 1.0 μg/l of each of the chlorobenzenes. See Table 1 for peak identifications.

200 ml. This method is simple and convenient, but sufficiently sensitive and selective.

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