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Journal of Chromatography A, 1033 (2004) 1–8
JOURNAL OF CHROMATOGRAPHY A
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Development of a solid-phase extraction method for the determination of polychlorinated biphenyls in water

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Received 19 August 2003; received in revised form 6 January 2004; accepted 20 January 2004

Abstract

Polychlorinated biphenyls (PCBs) in water were extracted with a rebuilt extraction unit using 47 mm C_{18} solid-phase extraction (SPE) disks. Three types of disks (SPEC, ENVI and Empore) were investigated for the extraction of seven PCBs from 1 l reagent water spiked at two concentration levels (20 and 1000 ng/l). The Empore disks produced the best analyte recoveries (91–107% with R.S.D. of 1–8%) at the low concentration level and displayed no leaking tendency. Empore disks were therefore considered superior to ENVI and SPEC disks for the conditions outlined in this work. The obtained extracts were dried and purified in an additional clean-up step using custom-made columns containing Florisil and Na_2SO_4. For water containing large amounts of organic matter, a pre-filtration was included. Final analysis was carried out on a dual-column GC–electron-capture detection system with on-column injection. The optimised extraction method, including clean-up, was less time-consuming and used less hazardous organic solvents than conventional liquid–liquid extraction (LLE) methods. Recoveries were 92–102% with R.S.D. of 3–8%.

Keywords: Solid-phase extraction; Water analysis; Environmental analysis; Polychlorinated biphenyls

1. Introduction

Recent global focus on fresh water supplies [1,2] has led to increased attention to the problems associated with water pollution caused by leachate from landfills and waste dumps. The complex composition of leachate, e.g. salts, heavy metals and various types of organic pollutants, pose a threat towards aquatic organisms and are also of great concern due to possible contamination of groundwater. Treatment of leachate is thus important since improvement of the quality of this type of waste water is necessary to improve the life conditions world-wide. Among common and ubiquitous persistent organic pollutants, which may occur in waste water, are polychlorinated biphenyls (PCBs), which if exposed to organisms are known to cause severe problems [3]. Numerous investigations have been performed during the last 35 years to evaluate their global distribution and transportation [4]. PCBs have very special properties whereby they found their way into various industrial applications as, for example, dielectric fluids in power transformers and capacitors. Unfortunately, much of this electrical equipment has been discharged on landfills and from there PCBs can leak out into our environment [5]. One possible route is the entrance of PCBs into leachate and from there to other types of water bodies such as ground and surface waters.

As an initial part of an ongoing Swedish–Baltic co-operation project a simple and reliable methodology had to be developed for different types of waters. Extraction of PCBs in water samples has classically been performed by means of liquid–liquid extraction (LLE). However, during the last decades, solid-phase extraction (SPE) has been utilised as a more sophisticated approach for such extractions resulting in lower hazardous solvent consumption, faster time for extraction and no emulsion formation [6]. SPE procedures have reached wide acceptance and the US Environmental Protection Agency (EPA) has methods available for the analysis of PCBs in drinking water using silica-bound sorbents packed in cartridges or embedded in

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doi:10.1016/j.chroma.2004.01.022

Table 1
A summary of previous methods extracting PCBs from spiked water samples using SPE disks and solvent elution

Year	Sample	Volume (l)	PCBs analysed (IUPAC)	Concentration (ppb)	Disk washing (A) and conditioning solvents (B)	Disk	Elution solvent	Average recovery (A), highest recovery (H), lowest recovery (L), average R.S.D. (R) (%)
1990 [10,11]	Spiked reagent water	1	1, 5, 29, 47, 98, 154, 188, 201	0.2 or 2	(A) 10 ml DCM; (B) 10 ml MeOH	47 mm Empore C_{18}	10 ml DCM	A: 98[a]; H: 141[a]; L: 78[a]; R: 22[a]
1990 [6]	Spiked surface water	0.5	Six major peaks from an Aroclor 1254 mixture	10	(A) 10 ml EtAc; (B) 10 ml MeOH	47 mm Empore C_8	20 ml EtAc	A: 90
1991 [12]	Spiked water	1	1, 5, 29, 47, 98, 154, 171, 201	0.2 or 2	(A) 10 ml EtAc–DCM (1:1); (B) 10 ml MeOH	47 mm Empore C_8	10 ml EtAc and 10 ml DCM	A: 80[a]; H: 106[a]; L: 30[a]; R: 39[a]
1993 [13]	Spiked reagent water	1	1, 5, 29, 47, 116, 153, 171	2	(A) 10 ml MeOH; (B) 10 ml MeOH	47 mm Empore C_{18}	CO_2 with 0.4 ml MeOH as modifier and 2 ml acetone as collection solvent	A: 90; H: 103; L: 72; R: 19
1994 [7]	Spiked reagent water	1	1, 5, 171, 154, 201, 98, 47, 29	0.5	(A) 5 ml EtAc–DCM (1:1); (B) 5 ml MeOH	47 mm Empore C_{18}	5 ml EtAc, 5 ml DCM and 6 ml EtAc–DCM (1:1)	A: 96; H: 100; L: 91; R: 5
1995 [14]	Spiked drinking water	1	77, 118, 105, 126, 153, 138, 128, 188, 187, 180, 170, 200, 195, 206, 209	0.5	(A) 30 ml hexane; (B) 20 ml MeOH	47 and 90 mm Empore C_{18}	30 ml DCM	A: 65; H: 74; L: 55
1995 [15]	Spiked reagent water	1	1, 5, 29, 47, 98, 154, 188, 201	2	(A) 10 ml acetone; (B) 20 ml MeOH	47 mm Empore C_{18}	15 ml DCM	A: 101; H: 124; L: 51; R: 26
1996 [16]	Spiked brackish water	1	Five congeners: tri-, penta-, hexa-, hepta- and octa-chlorinated	2	According to disk producer (A) 10 ml DCM; (B) 10 ml MeOH	47 mm Empore C_{18}	CO_2 with 4.8 ml acetone as modifier and trap eluted with 1.2 ml DCM	A: 106; H: 115; L: 98; R: 6
1996 [17]	Spiked reagent water	1	Five congeners: tri-, penta-, hexa-, hepta- and octa-chlorinated	2	(A) 10 ml DCM; (B) 10 ml MeOH	47 mm Empore C_{18}	CO_2 with 3.7 ml acetone as modifier and trap eluted with 1.2 ml DCM	A: 82; H: 91; L: 72; R: 7
1997 [18]	Spiked reagent water	5, 10 or 15	28, 52, 101, 118, 153, 138, 180	0.010 or 0.020	(A) 100 ml MeOH and 100 ml DCM; (B) 100 ml MeOH	90 mm Empore C_{18}	40 ml MeOH	A: 70[b]; H: 85[b]; L: 55[b]; R: 11[b]

DCM: dichloromethane.
[a] Values presented only for the 0.2 ppb concentration.
[b] Values presented are obtained from 51 samples.

disks [7]. For SPE of larger water samples (e.g. >0.5 l) containing suspended particles, disks have been reported superior to cartridges enabling faster flow rates, less channelling, reduced risk for plugging and lower solvent consumption [8]. LLE and SPE publications for PCB extraction from water have previously been reviewed [9]. An overview of the most important results presented until now based on disk extraction [6,7,10–18] are presented in Table 1.

Although new promising techniques such as solid-phase microextraction (SPME), stir-bar-sorptive extraction (SBSE) [19] and the use of 'microsized' SPE disks are available [20], this paper describes the development of a methodology for investigation of PCB contamination based on disk extraction with solvent elution. The reason for developing a new methodology is that many of the applications only measure PCBs in the ppb range while others utilise hazardous solvents such as dichloromethane (Table 1). Additionally, most disk methods, using solvent elution, show unsatisfactory recoveries for PCBs in reagent water. Three types of disks from well-known producers were investigated and the developed methodology was used for analysis of some Swedish waters, including ground water, tap water and leachate.

2. Experimental

2.1. Chemicals

Methanol, *n*-heptane, acetone (Pestanal grade, Riedel-de Haën, Seelze, Germany), isooctane and *n*-pentane (residue analysis, Fluka Chemie, Buchs, Switzerland) were used in the experiments. Millipore water (Milli-R04, Millipore, Bedford, MA, USA) was used as reagent water in spiking experiments and in blank extractions [7].

PCB solutions 1 and 2 contained a total of 10 PCBs, but only 7 of these were investigated in this study (52, 101, 138, 153, 170, 180 and 187, Larodan, Malmö, Sweden). The PCBs were dissolved in isooctane, and the concentrations in the two solutions (for each PCB congener) were 20 and 0.4 μg/ml, respectively. Reagent water spiked with PCB solutions 1 and 2 were used for SPE disk comparison, SPE method development, and clean-up evaluation.

PCB solution 3 was a certified reference material, NIST 2262 (US National Institute of Standards and Technology, Gaithersburg, MD, USA), utilised for preparation of calibration standards, containing 28 certified PCBs. Seven calibration solutions in *n*-heptane were prepared in the range of 1–40 ng/ml.

PCB solution 4 contained PCB 35 (as time reference) and PCB 169 (for quantification, Larodan) in *n*-heptane and was used as internal standard (IS). The concentrations in the solution were 540 and 400 ng/ml for PCB 35 and PCB 169, respectively.

2.2. Solid-phase extraction equipment

A standard Millipore 47 mm glass vacuum filtration apparatus (Millipore) was utilised after being rebuilt according to Fig. 1.

The normal sintered piece of glass, acting as support for the glass fibre filters and SPE disks, was removed and replaced by a removable PTFE O-ring and a removable stainless steel support with small holes (40% of the total area). This construction facilitated and reduced the time for cleaning of the extraction equipment. The vacuum source used was a MZ 2C vacuum pump (Vacuubrand, Wertheim, Germany).

Three different 47 mm SPE disks were compared in the initial spiking experiments with reagent water, ENVI disks (ENVI-18 DSK, C_{18}, Supelco, Bellefonte, PA, USA), SPEC disks (SPEC-47-C_{18} AR, C_{18}, SPEC Division of ANSYS, Los Angeles, CA, USA) and Empore disks (Empore, C_{18}, 3M Centre, St. Paul, MN, USA).

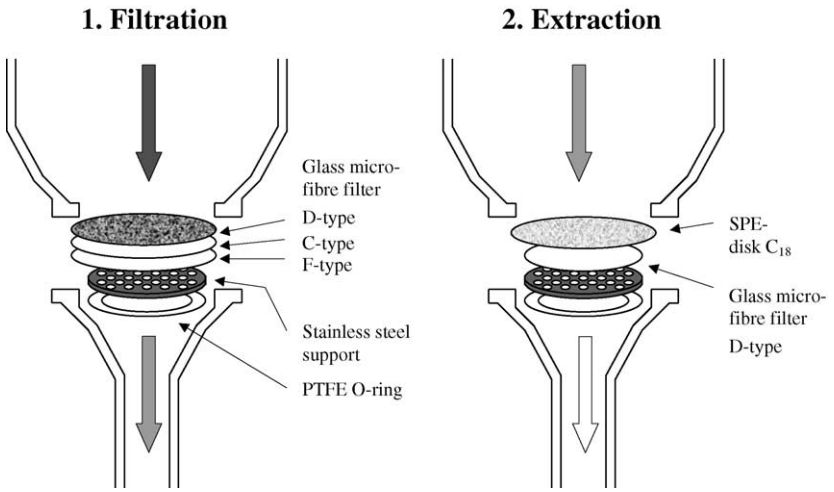

Fig. 1. Rebuilt solid-phase extraction unit used in all experiments. The sample was treated in two steps as indicated in the figure. The first step was a filtering step followed by an extraction step. Both are described in more detail in the text.

Three types of glass fibre filters were used as seen in Fig. 1 (D, C and F glass microfibre filters, 47 mm, Whatman, Maidstone, UK).

2.3. Solid-phase extraction procedure

2.3.1. SPE disk comparison

Fifty microlitres of PCB solution 1 or 2 was added to 1 l reagent water in a glass bottle, resulting in two PCB concentrations, 1000 and 20 ng/l for each PCB congener. The glass bottles were shaken vigorously for 5 min before performing the SPE procedure. The 47 mm glass vacuum filtration apparatus was mounted according to Fig. 1, step 2. A D-filter was placed under the SPE disk not to have the disk directly attached to the stainless steel support. This increased the total area available for the water sample to pass through the disk and prevented disk breakage. Before sample extraction, the disk was cleaned with isooctane followed by a disk conditioning step with methanol. Thereafter, reagent water was added prior to sample addition. All solvents were rinsed down the sides of the glass filtration apparatus. To avoid recovery losses, the disk may not go dry after adding the methanol until the sample is extracted. After sample extraction, the disk was allowed to air dry under vacuum for 10 min. Analytes were eluted into test tubes using isooctane. In this step, the elution solvent was rinsed down the sides of the glass filtration apparatus. Extracts were concentrated under a gentle stream of nitrogen and quantitatively transferred to 2 ml vials, followed by addition of 50 μl IS.

2.3.2. SPE method development

In these experiments, the 20 ng/l samples were used to have somewhat realistic concentrations. To avoid clogging, a filtering step was introduced. During the filtering step (Fig. 1, step 1), the water sample was passed through pre-washed glass microfibre filters. Cleaning of the filters was performed with *n*-pentane, methanol and reagent water. After filtration, the filters were dried for 10 min, and analytes were eluted into test tubes with *n*-pentane.

SPE of the filtrate was carried out in a similar way as in the SPE disk comparison experiments earlier. The only difference was the use of *n*-pentane as elution solvent. When *n*-pentane was used, 2 ml of *n*-heptane was added as a keeper to the extract. Some of the experiments also included a clean-up step as described further.

2.3.3. Clean-up procedure

Set-up 1 consisted of glass columns, 2 cm in diameter, packed with glass wool (Supelco), 8.0 g anhydrous Na_2SO_4 (Fluka Chemie) and 4.0 g Florisil (Supelco). Glass wool and Na_2SO_4 were heated at 400 °C overnight. The Florisil was activated at 130 °C overnight. The column was washed with 60 ml of *n*-pentane followed by sample addition. Samples were then eluted with 60 ml *n*-pentane and evaporated to ca. 1 ml under nitrogen followed by addition of 50 μl IS. Set-up 2 were pre-packed 15 ml custom-made disposable clean-up columns containing 2.0 g Florisil and 2.0 g Na_2SO_4 (International Sorbent Technology, Sorbent, V. Frölunda, Sweden). Set-up 3 consisted of two connected cartridges containing 2.0 g Florisil (Megabond Elut FL 2.0 g, Varian, Harbor City, CA, USA) and 2.2 g Na_2SO_4 (Bond Elut JR sodium sulphate 2.2 g, Varian). The vacuum source used during this step was a VacMaster-10 (International Sorbent Technology, Mid Glamorgan, UK).

For set-ups 2 and 3, the columns were washed with 15 ml of *n*-heptane. Samples were added and analytes were eluted with 20 ml *n*-heptane. Sample collection was done in 1.5 ml fractions and to each fraction 50 μl IS was added.

2.3.4. Final extraction procedure for real samples

All water samples were transferred into 1 l glass bottles. The tap water was taken from the Department of Analytical Chemistry, Lund University. The cold water was running for 5 min prior to sampling and during the 5 min of sampling as recommended by the EPA [7]. Sampling and extraction were conducted the same day. Three 1.5 l bottles of Ramlösa mineral water were decarbonised and transferred into glass flasks as described earlier. Ramlösa mineral water consists of filtered and carbonated ground water from an area close to the community of Ramlösa, located in the southern part of Sweden. The water was extracted within 24 h after the bottles were opened. Leachate from a waste dump located near Emmaboda, Sweden, were sampled in glass flasks and extracted within 3 days. Extraction of the real water samples was performed using the optimised method from the SPE section and the clean-up section described earlier. A summary of this method is presented in Table 2.

2.4. Gas chromatographic analysis

PCB extracts were analysed by injecting 1 μl of each sample on-column onto the gas chromatograph (GC 6890N) equipped with a 7683 series autosampler and injector (Agilent, Palo Alto, CA, USA). Detection was performed with two micro-electron-capture detection (μECD) systems (^{63}Ni-ECD). The detectors were held at 300 °C and purged with nitrogen at 60 ml/min (5.5, >99.9995% purity, AGA Gas, Sweden). Hydrogen was used as carrier gas at a constant linear velocity of 43 cm/s (Hydrogen Lab., AGA Gas).

The dual-column system utilised for separation of analytes was a HP-5ms (30 m × 0.25 mm, 0.25 μm, 5% phenylmethylpolysiloxane) column coupled in series to a HT-5 (25 m × 0.22 mm, 0.10 μm, 5% phenylpolycarboransiloxane, Scientific Glass Engineering Europe, Milton Keynes, UK) column and a parallel DB-17 (60 m × 0.25 mm, 0.25 μm, 50% phenylmethylpolysiloxane) column [21]. Parallel columns were coupled to the inlet via a deactivated retention gap (2 m × 0.530 mm deactivated fused silica) using a quick-seal glass “T”. The columns HP-5ms, DB-17 and the retention gap were manufactured by Agilent.

The temperature program was 90 °C for 2 min rising to 170 °C with a rate of 20 °C/min keeping the temperature

Table 2
Short summary of the optimised SPE method

Step	Procedure
1	Wash the filters and filtration unit with 10 ml *n*-pentane, methanol and water
2	Load sample and filter it
3	Dry filters with air for 10 min
4	Rinse sample container with 10 ml of *n*-pentane and load this solvent onto the filters
5	Elute analytes from filters into a test tube using the above 10 ml solvent
6	Load another 10 ml of *n*-pentane onto filters rinsing it down the sides of the filtration unit
7	Elute analytes from filters, into the same test tube as in step 5, using the above 10 ml solvent
8	Load a final 10 ml *n*-pentane fraction onto the filters and elute the solvent into the test tube
9	Wash and condition the SPE disk with 10 ml of *n*-pentane, methanol and water
10	Load filtrate from filtration and extract it
11	Dry SPE disk with air for 10 min
12	Elute analytes from SPE disk, in the same way as for filters, using 3× 10 ml of *n*-pentane
13	Add 50 μl IS and 2 ml of *n*-heptane to the pooled eluate
14	Evaporate the pooled eluate with nitrogen down to ca. 2 ml
15	Wash the drying and clean-up cartridge with 12 ml of *n*-pentane
16	Load evaporated sample eluate onto the drying and clean-up cartridge
17	Elute analytes with 9 ml of *n*-pentane into another test tube
18	Evaporate the dried eluate with nitrogen down to ca. 1 ml
19	Transfer the sample from the test tube to 2 ml vials
20	GC analysis

constant at 170 °C for 7.5 min. Thereafter, the temperature was raised to 285 °C with a speed of 3 °C/min keeping the temperature constant at 285 °C for 8 min.

Quantification was made by means of peak height measurements and the concentration in the samples were calculated from a seven point power-fit calibration curve in the concentration interval of 1–40 ng/ml for the individual PCB congeners. PCB 169 was used as IS. Recoveries were calculated against the theoretical added amount of PCBs using results from the detector giving the lowest signal.

3. Results and discussion

3.1. SPE disk comparison

High level concentrations (1000 ng/l) were used when investigating the elution procedure suggested by the disk producers. Elution was initially performed with 2× 5 ml of isooctane for ENVI and SPEC disks, and 2× 10 ml for the Empore disks. This gave rather unsatisfactory average recoveries of 76, 84 and 74% for ENVI, SPEC and Empore, respectively. However, the Empore disk instructions suggested the addition of a third elution step. New experiments were performed, eluting the PCBs with 3× 10 ml of isooctane (Table 3).

This had no effect on the ENVI and SPEC recoveries, while the Empore recoveries increased with 16% resulting in a recovery of 91%. Experiments at the low spiking level (20 ng/l) showed a recovery of 94% for the Empore disk, while ENVI and SPEC disks had recoveries below 86%. The leakage tendency was less pronounced for the Empore disks using our set-up. This is because this PTFE-based disk is thinner and more compressible (softer) compared to the glass fibre-based ENVI and SPEC disks. Consequently, Empore disks were used in further method development.

3.2. SPE method development

To decrease the solvent evaporation time, isooctane was replaced with *n*-pentane. Results from elution with *n*-pentane gave the same recovery (95%, Table 4(A)) as isooctane (94%, Table 3(B)). Thus, isooctane was replaced with *n*-pentane as washing and analyte elution solvent, resulting in a 15 min decrease in the total time of analysis.

When performing a pre-filtering step on glass microfibre filters, large amounts of PCBs are kept on the filters (Table 4(B)). However, an acceptable total recovery (average 110%) was achieved for the sum of the glass microfibre filter fraction and the SPE disk fraction (Table 4(B)).

Table 3
PCB recoveries from spiking experiments, using reagent water at two spiking levels and three types of C_{18} extraction disks (ENVI, SPEC and Empore)

PCB	(A) High level (1000 ng/l)						(B) Low level (20 ng/l)					
	ENVI		SPEC		Empore		ENVI		SPEC		Empore	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
52	68	3	79	3	88	2	85	18	116	7	107	8
101	74	5	81	5	91	3	77	12	80	19	92	4
138	80	7	87	4	93	4	84	12	82	15	93	1
153	78	6	85	5	91	5	80	9	80	18	91	1
170	78	6	86	4	93	6	83	17	80	16	92	3
180	78	9	85	4	91	4	80	15	81	16	94	4
187	77	6	86	5	92	5	82	16	81	17	92	1
Average	76	6	84	4	91	4	82	14	86	15	94	3

In all experiments, 3× 10 ml isooctane was used as elution solvent ($n = 3$).

Table 4
SPE of PCBs spiked at 20 ng/l in 1 l of reagent water, using Empore disks without (A) and with (B) pre-filtering through glass microfibre filters, with addition of clean-up of filter and SPE eluates using set-up 1 (C), with addition of clean-up of pooled filter and SPE eluates using set-up 1 (D), with addition of the internal standard to the pooled filter and SPE eluates and clean-up using set-up 2 (E)

PCB	(A) No pre-filtering, no clean-up		(B) Pre-filtering, no clean-up						(C) Pre-filtering, clean-up set-up 1						(D) Pre-filtering, clean-up set-up 1		(E) Pre-filtering, clean-up set-up 2	
	Recovery (%)	R.S.D. (%)	Filter		SPE		Filter + SPE		Filter		SPE		Filter + SPE		Filter + SPE		Filter + SPE	
			Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
52	98	8	7	38	104	7	111	6	4	26	66	12	70	13	73	1	97	4
101	92	14	30	31	83	6	113	6	17	27	56	13	72	16	82	1	92	5
138	92	11	63	46	58	14	121	23	31	30	42	7	73	17	80	6	102	3
153	93	10	55	39	59	11	114	19	29	27	43	6	73	14	85	2	96	4
170	104	6	61	28	47	21	108	10	37	24	31	10	69	18	52[a]	4	96	8
180	96	9	63	36	46	16	109	19	37	32	32	5	69	19	86	5	97	8
187	93	11	50	29	46	14	96	9	35	27	37	3	73	13	84	2	94	5
Average	95	10	47	35	63	13	110	13	27	28	44	8	71	16	82	3	96	5

Elution of all filters and SPE disks were performed with 3× 10 ml *n*-pentane ($n = 3$).

[a] Excluded from the average value due to unknown interfering peak.

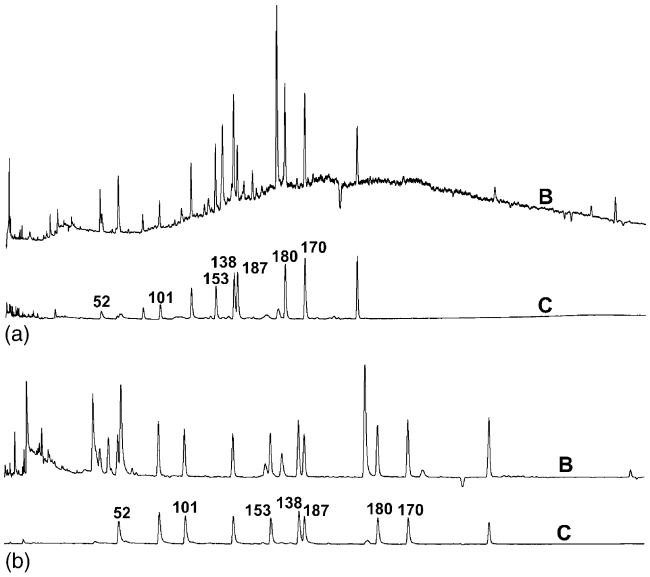

Fig. 2. Chromatograms from the glass microfibre filter eluate (a) and SPE disk eluate (b). Without clean-up (B) and with clean-up using set-up 1 (C). The investigated PCBs are marked in the C chromatograms. The B and C labelling refers to the B and C columns in Table 4.

A different problem in the A and B experiments (Table 4) was that unknown impurities were detected in some chromatograms (Fig. 2).

In order to measure PCBs at the 20 ng/l level an external drying and clean-up step was included. This was evaluated for a pure standard mixture of PCBs (50 μl PCB solution 2 dissolved in 2 ml *n*-heptane) by packing a glass column with glass wool, Na_2SO_4 and Florisil (set-up 1). Eluting the pure standard through the packed glass column (60 ml of *n*-pentane) gave quantitative recoveries for all seven PCBs (94–103% with R.S.D. of 1–7%, $n = 3$).

The results from a combined filtering/SPE/clean-up experiment are seen in Table 4(C). This gave a lower recovery (71%), but when comparing the baselines in the B and C experiments, it was clear that the C experiments had much less noise, nicer chromatography and no interfering peaks (Fig. 2). The low recovery is, however, a consequence of too much sample manipulation. Therefore, the two extracts (from the glass microfibre filter and the SPE disk) were pooled and passed through a single evaporation/clean-up step. This resulted in an increased recovery (82%) with maintained nice chromatographic behaviour and better R.S.D. (Table 4(D)). It was therefore decided to use this combined SPE/clean-up approach pooling the filter eluate and the SPE eluate. Unfortunately, the methodology required 60 ml of *n*-pentane for the elution of filters and disks, and 60 ml of *n*-pentane for washing the clean-up column. Consequently, pre-packed disposable clean-up columns (2 g of Na_2SO_4 and 2 g of Florisil) were investigated to decrease solvent usage (set-ups 2 and 3). A pure standard (50 μl PCB solution 2 dissolved in 2 ml *n*-heptane) was passed through these using a fractionated collection.

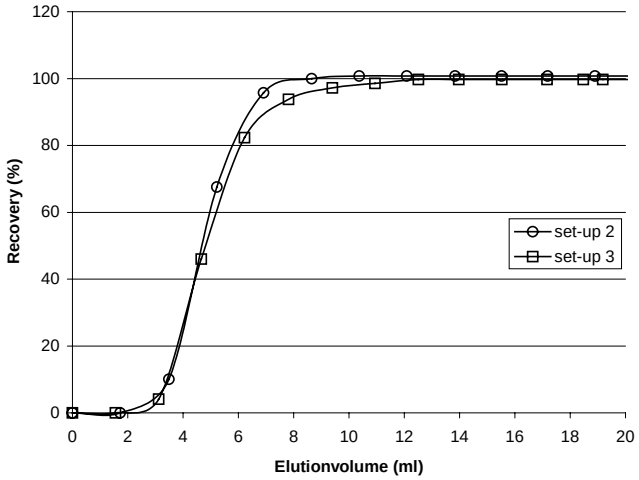

Fig. 3. PCB elution profiles for clean-up columns obtained using fractionated collection ($n = 2$). Set-up 2 is a custom-made column from IST containing 2.0 g Florisil and 2.0 g Na_2SO_4. Set-up 3 is two connected columns from Varian containing 2.2 g Na_2SO_4 and 2.0 g Florisil, respectively. The recovery for each data point is the mean recovery for the seven PCBs.

The elution profiles from these experiments can be seen in Fig. 3.

Both set-ups displayed no interfering peaks. Set-up 2 elutes all PCBs in 9 ml solvent, whereas set-up 3 requires 12 ml. Set-up 2 was the least costly alternative and considered superior to the other two set-ups. Parameters used in the finalised clean-up step were washing of the chosen clean-up column with 12 ml of *n*-pentane prior to sample addition and elution of sample with 9 ml *n*-pentane (Table 2).

Finally to overcome the losses observed in experiment D (Table 4), new experiments were performed where IS was added directly to the pooled eluate. In this case, the recovery of PCBs added to a level of 20 ng/l was 96% with individual recoveries in the range of 92–102% and R.S.D. of 3–8% (Table 4(E)). At this stage, the method was final and tested on natural matrices. The final optimised method is summarised in Table 2. For reagent water, the filtration time was 4 min and the extraction time was 7 min. The complete filtration/extraction cycle (including conditioning, drying and elution procedures) was 45 min. For leachate samples, the filtration and extraction times were slightly increased to 5 and 10 min, respectively. In no cases did plugging occur.

3.3. Real samples

In all of the waters investigated, none of the 28 congeners investigated were found. This result was somewhat expected, since levels of PCBs in Swedish tap and ground waters are usually below detection limits. The leachate taken from a landfill was, however, known to contain detectable levels of PCBs. An explanation for not finding PCBs might be that it rained heavily the day before sampling was conducted, thus diluting the leachate with rainwater. This might have lowered the PCB concentration below the limit of detec-

tion, which ranged from 0.25 to 1 ng/l for the investigated PCBs.

4. Conclusions

The developed SPE method was capable of handling various water samples with a reduced sample preparation time and solvent consumption compared to classical LLE methodologies. Since only PCBs were analysed, the commonly used solvent dichloromethane could be exchanged with *n*-pentane as elution solvent giving no apparent recovery losses compared to previous work.

As part of the on-going project, the method will be applied to a larger number of water samples. Further research will also be conducted to try and avoid the elution and clean-up steps with organic solvents by utilising supercritical fluid extraction followed by MS detection.

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