

DEVELOPMENT OF A SPE METHOD FOR THE DETERMINATION PCBs IN WATER

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Introduction

Recent global focus on fresh water supplies¹ has led to increased attention to the problems associated with water pollution caused by leachate from landfills and waste dumps. Leachate from landfills with its great complexity of 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 attending great interest since improvement of the quality of this type of waste water is necessary to improve the life conditions globally. Among common and ubiquitous persistent organic pollutants, which may occur in waste water, are polychlorinated biphenyls (PCBs), which exposed to organisms are known to cause problems of great concern. Numerous investigations have been performed during the last 35 years to evaluate their global distribution and transportation. 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 these PCBs can leak out into our environment². One possible route is the entrance of PCBs into leachate waters and from there to other types of water bodies such as ground water and surface waters.

As an initial part of an ongoing Swedish-Baltic cooperation 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 more recently, solid phase extraction (SPE) has been utilized as a more sophisticated approach for such extractions. There is a great diversity among the SPE methodologies used, including both cartridges and disks with various types of adsorbents such as diol, cyanopropyl, Florisil, C₈ and C₁₈. In this paper a methodology has been developed for investigations of PCB contamination based on SPE disk extraction. 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.

Methods and Materials

SPE methodology using extraction disks consists of well-defined steps. These are disk cleaning, disk conditioning, sample addition, disk drying and analyte elution. Different disk manufacturers and laboratories, however, utilize somewhat different conditions. Table 1 describe, in a relatively simplified way, the finalized SPE method and parameters used in this work.

SPE of aqueous samples with high levels of suspended solids can result in extremely long extraction times or even total clogging of systems. To avoid such problems a filtering step was

introduced (Figure 1 and Table 1). Gas chromatographic (GC) complications associated with water and impurities in the final extracts were minimized by the use of an external clean-up step. Here extracts were loaded onto cartridges containing 2g Na₂SO₄ and 2g Florisil (Table 1).

Table 1. A simplified overview of the SPE-methodology developed and applied on the analysed waters. The 1L samples were extracted in triplicates and a blank (reagent water) extraction was always performed whenever a sample was analysed.

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
4	rinse sample container with 10 mL of n-pentane and load this solvent onto the filters elute analytes from filters into a test tube using the above 10 mL
5	solvent
6	load another 10 mL of n-pentane onto filters rinsing it down the sides of the filtration unit elute analytes from filters, into the same test tube as in step 5, using the above 10 mL
7	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-disks with air
12	elute analytes from SPE-disks, in the same way as for filters, using 3x10 mL of n-pentane
13	add 50 µL internal standard and 2 mL of n-heptane to the pooled eluate
14	evaporate the pooled eluate with nitrogen down to ca 1mL
15	wash the drying and clean-up cartridge with 15 mL of n-heptane
16	load evaporated sample eluate onto the drying and clean-up cartridge
17	elute analytes with 15 mL of n-heptane 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

Throughout this study standard 47 mm glass vacuum filtration apparatus, were utilised after being rebuilt according to Figure 1. This rebuilding was done by removing the normal sintered piece of glass acting as support for the glass fibre filters and SPE disks. Instead a removable Teflon O-ring and a removable stainless steel support with small drilled holes (40% of the total area) were introduced. This new construction facilitated the cleaning of the extraction equipment. All solvents used were pesticide grade or equivalent and all glass used were, after machine wash, rinsed with n-heptane and acetone. Samples used in method development contained 1L Millipore water spiked with a PCB solution (containing PCB 52, 101, 138, 153, 170, 180 and 187) giving a concentration for each congener of 20 ng/L. Additionally PCB 169 was used as an internal standard. Quantification was based on a seven point calibration curve containing 28 certified PCBs in the range of 1-40 ng/mL for each PCB (NIST 2262, National Institute of Standards and Technology, Gaithersburg, MD, USA). Three types of waters, were analysed using the final method. The ground water was bottled by Carlsberg Sverige (Ramlösa mineral water), the tap water was taken

from the department of Analytical chemistry, Lund university. Leachate water came from a waste dump located near Emmaboda, Sweden. The GC system was equipped with an on-column injector, two electron capture detectors and a dual column system was installed. The choice of GC parameters was based on the work by Rahman et al.³. Three different SPE-disks were compared in the initial spiking experiments with reagent water, ENVI-disks (ENVI™-18 DSK, 47 mm, C₁₈, Supelco, Bellefonte, PA), SPEC-disks (SPEC-47-C18 AR, 47 mm, C₁₈, SPEC Division of ANSYS Inc., Los Angeles, CA) and Empore™-disks (Empore™, 47 mm, C₁₈, 3M Center, St. Paul, MN). All disks were packed with C₁₈-material. Three types of glass fibre filters were used and mounted according to Figure 1 (D-, C-, and F-filter with pore sizes of 2.7, 1.2 and 0.7 µm, respectively, glass microfibre filters, 47 mm, Whatman International Ltd, Maidstone, England).

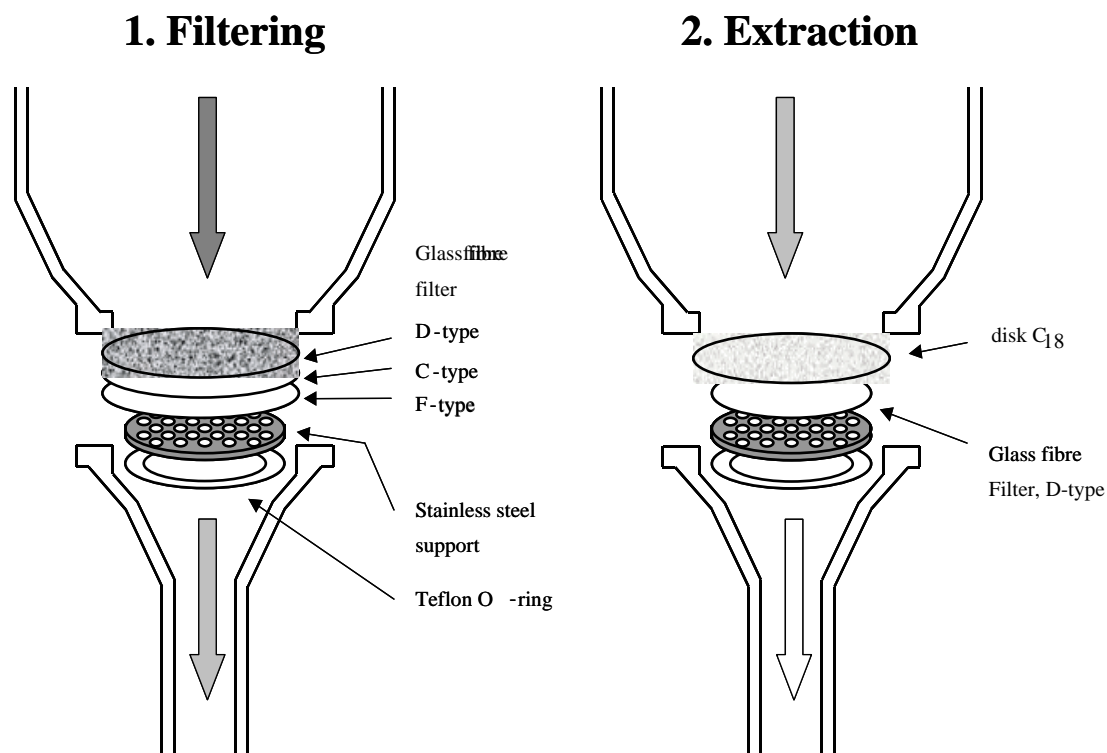


Figure 1. Rebuilt solid phase extraction unit used in all experiments.

Results and Discussion

Initial comparison experiments for the three types of disks using two different PCB spiking levels (1000 and 20 ng/L) in 1L samples are shown in Table 2. Best recoveries were obtained with Empore disks and since the leakage tendency also appeared to be less pronounced when these disks were used they were considered the best disk type (although the most expensive).

Table 2. Spiking experiments, using Millipore water at two spiking levels, performed for the 3 types of C₁₈-extraction (ENVI, SPEC and Empore) disks investigated using varying amounts of iso-octane as elution solvent.

	High level (1000ng/L)						Low level (20ng/l)					
	Improved elution (n=3)						Improved elution (n=3)					
	ENVI 3x10mL iso-octane		SPEC 3x10mL iso-octane		Empore 3x10mL iso-octane		ENVI 3x10mL iso-octane		SPEC 3x10mL iso-octane		Empore 3x10mL iso-octane	
PCB	Rec. (%)	RSD (%)	Rec. (%)	RSD (%)	Rec. (%)	RSD (%)	Rec. (%)	RSD (%)	Rec. (%)	RSD (%)	Rec. (%)	RSD (%)
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
153	78	6	85	5	91	5	80	9	80	18	91	0
138	80	7	87	4	93	4	84	12	82	15	93	0
187	77	6	86	5	92	5	82	16	81	17	92	1
180	78	9	85	4	91	4	80	15	81	16	94	4
170	78	6	86	4	93	6	83	17	80	16	92	3

Average recovery and relative standard deviation (RSD) obtained from samples containing 1L PCB spiked Millipore water using the final method was 96% and 6% respectively (n=3). In addition chromatograms displayed no interfering peaks and good baseline behaviour for both detectors.

In all of the waters investigated none of the 28 congeners investigated were found. For the tap and ground water samples investigated this result was expected since there are low background levels of PCBs in Swedish waters. 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 detection which ranged from 0.25 to 1 ng/L for the investigated PCBs.

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. Further research will be conducted to try and avoid the elution steps with organic solvents by utilizing supercritical fluid extraction.

References

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