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Short communication

Comparison of two extraction methods independently developed on two conceptually different automated supercritical fluid extraction systems for the determination of polychlorinated biphenyls in sediments

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Abstract

Two extraction methods that independently have been developed on conceptually different automated supercritical fluid extraction systems, ISCO SFX 3560 (syringe pump and liquid trapping) and Hewlett-Packard 7680T SFE (reciprocating pump and solid-phase trapping), were compared for the extraction of polychlorinated biphenyls from two Swedish sediments. The results demonstrated that the high-temperature ISCO method in some cases yields a more exhaustive extraction, but also less clean extracts due to co-extraction of unwanted matrix components which are all present in the trapping solvent. The medium-temperature Hewlett-Packard method may sometimes cause problems with quantitative recoveries, but on the other hand it yields very clean extracts due to the extra selectivity resulting from collection on a solid-phase trap. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Analytical supercritical fluid extraction (SFE) is still a relatively small discipline in environmental analysis. Nevertheless, manufacturer-designed SFE instruments for laboratory-scale analytical purposes are available from a couple of companies. SFE equipment typically consists of an extraction cell that can be heated and pressurized. This cell (containing the sample) is placed in an oven and connected to a

high-pressure pump supplying the supercritical fluid. Pumping of the extraction fluid can be done in two different ways, either continuously via a reciprocating pump, or by filling of a syringe pump which then delivers the fluid. Analyte collection can also be performed in basically two different ways; in solvents or on solid-phase traps [1–3]. A number of parameters are controlling the extraction process and therefore method development have been quite complex for the extraction of polychlorinated biphenyls (PCBs) from historically contaminated sediments [4–8]. As a consequence several different methods have been presented on various types of equipment. The objective of this study is to compare the results

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obtained for two such extraction methods that have been independently developed on conceptually different automated extraction systems. These systems are ISCO SFX 3560 with a syringe pump and liquid trapping, and Hewlett-Packard 7680T SFE with a reciprocating pump and a solid-phase trap. For both types of system, the extraction method developed is claimed to give quantitative recoveries for most types of solid environmental matrices [9,10]. Even though the extraction methods differ, they should generate the same data in order to be of equal applicability. Comparative studies are scarce in the literature but nevertheless it is important to find optimal systems and methods that can be used in routine laboratories.

2. Experimental

2.1. Sediments

Sediments from two different sources have been used in this study. One is a limnic sediment, originating from Lake Järnsjön (Småland, Sweden) and the other one is semi-limnic, originating from the Baltic bay Örserumsviken (Småland, Sweden).

2.1.1. Lake Järnsjön

This material is a surface sediment sampled in 1991 at 0–10 cm sediment depth. It has been stored in a freezer since then. The Lake Järnsjön sediment gives a minerogenic impression, containing fine-grained sand, with little visible organic material.

2.1.2. Baltic bay Örserumsviken

This sample consists of sediment plugs taken from a land deposit where sediment material from the bay was placed after dredging actions during the 1960s and 1970s. In comparison with the Lake Järnsjön sediment, the Örserumsviken sediment is much less dense, has a fluffy, almost cotton-like structure and, apparently, a much higher organic content.

2.2. Standards

The PCB standards for identification and quantification of target PCBs in sediment samples were

PCBs 28, 52, 101, 105, 118, 128, 138, 149, 153, 156, 170 and 180. Internal standards were PCBs 35 and 169 (all standards from Ultra Scientific, North Kingstown, USA).

2.3. Supercritical fluid extraction

An ISCO SFX 3560 automated system with a 260D syringe pump and a Hewlett-Packard 7680T supercritical fluid extractor were used. Both instruments were run with CO₂ (quality 4.8; >99.998%, AGA Gas, Sweden) as extraction gas and CO₂ (Food quality, AGA Gas) as cooling gas.

2.3.1. ISCO SFX 3560

Extractions were conducted with the ISCO system using the following parameter settings: 60 min dynamic extraction at 400 bar and 150°C, a CO₂ flow-rate of 1.5 ml/min and a restrictor temperature of 80°C. This method has previously been demonstrated to give quantitative recoveries for samples with a large variety of matrix characteristics [9]. Analyte collection was done in 10 ml of acetone at –10°C, utilizing the ISCO run option ‘pressurized collection’ and a solvent replenishment rate of 0.5 ml every 14 min. The extraction thimbles were prepared as follows: a glass fiber filter (type A/E, Gelman Sciences, USA) was placed on the bottom of a 10-ml extraction thimble. On top of that, 0.5 g of sample was placed, mixed with an equal amount of copper powder (to get rid of sulfur contaminants [11]), and then the thimble was filled up with Na₂SO₄ (analytical-reagent grade, Fluka, Germany). Finally another filter was placed on top and the thimble was closed. Four replicates were run for each sediment.

2.3.2. Hewlett-Packard (HP) 7680T

Extractions were done according to an established US Environmental Protection Agency (EPA) standard method for extraction of persistent organic pollutants from sediments and soils [10]. These extractions were performed with the following extraction parameter settings (EPA method 3562): CO₂ was used as extraction fluid for 10 min of static extraction at a density of 0.75 g/ml (305 bar) at 80°C, followed by 40 min of dynamic extraction at the same density and temperature with a flow of 1

ml/min. The nozzle temperature was kept constant at 45°C and the trap was kept at 20°C. The trap was filled with ~1 ml of Florisil (0.16–0.25 mm particle size) as trapping material and was eluted with 2×1.5 ml *n*-heptane and then 1.5 ml of dichloromethane followed by 2×1.5 ml *n*-heptane after every individual extraction. The extraction thimbles were prepared as follows: a glass fiber filter was placed at the bottom of the 7-ml extraction thimble and Na₂SO₄ was added to approximately 1 cm. On top of this, a mixture of ~0.5 g of sample and 0.5–1 g of copper powder (<63 μm, analytical-reagent grade, Merck, Germany) was placed and the thimble was filled up with Na₂SO₄ mixed with a small amount of copper powder. Finally, another filter was placed on top and the thimble was closed. Four replicates were run for each sediment.

2.4. Gas chromatographic analysis

Please refer to Ref. [11] for details of the gas chromatographic analysis.

3. Results and discussion

Individual congener concentrations in the Lake

Järnsjön sediment, as determined with the developed ISCO method, were generally higher than corresponding concentrations determined with the HP EPA method (Table 1). Only two concentrations did not differ significantly between the two methods; those of PCBs 101 and 153 (as determined by Student's *t*-test at the 0.05 level). For the Örserumsviken sediment, the HP EPA method and the ISCO method results differed to a lesser extent. Four congeners showed similar results with the two methods, namely PCBs 105, 156, 170 and 180, while the other eight congeners gave significantly lower results with the ISCO method (Table 1).

The major extraction-related difference between the two independently developed methods is the extraction temperature, with 80°C in the EPA method and 150°C in the ISCO method. This difference in temperature is probably the main reason for the observed higher ISCO recoveries for the Lake Järnsjön sediment. This theory is supported by previous investigations performed on the Lake Järnsjön sediment where 100°C gave incomplete recoveries [9]. The ISCO method gave on average 141% of the HP EPA method recovery, as based on individual PCB congener recoveries. Thus the HP EPA method is not exhaustive enough for the Lake Järnsjön sediment.

Table 1

Total amounts with RSD values of the individual PCB congeners in the Lake Järnsjön sediment and in the Baltic bay Örserumsviken sediment as determined by the developed ISCO method (*n*=4) and the HP EPA method (*n*=4)

PCB congener	ISCO Järnsjön (ng/g)	RSD (%)	HP Järnsjön (ng/g)	RSD (%)	ISCO Örserum (ng/g)	RSD (%)	HP Örserum (ng/g)	RSD (%)
PCB 28	1630	9.7	1200	7.4	363	2.4	398	2.7
PCB 52	705	5.9	572	7.5	119	0.4	145	1.8
PCB 101	135 ^b	3.6	130 ^b	5.1	40	6.4	51	2.1
PCB 105	94	5.1	64	9.0	20 ^b	7.6	18 ^b	2.2
PCB 118	137	7.7	119	6.3	31	3.6	35	2.3
PCB 128	11	4.7	5	8.0	17	7.9	5	4.2
PCB 138	35	1.4	26	6.0	27	2.7	37	3.8
PCB 149	26	4.3	20	6.6	29	0.3	32	2.6
PCB 153	29 ^b	3.9	27 ^b	6.8	37	2.6	42	2.8
PCB 156	8	11.5	5	5.1	6 ^b	– ^a	5 ^b	3.9
PCB 170	10	3.7	6	4.4	10 ^b	13	11 ^b	3.1
PCB 180	26	13.0	17	6.4	26 ^b	1.0	27 ^b	4.1

^a RSD could not be calculated since the compound could not be quantified in some of the analyses.

^b Concentrations do not differ significantly between the two methods, as determined by Student's *t*-test at the 0.05 level.

For the Örserum sediment, the developed ISCO method gives somewhat lower recoveries for most investigated congeners. However, the differences between the recoveries obtained with the developed ISCO method and the HP EPA method are small, with the ISCO method giving an average recovery of 92% of the HP EPA method recovery, as based on individual PCB congener recoveries. The HP EPA method is the preferable choice for this sediment, not

only because of the slightly higher recoveries but also because it gives lower and more homogeneous RSD values. The average RSD (based on individual congener RSD values) for the Örserumsviken extractions were 4.4% for the ISCO method and 3.0% for the HP EPA method. For this sediment, the RSD intervals differed substantially between the two methods. For the ISCO method, RSD values varied between 0.3 and 13%, while they only varied

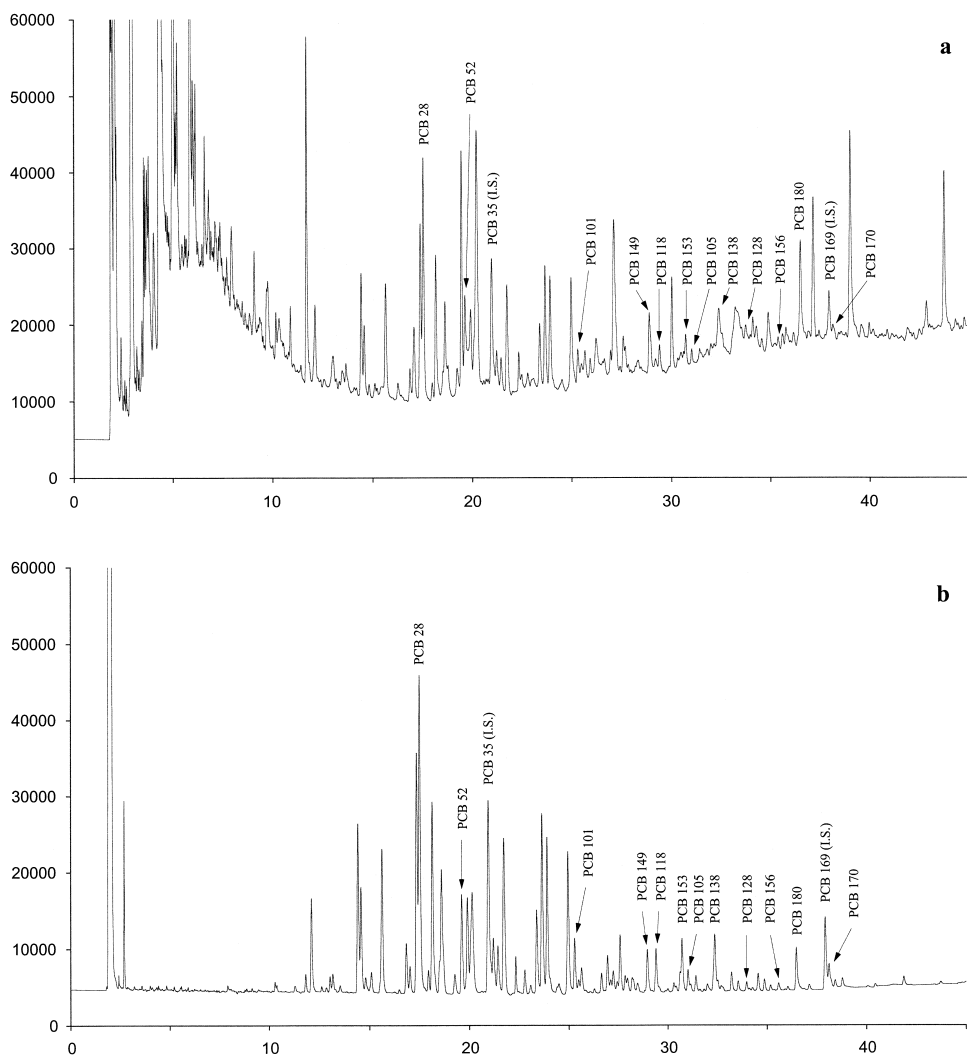


Fig. 1. Example chromatograms from the analysis of Örserumsviken sediment extracts obtained with the developed ISCO method (a) and with the HP EPA method (b). Time scales in minutes.

between 1.8 and 4.2% for the HP EPA method (Table 1). In the extractions of Lake Järnsjön sediment, the RSD values were of the same magnitude for the two extraction methods: On average 6.2 and 6.6% for the ISCO method and HP EPA method, respectively. However, the RSD values for the ISCO method varied between 1.4 and 13% while the corresponding interval for the HP EPA method was only 4.4–9.0%. The RSD values for the HP EPA method are somewhat higher for the Lake Järnsjön sediment than for Örserumsviken, which might reflect that the extraction of the Lake Järnsjön sediment is not complete.

There are probably two factors involved in the higher RSD values seen in the ISCO extractions. Firstly, the higher extraction temperature together with the longer extraction time in the ISCO method governs co-extraction of unwanted matrix components, resulting in dirtier extracts. Secondly, the analyte trapping on a solid sorbent in the HP EPA method provides additional selectivity to the sample preparation as demonstrated previously [12], resulting in cleaner extracts. Both factors are especially pronounced for difficult-to-extract matrices such as sediments, and Örserumsviken sediment in particular is known to cause dirty extracts [13]. The difference in extraction performance between the two systems is more clearly seen in Fig. 1a and b where typical chromatograms from extracts obtained with the ISCO method (a) and the HP EPA method (b) are presented for the Örserumsviken sediment. From these it is clear that the results will vary to a greater extent when applying the ISCO method.

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