

Short communication

Recoveries of organochlorine compounds (polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans) in water using steam distillation–solvent extraction at normal pressure

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Abstract

A simultaneous steam distillation–solvent extraction (SDE) procedure was used for determining polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCBs, PCDDs and PCDFs) at sub-ppb levels in water samples. Recoveries of 39.8–138.7% and a standard deviation of lower than 10% were achieved for the individual coplanar PCB and the 2,3,7,8-substituted PCDD/F congeners. SDE is a fast, clean, inexpensive and reproducible procedure for the determination of individual PCBs, PCDDs and PCDFs in waters at very low concentrations.

1. Introduction

Polychlorinated biphenyls (PCBs), polichlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been recognized as being highly toxic and ubiquitous environmental contaminants [1,2]. Of them, the most toxic are the PCB coplanar congeners (unsubstituted and mono- and di-*ortho*-substituted), with toxicity levels near that of the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin [3], and the PCDD and PCDF congeners with chlorines in the 2,3,7,8-positions.

The standard analytical procedure for monitoring the concentrations of organochlorine compounds in waste water utilizes either sequential or continuous liquid–liquid extraction [4,5]. Increasing concern about the use of large volumes of organic solvents, however, has resulted in efforts to develop alternative extraction approaches.

Solid-phase extraction (SPE) using many types of adsorbent (XAD-2 macroreticular resin, graphitized carbon, alumina, silica, etc), Sep-Pak C₁₈ cartridges and Empore discs is an alternative approach which has received considerable attention. This technology offers several significant advantages over the conventional liquid–liquid extraction techniques typically employed for water analysis. It reduces the volume of solvent

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required for extraction and provides a concentration step without the necessity for removing a large volume of solvent [6,7]. The disadvantages of the adsorption methods are the presence of organic impurities coming from some adsorbents and the long analysis time [8–11].

Steam distillation extraction (SDE) at normal pressure, in which the compounds were first distilled and then extracted into an organic solvent, has received much attention in recent years [12]. The small amounts of solvent used (2 ml) and the short analysis time (1 h) have made SDE a very attractive extraction–concentration technique for organochlorine compounds in waste water [13,14]. In addition, when the solvent was compatible with the analytical technique and the concentration of the analytes was high enough, the preconcentration step, before the chromatographic injection, could be avoided.

Since SDE was first used by Likens and Nickerson [12] in 1964, different modifications have been introduced to improve the results and extend the field of its applications, including the environmental field [15–20].

The objective of this study was to evaluate the steam distillation–solvent extraction at normal pressure procedure as an alternative to solid-phase extraction in determining organochlorine compounds (PCBs, PCDDs and PCDFs) in water at sub-ppb levels. For this purpose, a new micro-version of the SDE apparatus was proposed earlier [21]. So far, this SDE method has been found to be highly efficient for the extraction of compounds with different polarity, volatility and solubility from food products [22,23].

2. Experimental

2.1. Standard solutions

PCB standards

The 14 individual PCB coplanar congeners, selected by their abundance in environmental samples or by their toxicity (Table 1), were purchased from Ehrenstorfer (Germany).

PCDD and PCDF standards

EPA 1613 stock native standard solution, chemical purity >98% (Chemsyn Science Labs., Lenexa, KS, USA), consists of a mixture of 2,3,7,8-substituted congeners from tetra- to octa-PCDD and -PCDF, which are the most toxic congeners, at concentrations from 0.4 to 4.0 $\mu\text{g}/\text{ml}$ from tetra- to octa-PCDD/Fs.

PCB standard solutions

A working stock standard solution was prepared containing 1 $\mu\text{g}/\text{ml}$ of each of the 14 PCB individual congeners in *n*-pentane and stored at 4°C. Synthetic mixtures were prepared directly in the extraction flask by adding the appropriate volume of the stock standard solution to 100 ml of water purified in a Milli-Q system (Millipore). Final concentrations of 1, 0.1 and 0.01 ppb (ng/ml) of each PCB were prepared.

PCDD/F standard solutions

The EPA 1613 PCDD/F stock native standard solution was used as a working standard solution. Synthetic mixtures were prepared directly in the extraction flask by adding the appropriate volume of the working standard solution. The congener concentrations ranged between 2.5 and 2000 pg/ml (ppt) from the tetra- to octa-congeners (Table 2).

The extractions of PCBs and PCDD/Fs were carried out separately.

2.2. Simultaneous distillation and extraction

Sample extraction and concentration were carried out using the micro SDE equipment designed by Blanch et al. [21]. This microinstrument was basically a distiller with two distillation arms connected to two separate flasks. The flask containing the sample and that containing the extraction solvent were placed in different heating baths and each of them was distilled through the individual arms. After their vapours had condensed on the cool condenser surface, they were mixed in the separation chamber where the

extraction process took place. The continuous circulation and mixing of both the aqueous and the organic phases allowed efficient and rapid extraction to be achieved.

The new design of this SDE includes an enlarged surface condenser, which allows more effective mixing of the solvent vapour with sample vapour and, the fact that the distillation solvent and distillation sample arms enter the mixing chamber at the same height, allowing the use of both high- and low-density extraction solvents with only one configuration. The main advantage of this system is the high recovery in a very short time even for small amounts of analytes.

The experimental conditions for SDE were chosen according to the results obtained by Blanch et al. [21], who optimized the experimental variables using the modified sequential simplex method [24]. These optimized variables were chosen for a wide range of compounds of different natures, and it can be expected that the values of these variables would be adequate for PCBs and PCDD/Fs. Among the various possible solvents that could be used, *n*-pentane was chosen for the first experiments. The use of *n*-pentane allowed the direct injection of the extract obtained into a high-resolution gas chromatographic–electron-capture detection (HRGC–ECD) system without concentration for the higher concentrations. *n*-Pentane was replaced with dichloromethane in the analysis of PCDD/Fs at the lower concentrations (2.5–20 ppt for tetra- to octa-chlorinated congeners) to obtain better recoveries.

Thus, the experimental variables adopted were as follows: sample heating bath temperature, 149°C; solvent heating bath temperature, 67°C; coolant temperature, 3.4°C; and extraction time, 56 min. A volume of 2 ml of the solvent was used. The final extract was concentrated to 0.2 ml under a stream of nitrogen for the lower concentrations when *n*-pentane was used and 0.8–1.2 μ l of the extract were injected to the HRGC–ECD system. When dichloromethane was used it was necessary to evaporate to dryness and change the solvent.

2.3. HRGC–ECD

A Perkin-Elmer (Beaconsfield, UK) Model 8600 gas chromatograph equipped with a ^{63}Ni electron-capture detector was used.

The column was DB-5 (60 m \times 0.25 mm I.D., 0.25 μ m film thickness) (J&W Scientific, Folsom, CA, USA). The column temperature was programmed from 60°C (held for 1 min) at 50°C/min to 180°C, then at 4°C/min to 230°C (held for 40 min) and finally at 4°C/min to 270°C (held for 10 min). Nitrogen was used as the carrier gas at a flow-rate of about 22 psi. Samples of 0.8–1.2 μ l were injected in the splitless mode.

2.4. Quantitative analysis

Identification of individual PCB, PCDD and PCDF congeners was based on retention times relative to stock standard solution mixtures. The concentrations of individual congeners were determined by comparison of the individual peak-area responses with those for similar concentrations in the stock standard solutions, in the linear range of the detector used. The PCBs with IUPAC Nos. 12 and 209 [25], added before the injection, were used to correct for injection errors and detector fluctuations.

3. Results and discussion

3.1. PCB congeners

Table 1 shows the concentrations of PCB congeners investigated in different assays and their recoveries as an average of three experiments. In all instances the relative standard deviations (R.S.D.) was lower than 10%. Fig. 1 shows a chromatogram of a PCB standard mixture with ppb level concentrations.

The recoveries of all PCB congeners were around 100% for the higher concentrations (1 and 0.1 ppb). For lower concentrations (0.01 ppb), the recoveries were around 100% for all congeners except for PCB 101, 118, 126 and 156, for which they were between 56.8 and 75.5%.

Table 1
Recoveries of the method for PCB congeners (in *n*-pentane) at concentrations of 1, 0.1 and 0.01 ppb (ng/ml) in water

Peak No.	PCB structure	IUPAC No.	Recovery (%)		
			1 ppb	0.1 ppb	0.01 ppb
1	2,2',4,5,5'-P ₅ CB	101	97.7	95.0	56.8
2	3,3',4,4,4'-T ₄ CB	77	93.3	97.5	92.9
3	2,2',3,5,5',6'-HxCB	151	101.1	113.6	102.0
4	2,3',4,4',5-P ₅ CB	118	100.4	100.5	70.4
5	2,2',4,4',5,5'-HxCB	153	97.9	97.0	114.6
6	2,3,3',4,4'-P ₅ CB	105	97.9	92.3	102.6
7	2,2',4,4',5-P ₅ CB	138	99.8	108.2	126.4
8	3,3',4,4',5-P ₅ CB	126	101.9	104.7	68.2
9	2,3',4,4',5,5'-HxCB	167	102.6	93.3	104.8
10	2,3,3',4,4',5-HxCB	156	100.6	104.7	75.5
11	2,2',3,4,4',5,5'-HpCB	180	113.7	102.4	101.7
12	3,3',4,4',5,5'-HxCB	169	98.9	113.1	92.6
13	2,2',3,3',4,4',5-HpCB	170	103.4	102.6	111.8
14	2,2',3,3',4,4',5,5'-OCB	194	102.2	108.6	105.7

These values, however, are satisfactory in comparison with those obtained by other extraction methods, such as Soxhlet extraction and sonication [19,26].

The results are in accordance with those of other workers [13,15], who used older versions of SDE in the extraction of organochlorine compounds for water samples at ppb levels.

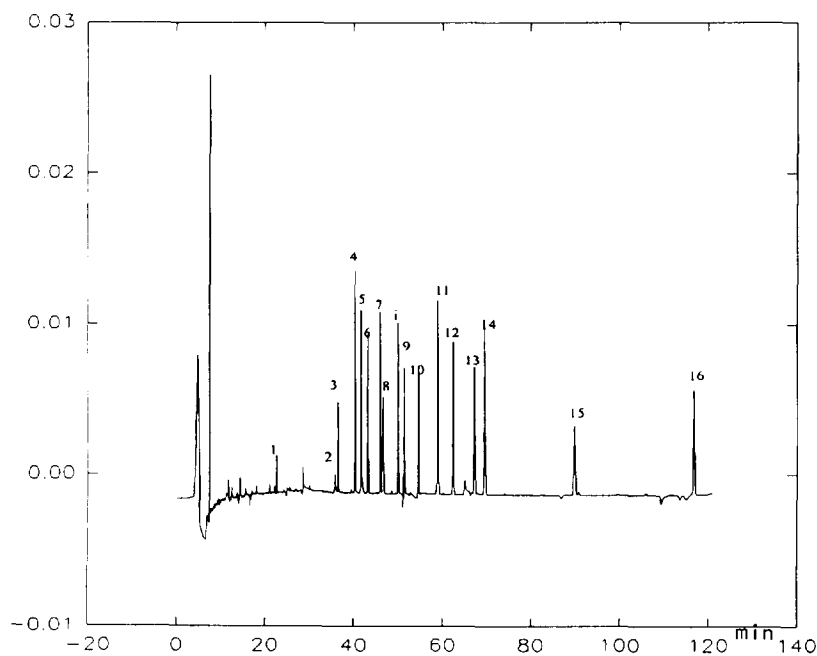


Fig. 1. Separation of 14 PCB congeners included in the standard mixture at ppb levels. Peaks 1 and 16 (PCB-12 and PCB 209) are internal standards; i = unknown. For other peak identifications, see Table 1.

The use of the new version of SDE developed by Blanch et al. [21] together with the implementation of modified sequential simplex optimization of the operating variables allowed the extraction of the individual PCBs from water samples at ppt levels, with high recoveries.

3.2. PCDD/PCDF congeners

Table 2 gives the concentrations of PCDD and PCDF congeners investigated in different assays and their recoveries as an average of three experiments. In all instances the relative standard deviation was lower than 10%. Fig. 2 shows a chromatogram of the PCDD and PCDF standard mixture at ppb levels.

The concentrations of the individual congeners were in the ppt range and the recoveries depended on both the concentration level and the physical characteristics of the different PCDD/F congeners. The recoveries decreased strongly

with decreasing concentration of PCDD/F congeners.

When SDE was carried out under the same conditions as for the PCB extractions, good recoveries were found from penta- to hepta-PCDD/F congeners at 0.1 and 1 ppb concentrations, and in general the recoveries decreased as the level of chlorination increased. The recoveries obtained for the lower chlorinated isomers (tetra-PCDD/F) were always lower than those found for penta- to hepta-congeners. This is probably due to the lower concentration of these two isomers in the standard commercial solution, which are four times lower than those of the penta-, hexa- and hepta-congeners. The recoveries of OCDD and OCDF isomers were around 50%. These two isomers have the highest molecular masses and the lowest vapour pressures [26], and probably these characteristics are related to the low recoveries.

The low efficiencies found at lower concentrations (2.5–20 ppt from tetra- to octa-PCDD/

Table 2
Recoveries of the method for PCDD and PCDF congeners down to sub-ppb (ng/ml) concentration levels

No.	Structure	<i>n</i> -Pentane solvent						Dichloromethane solvent	
		Recovery (%)	ppb ^a	Recovery (%)	ppb ^a	Recovery (%)	ppb ^a	Recovery (%)	ppb ^a
1	2,3,7,8-TCDF	49.0	0.25	46.9	0.025	55.5	0.0025	138.7	0.0025
2	2,3,7,8-TCDD	76.5	0.25	60.0	0.025	50.1	0.0025	105.6	0.0025
3	1,2,3,7,8-PCDF	94.7	1	70.1	0.1	48.1	0.01	108.7	0.01
4	2,3,4,7,8-PCDF	137.7	1	91.6	0.1	– ^b	0.01	89.6	0.01
5	1,2,3,7,8-PCDD	107.1	1	68.1	0.1	70.8	0.01	111.8	0.01
6	1,2,3,4,7,8-HxCDF	100.6	1	69.2	0.1	39.4	0.01	108.9	0.01
7	1,2,3,6,7,8-HxCDF	95.3	1	71.3	0.1	36.1	0.01	100.4	0.01
8	2,3,4,6,7,8-HxCDF	129.6	1	86.4	0.1	72.5	0.01	132.7	0.01
9	1,2,3,4,7,8-HxCDD	86.8	1	71.4	0.1	35.4	0.01	104.0	0.01
10	1,2,3,6,7,8-HxCDD	80.8	1	77.8	0.1	24.8	0.01	102.2	0.01
11	1,2,3,7,8,9-HxCDD	92.3	1	65.7	0.1	63.2	0.01	107.6	0.01
12	1,2,3,7,8,9-HxCDF	83.7	1	77.4	0.1	67.5	0.01	109.9	0.01
13	1,2,3,4,6,7,8, HpCDF	95.7	1	62.5	0.1	47.4	0.01	70.8	0.01
14	1,2,3,4,6,7,8, HpCDD	72.7	1	84.3	0.1	39.5	0.01	74.7	0.01
15	1,2,3,4,7,8,9-HpCDF	81.6	1	83.2	0.1	38.8	0.01	95.7	0.01
16	OCDF	40.5	2	39.1	0.2	42.4	0.02	55.9	0.02
17	OCDD	39.5	2	42.9	0.2	37.9	0.02	49.4	0.02

^a Concentration of each PCDD/F congener in water.

^b Not detected.

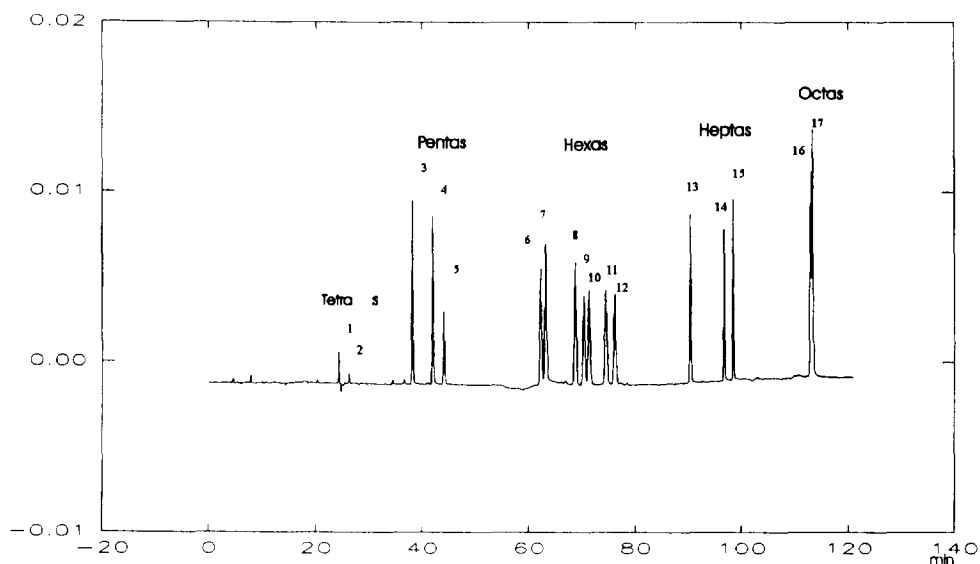


Fig. 2. Separation of the 2,3,7,8-substituted congeners of PCDD and PCDF standard mixture at ppb levels. For peak identifications, see Table 2.

PCDFs), usually lower than 50%, suggested the necessity for optimizing some of the experimental variables. The use of a stronger solvent with a higher affinity for organochlorine compounds, such as dichloromethane, gave better results (Table 2). It can be observed that the recoveries increased significantly, being almost 100% for all the isomers except for octachlorine isomers. Therefore, the use of dichloromethane is advisable when the PCDD/F concentrations in water are lower than 100 ppt, even when an additional step, changing to an electron-capture detector-compatible solvent, was necessary before the chromatographic analysis.

4. Conclusions

The SDE technique allows the determination of organochlorine compounds as individual PCDD, PCDF and PCB congeners at very low concentrations. The SDE apparatus offers, with some exceptions, excellent recovery efficiencies for the investigated compounds in the pg/ml or ng/ml range. In addition, it is inexpensive, fast and, as it needs only a small amount of solvent (2 ml), ecologically beneficial.

The good results obtained for the extraction of organochlorine compounds in water together with the versatility of the micro-SDE apparatus proposed, which allows the use of sample volumes five times larger than those previously used, without any modifications, suggest the possibility of applying this method to real water samples and other environmental samples. These aspects will be the topic of forthcoming works.

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