Journal of Chromatography, 626 (1992) 135–143
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 338

Supercritical fluid extraction of polychlorinated biphenyls and pesticides from soil

Comparison with other extraction methods

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ABSTRACT

A comparison is made of supercritical fluid extraction (SFE) with two other techniques widely used for the extraction of polychlorinated biphenyls (PCBs) and organochlorine pesticides in soil. Extraction conditions for the SFE of PCBs and pesticides were first determined. An experimental approach was set up to determine the influence of different extraction parameters such as pressure, extraction time, static and dynamic extraction, restrictor type and collection solvent for off-line SFE. The use of carbon dioxide at 50°C and 20 MPa, 10 min static followed by 20 min dynamic extraction with collection in iso-octane were been found to be the optimum conditions. Two types of soil, with a low and high content of organic carbon, respectively, spiked with 16 PCBs and organochlorine pesticides with a wide range of volatility and polarity at a level of 5 ng/g dry matter, were used as test materials. Conventional solvent extraction gives a good extraction yield for soil with a low content of organic carbon, but for peat soil the recoveries decrease dramatically to 30% for DDE, DDT and PCB 138 and 153. The recoveries with Soxhlet extraction are good, but an extra clean-up step before analysis is necessary. SFE gives good extraction yields for PCBs and organochlorine pesticides, varying between 85 and 105% with a reproducibility of 5% for each component for both types of soil. SFE is a fast, clean and reproducible method for the extraction of PCBs and organochlorine pesticides from these two soil matrices.

INTRODUCTION

Every five years a monitoring programme for organochlorine pesticides and polychlorinated biphenyls (PCBs) is carried out to observe trends in the levels of these components in soils in the Netherlands [1]. Several studies have shown that supercritical fluid extraction (SFE) results in good extraction yields for chlorinated contaminants in soils [2–12]. Therefore the application of SFE as an alternative extraction technique to conventional methods for the extraction of soil samples was evaluated in this laboratory. The latter techniques are laborious, time consuming and require large amounts of high purity solvents which produce problems of hazardous waste. In addition especially for the more nonpolar components [hexachlorobenzene (HCB), 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane (DDT) complexes and PCBs] solvent extraction often gives low extraction yields when applied to soils with high contents of organic carbon.

Several studies have described the use of SFE for the extraction of organic contaminants from different matrices. Lopez-Avila *et al.* [2] extracted several groups of organochlorine and organophosphorus pesticides spiked on sand with good recoveries (from 80 to 125%) using either CO_2 or, more advantageously, CO_2 modified with 10% methanol. Hawthorne and Miller [3–5] studied the extraction of polycyclic aromatic hydrocarbons from reference

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0021-9673/92/$05.00

materials and other matrices and obtained results in good agreement with certified values, in contrast to the results reported by Lopez-Avila *et al.* [2]. The extraction of total PCBs from a certified sediment sample was demonstrated by Onuska and Terry at 20 mPa, 40°C in 8 min using CO_2 with 2% methanol [6]. SFE of pesticides from soils and sediments has been studied using CO_2 saturated with water or with the direct addition of methanol to the extraction cell to increase recoveries [7–9]. Several studies have reported the optimization in terms of the modifier, pressure, temperature and flow-rate of the extraction of diuron and linuron from sand [10] and several chlorinated components [11] and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin from sediments [12].

SFE has many potential advantages compared with conventional solvent extraction methods, including reduced extraction times and amounts of extraction solvents. It also gives more efficient extractions, increased selectivity and the possibility of coupling with other chromatographic techniques. Based on their variable solvating power as a function of density, supercritical fluids have several characteristics that make them ideal extraction solvents to selectively extract and isolate discrete fractions from sample matrices. Rapid mass transfer during extraction is facilitated by the low viscosity and high solute diffusivities due to the liquid- and gas-like behaviour of supercritical fluids. In SFE CO_2 is most often chosen as the extraction solvent because of its moderate critical temperature (31°C) and pressure (73 atm), its non-flammable and non-toxic properties, low cost and minimized problems of waste.

In this paper results are presented for the optimization of SFE conditions for the determinations of organochlorine pesticides and PCBs in soils containing different amounts of organic carbon. Results are compared with those obtained by the application of conventional extraction techniques.

EXPERIMENTAL

Samples

Two types of soil characterized by the percentage of moisture, dry matter, pH and organic carbon were used as test materials: a peat soil with a relatively high organic carbon content (3.3%) and a sand with a low organic content (0.3%). Soils were air-dried, allowed to pass through a 2.8 mm sieve and subsequently homogenized in a ball mill. Individual soil samples were spiked just before analysis, waiting for 15 min to 1 h to allow evaporation of the solvents (the evaporation time depended on the amount of solvent used). Based on their occurrence in Dutch soils, the following compounds were selected for this study: α-hexachlorocyclohexane (α-HCH), HCB, β-HCH, γ-HCH, β-heptachlorepoxide (β-HEPO), 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethene (*p,p'*-DDE), dieldrin, 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethane (TDE), *o,p'*-DDT, *p,p'*-DDT and PCB 28, PCB 52, PCB 101, PCB 118, PCB 138 and PCB 153. PCBs were from CIL (Cambridge Isotope Laboratories, Woburn, MA, USA), pesticides from Promochem (Wesel, Germany). Spiking levels were chosen based on levels previously observed and were typically between 1 and 10 ng/g of dry soil.

Extraction procedures

Solvent extraction. Aliquots of 25 g of soil were extracted twice with 40 ml of acetone for 30 min using a shaking machine. The liquid fractions were mixed with 800 ml of water and a few millilitres of saturated sodium chloride, and were then extracted twice with 50 ml of hexane. The combined hexane fractions were dried and, after the addition of internal standards (PCBs 44 and 141), were concentrated in a Kuderna-Danish apparatus until 10 ml remained. All solvents used were pesticide-grade (hexane) or distilled (acetone, light petroleum).

Soxhlet extraction. Aliquots of 5 g of soil mixed (1:3, w/w) with quartz sand (Boom, Meppel, Netherlands) were placed in a modified Soxhlet extraction unit consisting of a fritted porosity glass extraction tube and were extracted for 14 hours with 150 ml of acetone–light petroleum (b.p. 30–60°C) (1:1, v/v). After cooling, 600 ml of water and a few millilitres of saturated sodium chloride were added for solvent extraction; light petroleum was separated and a second extraction with 50 ml of light petroleum was performed. The combined light petroleum fractions were dried and, after the addition of internal standards, were concentrated in a Kuderna-Danish apparatus until 5 ml remained.

Supercritical fluid extraction. The SFEs were performed on a Carlo Erba SFC 3000 instrument using a double 70-ml syringe pump (SFC 300) and an

SFE-30 extraction unit (Carlo Erba Instruments, Milan, Italy). The apparatus can be used in on-line and off-line modes; in the latter the restrictor is disconnected from the transfer tube and solvent sample collection can be performed. Extractions can be performed using constant pressure (varying from 15 to 50 MPa) or at constant flow and the temperature of the extraction unit can be varied between 40 and 150°C. The extraction process was pre-programmed using integrated software to perform valve switching and time programmed extractions with combinations of static and dynamic extraction conditions at various pressure settings. Supercritical pressure was maintained inside the extraction vessel using a deactivated fused-silica 1.5 m × 25 or 50 μm I.D. restrictor (SGE, Austin, TX, USA). Optimization experiments were carried out using glass beads (250 μm, acid washed and silanized; Supelco, Bellefonte, PA, USA) as the sample matrix, an 0.5-ml extraction vessel and sample collection into a 2-ml vial containing approximately 1 ml of organic solvent spiked with a known concentration of internal standard mixture (PCB 44 and 141). CO_2 was of SFC grade from Ucar (Union Carbide, Westerlo, Belgium).

Analysis

An HP 5890 gas chromatograph equipped with an HP 7673A autosampler, an electron-capture detector and a 50 m × 0.2 mm I.D. fused-silica capillary column (Ultra-2, HP, 0.33 μm film) was used for the chromatographic separation and was interfaced with an HP-Chem data system (Hewlett-Packard, Palo Alto, CA, USA). Helium was used as the carrier gas (2 ml/min) and argon–methane as the purge gas (60 ml/min). After the injection of 4 μl the temperature programme consisted of an initial temperature of 80°C, 2 min hold, then an increase to 170°C at 30°C/min, then 3°C/min to the final temperature of 290°C and held for 5 min. The injector temperature was 200°C and the detector temperature was 325°C. Quantification was performed by comparison with a reference standard mixture using PCB 44 and 141 as internal standards.

RESULTS AND DISCUSSION

Optimization of extraction conditions

Optimization experiments were carried out using glass beads spiked with a standard mixture of sixteen pesticides and PCBs in hexane followed by off-line SFE with sample collection in hexane. After each experiment a second extraction was performed to check if all the components had been extracted under the conditions used and to confirm that a clean system was used for the next experiment. Preliminary experiments were performed using different tapered and linear restrictors. Tapered restrictors caused clogging problems, so linear restrictors of 25 and 50 μm I.D. were used in spite of the disadvantages of a decrease in pressure over the whole linear range of the restrictor. The internal diameter of the restrictor in combination with its length (at fixed pressure) determines the flow-rate and the volume of CO_2 passing through the extraction cell during a certain time period. Table I gives the results for 25 and 50 μm restrictors for 20 and 50 min dynamic extractions, respectively. The same extraction yields (89 and 88%, respectively) can be obtained for a restrictor with a larger internal diameter in a shorter time (50 μm and 20 min) than for restrictors with a smaller I.D. (25 μm and 50 min). Finally 50-μm restrictors were chosen because of

TABLE I

COMPARISON OF EXTRACTION RECOVERIES (%) FOR 25 AND 50 μm LINEAR RESTRICTORS WITH DIFFERENT EXTRACTION TIMES (min)

Component	Restrictor (static/dynamic extra time) diameter		
	25 μm (10/20)	25 μm (10/50)	50 μm (10/20)
α-HCH	26	34	55
HCB	–	–	37
β-HCH	63	90	91
γ-HCH	44	–	64
β-HEPO	63	82	91
p,p'-DDE	69	96	106
Dieldrin	67	87	96
TDE	69	91	96
o,p'-DDT	73	116	107
p,p'-DDT	80	109	106
PCB 28	53	74	78
PCB 52	61	83	88
PCB 101	71	100	97
PCB 118	70	90	99
PCB 153	70	94	105
PCB 138	70	91	101
Mean	63	88	89

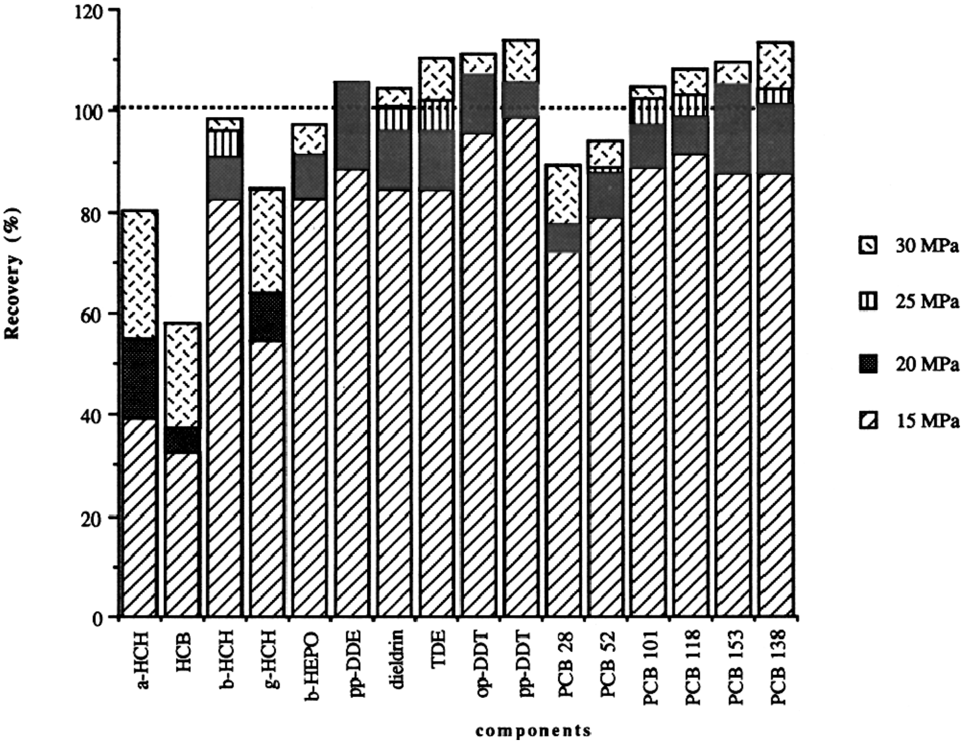

Fig. 1. Influence of variations in pressure on extraction recoveries. The largest improvement in recovery can be observed when increasing the pressure from 15 to 20 MPa. a = α; b = β; g = γ; pp = *p,p'*; op = *o,p'*.

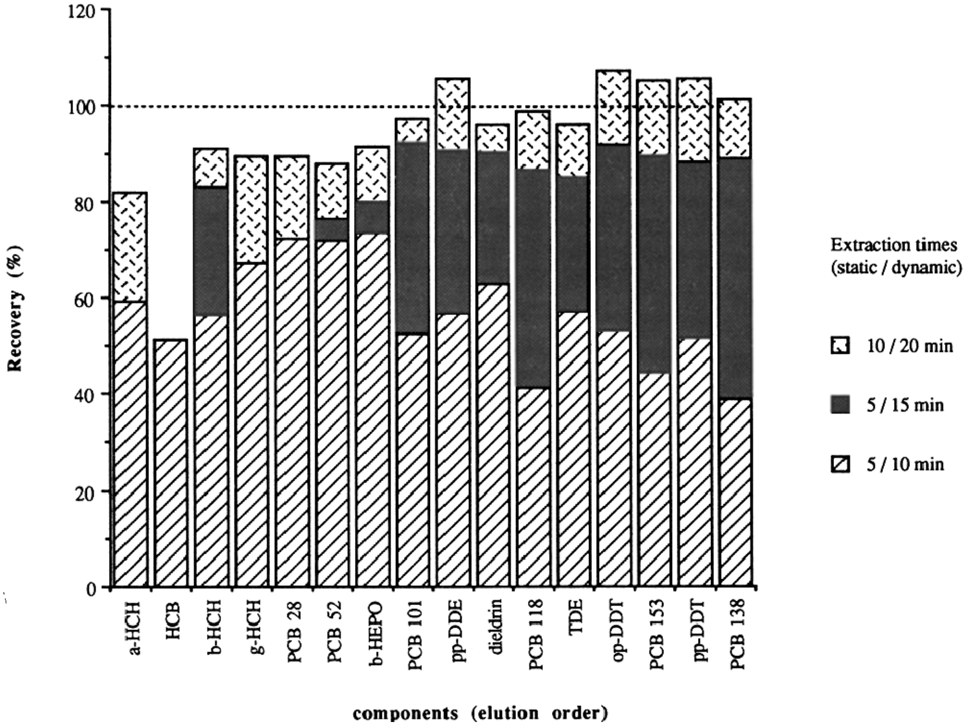

Fig. 2. Influence of extraction times (static/dynamic in min) on extraction yields. Better extraction yields are obtained, especially for the less volatile components, when using longer extraction times (note: components given in order of elution).

TABLE II

REPRODUCIBILITY OF EXTRACTION RECOVERIES (%) OF SFE PROCEDURE

Conditions: 20 MPa; 50°C; 10 min static and 20 min dynamic extraction.

Component	Reproducibility (%)			
	Experiment			Mean ± S.D.
	1	2	3	
α-HCH	55	56	54	55 ± 0.5
HCB	37	37	40	38 ± 1.0
β-HCH	91	98	90	93 ± 1.6
γ-HCH	64	63	64	64 ± 0.1
β-HEPO	91	93	87	90 ± 2.0
p,p′-DDE	106	103	96	101 ± 2.8
Dieldrin	96	97	92	95 ± 1.5
TDE	96	98	89	94 ± 2.6
o,p′-DDT	107	122	102	110 ± 4.2
p,p′-DDT	106	137	104	116 ± 5.7
PCB 28	78	88	80	82 ± 0.9
PCB 52	88	91	87	89 ± 0.8
PCB 101	97	101	93	97 ± 2.0
PCB 118	99	106	96	100 ± 2.3
PCB 153	105	100	94	100 ± 2.8
PCB 138	101	102	94	99 ± 2.5
Mean	89	93	85	89 ± 1.9

TABLE III

INFLUENCE OF COLLECTION SOLVENT ON EXTRACTION RECOVERIES (%)

Conditions: 20 MPa; 50°C; 10 min static and 20 min dynamic extraction.

Component	Hexane	Isooctane
α-HCH	55	95
HCB	38	78
β-HCH	93	105
γ-HCH	64	91
β-HEPO	90	103
p,p′-DDE	101	107
Dieldrin	95	105
TDE	94	102
o,p′-DDT	110	105
p,p′-DDT	116	101
PCB 28	82	105
PCB 52	89	102
PCB 101	97	108
PCB 118	100	110
PCB 153	100	104
PCB 138	100	101
Mean	89	101

the shorter time of analysis. Extraction pressure, combinations of static and dynamic extractions, extraction times and collection solvents were varied and the reproducibility of the system was tested. The extraction pressure was varied from 15 to 30 MPa at constant temperature of 50°C and 30 min extraction. Fig. 1 shows the recoveries for the different extraction conditions. A second extraction of the same sample did not give any increase in yield. A few components, α-HCH, HCB and γ-HCH, show relatively low recoveries compared with the other components, probably as a result of their volatility, which resulted in a less efficient trapping in the solvent used. Excluding the latter components, the largest improvement in recovery can be observed when increasing the pressure from 15 to 20 MPa, whereas only a slight increase in recovery is obtained from 25 to 30 MPa. As higher pressures increase the risk of co-extractants from the matrix, 20 MPa was chosen as the optimum pressure.

Several experiments were performed to establish the ideal extraction times at various combinations of static and dynamic extraction times. Earlier experiments with long static extractions and shorter dynamic extractions showed that the recoveries were low and that second extractions of these samples gave higher yields. Therefore experiments were carried out with 15, 20 and 30 min of extraction (Fig. 2). From Fig. 2 it can be seen that better extraction yields are reached, especially for the less volatile components, when using longer dynamic extraction times. Using the longest extraction time of 10 min static and 20 min dynamic extraction yields between 78 and 107% were found for all except the more volatile components.

The reproducibility of the extraction procedure was studied by triplicate extractions using the proposed conditions (50°C, 20 MPa, 10 min static and 20 min dynamic extractions). Table II shows that SFE gives reproducible extractions with good mean recoveries (89%) and low mean standard deviations (4.2%), with a range of 90.4 ± 3.2% to 115.5 ± 12.9% for all PCBs and chlorinated pesticides, excluding the more volatile pesticides.

To improve the recovery for the volatile pesti-

TABLE IV

COMPARISON OF EXTRACTION RECOVERIES (%) FOR PCBs AND PESTICIDES FROM SAND FOR DIFFERENT EXTRACTION TECHNIQUES

Conditions: 20 MPa; 50°C; 10 min static and 20 min dynamic; collection in iso-octane.

Components	Addition (ng/g)	Solvent extraction (n = 5)		Soxhlet extraction (n = 5)		SFE (n = 3)	
		Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)
α-HCH	2.3	86.9	4.3	100.7	1.3	98.8	2.1
HCB	0.9	94.0	5.2	113.0	1.9	88.7	7.2
β-HCH	3.3	93.3	4.0	120.0	4.7	100.5	5.1
γ-HCH	2.2	89.6	4.2	120.9	6.6	100.2	5.2
β-HEPO	3.2	88.3	4.2	106.0	2.7	94.2	1.9
p,p'-DDE	5.1	89.0	3.8	116.1	3.6	92.9	9.6
Dieldrin	4.8	88.1	3.2	101.3	2.8	92.9	3.5
TDE	8.2	87.8	8.2	95.6	2.8	96.2	5.0
o,p'-DDT	8.9	91.5	3.5	164.0	8.0	89.2	2.0
p,p'-DDT	10.1	96.9	3.8	–	–	91.2	5.4
PCB 28	4.9	96.3	4.8	139.6	3.1	98.0	1.5
PCB 52	4.6	92.0	5.3	121.3	4.4	–	–
PCB 101	2.9	94.9	5.0	125.5	4.8	88.2	1.9
PCB 118	2.3	93.2	4.4	136.8	5.3	90.2	6.9
PCB 138	2.4	94.1	3.8	126.0	4.4	86.5	4.7
PCB 153	2.1	94.6	4.4	120.3	3.5	96.2	3.9
Mean	4.3	91.9	4.5	120.5	3.7	93.6	4.1

cides iso-octane was investigated as a collection solvent. Table III shows that a considerable increase in recovery is obtained by chosing the most appropriate collection solvent. By changing to iso-octane acceptable recoveries are also found for α-HCH, HCH and γ-HCH. The mean recovery for all components was 101%, at a level of 5 ng absolute.

Comparison of SFE with other techniques

The optimized conditions (20 MPa, 50°C, 10 min static and 20 min dynamic extraction and solvent collection is isooctane) have been used for the SFE of compounds from two soil samples spiked with a standard mixture of sixteen pesticides and PCBs at a level of 5 ng/g of dry matter. Separate aliquots of the samples were also extracted with two conventional techniques: solvent extraction with acetone–hexane and Soxhlet extraction with acetone–light petroleum. All samples were extracted directly after a fixed time to evaporate the solvent after spiking, thus minimizing the influence of the spiking solvent acting as a modifier during extraction. In this way the analytical recovery was determined.

Tables IV and V give the recoveries and standard deviations for the various techniques applied to sand and peat soils. Solvent extraction of sand gives good recoveries with low standard deviations for all components, varying from 79 ± 3.8% for p,p'-DDT to 87 ± 4.3% for α-HCH. For peat soil the recoveries show more variation, with fairly low recoveries for p,p'-DDE (32 ± 6.5%), o,p'-DDT (41.6 ± 7.0%), p,p'-DDT (41 ± 9.6%), PCB 138 (18 ± 8.1%) and PCB 153 (12 ± 6.9%). These results are in agreement with values found for these components in the Dutch soil monitoring programme [1]. Rapid, almost irreversible, adsorption of these components takes place in soils with high organic carbon contents.

Using Soxhlet extraction, very high recoveries are found for sand (mean 121 ± 3.7%) and peat soils (125 ± 7.1%), probably caused by impurities coextracted during the more intensive Soxhlet extrac-

TABLE V

COMPARISON OF EXTRACTION RECOVERIES (%) FOR PCBs AND PESTICIDES FROM PEAT SOIL FOR DIFFERENT EXTRACTION TECHNIQUES

Conditions: 20 MPa; 50°C; 10 min static and 20 min dynamic; collection in iso-octane.

Components	Addition (ng/g)	Solvent extraction (n = 5)		Soxhlet extraction (n = 5)		SFE (n = 3)	
		Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)
α-HCH	2.3	98.2	7.5	103.6	5.2	83.9	1.8
HCB	0.9	78.2	7.7	127.4	7.6	88.3	2.2
β-HCH	3.3	115.6	9.2	137.7	8.4	108.0	1.6
γ-HCH	2.2	101.7	8.2	117.0	6.4	94.7	6.4
β-HEPO	3.2	110.3	9.0	124.2	5.8	107.0	3.9
p,p'-DDE	5.1	32.6	6.5	127.6	7.8	86.9	1.1
Dieldrin	4.8	90.8	8.3	108.9	5.6	89.2	2.5
TDE	8.2	71.9	8.3	88.9	14.2	86.7	3.1
o,p'-DDT	8.9	41.6	7.0	134.5	0.4	94.6	2.6
p,p'-DDT	10.1	40.9	9.6	–	–	98.0	1.9
PCB 28	4.9	79.1	7.9	148.1	8.3	101.0	6.5
PCB 52	4.6	63.9	6.6	114.1	1.8	–	–
PCB 101	2.9	53.3	6.9	133.2	18.8	101.3	1.9
PCB 118	2.3	53.9	7.3	154.1	6.3	96.0	2.7
PCB 138	2.4	18.4	8.1	116.4	6.5	90.8	1.7
PCB 153	2.1	11.9	6.9	134.6	11.2	86.4	2.3
Mean	4.3	66.4	7.8	124.7	7.1	94.2	2.6

tion procedure. In Fig. 3a and b, the chromatograms are shown for peat soil extracted with solvent and Soxhlet extraction, respectively. The chromatograms show several impurities giving increased baselines. An extra clean-up step before analysis, which was not applied here, is necessary to obtain reliable analytical data. SFE of sand and peat soils gives good recoveries for all components, varying from 87 ± 4.7% for PCB 138 to 101 ± 5.1% for β-HCH in sand, and from 84 ± 1.8% for α-HCH to 107 ± 3.9% for β-HEPO in peat soils. In Fig. 3c the chromatogram of a peat-soil extracted with SFE shows a clean extract giving a straight baseline, better than the results obtained for the other techniques. The reproducibility is fairly good (1.9–6.9%), and is comparable with that found in the optimization experiments on glass beads. SFE is comparable with the other techniques for sand with respect to reproducibility and gives better results for peat soils, especially for the more apolar components.

SFE is more efficient than conventional techniques, giving higher recoveries than solvent extraction and with no need for the clean-up steps required in Soxhlet extraction. Furthermore SFE is faster and requires less sample handling; an extraction with SFE takes only 30 min compared with solvent and Soxhlet extractions, which take one or two days for a series of samples. Automation of the SFE procedure will further increase the speed of analysis. The amount of extraction solvent is significantly reduced to only 1 ml.

CONCLUSIONS

SFE using CO_2 at 50°C and 20 MPa, 10 min static followed by 20 min dynamic extraction with collection in iso-octane, has been found to give the optimum extraction of organochlorine pesticides and PCBs from soils. After establishing the optimum conditions, SFE can be used for the extraction of organochlorine pesticides and PCBs from soils with high recoveries (85–105%) and good reproducibility. SFE is more efficient than solvent extrac-

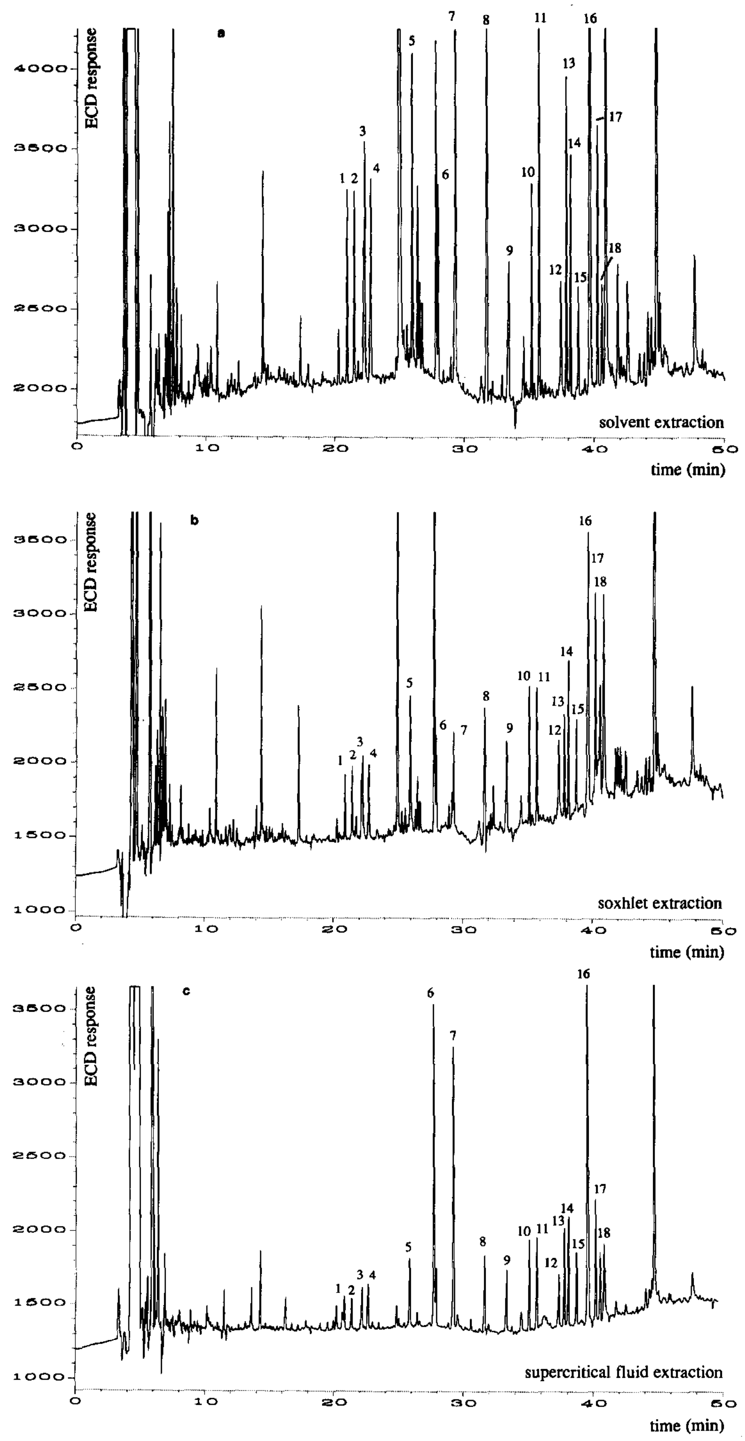

Fig. 3. Chromatograms of pesticides and PCBs extracted from peat soil. (a) Solvent extraction; (b) Sohxlet extraction; and (c) SFE. ECD = Electron-capture detection. 1 = α-HCH; 2 = HCB; 3 = β-HCH; 4 = γ-HCH; 5 = PCB 28; 6 = PCB 52; 7 = PCB 44 (I.S.); 8 = β-HEPO; 9 = PCB 101; 10 = *p,p'*-DDE; 11 = dieldrin; 12 = PCB 118; 13 = TDE; 14 = *o,p'*-DDT; 15 = PCB 153; 16 = PCB 141 (I.S.); 17 = *p,p'*-DDT; and 18 = PCB 138 (see under Experimental for gas chromatographic conditions).

tion for the extraction of more apolar components from soils with high organic carbon contents. No additional clean-up step is needed after the SFE of these components from soil, unlike Soxhlet extraction.

This work shows the potential of SFE for the determination of environmental contaminants in soil. The next step will be the SFE of real samples and the evaluation of extraction conditions for unknown matrices. Special attention should be devoted to the pretreatment and homogenization of small soil samples for analysis using SFE.

ACKNOWLEDGEMENT

R. Leenderts from Interscience Breda is gratefully acknowledged for his good advice and assistance by beginning the work with SFE.

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