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Optimization of supercritical carbon dioxide extraction for polychlorinated biphenyls and chlorinated benzenes from sediments

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Abstract

A method for the simultaneous extraction of polychlorinated biphenyls (PCBs) and chlorinated benzenes in sediments using supercritical fluid extraction (SFE) technique was developed. The best recovery of the above chlorinated pollutants was obtained by using non-modified carbon dioxide at 35 MPa and an extraction temperature of 100°C with a sediment moisture content in the 11 to 50% range. Cleanup of SFE extract was performed on a miniature Florisil column followed by sulfur removal with mercury. PCB levels were quantitated by a mixture of selected PCB congeners using a mass-selective detector so that the level of each PCB homologue series as well as the total PCB concentration in the sample extract could be evaluated. Under the optimized conditions, an extraction time of only 21 minutes was needed to produce PCB results comparable to a 7-h Soxhlet extraction. Meanwhile, the SFE recovery of chlorinated benzenes was up to 50% higher than for the Soxhlet results due to lower evaporative losses in the former procedure.

1. Introduction

Polychlorinated biphenyls (PCBs) contamination in the environment was first reported in 1966 [1]. Since then, there have been numerous indications of PCB pollution in various parts of the world. Because of their toxicity and suspected carcinogenicity to humans and wildlife [2], the levels of PCBs in water, sediments and biota samples are monitored in almost all water quality monitoring programs for organics. Considerable interest has also been focused on the determination of non-*ortho* substituted or copla-

nar PCB congeners as they exhibited toxicity at a level similar to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin [3]. Although the manufacture and use of PCBs have ceased in the 1970s, environmental pollution of PCB may still arise from leaking storage tanks and improper disposal in landfill sites. In contrast, the contamination of chlorinated benzenes was not as widespread as PCBs. Their occurrence has been documented in Lake Ontario, particularly near the Niagara River, as well as the connecting channels of the Great Lakes [4-7]. Due to their persistence and tendency to accumulate in sediments and biota samples, PCBs and chlorinated benzenes pollution will remain as an environmental concern for many years to come.

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In the past, several hundred millilitres of solvent were used in all extraction methodologies developed for the determination of PCBs and chlorinated benzenes in sediments [8]. With the exception of the steam distillation procedure, there was no substitute for organic solvent until the advent of supercritical fluid extraction (SFE). Solvent extraction not only generated a large amount of waste, but also required lengthy evaporation and cleanup steps. For the determination of chlorinated benzenes, improper evaporation of sample extracts also led to losses of these volatile compounds.

SFE extraction of Aroclor 1254 from sediment was first reported by Schantz and Chesler [9]. Comparable amounts of PCBs were obtained either by Soxhlet extraction with dichloromethane or by a 4-h extraction at room temperature using supercritical carbon dioxide at 35.5 MPa. Later on, quantitative recovery of total PCBs from sediments have also been reported by other investigators in shorter extraction times using carbon dioxide modified by methanol and higher extraction temperatures [10,11]. Recently, Langenfeld *et al.* [12] have studied the effects of temperature and pressure on the SFE efficiency for selected PCB congeners. Their results indicated that, at 200°C, PCBs were effectively extracted by pure carbon dioxide at 15.5, 36.2 or 67.2 MPa. Lower PCB recovery was obtained for all congeners at an extraction temperature of 50°C, regardless of the fluid pressure used. Yet, these authors did not study the recovery of PCBs

at extraction temperatures between the above extremes. Meanwhile, no results have ever been reported on the effect of SFE conditions on the recovery of PCBs at different level of chlorination, and there were few publications on the extraction of chlorinated benzenes by supercritical fluids. In this report, we describe the optimization of SFE conditions for PCBs and chlorinated benzenes in sediment samples.

2. Experimental

2.1. Reagents and chemicals

[²H₁₂]Chrysene and [²H₄]1,4-dichlorobenzene were products of MSD Isotopes (Pointe Claire, Canada). PCB congener standard solutions at 200 µg/ml in hexane were purchased from Ultra Scientific (North Kingstown, RI, USA). A mixture made up of the nine congeners (Table 1) at 10 µg/ml in isooctane was prepared by mixing appropriate amounts of the concentrated stock solutions. This mixture was further diluted to 1000, 250 and 100 pg/µl in the presence of [²H₁₂]chrysene (500 pg/µl) as internal standard. Chlorinated benzenes and hexachloro-1,3-butadiene (HCBd) were obtained from Aldrich (Milwaukee, WI, USA). Octachlorostyrene (OCS) was also obtained from Ultra Scientific. Calibration mixtures of chlorinated benzenes, HCBd and OCS from 50 to 500 pg/µl were prepared in isooctane. Distilled-in-glass grade

Table 1
List of PCB calibration congeners and their quantitation and confirmation ions

Chlorobiphenyl	BZ No.	Chlorine substitution	Quantitation ion	Confirmation ion
Mono-	1	2	188	190
Di-	5	2,3	222	224
Tri-	29	2,4,5	256	258
Tetra-	50	2,2',4,6	292	290
Penta-	87	2,2',3,4,5'	326	328
Hexa-	154	2,2',4,4',5,6'	360	362
Hepta-	188	2,2',3,4',5,6,6'	394	396
Octa-	200	2,2',3,3',4,5',6,6'	430	432
Nona-	209	2,2',3,3',4,4',5,5',6,6'	464	466
Deca-	209	2,2',3,3',4,4',5,5',6,6'	498	500

solvents were purchased from Burdick & Jackson (Muskegon, MI, USA). SFE-Grade carbon dioxide without a helium head pressure was supplied by Air Products (Nepean, Canada).

2.2. Extraction of sediments

All SFE extractions were performed with a Hewlett-Packard 7680T module. Typically, a 7-ml thimble was prepared by placing two layers of Whatman GFC filter paper and 200 mg of Celite after the bottom thimble cap was installed. A 1-g sample was weighed into the thimble and then it was mixed with 500 μ l of water by a vortex mixer. SFE was carried out at 100°C and 35 MPa (5000 p.s.i.) with unmodified carbon dioxide for 21 min (1 min static extraction and 20 min dynamic extraction). During the extraction, the octadecylsilane (ODS) trap was maintained at 15°C (see later discussion) for the sorption of extracts. Upon completion of extraction, the trap was warmed up to 45°C before the organics were eluted with two 1-ml aliquots of isooctane–hexane (1:1). The entire extraction–desorption cycle required *ca.* 35 min. For extractions using the modified carbon dioxide, a procedure previously described for polycyclic aromatic hydrocarbons (PAHs) was used [13].

For comparison, Soxhlet extraction was performed by refluxing the sediment with 300 ml of an acetone–hexane (59:41) mixture for 7 h. Evaporation of sediment extracts was performed with a three-stage Snyder column.

2.3. Cleanup procedure

The SFE extract was cleaned up on a 5-cm activated Florisil column packed in a 20 \times 0.7 cm I.D. disposable Pasteur pipette. After pre-elution with 3 ml of pentane, the combined SFE extract was applied to the cleanup column. The chlorinated pollutants were eluted by another 10 ml of pentane and this fraction was then evaporated down to *ca.* 1 ml in a 40°C bath under a gentle stream of nitrogen. (Note: if the determination of chlorinated benzenes is not needed, hexane can be used instead of the less commonly available pentane.) The concentrated extract was then vigorously shaken with a drop of mercury

and this step was repeated until the metal remained shiny. The extract was transferred to a calibrated test tube with several pentane rinses and the volume was brought down to just *ca.* 0.9 ml. Finally, 500 ng of the internal standard was added and the volume adjusted to 1 ml for GC–MS and GC–electron-capture detection (ECD) analyses.

2.4. Chromatographic analysis

Instrumental analysis of PCBs and chlorinated benzenes was carried out by a Hewlett-Packard (HP) 5890 Series II gas chromatograph equipped with a HP 5972A mass-selective detector, an electron-capture detector and a 30 m \times 0.25 mm I.D. HP-5-MS capillary column. Splitless injections (1 μ l) were made by the HP 7673A autosampler. The operation of the gas chromatograph, detectors, autosampler and the acquisition of data were all controlled by a personal computer running dedicated ChemStation and mass-selective detector softwares. The injection port and electron-capture detector were kept at 250 and 300°C, respectively while the mass-selective detector interface temperature was set at 280°C. The temperature program for PCB analysis was: initial oven temperature 70°C with a 1-min hold; programming rate 1, 30°C/min from 70 to 160°C; rate 2, 2.5°C/min from 160 to 260°C, and the final temperature was held for 10 min. The temperature program for chlorinated benzene analysis was: initial oven temperature 60°C with a 1-min hold; programming rate 1, 5°C/min from 60 to 150°C; rate 2, 10°C/min from 150 to 250°C and a 15-min hold at the final temperature. Splitless time was 1 min. Carrier gas was helium and constant column flow at 0.85 ml/min (MS work) or 1.2 ml/min (ECD work) was maintained by the electronic pressure controller. ECD make-up gas was argon–methane (95:5) at 30 ml/min. Electron energy and electron multiplier voltage of 70 eV and 2000 V, respectively, were used for all MS operations.

2.5. Acquisition of MS data

Prior to sample analysis, the mass-selective detector was tuned with perfluorotributyl-amine

(PFTBA) using the standard spectra autotune program. Mass spectral data for the PCBs were acquired in the selected ion monitoring mode using the characteristic and confirmation ions listed in Table 1 according to a previously published procedure [14]. Response factors for the calibration congeners relative to the internal standard [$^2\text{H}_{12}$]chrysene were determined. For samples, the peak areas for all PCB congeners at each level of chlorination were summed and quantitated against the calibration congener with the same number of chlorine atoms to yield the concentration of PCBs for each homologue series. Total PCB concentration in a sample was the sum of its PCB concentrations at each chlorination level. For better selectivity, dichlorobenzenes in sediment extracts were also analyzed by MS. In this case, masses m/z 146 and 148 (native dichlorobenzenes) and m/z 152 ($^2\text{H}_4$]1,4-dichlorobenzene, internal standard) were monitored.

3. Results and discussion

Two lake sediments, one collected from the Hamilton Bay and the other from Lake Ontario at a site near the Niagara River, were used in development and optimization of the SFE method. Conventional analyses have previously been performed on these samples: the Hamilton Bay sediment was shown to be naturally contaminated with PCBs, and the Lake Ontario one with chlorinated benzenes and a few other chlorinated hydrocarbons. Both samples have been freeze-dried and homogenized before use. In order to determine the efficiency of the new extraction procedure, the SFE recoveries relative to the Soxhlet results were generated.

There are numerous factors that can affect the results in a SFE experiment. The ones that have a more significant effect on the recovery include the selection of extraction fluid, the density or pressure of the supercritical fluid, extraction temperature, flow-rates and extraction times, the nature and amount of modifier(s), and the collection technique for the extracts. Many of these factors are inter-related and optimal recovery of

organics from a sample can often be obtained by different combinations of the above factors. Our aim in this work was to develop a method that is quantitative compared to Soxhlet, efficient (short extraction times), environmentally friendly and easy to adopt. Among all the supercritical fluid in use for extraction, carbon dioxide is by far the most widely used because of its availability, high purity, lower cost, ideal physical and chemical properties and environmental friendliness. Therefore other supercritical fluids were not evaluated in this study. Sorbent traps made of ODS have been shown to be highly efficient for the collection of a wide variety of semi-volatile and non-volatile organics in off-line SFE systems [15], thus they are most suitable for the collection of these chlorinated compounds. In our work, an extraction fluid pressure of 35 MPa and a flow-rate of 4 ml/min were chosen for more efficient extraction since the use of lower supercritical fluid pressures (or densities) usually and lower flow-rates usually requires a longer extraction time to achieve quantitative recovery.

3.1. SFE of PCBs from sediments

Nearly all sediment samples received for PCB analysis were wet, water was therefore added to our freeze-dried reference sample before the extraction was performed. In beginning of this work, the moisture content in our Hamilton Bay sediment was arbitrarily adjusted to 33%. Previously, we have shown that a higher extraction temperature results in a large improvement in the recovery of PAHs [13]. Using the Hamilton Bay sediment as a model sample, the recovery of PCBs in each homologous series was studied over the temperature range of 40 to 120°C in 20°C increments (Fig. 1). It should be noted that mono-, di-, nona- and decachlorobiphenyls are either undetected or present in minute amounts in our reference sample and nearly all other sediments, their results were not evaluated. When SFE was carried out at 35 MPa with a flow-rate of 4 ml/min, PCBs are readily extracted by supercritical carbon dioxide. Even at low extraction temperatures of 40 and 60°C, the recovery of *total* PCBs was 73 and 82%, respec-

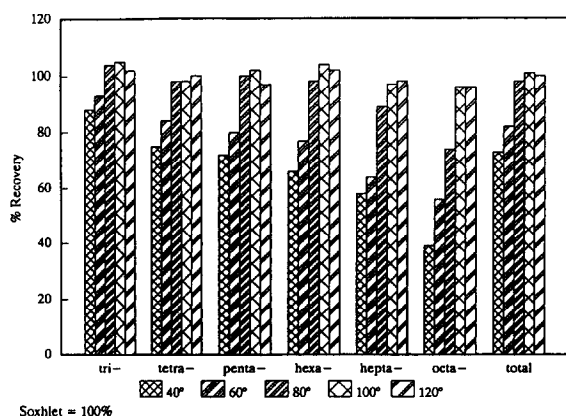


Fig. 1. Effect of extraction temperature ($^{\circ}\text{C}$) on the SFE recovery of chlorobiphenyls and total PCBs from the Hamilton Bay sediment.

tively of the Soxhlet result. A closer look at Fig. 1 indicates that while the trichlorobiphenyls were nearly 90% recovered at 40°C , the recoveries of other chlorinated biphenyls continuously dropped when the level of chlorination increased. For example, the recovery of octachlorobiphenyls was down to 39% at this temperature. Higher temperatures produced higher recoveries of all PCBs, particularly those with higher chlorination. This observation is consistent with our work on PAHs where the higher-molecular-mass PAHs were more readily recovered at higher extraction temperatures. Over 95% recovery of all PCBs was obtained at 100°C .

A further increase of extraction temperature to 120°C did not improve the recovery of PCBs, including the hepta- and octa-chlorobiphenyls.

The levels of PCBs from trichlorobiphenyls to octachlorobiphenyls in the Hamilton Bay sample determined by Soxhlet and SFE at 100°C were summarized in the second and third columns of Table 2. The precision and accuracy of the results indicated that both techniques produced data in good agreement with each other. Since the levels of hepta- and octachlorobiphenyls are relatively low in this sample, the total PCBs result obtained at 80°C was therefore nearly the same as the 100 or 120°C results (Fig. 1).

Sediment samples from the field had varying amounts of water, it was therefore interesting to find out if the moisture content in a sample also played a role in the recovery of PCBs under SFE conditions. Various amounts of water were added to the freeze-dried reference sample so that the resulting moisture content is 0, 11, 20, 33 or 50% before they were extracted by carbon dioxide at 100°C and 35.1 MPa (5000 p.s.i.). For all samples with 11 to 50% moisture content, the recoveries of PCBs in each homologous series were very similar to the results given in column three of Table 2. For the samples with zero moisture content, lower recoveries from 90 (for the trichlorobiphenyls) to 75% (for the hepta- and octachlorobiphenyls) were obtained. For this reason, extraction of completely dry sediment with pure carbon dioxide for PCB determination

Table 2

Mean levels of PCBs (ng/g) in the Hamilton Bay sediment by homologue series obtained under different extraction conditions

	Soxhlet ($n = 3$)	SFE 1 ($n = 6$)	SFE 2 ($n = 2$)	SFE 3 ($n = 2$)
Trichlorobiphenyls	275 ± 25	288 ± 17	287	299
Tetrachlorobiphenyls	681 ± 58	667 ± 49	654	687
Pentachlorobiphenyls	712 ± 63	726 ± 42	693	700
Hexachlorobiphenyls	310 ± 20	322 ± 21	298	341
Heptachlorobiphenyls	85 ± 12	82 ± 10	75	78
Octachlorobiphenyls	31 ± 3	29 ± 3	27	30
Total PCBs	2094 ± 182	2114 ± 161	2034	2135

Extraction conditions: Soxhlet: 300 ml of acetone-hexane (59:41, v/v), extraction time 7 h. SFE 1: 100°C extraction temperature and 35 MPa carbon dioxide pressure, no solvent modifier, extraction time 21 min. SFE 2: Same as SFE 1 except that $500 \mu\text{l}$ of dichloromethane-methanol (1:1, v/v) was spiked to the sediment prior to extraction. SFE 3: 120°C extraction temperature and 35 MPa carbon dioxide modified by 4% dichloromethane and 1% methanol, extraction time 42.5 min. See ref. 13 for details.

is not recommended. Attempts have also been made to extract PCBs from sediments in the presence of solvent modifier to see if higher recovery could be obtained. In these cases, the modifiers were introduced by either adding 500 μ l methanol–dichloromethane (1:1) directly to the sample before extraction or mixing with the carbon dioxide with the assistance of a high-pressure modifier pump during the dynamic extraction [13]. In contrast with the SFE of PAHs from sediment, the recovery of all PCBs could not be further improved in the presence of solvent modifiers (fourth and fifth columns of Table 2). Since fewer coextractives such as PAHs and humic substances were obtained by pure carbon dioxide, it is therefore suggested that no additional modifier should be used for the SFE of PCBs from sediments.

The effect of extraction time on the recovery of PCBs was also studied. Within experimental errors, the PCB results were the same for extraction times of either 20 or 10 min. Approximately 70% of the total PCB was recovered for a 5 minutes dynamic extraction time.

3.2. SFE of chlorinated benzenes and some chlorinated hydrocarbons

For the work on chlorinated benzenes and a few other chlorinated hydrocarbons, the Lake Ontario sediment sample collected near Niagara River, NY, USA, was used. Similar to the SFE of PCBs, our work on chlorobenzenes and HCBd in sediments were carried out with a 33% moisture content. As shown in Fig. 2, low extraction temperatures were again unfavourable for the extraction of all compounds of interest. For example, less than 65% of all chlorinated benzenes and HCBd were recovered at 40°C compared to the Soxhlet results. Higher extraction temperature improved recovery of all compounds, and the highest recovery was obtained at either 100 or 120°C. Since similar results were obtained at these two temperatures, 100°C was used for the result of the experiment as a shorter cycling time (heating and cooling) was achieved at a lower extraction temperature.

The concentrations of chlorinated benzenes in

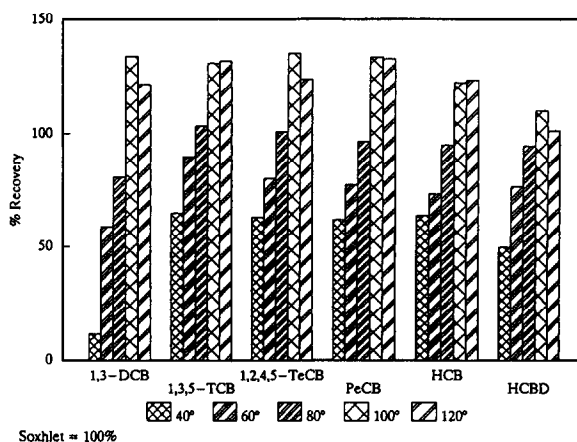


Fig. 2. Effect of extraction temperature (°C) on the SFE recovery of chlorinated benzenes and hexachloro-1,3-diene from the Lake Ontario sediment.

the Lake Ontario sediment obtained by Soxhlet as well as SFE procedures were summarized in Table 3. In contrast to the PCB results, at 100°C, the SFE recoveries of the chlorinated benzenes and HCBd were from *ca.* 10 to 35% higher than the Soxhlet values. Similar to our findings for naphthalene and methylnaphthalenes, the higher SFE results likely resulted from less evaporative losses in the SFE procedure since the latter required only one, instead of two, evaporations. This hypothesis was further supported by the results of the evaporation of Soxhlet extracts with known amounts of chlorobenzenes. Typically, only 65 to 85% of the chlorobenzenes could be recovered when 300 ml of the extract was concentrated to 1 to 2 ml, even if iso-octane was used as a keeper in the evaporation.

We have also examined the effects of modifiers, extraction time and the ODS trap temperature on the recovery of chlorinated benzenes. Again, the addition of modifier (500 μ l of dichloromethane–methanol, 1:1) to the sample prior to extraction did not improve the recovery of chlorobenzenes (Table 3, fourth column). Although there was no significant difference in chlorinated benzene results for extraction times of 15, 20 and 30 min, lower recoveries (from 55 to 85%) of all compounds were observed if the dynamic extraction time was reduced to 5 or 10 min. While lowering the trap temperature from

Table 3

Mean recovery of chlorobenzenes and chlorinated hydrocarbons (ng/g) in the Lake Ontario sediment by Soxhlet and SFE procedures

	Soxhlet (<i>n</i> = 3)	SFE 1 (<i>n</i> = 6)	SFE 2 (<i>n</i> = 2)	SFE 3 (<i>n</i> = 2)
1,3-Dichlorobenzene	84.8 ± 8	114 ± 10	105	156
1,4-Dichlorobenzene	66.0 ± 5	89.0 ± 8	87.2	127
1,3,5-Trichlorobenzene	72.5 ± 8.3	95.0 ± 8.3	95.7	97.3
1,2,4-Trichlorobenzene	100 ± 9	146 ± 12	151	143
1,2,4,5-Tetrachlorobenzene	114 ± 10	169 ± 11	174	169
1,2,3,4-Tetrachlorobenzene	30.8 ± 2.9	44.3 ± 3.1	42.4	43.9
Pentachlorobenzene	46.2 ± 5.8	64.5 ± 5.5	63.1	60.1
Hexachlorobenzene	195 ± 15	239 ± 13	225	227
Hexachloro-1,3-butadiene	42.8 ± 5.1	47.1 ± 3.6	43.9	46.2
Octachlorostyrene	36.4 ± 4.7	33.0 ± 2.9	37.4	31.9

Extraction conditions: Soxhlet: 300 mL of 51/49 (v/v) acetone–hexane (51:49, v/v), extraction time 7 h. SFE 1: 100°C extraction temperature and 35 MPa carbon dioxide pressure, no solvent modifier. Extraction time 21 min. SFE 2: Same as SFE 1 except that 500 μl of dichloromethane–methanol (1:1, v/v) was spiked to the sample prior to extraction. SFE 3: Same as SFE 1 except that the ODS trap temperature was kept at 0°C instead of 15°C during extraction.

15 to 0°C had no positive effects on the recoveries of trichlorobenzenes and other compounds of higher molecular masses, there was a *ca.* 40% increase in the recovery of the dichlorobenzenes (Table 3, fifth column). Trap temperatures of lower than 0°C were not used since plugging of the restrictor nozzle occasionally occurred during the extraction of wet sediments under such conditions.

3.3. Cleanup of SFE extracts

In addition to the chlorinated compounds of interest, the SFE extract also contained coextractives that could interfere with the GC analysis when ECD was used. In comparison to Soxhlet extraction, SFE was far more selective especially if no solvent modifier was used. Thus, a less stringent cleanup procedure can be used. In this work, PCBs, chlorinated benzenes and the other chlorinated hydrocarbons were eluted from a miniature (5 cm) fully activated Florisil column with pentane while the more polar coextractives in the sediment extracts stayed on the column. Pentane instead of hexane was used whenever the determination of the more volatile chlorinated benzenes was required since pentane has a lower boiling point and thus will minimize losses

in the solvent evaporation step. After concentration, the sample was further treated with mercury to remove elemental sulfur and sulfur-containing compounds which were not removed by the Florisil cleanup.

3.4. Final analysis of SFE extracts

Because of the large number of PCB congeners present in environmental samples, a total congener analysis is extremely tedious. That approach is further complicated by the availability and purity of authentic standards as well as the GC resolution of the congeners. For the purpose of this work, PCB samples were analyzed by MS using a method developed by Gebhart *et al.* [14]. In this case, a selected PCB congener from each homologue series was employed to quantitate all isomers at the same level of chlorination since the congener was shown to have a response factor nearly identical to the mean of the entire group. As PCB homologues have overlapping retention time windows, special precautions was taken to eliminate interferences by PCB congeners containing more chlorine atoms. Under electron impact ionization conditions, a chlorobiphenyl molecule undergoes fragmentation by the loss of two Cl, and to a

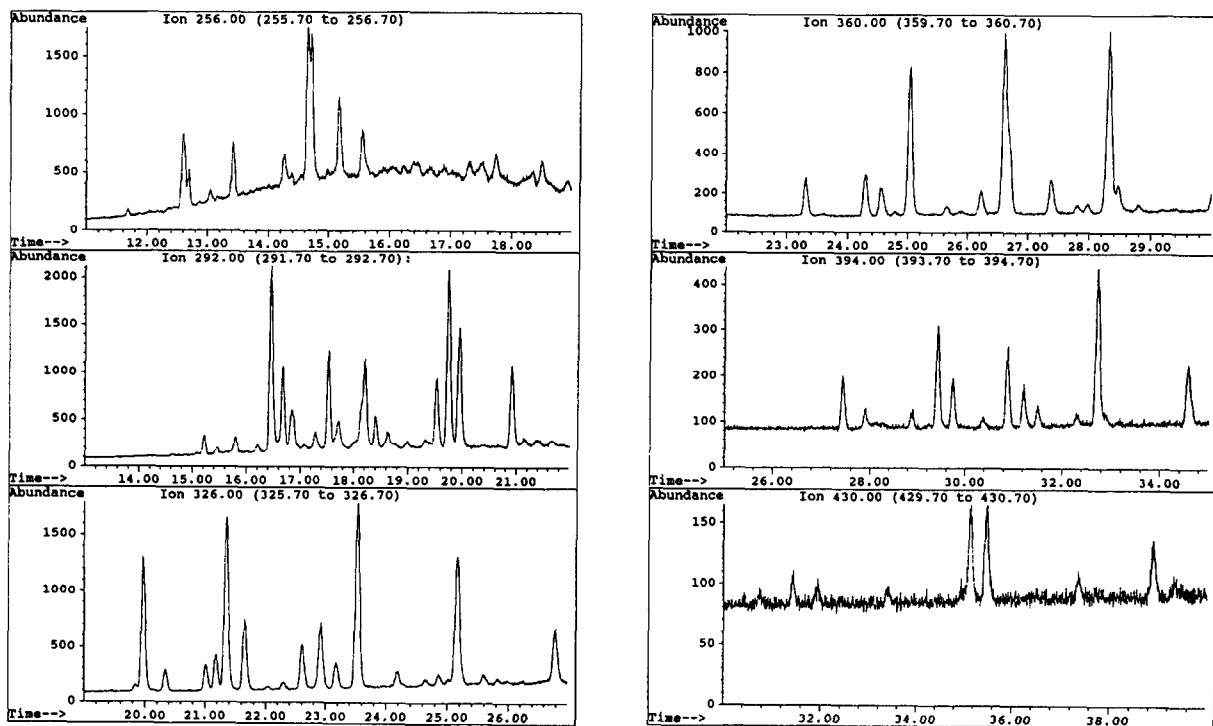


Fig. 3. Reconstructed single ion chromatograms for tri- (ion 256), tetra- (ion 292), penta- (ion 326), hexa- (ion 360), hepta- (ion 394) and octa- (ion 430) chlorobiphenyls in a SFE extract of the Hamilton Bay sediment after cleanup. Time in min.

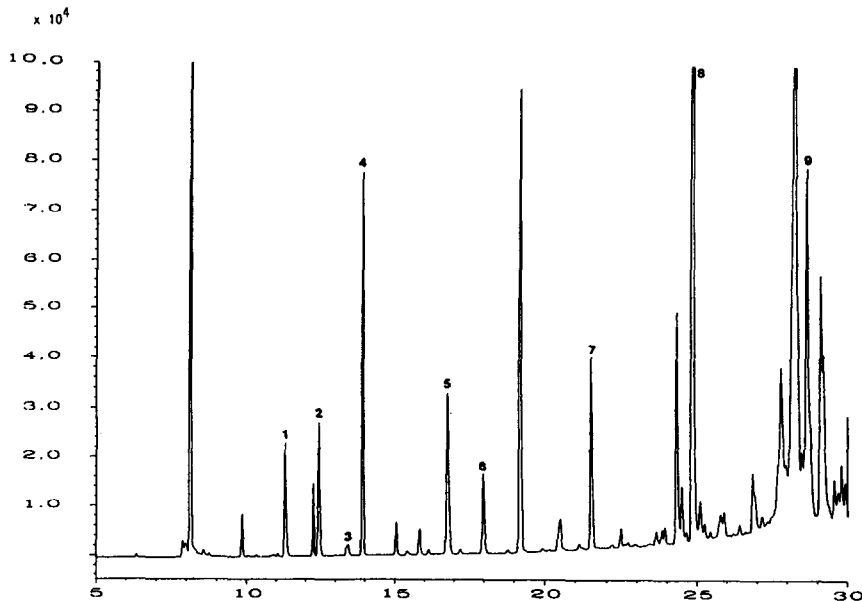


Fig. 4. Electron-capture chromatogram of a SFE extract for the Lake Ontario sediment contaminated by chlorobenzenes, hexachloro-1,3-butadiene and octachlorostyrene. Peaks: 1 = 1,3,5-trichlorobenzene; 2 = 1,2,4-trichlorobenzene; 3 = 1,2,3-trichlorobenzene; 4 = hexachloro-1,3-butadiene; 5 = 1,2,4,5-tetrachlorobenzene; 6 = 1,2,3,4-tetrachlorobenzene; 7 = pentachlorobenzene; 8 = hexachlorobenzene; 9 = octachlorostyrene. Time in min.

lesser extent, HCl and Cl, thus causing interference in the determination of PCBs with one or two less chlorine atoms [16,17]. Thus the absence of $(M + 70)^+$ and $(M + 35)^+$ ions was used to confirm the level of chlorination for each peak. With this selective quantitation technique, we were able to evaluate the recovery of chlorobiphenyls at each level of chlorination as well as the total PCB concentration of a sample in the SFE experiments. While the dichlorobenzenes were also analyzed by MS, the other chlorinated benzenes, hexachloro-1,3-butadiene and octachlorostyrene were analyzed by ECD for better sensitivity. Reconstructed single ion chromatograms depicting the PCB from tri- to octachlorobiphenyls in the SFE extract of the Hamilton Bay sample are shown in Fig. 3. An ECD chromatogram illustrating the chlorinated benzenes in the extract of a Lake Ontario sediment is shown in Fig. 4.

4. Conclusions

In summary, a SFE method using unmodified supercritical carbon dioxide was developed and optimized for the simultaneous extraction of native PCBs, chlorinated benzenes, hexachloro-1,3-butadiene and octachlorostyrene from sediments. While PCBs were similarly recovered by either SFE and Soxhlet extraction, the SFE recovery for chlorinated benzenes and HCBd exceeded the Soxhlet results due to less evaporative loss. The new technique is more efficient since it requires only 21 min and no organic solvent in the extraction steps. A simplified cleanup procedure and much less solvent evapora-

tion are also the other advantages of the SFE approach. For the above reasons, the SFE approach is a better alternative than conventional solvent extraction techniques in routine and analyses of PCBs and chlorinated benzenes.

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