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Short Communication

Reduction/elimination of sulfur interference in organochlorine residue determination by supercritical fluid extraction

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ABSTRACT

Supercritical fluid extraction (SFE) was used for selective extraction of polychlorinated biphenyls and chlorinated pesticides from sediment samples fortified with elemental sulfur. The results obtained showed that use of SFE in static mode can lead to significant reduction in sulfur interference.

INTRODUCTION

Organochlorines as a class are some of the most persistent organic contaminants in the environment. These chemicals have found wide application in the past; however, due to adverse effect of these chemicals on human health and

the environment, their use has been severely curtailed during the past decade. Despite the discontinuation of their use, these compounds are still prevalent in all compartments of the environment. Due to direct link of aquatic systems to human exposure, the contamination of aquatic systems is of special concern. In aquatic systems sediments are the primary reservoir of all hydrophobic compounds and monitoring pro-

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grams for environmental quality of aquatic systems generally involve measurements of contaminants in sediments. The traditional analytical methodologies employed for this purpose are quite laborious, a major problem in the sediment residue monitoring being the interference caused by elemental sulfur. The elemental sulfur in sediments results from degradation of biological materials, especially under anoxic conditions. The interference is quite serious when electron-capture detection (ECD) is used. The sulfur interference is linked to three factors.

(1) Aggregates of elemental sulfur exhibit partition behavior similar to organochlorine compounds in system where the fluid phase is a non-polar or a moderately polar organic solvent. As a result, elemental sulfur aggregates are extracted and carried through most adsorbent-based clean-up techniques.

(2) Sulfur aggregates exhibit chromatographic characteristics similar to a number of organochlorine compounds of interest in gas chromatography.

(3) Sulfur aggregates possess high affinity for thermal electrons and give strong ECD responses, which continues to be the primary detection method for polychlorinated organics.

In traditional analytical schemes, the sulfur interference problem has been dealt with using three different approaches. The first approach involves removal through size-exclusion chromatography (SEC). SEC is used extensively for removal of large interfering and/or other problematic molecules such as lipids. The technique has also been used to remove low levels of sulfur from extracts containing organochlorine compounds [1]. The removal is based on the fact that the most prevalent sulfur aggregates, such as S_8 , possess a condensed cyclical structure and can exhibit total penetration on a selected SEC column. By proper selection of column gel packing, sulfur can be separated from the organochlorine compounds of environmental concern. Since the technique is based on physical separation, no artifacts or anomalies are introduced by its use. The primary limitation of the technique is due to the small column capacity which leads to the overloading of the column;

this results in loss of separation between analytes of interest and sulfur.

The other techniques for removal of sulfur involve either reaction with metallic copper, mercury or tetrabutylammonium sulfite. The treatment with metallic copper is perhaps the most frequently used method and results in precipitation of sulfur as sulfide [2]. The methodology is very effective; however, its use results in degradation of a number of analytes of environmental interest.

It is quite logical that the performance of analytical methodology can be enhanced if a selective extraction procedure is employed to decrease the amount of sulfur in the extract. Supercritical fluid extraction (SFE) offers selectivity and has been shown to be applicable for a variety of small non-polar analytes in different matrices [3–5]. The present study was designed to monitor the effectiveness of SFE for reducing sulfur interference during organochlorine residues determinations.

Studies were also undertaken to improve the SFE process by optimization of adsorbent material for trapping extracted components.

EXPERIMENTAL

All SFE experiments were carried out with a multichamber SFE system, the details of which have been provided elsewhere [4]. The system consists of a pneumatic amplifier, extraction vessels [capable of withstanding up to 400 atm (1 atm = 101 325 Pa) pressure] and adsorbent traps. A schematic of the system is given in Fig. 1.

All experiments were conducted with sediment samples collected from streams in Missouri, USA. All evaluations were carried out with the material balance approach, which involved fortification of samples aliquots with known concentrations of elemental sulfur (0.15%) and organochlorines of interest, such as hexachlorobenzene, hexachlorocyclohexanes, chlordane, heptachlor, heptachlor epoxide, *p,p'*-DDT (and metabolites) and polychlorinated biphenyls (PCBs). The concentration of pesticides in the experiments was varied from 20 to 200 parts per billion (ppb, w/w). A 1-kg batch of samples was

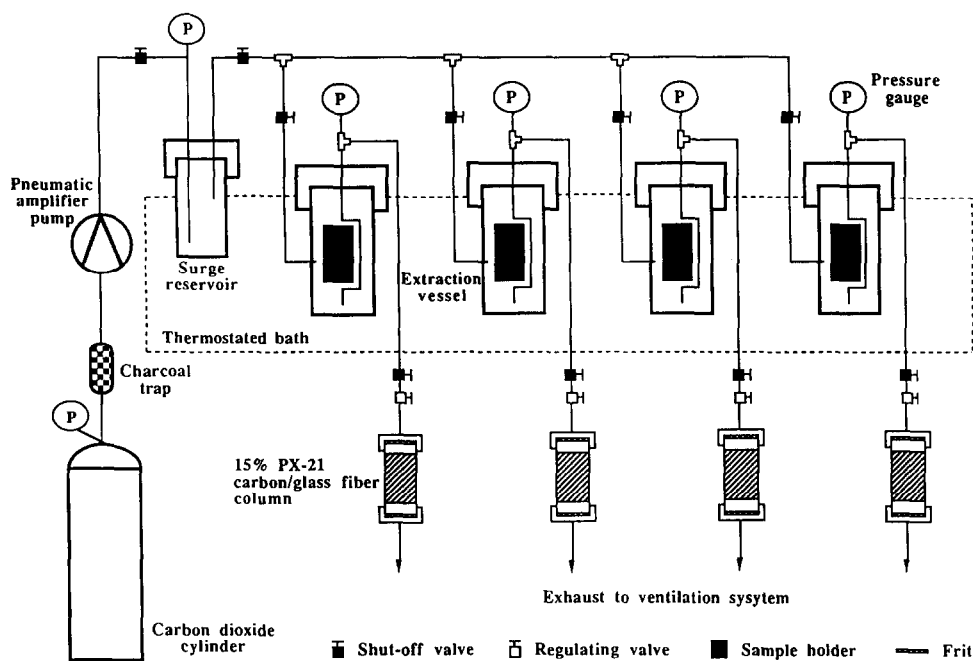


Fig. 1. Schematic diagram of SFE system.

homogenized, air dried, and sieved to remove stones and aggregates larger than 2 mm. Aliquots (5–10 g) were used for organochlorines residue determination. The samples were homogenized with anhydrous sodium sulfate and clean Pyrex wool, and the mixture was placed in a stainless-steel wire mesh sample holder. The sample holders were placed in the SFE vessels which were submerged in a thermostated water bath. The vessels were sealed and pressurized with either CO_2 or N_2O . All extractions were carried out in the static mode. Effects of density, temperature and equilibration period on extractability and the selectivity were monitored.

The extracted sediment components were trapped in solid adsorbent traps. Experiments to optimize the composition of adsorbent materials were carried out independently. The criteria for selection of optimal adsorbent material were minimum breakthrough and high desorption efficiency. To ascertain the breakthrough a series configuration was employed. The high-pressure cartridges used as adsorbent traps, were of an easy-to-operate snap-on/snap-off type, designed in our laboratories. A number of adsorbent

materials were used, including silica gel Davidson grade 923, Florisil and graphitized carbon.

For comparative purposes, samples were also extracted in Soxhlet and subjected to classical clean-up steps including chromatographic fractionation on Florisil, size-exclusion and silica gels.

When required, the Cu metal treatment was used for removing elemental sulfur. Cu for this purpose was obtained by rinsing fine granular Cu with diluted nitric acid, followed by thoroughly rinsing with water, acetone and hexane. Approximately 0.6 g of the clean Cu was added to each sample extract, the contents were shaken for 10 min, the supernatant was separated and a $2\text{-}\mu\text{l}$ portion injected into a gas chromatograph. The gas chromatographic analyses were performed on a capillary gas chromatograph, Perkin-Elmer Model 8500 equipped with a split-splitless injector and an electron-capture detector. Gas chromatographic separations were carried out with a $30\text{ m} \times 0.25\text{ mm}$ fused-silica capillary column coated with 95% methyl and 5% phenyl polysiloxane; helium was used as the carrier gas.

Gas chromatographic conditions were: injector

temperature 255°C; oven temperature program 1 min isothermal at 80°C, then at 10°C min⁻¹ to 180°C, then at 3°C min⁻¹ to 255°C, isothermal for 9 min. Determinations of polychlorinated dibenzo-*p*-dioxins (PCDDs) were carried out with a quadruple mass spectrometer (Hewlett-Packard MSD Model 5970B) interfaced with a gas chromatograph (Hewlett-Packard Model 5890). The mass spectrometer was operated in selected ion monitoring mode. The quantitation of PCDDs was accomplished with ¹³C-labeled internal standards.

RESULTS AND DISCUSSION

The applicability of supercritical fluids for the extraction of non-polar and moderately polar analytes from soils or sediments has been demonstrated by a number of researchers [6–9]. Extraction efficiencies approaching 100% can be obtained even under moderate operating parameters, in the near critical region, especially in the presence of polar modifiers/wetting agents [6]. However, the acceptance of this technique for routine applications has been slow due to the relatively high cost of the extraction systems and poor precision. The latter problem is related to inefficient trapping of extracted analytes. An ideal trapping system is one which retains all analytes while allowing all of the extracting fluid to escape. The most common approach involves expansion of condensed fluid through a restrictor, where the expansion leads to a drop in the solubility of analytes. Analytes are then collected either on the walls of an expansion vessel or in an adsorbent trap or liquid impingers. The breakthrough of analytes in condensed CO₂ aggregates is the most severe problem in all trapping systems. The problem can be alleviated by using low-volume thermostated restrictors; however, this results in long decompression periods. For large extraction vessels, decompression periods often exceed extraction equilibration periods. The proper selection of trapping system is thus an important consideration for analytical SFE.

Application of adsorbent traps, in cases where the trap can serve a dual purpose of fractionation and clean-up, is quite attractive. For the present

application, a dual adsorbent trap was found to give the best results. The trap consisted of a stainless steel tube (150 mm × 9 mm I.D.) designed to fit into a Swagelok quick-connecting fitting. The trap was packed with a 20-mm layer of Florisil and topped with a 20-mm layer of graphitized carbon PX-21 (10%, w/w, on glass fiber).

The choice of adsorbent combination was made to facilitate fractionation of PCDDs, PCBs, chlorinated pesticides and polar co-extractants. This fractionation was accomplished by forward elution with hexane, hexane–dichloro-

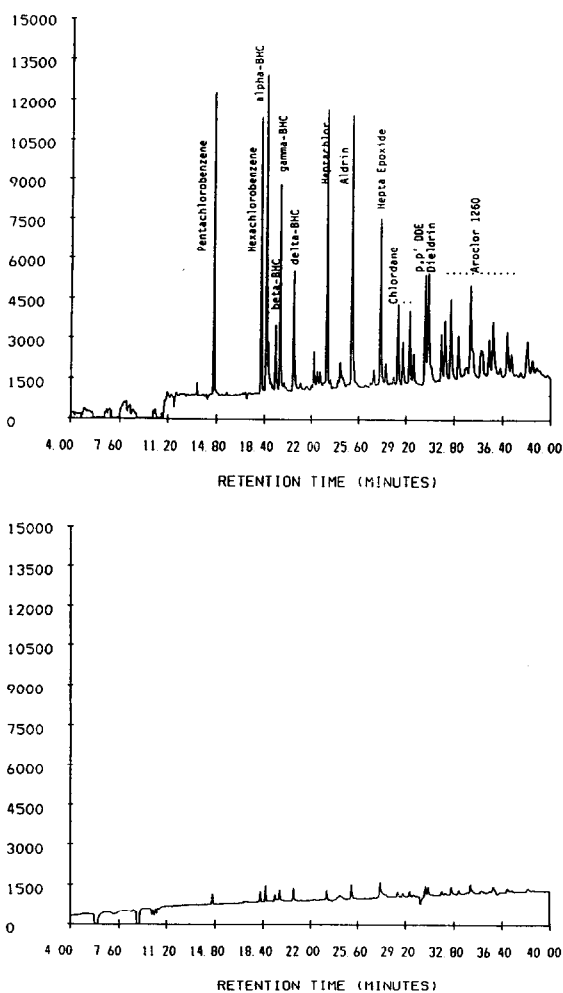


Fig. 2. Gas chromatographic output for SFE breakthrough experiment: chlorinated pesticides and PCBs. Hexane–diethyl ether (94:6); top: trap 1, bottom: trap 2. BHC = Benzene hexachloride.

methane (50:50) followed by a reverse extraction with toluene. Further fractionation into subclasses is feasible but was not optimized for the present study. The evaluation of traps included breakthrough and recovery experiments.

The breakthrough experiments were carried out by assembling two traps in a series. The carbon layer in the first trap was spiked with a mixture containing PCDDs, pesticides and PCBs. The extraction system was assembled and pressurized with CO₂ to 200 atm at 50°C. The fluid was then released through the serial trap. Both traps were eluted with hexane and hexane-dichloromethane mixture in the forward direc-

tion followed by extraction with toluene in the reverse direction. All components of the mixture were quantitatively recovered from the first trap indicating essentially zero breakthrough. The results are shown in Figs. 2 and 3, which depict the chromatographic traces of pesticides/PCBs extracts (hexane-dichloromethane fraction) and PCDDs extract (toluene fraction), respectively. The total concentration of components in the second trap extract was $\leq 2.0\%$ indicating minimal breakthrough.

The SFE experiments were carried out after optimization of trapping systems. The fortified sediment, containing 20–200 ppb of pesticides and PCBs and 0.15% (w/w) elemental sulfur, was placed in the extraction vessel. Results of extraction carried out at different densities (constant temperature) are given in Table I. The results show that all analytes were extracted quantitatively; recoveries were generally better

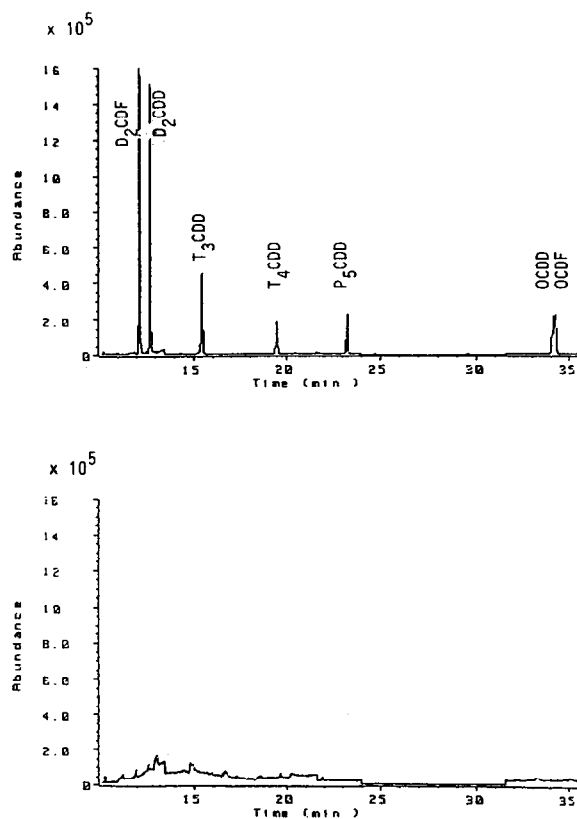


Fig. 3. Gas chromatographic output for SFE breakthrough experiment: polychlorinated dibenzo-*p*-dioxins. Reverse toluene extract; top: trap 1, bottom: trap 2. D₂CDF = dichlorodibenzofuran; D₂CDD = dichlorodibenzodioxin; T₃CDD = trichlorodibenzodioxin; T₄CDD = tetrachlorodibenzodioxin; P₅CDD = pentachlorodibenzodioxin; OCDD = octachlorodibenzodioxin; OCDF = octachlorodibenzofuran.

TABLE I

RECOVERY AT DIFFERENT EXTRACTION PRESSURES AND CONSTANT TEMPERATURE (323 K)

Results are averages of five determinations. Standard deviation for the recovery was 3.6.

Analyte	Recovery (%)			
	Extraction pressure (atm)			
	136	156	177	197
γ -Benzene hexachloride	98	98	92	93
Hexachlorobenzene	92	95	98	93
Heptachlor	105	96	96	95
Heptachlor epoxide	89	96	98	97
<i>trans</i> -Chlordane	98	96	96	96
<i>cis</i> -Chlordane	95	94	95	98
Dieldrin	98	93	91	94
<i>p,p'</i> -DDE	95	92	93	93
<i>p,p'</i> -DDD	89	85	84	83
<i>p,p'</i> -DDT	85	86	94	87
2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin	78	73	85	92
2,3,6,7,8-Pentachlorodibenzo- <i>p</i> -dioxin	73	76	81	90
Octachlorodibenzo- <i>p</i> -dioxin	65	66	78	85

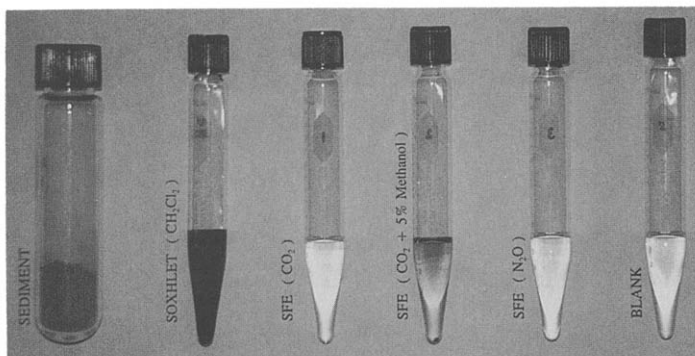


Fig. 4. Photograph of supercritical fluid and liquid solvent extracts of sulfur- and organochlorine-fortified soil.

than 85%, while the recovery for fortified sulfur ranged between 1-3%. By contrast, $\geq 90\%$ of the fortified sulfur was recovered with liquid solvent extraction. The results of relative extractability of sulfur and other contaminants from soil/sediment samples are shown in Fig. 4. Quantitation of sulfur content in liquid extract and supercritical extract reveal that a 50-fold increase in selectivity for organochlorines over sulfur was obtained. However, the residual sulfur in SFE extract still caused considerable interference problems (Fig. 5). The interference problem was easily eliminated by mild treatment with Cu or SEC. The results obtained are shown in Fig. 6. By contrast, the sulfur content in fortified samples extracted in liquid solvent remained high even after Cu treatment and pre-

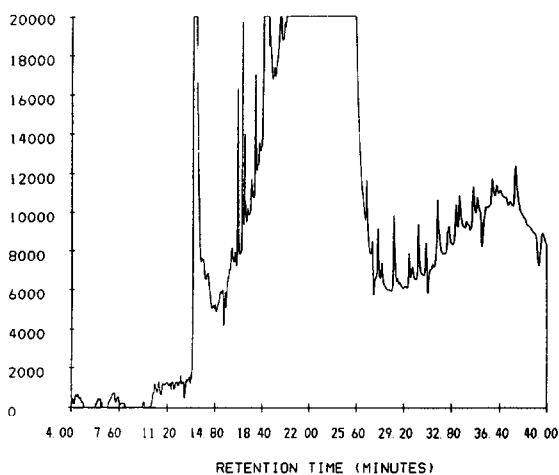


Fig. 5. Chromatographic output of supercritical fluid extract of sulfur-fortified soil. Extraction fluid CO₂, 136 atm, 50°C.

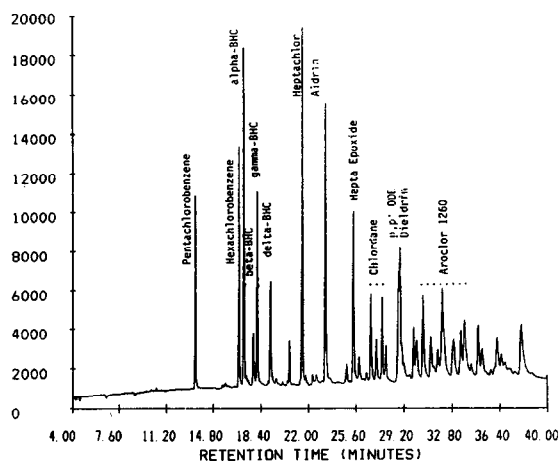


Fig. 6. Chromatographic output of Cu-treated SFE extract. Extraction fluid CO₂, 136 atm, 50°C.

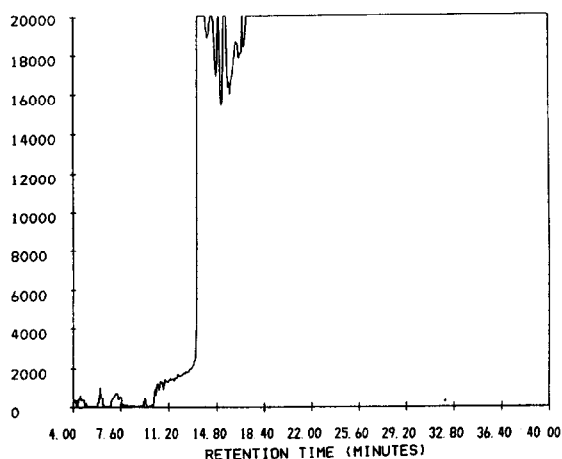


Fig. 7. Chromatographic output of liquid solvent extract after Cu treatment.

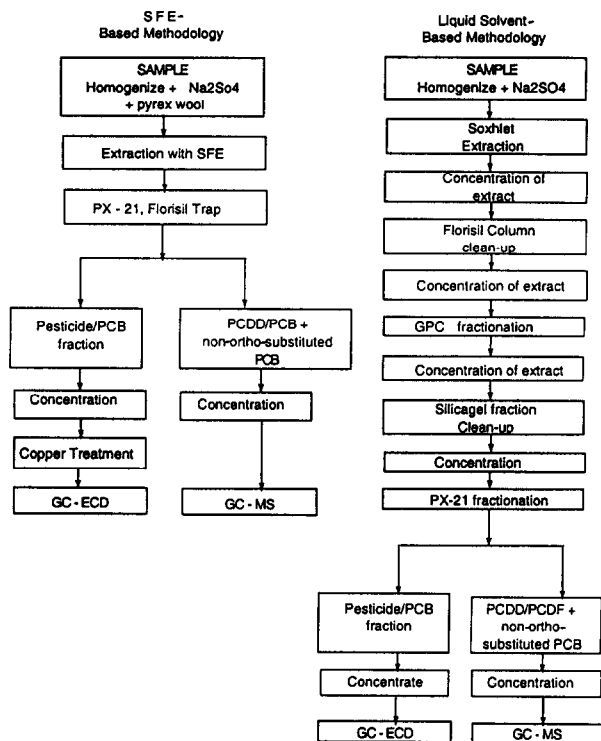


Fig. 8. Flow schematic of analytical methodologies. PCDD = Pentachlorodibenzodioxin; PCDF = pentachlorodibenzofuran.

vented detection and quantitation of any analytes. Chromatographic results obtained for a sample extracted in liquid are shown in Fig. 7. The results clearly demonstrate the superiority of SFE in reducing interference problems associated with the presence of elemental sulfur. Furthermore, the SFE and associated clean-up methodology is considerably faster. The methodology is essentially a two-step process com-

pared to multi-step liquid solvent-based methodologies. The flow diagrams of the two approaches are given in Fig. 8.

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