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Matrix effect on supercritical fluid extraction of organochlorine pesticides from sulfur-containing soils

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Abstract

The influences of spiking method and matrix properties of total organic carbon, pH, moisture content, and grain size on supercritical fluid extraction efficiency of 16 organochlorine pesticides (OCPs) from soils were investigated. A direct on-line method using selective adsorbents of AgNO₃ loaded silica in the extraction cell for simultaneous extraction and clean-up of sulfur-containing soils is developed. The procedures are simple, rapid, and require only small amounts of samples and solvents. With the right choice of extraction conditions and trapping materials, it may serve to analyze OCPs in sulfur-containing soils on a routine basis.

Keywords: Soil; Environmental analysis; Matrix effects; Extraction methods; Pesticides; Organochlorine compounds

1. Introduction

The persistence and extended use of organochlorine pesticides (OCPs) have resulted in the widespread distribution of those compounds in the environment. Negative environmental impacts due to OCPs are of great concern and widely recognized [1,2]. The poor solubility of OCPs in water [3] needs the investigation of OCPs impact on human health and surrounding ecosystems to focus on the analysis of soil and biota samples [4–13].

OCPs in solid matrices are currently determined using liquid extraction to separate OCPs from the matrices followed by clean-up and concentration procedures before the GC determination [14,15]. The general drawbacks, such as the use of large amounts of solvents, time-consuming, labor-intensive and considerable waste production, associated with these classical extraction techniques could be reduced using supercritical fluid extraction (SFE). SFE has

shown to be an efficient and rapid method for the isolation of OCPs from solid matrices [6–8,10–13]. The quantitative recoveries obtained using spiked samples were sometimes reported to be lower when extracting real samples of different matrices [16,17]. Nevertheless, the benefits in speed, cost, and the small amounts of solvents used have made SFE a viable alternative to classical solvent and sonication extractions.

The soil matrices are complex because of the presence of sulfur (S), which will deteriorate the separation capability of GC capillary column and the sensitivity of electron-capture detection (ECD). To provide reliable results, the minimization of S interferences in SFE extracts before GC determination is compulsory. Soil S is predominately in inorganic and organic forms. The ratio of the two forms varies with soil properties such as pH, moisture, organic matter and clay contents, depth, and climatic conditions [18]. Previous studies concluded that the presence of elementary S was the major problem in sediment analysis [19,20]. The S interferences could be dealt

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with using size-exclusion chromatography [21], conversion of S to thiosulfate by tetrabutylammonium sulfite [22] and to sulfide by metallic copper (Cu) [23]. The use of Cu is the most frequently used method. It has recently been used to reduce the S interferences in a soil spiked with 0.15% elementary S after SFE extraction of OCPs [13].

In this study, the influences of spiking method, soil composition, soil moisture, and grain size on SFE extraction efficiency of 16 OCPs (α -BHC, γ -BHC, β -BHC, heptachlor, δ -BHC, aldrin, heptachlor epoxide, endosulfan I, 4,4'-DDE, dieldrin, endrin, 4,4'-DDD, endosulfan II, 4,4'-DDT, endrin aldehyde, and endosulfan sulfate) from soils were investigated. A feasibility study of adding selective adsorbents of Cu (or AgNO_3 loaded silica) to the extraction cell for on-line clean-up of sulfur-containing soils was conducted. To overcome the concern of great discrepancies between the SFE extraction efficiencies of spiked and real samples contaminated at trace level [17,24,25], the effectiveness of AgNO_3 loaded silica for simultaneous extraction and clean-up of sulfur-containing species in the soils was demonstrated using a NIST Standard Reference Material (SRM) 1941a marine sediment.

2. Experimental

2.1. Chemicals

The solvents (acetone, *n*-hexane, acetonitrile, methanol) used were all HPLC grade from Tedia (Fairfield, OH, USA). The EPA method 608 OCPs mixture and internal standards of hexachlorobenzene (HCB) and mirex were obtained from AccuStandard (New Haven, CT, USA). The HCB was added to the sample at the beginning of the extraction. It was used to check the possible loss of analytes during extraction. Standard calibration mixtures containing 100 ppb mirex as the quantitation standard were prepared by diluting the OCPs mixtures in *n*-hexane by volume. The CO_2 extraction fluid was SFE grade from Scott Specialty Gases (Plumsteadville, PA, USA). The Cu (purity, >99.7%; particle size, <63 μm) and AgNO_3 (purity, >99.8%) powders as well as silica gel (100–200 mesh, ASTM 923 grade) were obtained from Merck (Darmstadt, Germany). HNO_3

of reagent grade was obtained from Fisher (Pittsburgh, PA, USA). The Cu was treated prior to use by rinsing it with 20% (v/v) HNO_3 for ~1 min, followed by thoroughly rinsing with deionized water, acetone and *n*-hexane [13]. The cleaned Cu was kept in the *n*-hexane. The AgNO_3 loaded silica was prepared by dissolving 2.5 g of AgNO_3 in ~30 ml of deionized water and then homogeneously mixed with 22.5 g of silica gel. The mixture was dried in an oven at 50°C first and then activated at 150°C prior to use.

2.2. Soil samples and spiking methods

Five kinds of soils were used in this study. Samples A and C were top soils collected at different sites in the campus. Sample B was sea-sand purchased from Merck with particle size between 0.1~0.3 mm. Sample D was sea-sand collected from southern Taiwan. Sample E was a Standard Reference Material (SRM) 1941a marine sediment from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). The samples were air-dried at ~30°C. Visible twigs and rocks were picked out. The samples were then ground mechanically to obtain a homogeneous powder and sieved through a No. 60 mesh sieve. Soil samples used for fortified and control studies were obtained by extracting ~50 g of sieved soils with 250 ml of acetonitrile for 18 h, followed by extracting with 250 ml of methanol, *n*-hexane, and acetone, each for 8 h. The cleaned soils were dried at 50°C and kept in a desiccator prior to use. Chemical analysis revealed the thus obtained soil blanks were free of OCPs residues. The moisture content, the total organic carbon (TOC), and the pH for samples A to D were listed in Table 1.

Contaminated soil samples fortified at 40 ppb levels were prepared using two methods [16]. In the spot method, 2 g of soil blanks were weighed into a 5-ml extraction cell. The soil blanks were then fortified with a known amount of OCPs by homogeneously adding 0.04 ml of 2 ppm OCPs stock standard solutions directly to the soil. The solvent was evaporated to dryness at ambient temperature for ~5 min. In the slurry method, 40 g of soil blanks were weighed into a 100 ml flask. After an appropriate volume of *n*-hexane was added to totally

Table 1
Properties of soil samples A to D

Sample No.	Property		
	Moisture content (%) ^a	Total organic carbon (%) ^b	pH ^c
A ^d	0.9	4.4	4.9
B	0.2	0.1	6.9
C	0.6	1.6	7.1
D	0.2	1.9	8.8

^a The moisture content of the dried soil was measured at the time of SFE.

^b Total organic carbon determinations were based on the oxidation of organic carbon and thermal decomposition of carbonates in a furnace. The liberated carbon dioxide was trapped and measured.

^c The pH was obtained by measuring the homogeneous solution containing 95 ml water with 5 ml soil.

^d The particle distribution was <0.002 mm 55.6%, 0.002–0.53 mm 31.0%, 0.53–2.00 mm 13.4%.

immerse the soil, 0.8 ml of 2 ppm OCPs stock standard solutions were added to the soil and stirred for 10 min. The solvent was evaporated to dryness at ambient temperature in a hood for at least 8 h.

2.3. Supercritical fluid extraction

All extractions were performed on a Suprex (Pittsburgh, PA, USA) PrepMaster equipped with an AccuTrap collecting device. The CO₂ extracts containing the analytes were trapped by the deactivated fused silica beads (140–270 mesh, Sigma, MO, USA) in the AccuTrap first at –30°C. They were then eluted out at 30°C using an appropriate volume of *n*-hexane. The restrictor temperature was fixed at 80°C. Extractions were generally performed on 2 g of soils in an extraction cell with 5 ml in volume. Initial extraction conditions were adopted from the literature [10]. Optimized extraction conditions were obtained by sequentially varying one experimental parameter while all other parameters remained fixed. The parameters were varied in the order of modifier species, extraction pressure, extraction temperature, static extraction time, dynamic extraction time, modifier amount, eluant volume and size of the extraction cell. Results of the current test were used to determine the next extraction parameter change for optimization. Details of the optimization study were reported elsewhere [20]. The optimized extraction conditions obtained using the soil blanks

fortified at 40 ppb levels were: 0.1 ml of acetone modifier, extraction pressure at 250 atm, extraction temperature at 50°C, static extraction for 5 min, dynamic extraction for 20 min, 6 ml of *n*-hexane eluting at 1 ml/min and a 5-ml extraction cell. The modifier was introduced by adding an appropriate volume of modifier solution to the soil loaded in the extraction cell. About 1.5 g of activated Cu (or 1.5 g of AgNO₃ loaded silica) was added to the extraction cell for selective trapping of sulfur-containing species. The extraction conditions were used throughout the study, unless otherwise specified.

The *n*-hexane eluate in the collection vial was then transferred into a concentration tube and purged with nitrogen to a volume of ~0.8 ml. 0.1 ml of mirex quantitation standard was added. The final volume of the eluate was adjusted to 1.0 ml and subjected to GC–ECD analysis.

2.4. Gas chromatography

GC–ECD analyses were carried out using a HP-5890 Series II gas chromatograph equipped with a SPB-608 capillary column (30 m×0.25 mm I.D., 0.25 μm film thickness) and a ⁶³Ni electron-capture detector. Samples were introduced into the GC column via an on-column injector system. The injector temperature was programmed similar to that for the column, except being maintained at 3°C higher. ECD was at 300°C. Helium was used as the carrier gas at a constant flow-rate of 1.3 ml/min. Nitrogen was used as the make-up gas at a constant flow pressure of 44 p.s.i. (1 p.s.i.=6894.76 Pa). The column temperature was initially held at 60°C, then programmed at 30°C/min to 150°C and held for 2 min, then at 7.3°C/min to 285°C and held for 10 min.

3. Results and discussion

3.1. SFE of contaminated soils spiked by spot and slurry methods

The movement and fate of organic chemicals, including OCPs, in the soils are determined by chemical, physical and biological process occurring in the soils. Among the known processes, sorption–

desorption behavior is considered the most important process affecting organic contaminants [18]. Recent kinetic study of SFE of organic contaminants from heterogeneous environmental samples of sediments and soils suggests that strong analyte–matrix interactions are responsible for the great discrepancies between the extraction efficiency of samples with spiked and native analytes [26]. To investigate the influence of analyte–matrix interactions on SFE extraction efficiency of OCPs, two different spiking methods were tested first on contaminated soils prepared by spiking soil blanks from sample A. It was selected because it contained large amounts of TOC and could undergo stronger interactions with OCPs than other soil samples.

Table 2 lists the percent recovery and standard deviation for the 16 OCPs from spot- and slurry-spiked soils. The recoveries for α -BHC, γ -BHC, β -BHC, heptachlor, δ -BHC, aldrin, heptachlor epoxide, endosulfan I, 4,4'-DDE, dieldrin, endrin, 4,4'-DDD, and 4,4'-DDT [referred as group I OCPs thereafter] from spot-spiked soils are comparable ($\geq 70\%$) to those reported previously for sand [10], except endosulfan II, endrin aldehyde, and endosulfan sulfate [referred as group II OCPs thereafter]. The recoveries for group I OCPs from spot-spiked

soils are in the range of 71–111% and decrease to 67–104% from slurry-spiked soils. Decreasing recovery as high as 30% was observed for aldrin. The results indicate that group I OCPs interact with most of the active sites in the matrix under the slurry-spiked conditions. This is expected since the spiked OCPs could spread over the total surface of the soil during the slurry stirring process. In addition, the OCPs could partition from the liquid phase into the wetted soil surface and interact with the active sites which are located in the organic matter and clay fraction [27]. For group II OCPs, the differences in recoveries (all $\leq 55\%$) are not significant. The lack of solubility data for most OCPs in supercritical CO₂ [28] prevents us identifying whether the strong analyte–matrix interactions or poor partitioning into the fluid is the limiting factor for extraction efficiency. The standard deviations for the 16 OCPs appear not affected by the spiking method. The results indicate the decrease in recoveries when extracting real samples is probably due to the adopted spiking method's failure to completely simulate the real-world samples.

3.2. SFE of slurry-spiked soils with different matrices

Various analyte–matrix interaction forces ranging from van der Waals forces, water bridging, H-bonding, to covalent bonding are involved in the sorption of organic chemicals by soils [18,29]. To investigate the influence of soil matrix on SFE extraction efficiency of OCPs, four different kinds of slurry-spiked soils possessing known and different TOC contents, moisture content, and pH were extracted. It should be pointed out that these four soils might theoretically differ in more properties other than those mentioned above.

Table 3 lists the percent recovery and standard deviation for the 16 OCPs from slurry-spiked soils with different matrices. The corresponding TOC, moisture content, and pH values are listed in Table 1. The average recoveries \pm standard deviations for the 16 OCPs are $75 \pm 17\%$, $85 \pm 31\%$, $85 \pm 17\%$, and $78 \pm 12\%$ for samples A, B, C, and D, respectively. Clay, metal oxide surfaces and organic matter are the dominant materials responsible for the sorption of organic contaminants [18,29]. The hydrolysis or

Table 2
Influence of spiking method on OCPs percent recovery from soil sample A

Compound	Spiking method	
	Spot ($n=7$)	Slurry ($n=7$)
α -BHC	104 \pm 6	78 \pm 7
γ -BHC	95 \pm 6	76 \pm 5
β -BHC	93 \pm 4	70 \pm 3
Heptachlor	95 \pm 5	72 \pm 5
δ -BHC	96 \pm 7	92 \pm 9
Aldrin	97 \pm 6	67 \pm 6
Heptachlor epoxide	91 \pm 5	82 \pm 3
Endosulfan I	71 \pm 4	83 \pm 6
4,4'-DDE	111 \pm 6	95 \pm 4
Dieldrin	85 \pm 5	87 \pm 5
Endrin	90 \pm 13	83 \pm 11
4,4'-DDD	108 \pm 7	104 \pm 8
Endosulfan II	46 \pm 5	55 \pm 10
4,4'-DDT	85 \pm 7	71 \pm 7
Endrin aldehyde	45 \pm 8	46 \pm 6
Endosulfan sulfate	49 \pm 11	41 \pm 6

Spiked at 40 ppb level, mean \pm standard deviation.

Table 3
Influence of matrix on OCPs percent recovery from soil samples A to D

Compound	Sample			
	A (n=7)	B (n=5)	C (n=4)	D (n=3)
α -BHC	78 \pm 7	74 \pm 7	80 \pm 4	81 \pm 4
γ -BHC	76 \pm 5	84 \pm 5	85 \pm 6	81 \pm 4
β -BHC	70 \pm 3	83 \pm 7	77 \pm 6	72 \pm 2
Heptachlor	72 \pm 5	74 \pm 5	78 \pm 5	84 \pm 4
δ -BHC	92 \pm 9	93 \pm 9	92 \pm 7	101 \pm 5
Aldrin	67 \pm 6	3 \pm 1	61 \pm 6	65 \pm 3
Heptachlor epoxide	82 \pm 3	99 \pm 7	101 \pm 5	87 \pm 4
Endosulfan I	83 \pm 6	97 \pm 5	94 \pm 5	89 \pm 5
4,4'-DDE	95 \pm 4	95 \pm 7	107 \pm 9	87 \pm 3
Dieldrin	87 \pm 5	163 \pm 11	103 \pm 3	82 \pm 3
Endrin	83 \pm 11	87 \pm 8	102 \pm 10	65 \pm 7
4,4'-DDD	104 \pm 8	97 \pm 8	104 \pm 12	87 \pm 4
Endosulfan II	55 \pm 10	91 \pm 7	82 \pm 7	78 \pm 6
4,4'-DDT	71 \pm 7	85 \pm 7	77 \pm 12	69 \pm 9
Endrin aldehyde	46 \pm 6	66 \pm 6	48 \pm 4	54 \pm 10
Endosulfan sulfate	41 \pm 6	71 \pm 11	64 \pm 8	63 \pm 10

Spiked at 40 ppb level, mean \pm standard deviation.

protonation of some pesticides at acidic or basic conditions were reported to be responsible for the lower SFE recoveries [12]. A pronounced difference in recoveries was observed for group II OCPs between sample A (47 \pm 6%) and other samples (76 \pm 11%, 65 \pm 14%, and 65 \pm 10% for samples B, C, and D respectively). The organic matter and pH in sample A apparently influence the OCPs recovery. The lower recoveries for sample A were therefore ascribed to the combining effect of high TOC content and low pH. The strong analyte–matrix interactions are therefore responsible for the low recoveries of group II OCPs. Another remarkable difference in recoveries is for aldrin and dieldrin. The recovery for aldrin was almost null (3%) while that for dieldrin was more than full recovery (162%) in sample B. This unusual behavior was responsible for the poor standard deviation observed for sample B and was caused by the oxidation of aldrin to form dieldrin. Dieldrin is known to be the major product when aldrin has undergone chemical and biological degradation process [30]. The real cause for this degradation behavior of aldrin in sample B is still unknown. However, the results indicate that soil properties such as the TOC and pH significantly

influence the extraction efficiency. In addition, the type and nature of functional groups on an organic chemical also influence the extraction efficiency presumably via different interactions with the matrix.

Moisture in the soils might be regarded as a modifier. It might increase the polarity of the supercritical fluid and enhance the partitioning of polar analytes into the fluid. In addition, it might compete with polar analytes for the active sites in the matrix and displaced them into the fluid. Finally, it might swell the soil matrix and expose the small internal cavities, allowing the supercritical fluid better access to adsorbed analytes [12]. Table 4 lists the percent recovery and standard deviation for the 16 OCPs from slurry-spiked soil sample A with different moisture content. The average recoveries \pm standard deviations are 75 \pm 17%, 71 \pm 14%, and 70 \pm 14% for samples with 0.9%, 2.5%, and 5.0% moisture content, respectively. The recoveries appear close among these three samples, indicating that the modifier (0.1 ml of acetone) works well. This finding indicates that small variations of moisture content in the soils could be compensated by the added modifier and will not significantly influence the extraction efficiency. This is of practical importance for SFE applications because it is difficult to exactly control the moisture in soils. The most pronounced improvement in

Table 4
Influence of moisture content on OCPs percent recovery from soil sample A

Compound	Moisture (%)		
	0.9 (n=7)	2.5 (n=2)	5.0 (n=2)
α -BHC	78 \pm 7	71 \pm 3	64 \pm 6
γ -BHC	76 \pm 5	72 \pm 3	66 \pm 7
β -BHC	70 \pm 3	72 \pm 3	69 \pm 3
Heptachlor	72 \pm 5	63 \pm 3	62 \pm 1
α -BHC	92 \pm 9	88 \pm 4	92 \pm 1
Aldrin	67 \pm 6	62 \pm 3	59 \pm 4
Heptachlor epoxide	82 \pm 3	79 \pm 3	77 \pm 3
Endosulfan I	83 \pm 6	66 \pm 3	67 \pm 0
4,4'-DDE	95 \pm 4	83 \pm 1	86 \pm 1
Dieldrin	87 \pm 5	76 \pm 3	75 \pm 2
Endrin	83 \pm 11	80 \pm 3	82 \pm 9
4,4'-DDD	104 \pm 8	86 \pm 3	75 \pm 8
Endosulfan II	55 \pm 10	55 \pm 2	54 \pm 2
4,4'-DDT	71 \pm 7	65 \pm 3	71 \pm 8
Endrin aldehyde	46 \pm 6	86 \pm 4	90 \pm 11
Endosulfan sulfate	41 \pm 6	34 \pm 1	34 \pm 8

Spiked at 40 ppb level, mean \pm standard deviation.

recovery was observed for endrin aldehyde. The recovery increases from ~46% in sample containing 0.9% moisture to almost twice ~86% or ~90% in samples containing 2.5% or 5.0% moisture. This dramatic increase in recovery is ascribed to the formation of H-bonding between the carbonyl group in the endrin aldehyde and the water molecule, enhancing the partitioning of endrin aldehyde into the fluid. The adverse effect of restrictor plug (I.D. 30 μm) via ice formation for samples with high moisture content was avoided in this study by placing 1 g of anhydrous sodium sulfate on top of the soil in the extraction cell.

The soil matrix is composed of particles partially covered by an organic or moisture layer. The analytes must be desorbed from the soil surface first, followed by diffusion through an occluding layer of organic or moisture, then partition into the supercritical fluid before being extracted. Soils with different grain size possessing different surface area might therefore influence the extraction efficiency if the extraction solvent can not reach the total surface of the soil. The influence of grain size on SFE extraction efficiency was therefore investigated. Soil blanks from sample A were sieved through a No. 10 mesh, a No. 30 mesh, and a No. 60 mesh sieve to yield coarse (<2.00 mm), medium (<0.595 mm),

and fine (<0.250 mm) sands. Each sand was separately fortified at 40 ppb levels using slurry-spike method. Table 5 lists the percent recovery and standard deviation for the 16 OCPs from slurry-spiked soil sample A with different grain size. The average recoveries \pm standard deviations for the 16 OCPs are $73 \pm 22\%$ for coarse sand, $81 \pm 22\%$ for medium sand and $77 \pm 20\%$ for fine sand. The recoveries appear close among group I OCPs in these three samples, indicating that variations in grain size did not significantly influence the extraction efficiency. This might imply that group I OCPs distribute evenly on the soil surface. The cause for the unusually low aldrin and high endrin contents in medium sand sample is not clear yet but is more likely due to spiking error. For group II OCPs, the lowest recoveries are observed for coarse sand. The results indicate that variations in grain size have marked influence on the SFE extraction efficiencies for group II OCPs. The cause of stronger analyte-matrix interactions for group II OCPs in coarse sand warrants further investigations.

3.3. SFE of sulfur-containing soil samples

The combination of extraction and clean-up process in one step, i.e., selective extraction, could

Table 5
Influence of grain size on OCPs percent recovery from soil sample A

Compound	Grain size		
	Coarse ($n=3$)	Medium ($n=3$)	Fine ($n=3$)
α -BHC	83 \pm 6	80 \pm 1	86 \pm 7
γ -BHC	83 \pm 5	84 \pm 4	86 \pm 5
β -BHC	80 \pm 4	82 \pm 2	82 \pm 3
Heptachlor	76 \pm 6	74 \pm 2	70 \pm 5
δ -BHC	83 \pm 5	89 \pm 3	91 \pm 5
Aldrin	58 \pm 4	26 \pm 1	65 \pm 6
Heptachlor epoxide	89 \pm 5	90 \pm 2	89 \pm 3
Endosulfan I	87 \pm 4	93 \pm 1	79 \pm 6
4,4'-DDE	86 \pm 5	88 \pm 4	90 \pm 4
Dieldrin	88 \pm 5	90 \pm 1	90 \pm 5
Endrin	106 \pm 8	134 \pm 5	105 \pm 11
4,4'-DDD	82 \pm 6	88 \pm 1	91 \pm 8
Endosulfan II	25 \pm 4	61 \pm 18	46 \pm 10
4,4'-DDT	73 \pm 8	92 \pm 3	90 \pm 7
Endrin aldehyde	44 \pm 2	64 \pm 7	40 \pm 6
Endosulfan sulfate	31 \pm 2	62 \pm 14	40 \pm 6

Spiked at 40 ppb level, mean \pm standard deviation.

significantly enhance the performance of an analytical method via saving time and minimizing the loss of analytes. The ease and compatibility of adding solid-phase adsorbents to the SFE extraction cell for selective trapping of interfering materials has made SFE an ideal tool for analyzing solid matrices. The advantage of this direct on-line clean-up approach has been exploited in the analysis of PCBs in fish tissue [31,32], PCBs in sludge [33,34], carbamates in tissues [35], and OCPs in aquatic plants [8]. A feasibility study of this approach for selective extraction of OCPs from sulfur-containing soils was conducted. Cu powder (or AgNO_3 loaded silica) was evaluated for their S trapping efficiency. The dominant form of S in most soil and aquatic environments is organic S [18]. The complex nature of the organic S makes the preparation of sulfur-containing samples to simulate the real samples difficult. Therefore, a real sediment with a high level of S collected from a local DarPu dam was used to reduce the discrepancies between the SFE of spiked and real sulfur-containing samples during method development. The saturation of the ECD throughout the whole GC-ECD chromatogram (Fig. 1A) of the SFE extracts from the sediment sample indicates that it is appropriate for this study.

The use of Cu in the extraction cell to clean-up the S interferences in the soils appears not very effective. Strong S interferences as shown by the huge S background peak are still apparent (Fig. 1B), indicating that certain residual S exists in the extracts. The S background peak disappears after the SFE extracts were put to rest for seven days (Fig. 1C). This indicates that small amounts of Cu were co-extracted with the S and OCPs by the supercritical CO_2 fluid into the collection vessel. The selectivity of SFE for OCPs over S appears not significant. Our observation accords with those reported by Louie et al., [36] and Bøwadt [19]. In addition, the recoveries of most OCPs found from spiking studies are on the low side (~20%). The use of Cu in the extraction cell for direct on-line clean-up of S interference is therefore not recommended. Possible causes for these low recoveries include: not enough Cu used, the presence of S co-extracted with the OCPs, the change of catalytic effect of Cu in the supercritical fluid environment, and/or not enough static extraction time for the Cu to react with the S. Using AgNO_3

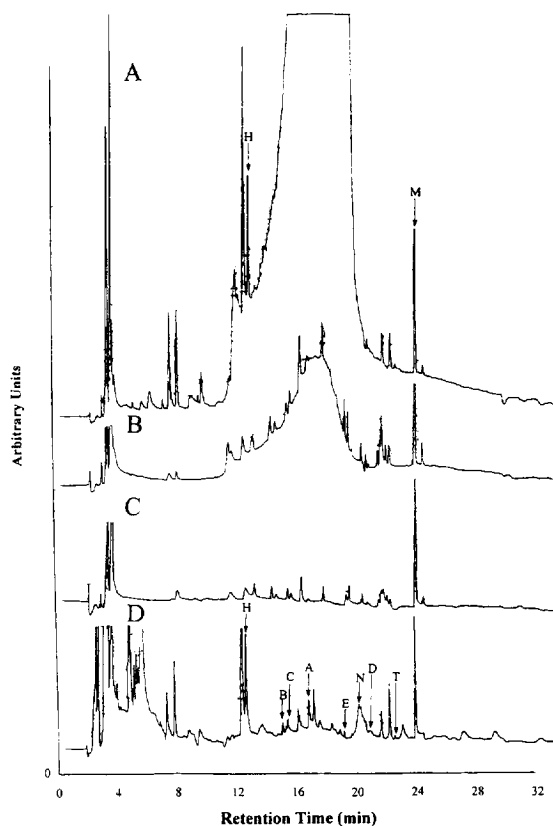


Fig. 1. GC-ECD chromatograms of SFE extractions of DarPu dam sediments: (A) No trapping material in the extraction cell; (B) Using Cu powder as trapping material in the extraction cell, (C) as for (A) but the SFE extracts were put to rest for 7 days before GC-ECD measurement; (D) Using as AgNO_3 loaded silica as trapping material in the extraction cell. Compounds: H: HCB; B: α -BHC, C: γ -BHC, A: aldrin, E: 4,4'-DDE, N: endrin, D: 4,4'-DDD, T: 4,4'-DDT, and M: mirex. See Section 2.3 for extraction conditions.

loaded silica as selective adsorbents, on the other hand, yields S-free extracts (Fig. 1D). The recoveries from spiking studies remain the same ($\geq 70\%$), indicating that this approach is more desirable. The unusually low recovery for heptachlor ($\leq 30\%$) is presumably due to the degradation into heptachlorepoxide caused by the AgNO_3 . In fact, the S odor was smelled during the extractions when the adsorbents were not used. The restrictors were plugged easily by the S. This situation was improved with the use of Cu. The S odor and the plug problems were eliminated with the use of AgNO_3 loaded silica.

To further check the feasibility of AgNO_3 loaded silica as selective adsorbents for direct on-line clean-up of S interferences in the soils, a SRM 1941a marine sediment was simultaneously analyzed. This SRM contains $0.9589 \pm 0.0058\%$ of S and is provided with certified concentrations for 23 PAHs, 21 PCBs, and 6 OCPs. The comparison between the SFE extraction without and with the use of AgNO_3 loaded silica adsorbents can be seen in Fig. 2. The complex nature of this matrix is clearly reflected in the complicated GC-ECD chromatogram. Similar saturation of the ECD throughout the GC-ECD chromatogram of the SFE extracts was observed (Fig. 2A). The S interferences could be easily eliminated by treatment with AgNO_3 loaded silica (Fig. 2B). From these two chromatograms, the effectiveness of AgNO_3 loaded silica for direct on-

line clean-up of S interferences is apparent. The measured values are in accordance with the certified values for three determined OCPs of 4,4'-DDE, dieldrin, and 4,4'-DDD (Table 6). The abnormally high result for 4,4'-DDT is ascribed to the interferences that cannot be resolved by the proposed method. The identity of it cannot be determined using GC-MS because of the small amounts of sample, 2 g, used in this study rather than the 100 g used by the NIST [37]. Nevertheless, the efficiency of AgNO_3 loaded silica for direct on-line clean-up of S interferences in real soil samples is evident.

4. Conclusions

This study reveals that spiking method significantly influences the SFE extraction efficiency of OCPs from soils. The decrease in recovery when extracting real samples is probably due to the spiking, i.e., spot-spiking, method used to prepare fortified samples fails to completely simulate the real-world samples. Analyte-matrix interactions have predominant effect on the SFE extraction efficiency of endosulfan II, endrin aldehyde and endosulfan sulfate. Soil properties of TOC and pH were found to significantly influence the extraction efficiency. Small variations of moisture content from 0.9% to 5.0% in soils do not effect the recovery much if appropriate modifier was used. The dramatic increase in recovery of endrin aldehyde with increasing amount of moisture content is ascribed to the formation of H-bonding between the carbonyl group in the endrin aldehyde and the water molecule. Difference in grain size has marked influence on the SFE extraction efficiency of endosulfan II, endrin aldehyde and endosulfan sulfate. The efficiency of adding AgNO_3 loaded silica to the extraction cell for simultaneous extraction and clean-up of sulfur-containing soils is demonstrated. The degradation of heptachlor into heptachlorepoxide by the AgNO_3 renders this method less desirable for determining heptachlor. Nevertheless, the procedures are simple and rapid and require only small amount of samples and solvents. The total amount of time needed from SFE extraction to GC-ECD analysis is less than 2 h. With the right choice of extraction conditions and



Fig. 2. GC-ECD chromatograms of SFE extractions of a NIST SRM 1941a, a marine sediment: (A) No trapping material in the extraction cell; (B) Using as AgNO_3 loaded silica as trapping material in the extraction cell. Compounds: H: HCB, E: 4,4'-DDE, L: dieldrin, D: 4,4'-DDD, T: 4,4'-DDT, and M: mirex. See Section 2.3 for extraction conditions.

Table 6
Method detection limit [20], certified value and measured value of SRM 1941a

Compound	MDL (ppb) ^a	Certified value (ppb)	Measured value (ppb)
α -BHC	1.0	NA ^b	ND ^c
γ -BHC	0.8	NA	ND
β -BHC	2.2	NA	ND
Heptachlor	1.6	NA	ND
δ -BHC	0.8	NA	ND
Aldrin	1.9	NA	ND
Heptachlor epoxide	1.3	NA	ND
Endosulfan I	2.9	NA	ND
4,4'-DDE	2.2	6.85±0.32	7.0
Dieldrin	2.8	1.26±0.55	ND (2.0) ^d
Endrin	2.4	NA	ND
4,4'-DDD	7.7	4.96±0.23	ND (5.5)
Endosulfan II	4.4	NA	ND
4,4'-DDT	8.4	1.25±0.12	14.1
Endrin aldehyde	6.1	NA	ND
Endosulfan sulfate	12.9	NA	ND

^a 3.14 times the standard deviation of 7 replicate analyses of blank soil fortified at 2.0 ppb for α -BHC, γ -BHC, heptachlor, δ -BHC, heptachlor epoxide; 4.0 ppb for β -BHC, aldrin, endosulfan I, 4,4'-DDE, dieldrin, endrin, endosulfan II; 12.0 ppb for 4,4'-DDD, 4,4'-DDT, endrin aldehyde, endosulfan sulfate.

^b Not available.

^c Not detectable.

^d (Measured value).

trapping materials, it may serve to analyze OCPs in sulfur-containing soils on a routine basis.

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