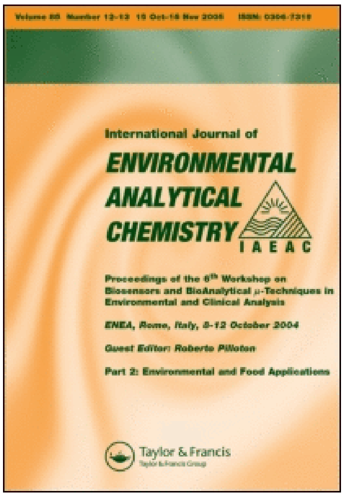

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Practicality of Supercritical Fluid Extraction/Ir for the Measurement of Petroleum Hydrocarbons in Aged Soil: A Comparative Study Between Two Commercial Extractors

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PRACTICALITY OF SUPERCRITICAL FLUID EXTRACTION/IR FOR THE MEASUREMENT OF PETROLEUM HYDROCARBONS IN AGED SOIL: A COMPARATIVE STUDY BETWEEN TWO COMMERCIAL EXTRACTORS

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Petroleum hydrocarbons (PHCs) were determined in two industrial soils, a refinery sandy soil and a wood preserving (clayey) soil, using supercritical CO_2 (SC-CO_2) and IR detection (2932 cm^{-1}). Two commercial extractors, a Dionex SEE –703 and an HP 7680A Module were used to extract the soils under various drying conditions ($MgSO_4/Na_2SO_4$, 3:0, 3:1, 3:3, 1:3, 0:6) and soil water content (< 2% - 60 % v/w). In the case of the clayey soil, both SFE extractors produced bell-shaped recovery curves, relating extracted amounts of PHCs with $MgSO_4/Na_2SO_4$ ratio, with optimal recoveries occurring when both drying agents ($MgSO_4/Na_2SO_4$, 3:1) were used to dry the soil. The lowest concentrations were obtained when only Na_2SO_4 was used to dry the soil. For the sandy soil the variation in the extracted amounts of PHCs did not exceed 10 % with the HP extractor, however, in the case of Dionex the extracted PHCs dropped by > 65 % when using Na_2SO_4 and by > 35 % when using $MgSO_4$ as drying agent. Similar bell-shaped recovery curves, relating soil water content with extracted amounts of PHCs, were also produced from the sandy soil using the Dionex extractor with optimal concentrations achieved at around 20 % H_2O that reduced by as much as 50 % when the soil was either dry (< 2%) or saturated (> 45 %) with water. Whereas in the case of HP extractor the variation in PHCs recovery did not exceed 10 % and extracted amounts of PHCs were similar to those obtained by standard Soxhlet techniques (EPA Methods 418.1/3450 and APHA Method # 8520).

Keywords: SFE, Soxhlet, petroleum hydrocarbons, soil, drying agents

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INTRODUCTION

Several literature reports[1,2] clearly address the lack of consistency among various methods used to analyze petroleum hydrocarbons (PHCs) in soil. Standard methods, such as the Environmental Protection Agency (EPA) Methods # 418.1/418.2 and #3540[3] are found inappropriate for the measurement of PHCs in contaminated soil[4] as well as in bioremediated soil and bioslurries.[5] These methods are derived from the American Public Health Association Method (APHA # 5520), originally developed to analyze oil and grease in water and sludges.[6] According to the APHA method, any extractable chemical with a -C-H bond that absorbs in the IR region 2700 to 3200 cm^{-1} is measured as oil and grease.

To reduce the amount of solvents and time required for analysis, researchers have recently focused their attention on solventless sample preparation methods such as supercritical fluid extraction (SFE).[7] In contrast to the century old Soxhlet method, extractability of analytes by SC-CO_2 depends on the type of SFE extractor and on the type of matrix used in the extraction cell. SFE often requires extensive optimization of several instrumental (extractor type, pressure, flow rate, restrictor)[8] and experimental parameters (soil type, compaction and modifiers) [9-11] to assure reproducibility and accuracy. Also estimates on the actual SFE concentrations of TPHs in soil are often established through extensive collection study or by comparing SFE recoveries with those obtained by other established techniques such as the Soxhlet.

Recently several laboratories were involved in an intensive interlaboratory study that involved several commercial SEE extractors including Dionex and HP extractors to determine the concentrations of PHCs in several soils using several instrumental and experimental parameters. The study led to the recent release of an SFE/IR method for the determination of PHCs in soil by the Environmental Protection Agency/USA (EPA Method # 3560).

Our main interest from this study is to have a reliable method capable of measuring hydrocarbon related products in soil with acceptable reproducibility and accuracy. Most environmental analytical laboratories dealing with pollution control and remediation assessment have the mandate to produce data on the actual concentration of pollutants in soil. Presently many laboratories are facing the challenge of sometimes reproducing their own data when it comes to the measurements of petroleum hydrocarbons in soil using available standard techniques.

To test this hypothesis, a comparative study involving two commercial SEE extractors (Dionex and HP) and SC-CO_2 is undertaken to determine PHCs in two contaminated soils, a refinery sandy soil and a clayey soil taken from a wood preserving facility. A quantitative detailed study is undertaken to investigate the effect of soil water content and type and amounts of drying agents, $MgSO_4$, and

Na_2SO_4, on the extracted amounts of PHCs. Results are then compared with those of EPA Method 3560 and the Soxhlet based EPA Method 418.1.

EXPERIMENTAL

Materials and Reagents

Hexadecane, iso-octane, benzene and p-terphenyl were from Aldrich (Milwaukee, WI). Glass distilled Freon–113 (1,1,2-trichloro–1,2,2-trifluoroethane) was obtained from Caledon, (Georgetown, ON). Silica gel (100–200 mesh), Fisher Davisil grade 644, was obtained from Fisher Scientific (Montreal, Canada) and was activated in an oven at 150 °C for 16 h before use. Whatman cellulose thimbles for the Soxhlet extractor were washed with pesticide grade hexane in a sonicator for 2.5 h prior to extraction. Anhydrous magnesium sulfate ($MgSO_4$) and anhydrous sodium sulfate (Na_2SO_4) were from Fisher Scientific (Montreal, Canada). Both drying agents were activated at 105 °C for 16 h. The granular size distribution of each drying agent was determined by screening through several wire screens of different meshes. More than 60 % of the $MgSO_4$ granular size distribution was < 0.2 mm, whereas close to 90 % of Na_2SO_4 granular size distribution was > 0.3 mm.

Soil sampling preparation

Two soils, a sandy soil from a refinery site (% of clay, sand, silt and soil organic matter, 15, 58, 27 and 8,. respectively) and a clayey soil from a wood preserving facility (% of clay, sand, silt and soil organic matter, 27, 40, 33 and 11, respectively), both with at least 10-15-years history of contamination were selected in the present study. The refinery soil was contaminated with bunker crude oil while that of the wood preserving soil was contaminated with creosote. Each of the soil samples was sieved (10 mesh), homogenized and then dried inside a fume hood at room temperature.

Soxhlet extraction

The refinery sandy soil (20 g) was mixed with the drying agent, $MgSO_4$ (20 g) and extracted as described in EPA Method # 3450 using Freon for a total of 80 cycles. Final extracts were dried over sodium sulfate and then concentrated to 10 ml using a water pump (18–20 mm Hg) before clean up on a silica gel column and analysis by IR. All measurements were based on triplicate extractions followed by IR analysis. Hexadecane and *p*-terphenyl were used as recovery standards using GC-MS analysis (standard recovery > 95 %).

SFE Extraction

Two commercial SFE extractors were used: Dionex extractor (SFE - 703, Dionex Ltd., Sunnyvale, CA) and an Hewlett Packard extractor (HP 7680A SFE Module, Orangeville, Ontario). Extraction was carried out using conditions similar to those used in EPA Method # 3560. In a typical experiment and in the case of Dionex, the soil (3 g) was mixed with $MgSO_4$ (1:1 w/w) and extracted with SC-CO_2 (340 atm and 350 - 400 mL gas /min) for 60 min. Oven temperature was maintained at 80 °C while that of the restrictor (250 mL/min) was kept at 150 °C. Analytes were collected in vials containing Freon–113 (10 mL). The extract was readjusted to 10 ml and cleaned up through a silica column (as described below). All analyses were based on triplicate extractions.

In the case of HP extractor, extractions were conducted using 2 g of the soil in 7 mL extraction thimbles using SC-CO_2. The frit was protected using clean Ottawa sand. The SC-CO_2 extract was allowed to pass through an adsorption column coated with ODS. The nozzle and trap temperatures were kept at 85 °C and 15 °C, respectively. The analytes were desorbed into a collection vial using Freon–113 at a flow rate of 1 mL/min (3 x 2 mL) at 40 °C (Nozzle and trap). The collected solution was diluted to 10 mL for subsequent IR analysis.

Clean-up of soil extracts on a silica column

Portions of each of the above described crude extracts from either Soxhlet (0.5 ml) or SFE (2 ml) were successively eluted on a silica gel column (i.d. 10.5 mm) using 8 g silica for the Soxhlet extract and 2 g for the SFE extract. The petroleum hydrocarbon fraction was obtained using 65 mL Freon in the case of Soxhlet and 15 mL in the case of SFE. Methylene chloride (20 %) in hexane was used to elute the aromatic fraction including PAHs. The clean-up process was monitored by using hexadecane as aliphatic marker (100 µl) and *p*-terphenyl (100 µl) as an aromatic marker.

Water effect on the recovery of PHCs.

The soil was dried in a fume hood at room temperature overnight (only semi-volatiles were studied). Once the soil was dried (ca 1 %) the soil water content was adjusted to the desired level by adding deionized water. The following soil/water formulations were prepared : dry soil (H_2O 1.6 %), natural soil (H_2O, 10, 20 % and 30 %), saturated soil (H_2O, 45 %) and finally soil in the form of slurry

(H_2O, 60 %). Each composition was extracted by SC-CO_2 and Soxhlet as described above.

Effect of the type and amount of drying agent on the measured concentrations of PHCs

In one study, the refinery sandy soil (2 g) was mixed with the drying agent $MgSO_4$ or Na_2SO_4 in several ratios (soil/drying agent; 1:1, 1:2 and 1:3 w/w). Each soil mixture was divided into two parts: one part was extracted by Soxhlet (with Freon) and the other part by SC-CO_2, keeping the water content for each soil sample at around 20 % w/w by the addition of the required amount of deionized water to the dry soil. In both Soxhlet and SFE, extractions were carried out as described above.

In a second study the soil was mixed with both drying agents in the following ratios: soil/$MgSO_4$/Na_2SO_4 ; 3/3/0, 3/3/1, 3/3/3, 3/1/3, and 3/0/6 w/w/w, respectively. Each mixture was then extracted with SFE as described above.

IR analysis and quantitative procedure

IR analysis of hydrocarbons was carried out on a Philips Pye Unicam PU 9512 IR Spectrometer using 1 cm Infrasil quartz cells and a wavelength range of 2700–3200 cm^{-1} ($\upsilon_{C\text{-}H}$, 2932 cm^{-1})

Hexadecane/iso-octane (1:1 w/w) was used as a quantitative standard, instead of the composition (benzene, hexadecane, iso-octane) because the soil extracts showed mainly aliphatic hydrocarbons with no sign of aromatics (GC-MS data not shown). In all cases, triplicate extractions were carried out to determine the precision of measurements.

RESULTS AND DISCUSSION

Effect of the drying agent on the recovery of PHCs from the refinery sandy soil

The refinery soil was first extracted with Soxhlet to establish the level of contamination of PHCs in the soil. The extraction was then performed by SFE with different ratios of drying agents (Table I). There are clearly some interesting differences between SC-CO_2 recoveries as obtained by Dionex extractor and those of the Soxhlet. Firstly, the SC-CO_2 concentration of PHCs was always lower, sometimes by as much as 50 %, than that of the Soxhlet method, and, secondly, the range of the RSD values among SFE measurements was wider. For example, the RSD values for Soxhlet recoveries ranged between 0.2 and 2.9 whereas those for SFE ranged between 0.6 and 20.6. The precision in the SFE measurements, although less than that of the Soxhlet, was well within the 20 % (RSD) reported for EPA Method # 3560.[12] The wider variation in the RSD values of SFE may be a consequence of the parallel type orientation of the extraction cell used (Dionex # 703). This horizontal orientation may lead to a channeling effect, i.e., the creation of free flow channels within the soil matrix that differ from sample to another. Both SFE and Soxhlet techniques gave lower PHCs concentrations when the soil drying agent $MgSO_4$ was replaced by Na_2SO_4, i.e., a reduction from 15,690 mg/Kg to 12,179 mg/Kg in the case of Soxhlet and a reduction from 13,150 mg/Kg to 6,627 mg/Kg in the case of SFE. The observed reduction in both Soxhlet and SFE recoveries (i.e., a reduction of 22 % and 50 %) respectively, were larger than the corresponding RSD range, i. e., 2.5 to 6.4 in the case of Soxhlet and 7.7 to 5.3 in the case of SFE, indicating that the observed changes in concentrations were real experimental differences.

TABLE I Effect of drying agent on the recovery of PHCs from a refinery sandy soil contaminated with bunker crude oil (% H_2O, 20 as w/w) using Soxhlet with Freon and SC-CO_2 with Dionex # 709. Concentrations of PHCs were measured using IR and a standard composition made of hexadecane/iso-octane (50:50, v/v)

Method of Extraction	*Soil/$MgSO_4$ w/w*	*PHCs mg/Kg*	*RSD %*	*Soil/Na_2SO_4 w/w*	*PHCs mg/Kg*	*RSD %*
Soxhlet	1:1	15,690	2.5	1:1	12,179	6.4
Soxhlet	1:2	16,004	0.2	1:2	14,155	2.4
Soxhlet	1:3	16,455	2.9	1:3	15,874	1.4
SFE	1:1	13,150	7.7	1:1	6,627	5.3
SFE	1:2	11,910	0.6	1:2	7,521	4.8
SFE	1:3	11,623	20.6	1:3	7,950	8.5

Furthermore, we found that increasing the concentration of $MgSO_4$ had very little effect on either Soxhlet or SFE recovery since observed variations in the concentration of PHCs were lower than the RSD values (Table I). Increasing the concentration of Na_2SO_4, however, led to an increase in both Soxhlet and SFE recoveries. For example, increasing the concentration by three fold (from a soil/Na_2SO_4 ratio of 1/1 to 1/3) led to a 30 % and 20 % increase in the PHCs concentration of Soxhlet and SFE techniques, respectively (Table I). There is still a lot of controversy surrounding the type of the drying agent that can best be used to enhance SC-CO_2 analyte recovery from soil. For example, $MgSO_4$,[13] diatomeaus earth,[14] and Na_2SO_4[15] have all been reported as potential drying agents in the SC-CO_2 extraction of contaminated soil. The results of the present study seems to favor $MgSO_4$, as soil additive for both SFE and Soxhlet extraction.

It is not certain if the observed variation in the SFE recovery of PHCs in the presence of these salts is attributed to a water removal efficiency, to the ability to introduce certain changes into the soil fabric (e.g., compaction, channeling, porosity and swelling, ... etc) or to a combination of both. We found that when using Na_2SO_4 water was observed in the SFE collection vial which was not the case with $MgSO_4$. Also $MgSO_4$ has more fine particles (> 60 % of $MgSO_4$ < 0.2 mm) than Na_2SO_4 (> 90 % of Na_2SO_4 > 0.3 mm). Presumably, Na_2SO_4, with a much lower surface area, acted as a poor drying agent and subsequently some of the remaining free water might have occupied the inner pores of the soil thus restricting CO_2 access to the analyte.

Alternatively, the granular Na_2SO_4 may create large free flow channels thus resulting in an inefficient contact between SC-CO_2 and the matrix and its analyte. Interestingly, such channels were only observed when $MgSO_4$ was used as drying agent; channels close to 2 mm in diameter were clearly seen at the top of the extraction cell that extended from one end of the cell to the other. These free flow channels would undoubtedly affect the contact between the analyte and subsequently analyte extractability in the case of Dionex with horizontal cell orientation. A Method to increase recovery despite of this impractical orientation of the extraction cell will be described later.

Dionex Extractor VS HP Module: effect of drying agent

Both SFE extractors, Dionex and HP, showed that extracted amounts of PHCs depended on the type of the drying agent and its mixing ratio with the soil. The sandy soil gave a bell shaped recovery curve, relating extracted amounts of PHCs with $MgSO_4/Na_2SO_4$ using the Dionex extractor (Figure 1) The same soil produced smaller variations in recovery which in most cases did not exceed the RSD values when using the HP extractor (Figure 1). On the other hand, the clayey soil showed bell-shaped recovery curves when using both Dionex and HP extractors (Figure 2).

An important observation in Figure 2 is that optimal extractions were obtained in both extractors when the two drying agents ($MgSO_4/Na_2SO_4$) were mixed together with the soil. Maximized PHCs concentrations, i.e., 905 mg/kg with Dionex and 1038 mg/kg with HP, occurred using the following soil composition ratio, soil/$MgSO_4/Na_2SO_4$; 3:2:1 w/w (Figure 2). These optimized values for PHCs concentrations were reduced when either drying agent was used on its own as soil additives. The biggest reduction occurred when $MgSO_4$ was completely

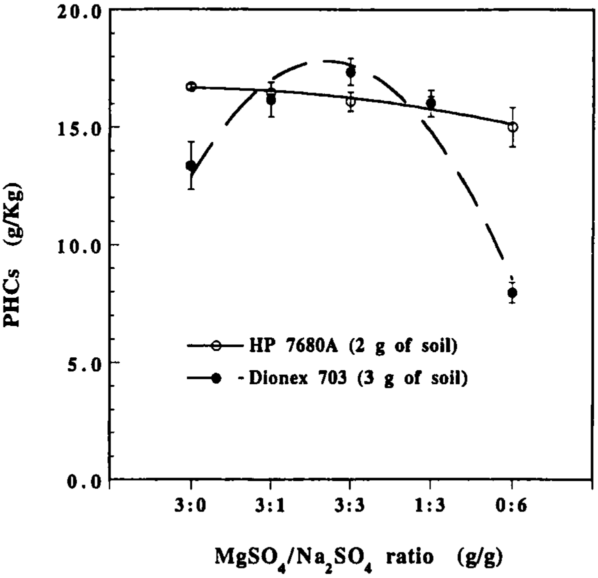

FIGURE 1 Effect of the drying agent $MgSO_4$ and Na_2SO_4, on the SC-CO_2 extracted amounts of petroleum hydrocarbons (PHCs) from a refinery sandy soil contaminated with bunker crude oil using HP and Dionex extractors

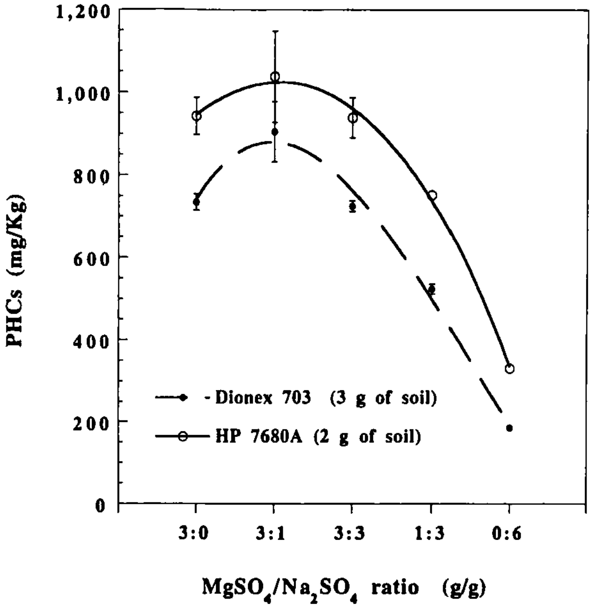

FIGURE 2 Effect of the drying agent $MgSO_4$ and Na_2SO_4 on the SC-CO_2 extracted amounts of petroleum hydrocarbons (PHCs) from a wood preserving clayey soil contaminated with creosote using HP and Dionex extractors

replaced by Na_2SO_4. For example, in the case of the sandy soil a reduction of 63 % and 67 % were observed using both HP and Dionex, respectively.

These results indicate that $MgSO_4$ and Na_2SO_4 dictate SFE extractability of PHCs from the soil. Besides their role as drying agents these additives may also act to introduce certain changes into the soil fabric causing fluctuations in measurements. As was previously mentioned, in the case of Dionex we found that after completing the extraction cycle a free flow channel (up to 2 mm in diameter) was located inside the cell containing the soil/$MgSO_4$ composition. The formation of these free flow channels allow CO_2 to pass through the matrix without encountering the analyte thus lowering extraction efficiency. Such phenomena was not observed in the case of the HP extractor whose extraction cell is vertically oriented, perhaps explaining why HP extractor showed higher PHCs recoveries than those of Dionex (Figures 1 and 2).

Also Na_2SO_4 is coarsed and granular (1 % < 0.2 mm) whereas $MgSO_4$ is a fine powder (60 % < 0.2 mm). In general, fine grained-matrix can be compacted to higher densities than course grained one. Therefore, blending the soil with the granular Na_2SO_4 is expected to give a torturous matrix with free flowing channels thus reducing extractability. Finally, Na_2SO_4 is a poor drying agent compared to $MgSO_4$ and this may become a problem in the case of the clayey soil (high affinity to water), where remaining water restrict CO_2 access to the inner pores of the soil thus shielding the analyte from extraction. In fact water was observed inside the collection vials of the SC-CO_2 extracts coming from the soil/sodium sulfate mixtures.

Dionex Extractor VS HP Module: water effect on recovery

The refinery sandy soil and the wood preserving clayey soil were each mixed with $MgSO_4$ (soil/$MgSO_4$, 1/1 w/w) and the resulting mixtures were subdivided into 2–3 g batches. The water content of each batch was adjusted by adding deionized water (H_2O 1.6 to 60 % v/w) before extraction with SC-CO_2 using both HP and Dionex extractors. When plotting the extracted concentration of PHCs against soil water content each extractor produced a distinctive curve for each type of soil (Figures 3 and 4).

Once again the Dionex extractor produced bell shaped recovery curves for both the sandy soil and the clayey soil with optimal concentration occurring when soil water content was kept around 20 to 30 %. Whereas in the case of HP extractor the variation in the extracted amounts of PHCs did not vary much for both types of soil and in most cases these changes did not exceed RSD values (Figures 3 and 4). Furthermore, concentration values obtained with the HP extractor correlated with those obtained by Soxhlet (Figure 5). Also, we observed that extracted

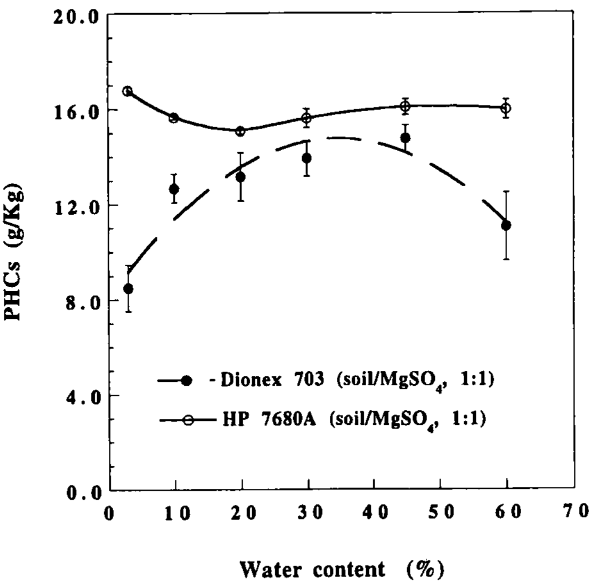

FIGURE 3 Effect of water on the SC-CO$_2$ extracted amounts of petroleum hydrocarbons (PHCs) from a refinery sandy soil contaminated with bunker crude oil using HP and Dionex extractors

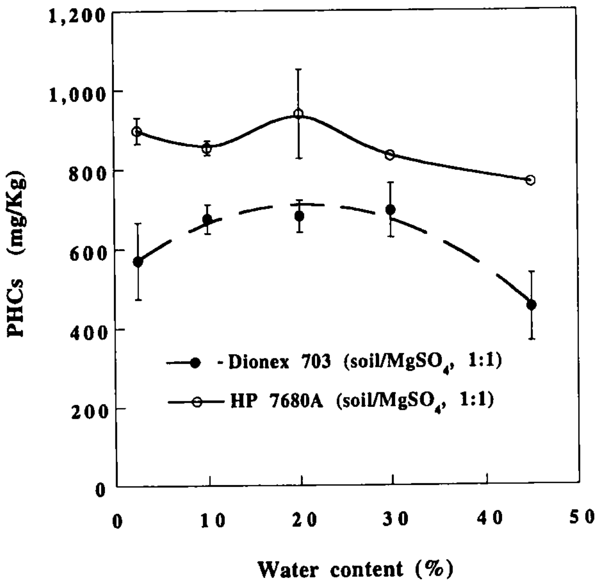

FIGURE 4 Effect of water on the SC-CO$_2$ extracted amounts of petroleum hydrocarbons (PHCs) from a wood preserving clayey soil contaminated with creosote using HP and Dionex extractors

amounts of PHCs by the HP extractor were always higher than those obtained by Dionex (Figures 3 and 4). The difference in performance between the two extractors was more drastic when the soil was either dry (% water 1.6) or saturated (% water > 50), i.e., the amounts extracted by HP were higher than those obtained by Dionex by 57 % and 86 % for the clayey soil and by 35 % and 56 % for the sandy soil.

There have been several studies on the effect of various experimental and instrumental parameters on the extraction of analytes from soil by SFE.[16-19] This is the first time that such a detailed quantitative study using two commercial extractors (used in EPA Method # 3560) and two real contaminated soils is undertaken. Snyder et al.[8] has reported that SC-CO_2 recovery of polar pesticides is maximized (> 80 %) when soil water content is kept in the range of 5 % to 10 % but drops to less than 5 % when water content reaches 25 %. EPA (Method # 3560) has also made the recommendation that a soil water content of 20 % would lead to optimal SC-CO_2 extraction of PHCs from soil without specifying the effect that the extractor or soil type may have on recovery. Apart from the fact the soil is subject to compactive pressure (340 atm) from CO_2, the exact mechanical status of the soil in the SFE cell is not known. However, when the soil is very dry its particles are expected to be stiff and very difficult to compact. Under severe drying conditions, the soil is characterized by having wide free flow channels resulting in a less dense and poorly extracted soil. Therefor, the

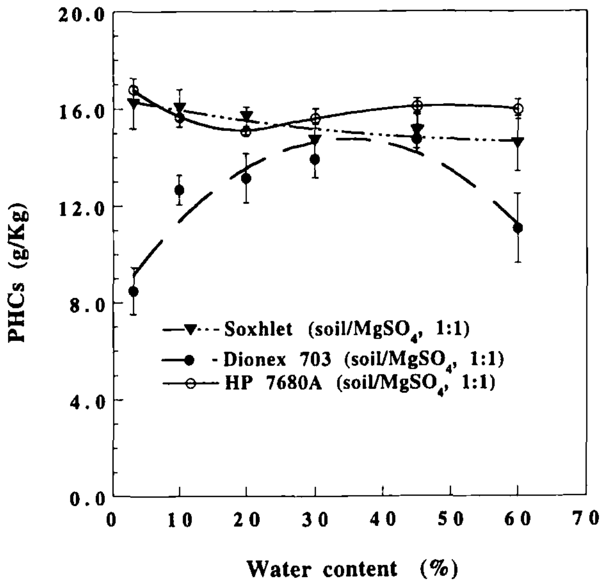

FIGURE 5 Extracted amounts of PHCs from the refinery soil using SFE (SC-CO_2) and Soxhlet (Freon): a comparative study

$SC\text{-}CO_2$ fluid would permeate through these channels without encountering the analyte. Also it has been suggested that elasticity[19] and compaction[20-25] of soil particles would be affected by changing soil water content. It has been widely known that soil compaction, which is influenced by soil water content and pressure, affects soil permeability which in turn may affect analyte extractability.[21]

On the other extreme, when the soil is very wet ($> 40\ \%\ H_2O$) it is difficult for the soil to undergo compaction because most of the air in the soil void is now replaced by water thus restricting $SC\text{-}CO_2$ from reaching the analyte entrapped in the inner regions of the soil. It has been suggested that soil swelling, caused by the presence of water, exposes small internal cavities giving $SC\text{-}CO_2$ a better access to the adsorbed analyte.[8]

In conclusion, the present study shows that $SC\text{-}CO_2$ extraction of PHCs from aged soil is not a straight forward laboratory practice for agencies involved in environmental monitoring and remediation assessment. Variations as high as 80 % in the recovery of PHCs from aged soils are observed by simply changing the type and amount of the drying agent. Extracted amounts of PHCs also depend on the commercial source of the SF extractor. In contrast, the century old laborious Soxhlet seems to produce more realistic data than the SFE on the actual concentration of PHCs in aged soil. At the least an exhaustive optimization of all experimental and instrumental parameters associated with SFE must be thoroughly searched for each soil tended for analysis.

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