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# Comparison of sorbent and solvent trapping after supercritical fluid extraction of volatile petroleum hydrocarbons from soil

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## Abstract

Supercritical fluid extraction (SFE) with sorbent and solvent traps was used for extracting total petroleum hydrocarbons (TPH) from real-world soil samples contaminated with gasoline- or diesel-range hydrocarbons. Quantitative extractions using two SFE systems were performed at 80°C and 340 atm with a flow-rate of 1.5 ml/min. Both sorbent and solvent trapping could effectively ( $\geq 90\%$ ) collect BTEX (benzene, toluene, ethylbenzene, and xylenes). Sorbent trapping yielded quantitative collections ( $\geq 88\%$ ) of *n*-alkanes as volatile as *n*-hexane, while the solvent trapping effectively collected *n*-alkanes as volatile as *n*-heptane (pressurized trapping system) or *n*-octane (normal trapping system). The quantitation of BTEX, TPH, and individual species from contaminated soils obtained by the two SFE systems agreed well. Because of the greater losses of BTEX and volatile *n*-alkanes, Soxhlet extraction yielded significantly lower BTEX, TPH, and individual species values than SFE.

## 1. Introduction

Supercritical fluid extraction (SFE) has been rapidly developed because of the interest in reducing the use of organic solvents [1–3]. Off-line SFE with infrared detection for determining total petroleum hydrocarbon (TPH) content in contaminated soils has shown good agreement with conventional Soxhlet extraction using Freon-113 for gasoline- and diesel-range hydrocarbons (e.g., up to ca. C<sub>20</sub> alkanes) [4–9] and heavy hydrocarbons (up to C<sub>50</sub> alkanes) [10], and reduces the amount of liquid solvent required from ca. 150 ml to ca. 10 ml per sample extraction [4–10]. Although solventless trapping

has been used in on-line SFE–GC for the determination of volatile petroleum hydrocarbons [11], most of the off-line SFE applications for TPH have been done by solvent trapping which may not efficiently collect the very volatile hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX) components and low-molecular-mass *n*-alkanes. It should be pointed out that the collection efficiency of solvent trapping also depends on the configuration of the solvent trap. For example, systems that depressurize the CO<sub>2</sub> effluent into a gas-phase in a transfer tube before contacting the solvent have been reported to yield poor collection efficiencies for polycyclic aromatic hydrocarbons (PAHs) [12] and polychlorinated biphenyls (PCBs) [13]. In contrast, when the CO<sub>2</sub> is

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depressurized directly in the collection solvent. PAHs as volatile as naphthalene, all PCB congeners, and many more volatile organics can be efficiently collected [14,15]. SFE extracts can also be collected on sorbents such as silica gel or bonded-phase packings and this technique has been used to collect PCBs [16,17], PAHs [16,18], and pesticides [19] from different matrices after SFE. Because sorbent trapping may avoid the loss of volatile analytes which can occur in solvent trapping, sorbent trapping may more efficiently collect volatile organics. The purpose of the present study is to compare the trapping efficiencies of SFE systems using sorbent traps (Hewlett-Packard) and solvent traps (ISCO). The SFE efficiencies are evaluated by comparing BTEX, TPH, and individual species concentrations with Soxhlet extraction for real-world soils containing gasoline- to diesel-range organics.

## 2. Experimental

### 2.1. Samples

A standard hydrocarbon mixture or gasoline spiked XAD-2 sorbent resin (Supelco, Bellefonte, PA, USA) was used for determining the SFE trapping efficiencies. However, several "real-world" soil samples were used in this work since previous studies [20] have shown that spiked organics are often easier to extract than soils that have been contaminated under environmental conditions. Two of those soil samples were contaminated by volatile petroleum hydrocarbons such as BTEX and *n*-alkanes up to  $C_{12}$  and the other samples contained *n*-alkanes with a range from  $C_{10}$  to  $C_{20}$ . All soils were extracted exactly as received (e.g. no air drying or other preparation) and had water contents ranging from 2 to 15% (w/w).

### 2.2. SFE with sorbent traps

A Hewlett-Packard 7680T supercritical fluid extractor was used for the sorbent trapping SFE extractions. For spiked hydrocarbon studies a stainless-steel HP extraction cell (7 ml, 90 mm

length  $\times$  10 mm I.D.) was filled first with ca. 6 g precleaned "Ottawa" sand (Fisher Scientific, Fair Lawn, NJ, USA) then with 1 g XAD-2 on the top of the sand. The XAD-2 resin was spiked with 2  $\mu$ l of a mixture of pure BTEX and  $C_5$  to  $C_{20}$  *n*-alkanes, or with 2  $\mu$ l of gasoline. The cell was sealed immediately after the spiking. The XAD-2 end of the cell was placed at the outlet (upper for the HP system) of the  $CO_2$  flow. For real-world samples, the cell was filled completely with soil (ca. 10 g). The samples were extracted at 340 atm (1 atm =  $10^5$  Pa) and 80°C (chosen because the reference data can be found at these identical conditions [4,8]) with SFC-grade  $CO_2$  (Scott Specialty Gases, Plumsteadville, PA, USA) at a flow-rate of 1.5 ml/min for 30 min.  $CO_2$  without helium head pressure was used with the HP extractor as specified by the manufacturer. Collection traps were filled with ca. 1 ml of trapping material (Porapak Q, 60/80 mesh). During the extractions the collection trap was kept at a temperature of either  $-5^\circ C$ ,  $5^\circ C$ , or  $-5^\circ C$  (15 min)/ $5^\circ C$  (15 min), respectively, so that the trapping temperature could be optimized. The restrictor nozzle was held at  $55^\circ C$  for all extractions. After a 30-min extraction (for the trapping temperature at  $-5$ , or  $5^\circ C$ ) the sorbent trap was rinsed three times with 1.6 ml methylene chloride. The three rinse fractions were combined and the internal standard (1,3,5-triisopropylbenzene) was added. For the two-step extraction [trapping temperature at  $-5^\circ C$  (15 min)/ $5^\circ C$  (15 min)] the traps were rinsed two times with 1.2 ml methylene chloride after each 15-min extraction step. All of the four rinse fractions were combined and internal standard was added.

### 2.3. SFE with solvent traps

The normal (atmospheric pressure) solvent trapping SFE extractions were performed using an ISCO SFX-210 extraction unit (ISCO, Lincoln, NE, USA) supplied with SFC-grade  $CO_2$  with helium head pressure (Scott Specialty Gases) by an ISCO Model 260D pump. The same weight of XAD-2 (1 g) and soil (ca. 10 g) was used as for the HP cells. Since the ISCO

cells were 10 ml (vs. 7 ml for the HP cells) the additional void volume was filled with pre-cleaned "Ottawa" sand. Extractions were performed using the same pressure (340 atm) and temperature (80°C) as used for the HP system. The flow-rate of CO<sub>2</sub> was controlled at ca. 1.5 ml/min with a coaxially heated restrictor set to 80°C. Collection of the extracts was performed by inserting the outlet of the restrictor into either 15 ml of methylene chloride contained in a 26-ml (150 mm high × 15 mm I.D.) glass vial supplied with the ISCO extractor or 8 ml of methylene chloride in a 22-ml (85 mm high × 18 mm I.D.) Supelco glass vial. During SFE, the collection solvent volume was reduced by the heating of the restrictor and the purging of CO<sub>2</sub>, therefore, the volume was maintained at ca. 6 ml by small additions of methylene chloride. Internal standard was added to the extracts after the extraction but prior to GC-flame ionization detection (FID) analysis as described above.

Additional collection studies from spiked XAD-2 samples were performed using the pressurized solvent trapping system available with the ISCO SFX-3560 automated extractor and the 26-ml collection vials described above. All extraction conditions were identical to those used with the SFX-210, except that the collection solvent vial was pressurized to ca. 2 atm (above ambient), and cooled to -20°C. Since these steps greatly reduced solvent loss, only 7 ml solvent was used for each collection.

#### 2.4. Soxhlet extractions

Soxhlet extractions of 10-g soil samples were performed for 4 h with 150 ml Freon-113 (trichlorotrifluoroethane) similar to APHA method 5520 D [21]. After extraction, the samples were concentrated by evaporating the solvent to ca. 6 ml which is the same final volume of the SFE extracts using either sorbent or solvent traps.

#### 2.5. Extract analysis

All extracts were analyzed by a Hewlett-Packard 5890 II gas chromatograph equipped with a flame ionization detector using a 30-m DB-5

column with 0.32 mm I.D. and 1 μm film thickness (J&W Scientific, Folsom, CA, USA). Autosampler injections were performed either in the splitless mode for 0.3 min or in the split mode with a ratio of 1:30 depending on the analyte concentration. The oven temperature remained at 30°C for 3 min and was then ramped to 320°C at a rate of 6°C/min. The total TPH quantitations were based on the total peak area except the solvent peak (compared to the internal standard), while the individual BTEX and *n*-alkanes were evaluated using standard calibration curves generated from appropriate dilutions of a mixture containing neat BTEX and C<sub>5</sub> to C<sub>20</sub> *n*-alkanes (also compared to the internal standard), where the dilutions were prepared in either Freon-113 or methylene chloride for Soxhlet and SFE extractions, respectively.

### 3. Results and discussion

#### 3.1. Trapping efficiencies of SFE systems

Previous work has shown that SFE with pure CO<sub>2</sub> can effectively extract light hydrocarbons from contaminated soils [8–11]. However, only solvent traps were used to collect the TPH in off-line SFE applications [4,8–10]. Because of the loss of the more volatile hydrocarbons which can occur during SFE, an effort has been made in this study to compare the trapping efficiencies of optimized sorbent and solvent traps with the ultimate goal of efficiently collecting organics as volatile as benzene so that both BTEX and TPH can be determined with a single extraction.

In order to optimize the sorbent trapping, extractions were performed at three trapping conditions, either 30 min at -5°C, 30 min at 5°C, or 15 min at -5°C/15 min at 5°C (two-step extraction), respectively. As shown in Table 1, all BTEX and *n*-alkanes as volatile as *n*-hexane were quantitatively collected (≥ 87%) under all three trapping conditions. Because the trapping at -5°C required more cooling CO<sub>2</sub> and could cause system plugging by frozen water from the soil samples (see Table 3) and the two-step trapping took longer time (ca. 1 h) to complete

Table 1  
SFE trapping efficiencies of hydrocarbons using sorbent and solvent traps

Analyte	Percent recovery (%R.S.D. <sup>a</sup> )					
	Sorbent trap (HP)			Solvent trap (ISCO)		
	Trapping temperature			Initial solvent volume (ml)		
	– 5°C	5°C	– 5°C (15 min)/ 5°C (15 min)	Normal trapping		Pressurized trapping
			8	15	7	
C <sub>6</sub>	88 (4)	90 (4)	87 (9)	ND <sup>b</sup>	18 (13)	59 (14)
Benzene	96 (3)	93 (4)	98 (9)	60 (10)	90 (6)	102 (9)
C <sub>7</sub>	100 (4)	100 (3)	98 (9)	34 (8)	69 (10)	92 (9)
Toluene	101 (3)	101 (3)	99 (7)	89 (6)	103 (5)	108 (6)
C <sub>8</sub>	102 (4)	101 (3)	99 (8)	75 (6)	95 (6)	102 (8)
Ethylbenzene	102 (4)	101 (3)	100 (7)	97 (4)	104 (6)	107 (5)
<i>m</i> -, <i>p</i> -Xylene <sup>c</sup>	102 (4)	101 (3)	100 (7)	98 (4)	104 (6)	107 (5)
<i>o</i> -Xylene	102 (4)	101 (3)	100 (7)	98 (4)	104 (7)	106 (5)
C <sub>9</sub>	102 (5)	100 (3)	100 (7)	92 (6)	102 (7)	104 (7)
C <sub>10</sub>	102 (5)	99 (3)	100 (7)	96 (9)	102 (7)	104 (6)
C <sub>11</sub>	102 (4)	99 (3)	100 (7)	96 (12)	102 (7)	103 (5)
C <sub>12</sub>	102 (4)	99 (3)	100 (7)	96 (15)	102 (7)	102 (4)
C <sub>13</sub>	102 (4)	99 (3)	100 (7)	95 (16)	101 (7)	102 (3)
C <sub>14</sub>	101 (4)	99 (3)	101 (7)	94 (16)	101 (7)	101 (1)
C <sub>15</sub>	100 (3)	99 (3)	100 (7)	93 (16)	100 (7)	100 (1)
C <sub>16</sub>	99 (3)	99 (3)	100 (7)	91 (16)	100 (7)	101 (1)
C <sub>17</sub>	99 (2)	99 (3)	100 (6)	91 (16)	101 (8)	101 (2)
C <sub>18</sub>	98 (1)	99 (3)	99 (6)	92 (17)	101 (8)	104 (4)
C <sub>19</sub>	98 (1)	99 (3)	100 (6)	93 (17)	103 (8)	109 (5)
C <sub>20</sub>	98 (1)	99 (3)	100 (6)	95 (17)	104 (9)	107 (7)

<sup>a</sup> %R.S.D. based on quadruplicate extractions.

<sup>b</sup> Not detected.

<sup>c</sup> The sum of *m*- and *p*-xylene is reported because these two species were not resolved with the chromatographic conditions used.

the extraction, trapping at 5°C was chosen for all subsequent extractions.

The normal (atmospheric pressure) solvent trapping was performed using either a 22-ml Supelco vial (85 mm high × 18 mm I.D.) or a 26-ml ISCO vial (150 mm high × 15 mm I.D.). The results shown in Table 1 demonstrate that the longer ISCO vials with 15 ml methylene chloride could quantitatively (≥ 90%) collect the hydrocarbons as volatile as benzene, toluene, and *n*-octane, while the shorter Supelco vials with 8 ml methylene chloride only effectively trap the hydrocarbons as volatile as ethylbenzene and *n*-nonane. Therefore, the larger vials were used for all of the later solvent trapping SFE

extractions. In order to further improve the trapping efficiencies of the very volatile *n*-alkanes, additional extractions have been done using a pressurized trapping system (ca. 2 atm) with solvent cooling to –20°C which has recently become available from ISCO. With this system, the collection solvent loss was only ca. 1 ml (compared to ca. 10 ml with the open solvent vials) and the trapping efficiencies of *n*-hexane and *n*-heptane were improved (Tables 1 and 2). However, the pressurized solvent trapping could still not effectively collect *n*-hexane, while the sorbent trapping at 5°C could.

The gasoline spiked XAD-2 samples were extracted under optimized sorbent trapping

Table 2  
SFE trapping efficiencies of gasoline components using sorbent and solvent traps

Analyte	Percent recovery (%R.S.D. <sup>a</sup> )		
	Sorbent trap (HP)	Solvent trap (ISCO)	
		Normal trapping	Pressurized trapping
C <sub>6</sub>	86 (13)	19 (22)	51 (8)
Benzene	100 (14)	92 (5)	92 (10)
C <sub>7</sub>	100 (9)	63 (10)	90 (14)
Toluene	96 (5)	91 (7)	102 (7)
C <sub>8</sub>	98 (9)	87 (4)	103 (9)
Ethylbenzene	98 (6)	95 (5)	102 (6)
<i>m</i> -, <i>p</i> -Xylene <sup>b</sup>	97 (6)	95 (4)	102 (6)
<i>o</i> -Xylene	98 (5)	95 (4)	102 (5)
C <sub>9</sub>	98 (10)	92 (5)	106 (9)
C <sub>10</sub>	88 (12)	92 (6)	103 (5)
C <sub>11</sub>	88 (10)	88 (16)	105 (4)
C <sub>12</sub>	92 (8)	91 (6)	97 (1)
C <sub>13</sub>	97 (4)	92 (6)	105 (2)
C <sub>14</sub>	104 (3)	95 (4)	102 (8)

<sup>a</sup> %R.S.D. based on quadruplicate extractions.

<sup>b</sup> The sum of *m*- and *p*-xylene is reported because these two species were not resolved with the chromatographic conditions used.

(5°C), normal solvent trapping (26-ml ISCO vials), and pressurized solvent trapping conditions. As shown in Table 2, both sorbent and solvent trapping yielded reasonable collection efficiencies ( $\geq 86\%$ , except *n*-hexane and *n*-heptane by normal solvent trapping and *n*-hexane by

pressurized solvent trapping) of the majority of volatile species and quantitative collection of all of the less volatile species.

As discussed above, the trapping must be carefully performed to efficiently collect the analytes for both sorbent and solvent trapping

Table 3  
TPH concentrations obtained by SFE with sorbent and solvent trapping vs. Soxhlet extraction from soil samples

Sample No.	Range of hydrocarbons	Water content [% (w/w)]	TPH concentration ( $\mu\text{g/g}$ ) (%R.S.D. <sup>a</sup> )		
			SFE		Soxhlet
			Sorbent (HP)	Solvent <sup>b</sup> (ISCO)	
1	C <sub>8</sub> -C <sub>14</sub> (Fig.1)	8	410 (18)	310 (13)	250 (12)
2	C <sub>6</sub> -C <sub>12</sub> (Fig.1)	10	1880 (8)	1470 (4)	660 (6)
3	C <sub>10</sub> -C <sub>22</sub> (Fig.2)	13	150 (3)	110 (8)	130 (8)
4	C <sub>10</sub> -C <sub>22</sub> (Fig.2)	2	5340 (9)	5300 (6)	3880 (9)
5	C <sub>13</sub> -C <sub>20</sub> (Fig.3)	13	7 (19)	7 (22)	6 (19)
6	C <sub>11</sub> -C <sub>16</sub> (Fig.3)	5	1500 (2)	1320 (11)	1000 (11)
7	C <sub>6</sub> -C <sub>14</sub> (Fig.3)	15	870 (11)	730 (2)	610 (4)

<sup>a</sup> %R.S.D. based on triplicate extractions.

<sup>b</sup> Normal (atmospheric pressure) solvent trapping.

Table 4  
Concentrations of individual hydrocarbons from soil contaminated with gasoline-range organics

Analyte	Concentration ( $\mu\text{g/g}$ ) (%R.S.D. <sup>a</sup> )		
	SFE/sorbent (HP)	SFE/solvent <sup>b</sup> (ISCO)	Soxhlet
<i>Sample 1</i>			
Benzene	0.15 (22)	0.12 (36)	0.07 (24)
Toluene	3.8 (23)	2.8 (26)	1.30 (18)
Ethylbenzene	0.77 (23)	0.40 (24)	0.24 (32)
<i>m</i> -, <i>p</i> -Xylene <sup>c</sup>	3.9 (15)	2.2 (28)	2.0 (16)
<i>o</i> -Xylene	2.9 (18)	1.6 (30)	1.4 (30)
BTEX	12	7.1	5.0
C <sub>6</sub> -C <sub>12</sub>	22	12	15
C <sub>13</sub> -C <sub>20</sub>	6.2	4.1	6.1
<i>Sample 2</i>			
Benzene	5.1 (25)	2.6 (8)	0.26 (45)
Toluene	110 (13)	78 (6)	3.5 (9)
Ethylbenzene	32 (7)	24 (3)	4.7 (7)
<i>m</i> -, <i>p</i> -Xylene	169 (4)	125 (5)	38 (8)
<i>o</i> -Xylene	77 (5)	57 (5)	20 (7)
BTEX	390	290	67
C <sub>6</sub> -C <sub>12</sub>	140	85	16
C <sub>13</sub> -C <sub>20</sub>	10	7.6	4.4

<sup>a</sup> %R.S.D. based on triplicate extractions.

<sup>b</sup> Normal (atmospheric pressure) solvent trapping.

<sup>c</sup> The sum of *m*- and *p*-xylene is reported because these two species were not resolved with the chromatographic conditions used.

Table 5  
Concentrations of individual hydrocarbons from soil contaminated with diesel-range organics

Analyte	Concentration ( $\mu\text{g/g}$ ) (%R.S.D. <sup>a</sup> )		
	SFE/sorbent (HP)	SFE/solvent <sup>b</sup> (ISCO)	Soxhlet
<i>Sample 3</i>			
Benzene	0.068 (45)	0.043 (53)	ND <sup>c</sup>
Toluene	0.10 (36)	0.062 (38)	ND
Ethylbenzene	0.047 (50)	0.036 (53)	ND
<i>m</i> -, <i>p</i> -Xylene <sup>d</sup>	0.13 (37)	0.081 (33)	ND
<i>o</i> -Xylene	0.11 (10)	0.078 (39)	ND
BTEX	0.46	0.30	ND
C <sub>6</sub> -C <sub>12</sub>	4.8	3.7	3.3
C <sub>13</sub> -C <sub>20</sub>	20	16	22
<i>Sample 4</i>			
BTEX	ND	ND	ND
C <sub>6</sub> -C <sub>12</sub>	250	240	200
C <sub>13</sub> -C <sub>20</sub>	1700	1700	1200

<sup>a</sup> %R.S.D. based on triplicate extractions.

<sup>b</sup> Normal (atmospheric pressure) solvent trapping.

<sup>c</sup> Not detected.

<sup>d</sup> The sum of *m*- and *p*-xylene is reported because these two species were not resolved with the chromatographic conditions used.

SFE. For sorbent trapping the trapping materials, trapping temperature, and the identity, volume, and temperature of rinsing solvent have to be optimized for target analytes. For solvent trapping systems the identity and volume of the collection solvent, the height of the collection vials, the head pressure on the top of the trapping solvent, and the solvent temperature could play a significant role in solvent trapping

efficiencies. In addition (as described above in the Introduction), the choice of solvent collection system, (i.e., whether the CO<sub>2</sub> expands directly in the solvent, or the CO<sub>2</sub> expands before the collection solvent) can greatly affect collection efficiencies. However, the results shown in Tables 1 and 2 clearly demonstrate that very volatile species can be collected with depressurization directly in a suitable solvent.

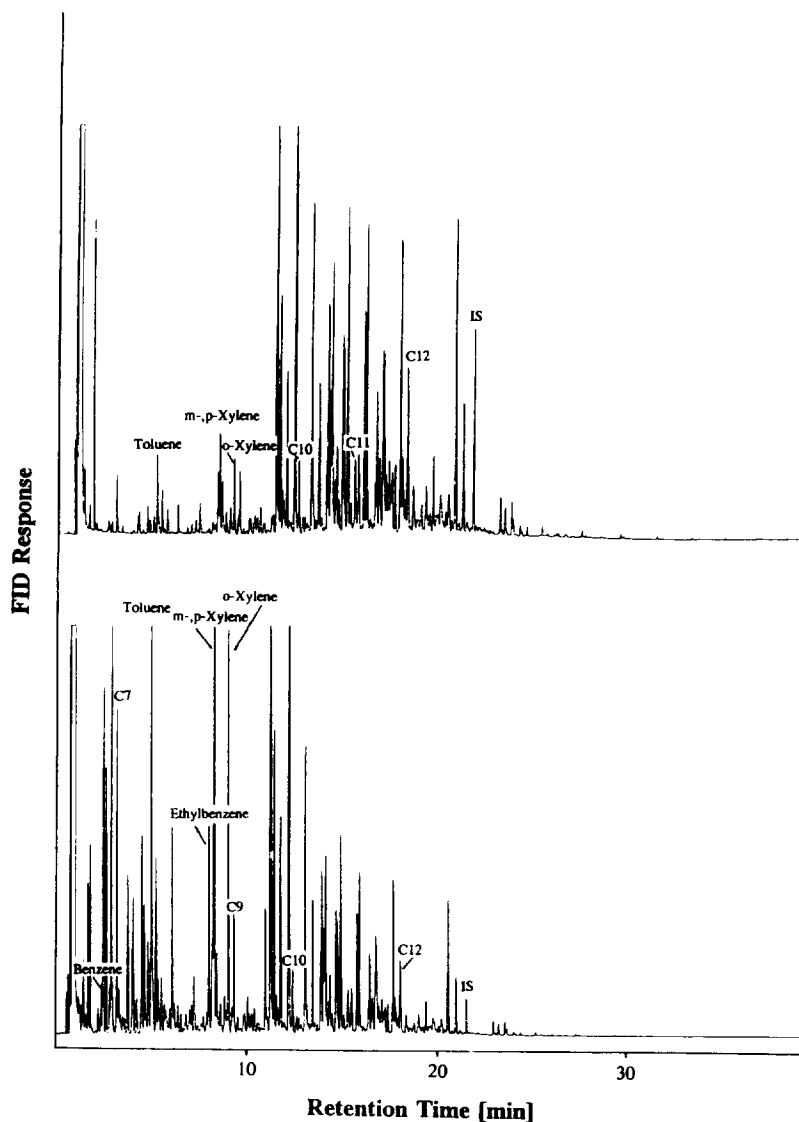


Fig. 1. GC-FID chromatograms of SFE extracts (sorbent trapping) of soils contaminated with gasoline-range organics for sample 1 (top) and sample 2 (bottom). IS = internal standard (1,3,5-triisopropylbenzene).

### 3.2. Comparison of the extraction efficiencies using sorbent and solvent trapping SFE and Soxhlet extraction

Since previous studies reporting SFE of petroleum hydrocarbons from soil used samples that were highly contaminated [4,8–10], this study included soils with low contamination levels. As

shown in Table 3, the samples were contaminated from low  $\mu\text{g/g}$  to low  $\text{mg/g}$  levels of TPH. The lowest TPH concentration was found in the sample 5 that contained only ca.  $7 \mu\text{g/g}$  TPH. Representative chromatograms for each sample are shown in Figs. 1–3, where we can see that the samples 1 and 2 were contaminated with gasoline-range hydrocarbons, while the samples

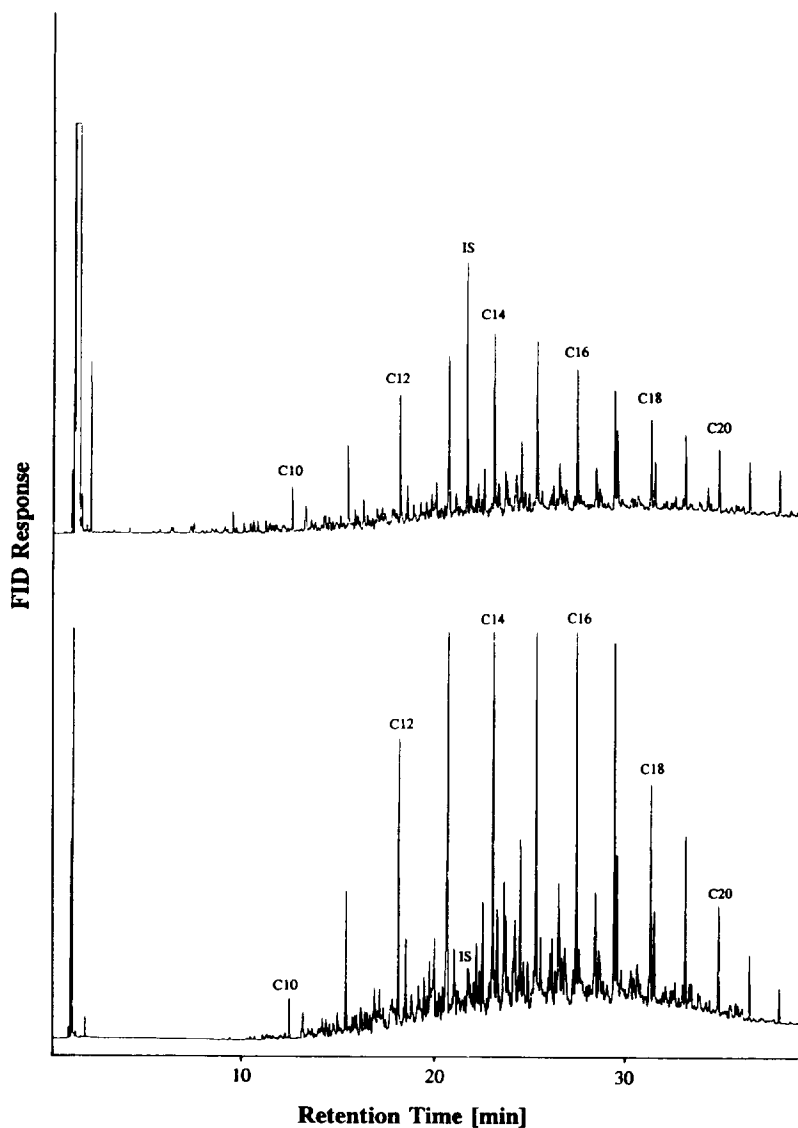


Fig. 2. GC-FID chromatograms of SFE extracts (sorbent trapping) of soils contaminated with diesel-range organics for sample 3 (top) and sample 4 (bottom). IS = internal standard (1,3,5-diisopropylbenzene).



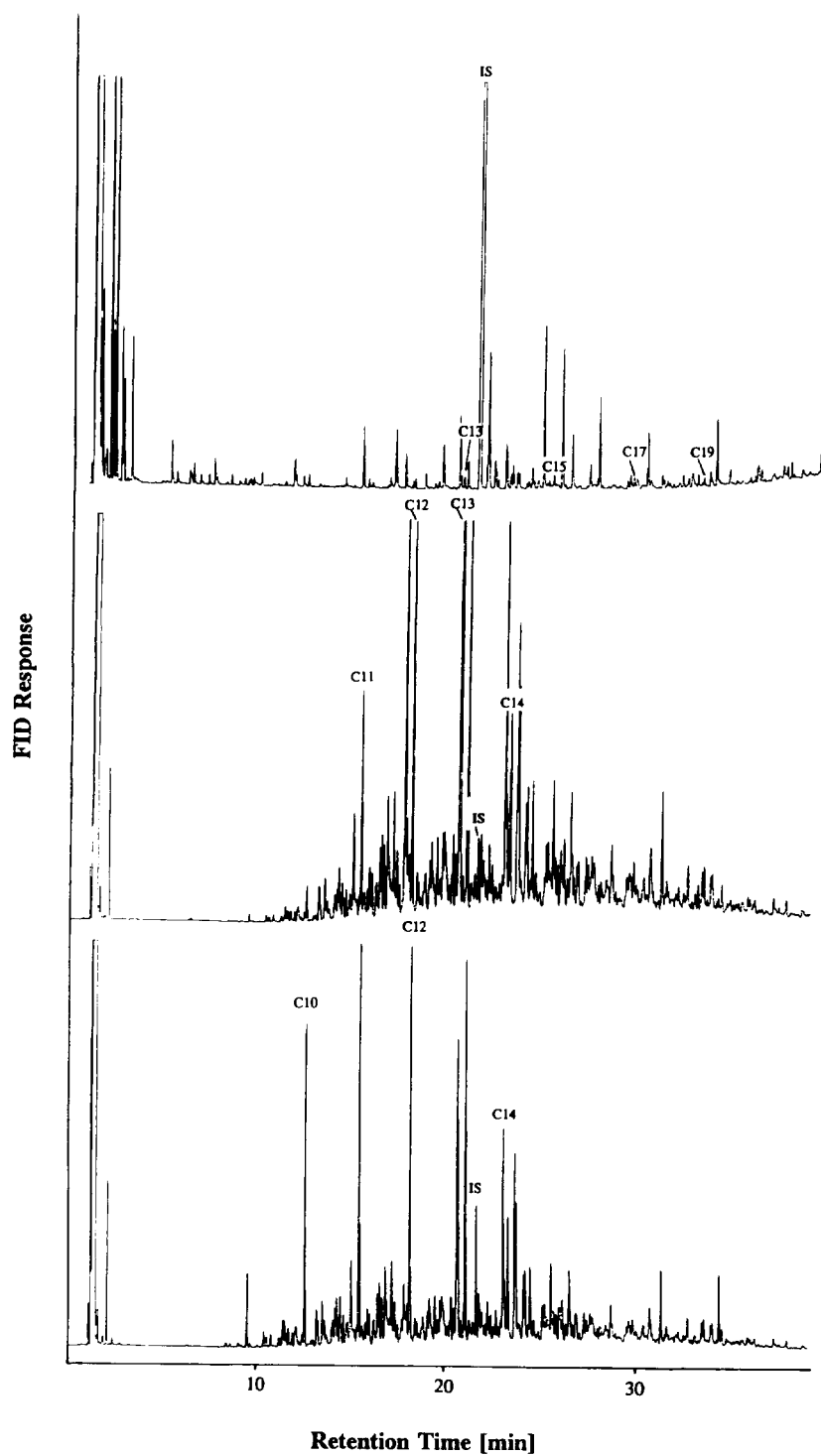


Fig. 3. GC-FID chromatograms of SFE extracts (sorbent trapping) of contaminated soils for sample 5 (top), sample 6 (middle), and sample 7 (bottom). IS = internal standard (1,3,5-diisopropylbenzene).

3 and 4 were typically contaminated with diesel-range hydrocarbons.

The TPH concentrations in Table 3 demonstrate that the sorbent and solvent SFE systems gave reasonable agreement, although the Soxhlet values were generally significantly lower for the samples containing more volatile species. (Note that all of the solvent collection results in Tables 3–6 utilized the SFX-210 system with solvent collection at atmospheric pressure since the pressurized collection system was not available for this part of the study). Similar results were

reported in previous work [10] for the heavy hydrocarbon quantitations, where SFE yielded 5 to 45% higher TPH recoveries than Soxhlet. Because the hydrocarbons determined in this study are more volatile than those in Ref. 10, the higher SFE recoveries appear to result from higher losses of volatile analytes from the Soxhlet extractions.

The concentrations of individual BTEX compounds for each sample are shown in Tables 4–6. The individual *n*-alkanes ranging from C<sub>6</sub> to C<sub>20</sub> were also quantified and the data were reported

Table 6  
Concentrations of individual hydrocarbons from contaminated soil

Analyte	Concentration ( $\mu\text{g/g}$ ) (%R.S.D. <sup>a</sup> )		
	SFE/sorbent (HP)	SFE/solvent <sup>b</sup> (ISCO)	Soxhlet
<i>Sample 5</i>			
Benzene	0.051 (19)	0.031 (44)	ND <sup>c</sup>
Toluene	0.014 (45)	0.034 (60)	0.0094 (40)
Ethylbenzene	0.0017 (47)	0.0047 (58)	0.0069 (56)
<i>m</i> -, <i>p</i> -Xylene <sup>d</sup>	0.0033 (42)	0.018 (57)	0.018 (62)
<i>o</i> -Xylene	0.0035 (37)	0.010 (56)	0.013 (41)
BTEX	0.074	0.098	0.047
C <sub>6</sub> –C <sub>12</sub>	0.060	0.099	0.032
C <sub>13</sub> –C <sub>20</sub>	0.40	0.49	0.63
<i>Sample 6</i>			
Benzene	0.092 (32)	0.11 (42)	ND
Toluene	0.061 (5)	0.088 (41)	ND
Ethylbenzene	ND	ND	ND
<i>m</i> -, <i>p</i> -Xylene	0.18 (9)	0.21 (22)	ND
<i>o</i> -Xylene	0.093 (10)	0.092 (30)	ND
BTEX	0.43	0.50	ND
C <sub>6</sub> –C <sub>12</sub>	84	72	60
C <sub>13</sub> –C <sub>20</sub>	140	110	110
<i>Sample 7</i>			
Benzene	ND	ND	ND
Toluene	ND	ND	ND
Ethylbenzene	0.097 (19)	0.096 (5)	0.037 (7)
<i>m</i> -, <i>p</i> -Xylene	0.68 (13)	0.59 (6)	0.28 (12)
<i>o</i> -Xylene	0.68 (11)	0.53 (28)	0.23 (6)
BTEX	1.4	1.2	0.55
C <sub>6</sub> –C <sub>12</sub>	130	110	63
C <sub>13</sub> –C <sub>20</sub>	51	42	34

<sup>a</sup> %R.S.D. based on triplicate extractions.

<sup>b</sup> Normal (atmospheric pressure) solvent trapping.

<sup>c</sup> Not detected.

<sup>d</sup> The sum of *m*- and *p*-xylene is reported because these two species were not resolved with the chromatographic conditions used.

as two groups ( $C_6$ – $C_{12}$  and  $C_{13}$ – $C_{20}$ ) in Tables 4–6. The %R.S.D. for the determination of individual *n*-alkanes was typically 5–20% for samples 1, 2, and 3; 5–10% for samples 4, 6, and 7; and 20–40% for sample 5 [where the concentrations of individual compounds were very low, ca. in the ppb (w/w) level], respectively. The results of two SFE systems agreed quite well, although the yield of solvent trapping was generally lower than that of sorbent trapping for the more volatile hydrocarbons. It should be noted that all of the collections for Tables 3–6 were performed with the normal (not pressurized) solvent trap. However, as shown in Tables 1 and 2, the collection efficiencies of the more volatile species could be improved by utilizing the pressurized solvent trap system. In most cases, the extraction yield of individual hydrocarbons obtained by the two SFE systems was higher than that of the Soxhlet extractions. This would be expected based on the losses of volatiles from Soxhlet process (note that Soxhlet extracts were evaporated from 150 ml to ca. 6 ml before GC analysis). The data shown in Tables 4–6 demonstrate that the yield of BTEX (volatile hydrocarbons) using Soxhlet extractions was very low (the lowest one was only ca. 17% of the SFE yield). The poor collection efficiencies of the volatile hydrocarbons using Soxhlet were also reported in Ref. [9].

The results shown in Tables 3–6 demonstrate that both types of SFE instrumentation (sorbent traps and solvent traps) can be used for quantitative determinations of BTEX, TPH, and individual organic compounds for gasoline and diesel range organics with a single SFE extraction condition. While the trapping must be carefully performed (especially for the solvent trapping) to efficiently recover volatile species like benzene, commercially available instrumentation is available that is capable of such operation.

#### 4. Conclusions

Both SFE systems using sorbent and solvent traps effectively trapped BTEX and the *n*-alkanes as volatile as *n*-hexane (sorbent trap),

*n*-octane (atmospheric pressure solvent trap), and *n*-heptane (pressurized/cooled solvent trap). SFE using either sorbent or solvent trapping gave reasonable agreement for BTEX, TPH, and individual compound concentrations, although the Soxhlet values were generally significantly lower because of the losses of the volatile compounds. With both types of SFE instrumentation, total solvent used is only ca. 6–15 ml compared to 150 ml with the Soxhlet method, and extraction times are reduced to 30 min compared to 4 h for Soxhlet extraction.

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