ELSEVIER

Journal of Chromatography A, 685 (1994) 95–111

JOURNAL OF CHROMATOGRAPHY A

Analysis of volatile organics by supercritical fluid extraction coupled to gas chromatography II. Quantitation of petroleum hydrocarbons from environmental sample

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First received 6 April 1994; revised manuscript received 5 July 1994

Abstract

A coupled supercritical fluid extraction–gas chromatography (SFE–GC) method has been developed for the quantitative extraction and analysis of gasoline and diesel range organics from real world environmental samples. Petroleum-contaminated samples containing gasoline- to diesel- and motor oil-range hydrocarbons (total hydrocarbon content typically ranging from 2 to 26 mg/g) could be quantitatively extracted by a 15-min SFE–GC extraction using 400 atm (1 atm = 101 325 Pa), 60°C CO_2. The SFE–GC hydrocarbon recoveries from real-world samples were comparable to those obtained by sonicating the samples in methylene chloride for 14 h, except for the gasoline recovery which was higher by SFE–GC analysis due to the more efficient collection of the more volatile analytes. Reproducibilities for replicate SFE–GC extractions and analyses were typically $<5\%$ (R.S.D.) for the quantitation of both individual organics and total hydrocarbon content. Gasoline- to diesel-range organics (as volatile as *n*-pentane) could be quantitatively retained during the SFE step of the SFE–GC analysis using a thick-film (30 m × 0.32 mm I.D., 5 μm film thickness) DB-1 column operated at a cryogenic trapping temperature of −25°C. Using split SFE–GC operated at a high split ratio (100:1) relatively large 1-g sample sizes could be extracted, and by using a drying agent (molecular sieve 3A) very wet (25%, w/w, water) samples could be analyzed without extracted water freezing and plugging in the GC column during the SFE step.

1. Introduction

Contamination of the environment by fuel leaks from underground storage tanks and by fuel spills during production and transport has become a major environmental issue which has prompted routine soil monitoring for TPH (total petroleum hydrocarbons) and BTEX components (benzene, toluene, ethylbenzene, *m*-xylene and *o*-xylene). Head space [1] or purge and trap [2–4] techniques are typically used for the recovery of volatile petroleum hydrocarbons such as the gasoline range organics (defined as compounds in the C_6–C_{10} boiling point range [1]). However, samples containing less volatile hydrocarbons such as diesel range organics (C_{10}–C_{25} boiling point range) require more rigorous extraction conditions using organic solvents such as Freon-113 (trichlorofluoroethane) [5,6], methylene chloride [7,8], or alkalized methanol [9].

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0021-9673/94/$07.00
SSDI 0021-9673(94)00639-3

Although both purge-and-trap and liquid solvent techniques are valuable methods for the extraction and recovery of petroleum hydrocarbons, each method has its limitations. For example, the suitability of head space and purge-and-trap analysis is severely limited by the volatility of the analyte species; thus, moderately volatile samples such as kerosene and diesel fuel are virtually non-detectable by these techniques [1,4]. Conversely, liquid solvent extraction may yield low recoveries for the volatile gasoline range organics due to sample losses during processing, and can require several hs to perform, generating large volumes of hazardous waste solvent [10]. Furthermore, one of the most common organic solvents used for petroleum hydrocarbon analysis, namely Freon-113, is be phased out of production in accordance with the Montreal Protocol on Substances that Deplete the Ozone Layer [10,11].

A recent alternative to these established extraction techniques is the use of supercritical fluid extraction (SFE). The most commonly used supercritical fluid, carbon dioxide, can extract polycyclic aromatic hydrocarbons [12–14], and alkyl and aromatic hydrocarbons [10,11,15,16] with recoveries that are comparable to liquid solvent extraction. Under SFE conditions carbon dioxide has a solvent strength that approaches that of a liquid enabling the solvent to extract analytes from the gasoline- to diesel-range organics, which is desirable as petroleum hydrocarbon contamination in the environment often involves a mixture of fuels. Another advantage of carbon dioxide is that at ambient conditions the solvent is a gas, which greatly simplifies the concentration of extracted analytes and, most importantly for this paper, allows the direct coupling of SFE with capillary gas chromatography (GC) without introducing large volumes of liquid solvent onto the chromatographic column [12,16–20].

Coupled (on-line) SFE with capillary GC is very attractive, as the extracted analytes are deposited directly into the gas chromatograph, greatly reducing sample preparation and handling steps and minimizing the potential for analyte loss. On-line SFE is, therefore, very suitable for petroleum hydrocarbon analysis as the technique can efficiently extract and collect very volatile analytes such as the gasoline-range organics. For example, on-line SFE can recover analytes as volatile as *n*-butane [21] compared to off-line SFE (analyte collected in an organic solvent) which is only suitable for analytes as volatile as *n*-octane [22]. Furthermore, as no organic solvent is used in the on-line SFE technique, there is no solvent peak present which can chromatographically co-elute with the volatile analytes.

The aim of this study is to develop a simple and reliable coupled SFE–GC method for the analysis of petroleum hydrocarbons from a variety of environmental samples without the need for any pre-preparation (e.g., air drying). The method uses a conventional split/splitless injection port operated at the optimized SFE–GC conditions developed in the first part of this study [21]. Only slight modifications need to be made to the gas chromatographic equipment as previously described [21] and a drying agent is used to enable very wet samples to be analyzed. The quantitative recovery of gasoline- and diesel-range organics (including BTEX) from real world environmental samples using SFE–GC analysis are reported and compared to the recoveries obtained by a conventional organic solvent extraction.

2. Experimental

2.1. Instrumentation and methods

Coupled SFE–GC analysis with flame ionization detection (FID) was performed using a Hewlett-Packard 5890 gas chromatograph modified as described in Part I of this study [21] with helium as the carrier gas and a wide-bore (30 m × 0.32 mm I.D., 5 μm film thickness) DB-1 column supplied by J & W Scientific, Folsom, CA, USA. The injection port and FID system were both operated at 300°C. The split ratio (under SFE–GC conditions) was maintained at 100:1 [21].

Supercritical fluid extractions were performed

with CO_2 (supercritical-fluid grade, Scott Specialty Gases, Plumsteadville, PA, USA) and an ISCO Model 260D syringe pump (ISCO, Lincoln, NE, USA). Samples were placed in a 3.5-ml extraction cell from Keystone Scientific (Bellefonte, PA, USA). The flow-rate of the supercritical fluid through the extraction cell was controlled at 0.6 ml/min (as liquid CO_2 measured at the pump) by a 9-cm-long restrictor (26 μm I.D. × 150 μm O.D.) cut from fused-silica tubing (Polymicro Technologies, Phoenix, AZ, USA). During the extraction, the extraction cell and a pre-equilibration coil were placed inside a thermostated tube heater which was situated directly above the injection port.

To avoid the loss of volatile hydrocarbon components, sample handling and processing during SFE–GC was kept to a minimum and the contaminated samples were analyzed without drying. Prior to weighing the sample into the extraction cell, the internal standard (octahydroanthracene in methylene chloride) was spiked onto an 8-mm O.D. circular piece of Whatman No. 1 filter paper (Maidstone, UK). The methylene chloride was then allowed to completely evaporate as determined by weighing the filter paper. The 3.5-ml extraction cell was filled with 2 g of drying agent, molecular sieve 3A (Alltech, Deerfield, IL, USA). With the internal standard spiked on the filter paper and the drying agent loaded inside the extraction cell, the sample (1 g) was quickly placed on top of the drying agent, the spiked filter paper was placed on top of the sample, and the cell immediately sealed and extracted so that the SFE flow went sequentially through the filter paper, sample, and drying agent (from top to bottom). The extraction effluent was depressurized inside the split/splitless injection port (split set at 100:1) and the analytes were cryogenically trapped (−50 or −25°C depending on the sample) in the chromatographic column as previously described [21]. During SFE the GC carrier gas was then shut off with a toggle valve and the sample extracted for 15 min with 400 atm (1 atm = 101 325 Pa), 60°C CO_2. At the end of the extraction the restrictor was withdrawn from the injection port, the carrier gas was turned on, and analysis begun by rapidly heating the GC oven to 40°C, then at 8°C/min to 300°C.

After SFE–GC analysis, the sample residue was either re-extracted by SFE–GC, or the sample, drying agent and filter paper were removed from the extraction cell and sonicated in 10 ml of methylene chloride for 14 h. After sonication, the extract was centrifuged at 300 *g* for 10 min to remove debris, the solvent was evaporated to 1 ml (for samples containing volatile components) or 100 μl (for samples containing less volatile components) and an internal standard (octahydroanthracene) added for GC–FID analysis. Fresh samples (1 g) were also extracted by sonicating in 10 ml methylene chloride for 14 h. The solvent extract was centrifuged and evaporated to 1 ml and an internal standard (octahydroanthracene) added for GC–FID analysis. The methylene chloride extracts were analyzed using the same GC column as the SFE–GC analysis but operated in the GC mode by injecting 1 μl of the extract into the split/splitless injection port in the splitless mode.

Since on-line SFE–GC introduces all of the extracted organics into the injection port (while this is not possible with the methylene chloride extract), SFE–GC can yield much larger peak areas than conventional solvent injections which could, in turn, lead to integration errors in comparing the two methods. This was not a problem with the samples using individual peak integration (i.e., the samples with the more volatile fuel components). Therefore, the methylene chloride extracts from these samples were concentrated only to 1 ml to avoid any unnecessary loss of volatiles. However, many of the components of the diesel- and motor oil-contaminated samples were poorly resolved (Figs. 5 and 6). Therefore, integration using an extended baseline was required for accurate determination of TPH. For these samples it was necessary to introduce equivalent quantities of extracted hydrocarbons into the GC column, both by SFE–GC and by conventional injection of the methylene chloride extracts, to allow accurate comparisons of the extraction efficiencies. To accomplish this, the SFE–GC analyses were performed with a 100:1 split ratio, and the

methylene chloride extracts were concentrated to 100 μl before injection of 1 μl in the splitless mode. Therefore, a comparable amount (1%) of the total extracted analytes were injected by both methods, and the peak areas were equivalent for the two techniques (assuming equivalent extraction efficiencies). To further ensure that the quantitative comparisons were valid, all quantitative results for all of the samples used in this study were based on the internal standard (octahydroanthracene).

2.2. Samples and standards

Six environmental samples contaminated with petroleum hydrocarbons, but with varying organic and water contents, were collected locally (North Dakota, USA), sieved to <2 mm to remove any sticks and other debris, and stored at -10°C until analyzed. The type of hydrocarbon contamination was confirmed by GC–mass spectrometry (MS) analysis using a Hewlett-Packard Model 5988 with electron impact ionization (70 eV). Scan range was 50–400 u.

Contaminated sediment was collected from an aquifer under an oil refinery at about a 2 m depth and contained ca. 5.0% (w/w) water and 0.8% (w/w) organic matter (determined by thermogravimetric analysis). A second sediment was obtained from an aquifer near underground fuel storage tanks. Two sandy soil samples were collected, each containing 0.4% organic matter and 25% (w/w) and 17% (w/w) water, respectively. A top soil collected next to an above ground diesel storage tank contained ca. 1.0% (w/w) water and 7.1% (w/w) organic matter. A motor oil-contaminated soil was taken from a railroad embankment and contained ca. 1.6% (w/w) water and 7.4% (w/w) organics. A gasoline-contaminated charcoal filter was obtained from a 1974 Chevette automobile. The filter was situated between the gasoline tank and carburetor and consisted of 1-mm O.D. carbon particles which contained ca. 3.4% (w/w) water.

The final sample was a "clean" agricultural top soil which contained ca. 16% (w/w) water and 4.7% (w/w) organic matter. This soil was spiked with gasoline by placing the unspiked soil on top of a bed of drying agent inside a 3.5-ml extraction cell (as discussed in the *Instrumentation and methods* section) and then injecting 1 μl of fresh unleaded gasoline into the middle of the 1-g sample. A piece of filter paper containing the internal standard was placed on top of the sample (as discussed in the *Instrumentation and methods* section) and the cell was then immediately sealed and connected to the SFE–GC apparatus.

For all samples, the internal standard, octahydroanthracene, was spiked onto filter paper or into the methylene chloride sonication extract at a concentration similar to that of the native analytes in the environmental samples, namely: 53 μg (contaminated sediment from an oil refinery), 214 μg (sediment from near the underground storage tanks), 428 μg (diesel contaminated soil), 107 μg (motor oil contaminated soil), 535 μg (gasoline contaminated charcoal filter) and 53 μg (soil spiked with gasoline). Quantitation of well-resolved individual species was based on peak areas (compared to the internal standard). For poorly resolved species (e.g., motor oil organics), quantitation of total petroleum hydrocarbons was based on a total integrated FID area using an extended baseline compared to the peak area of the internal standard [11]. Quantitative recovery of the spiked gasoline sample was determined by comparing the SFE–GC recoveries to a conventional split injection of the neat gasoline containing octahydroanthracene (53 mg/ml).

To determine the detection limit of the SFE–GC system a neat mixture of BTEX and C_4–C_{20} *n*-alkanes (ca. 0.5 g each) was prepared and diluted in ethanol (1 mg neat mixture/ml) [21]. A sorbent resin, Tenax-TA (Supelco, Bellefonte, PA, USA) was prepared by weighing 400 mg of the 60–80 mesh (180–250 μm) resin into a 2.5-ml extraction cell, and pre-extracting for 30 min with 400 atm CO_2 (60°C) to remove contaminants. The hydrocarbon–ethanol solution (1, 0.4 or 0.2 μl) was injected into the center of the clean Tenax-TA. The spiked sorbent resin was flushed with dry helium for 10 min at 300 ml/min to remove the ethanol. The sample was then

analyzed under identical SFE–GC conditions as the environmental samples using the 100:1 split ratio.

3. Results and discussion

3.1. Quantitative SFE–GC

The success of SFE–GC is dependent upon the correct choice of the SFE flow-rate, the GC column stationary phase thickness, and the oven temperature used for the cryogenic trapping of extracted analytes as optimized in the first part of this study [21] and as now used for the analysis of petroleum-contaminated environmental samples. The samples were extracted at a suitable extraction flow-rate (0.6 ml/min CO_2 as liquid CO_2 measured at the pump) using the appropriate split ratio (100:1), chromatographic column (5 μm film thickness), and cryogenic trapping temperature (−50 or −25°C).

The ability of split SFE–GC analysis to quantitatively extract and recover petroleum hydrocarbons from environmental samples was first investigated by analyzing replicate 1-g samples of agricultural soil spiked with neat gasoline. Complete extraction and trapping of the spiked soil should yield the same quantity of gasoline (1 μl spike) as 1 μl of gasoline injected into the gas chromatograph. Initially, analyte recoveries were calculated by comparing the raw chromatographic areas obtained by the SFE–GC and conventional injection techniques. However, this proved to be unreliable because the split ratio changed between the SFE–GC and GC analysis [21,23]. Therefore, to determine the recoveries internal standardization was used as this quantitative method is independent of the split ratio. The analyte response factors (area ratio of analyte to internal standard, octahydroanthracene) produced from the SFE–GC method were compared with those generated from the conventional split injection of the gasoline spike and internal standard.

The SFE–GC technique gave chromatograms with virtually identical peak shapes as those generated by a conventional split injection of neat gasoline, demonstrating that the use of coupled SFE–GC did not cause any loss in the quality of the chromatographic separations (Fig. 1). Furthermore, no peak tailing or split peaks associated with poor trapping were observed, as

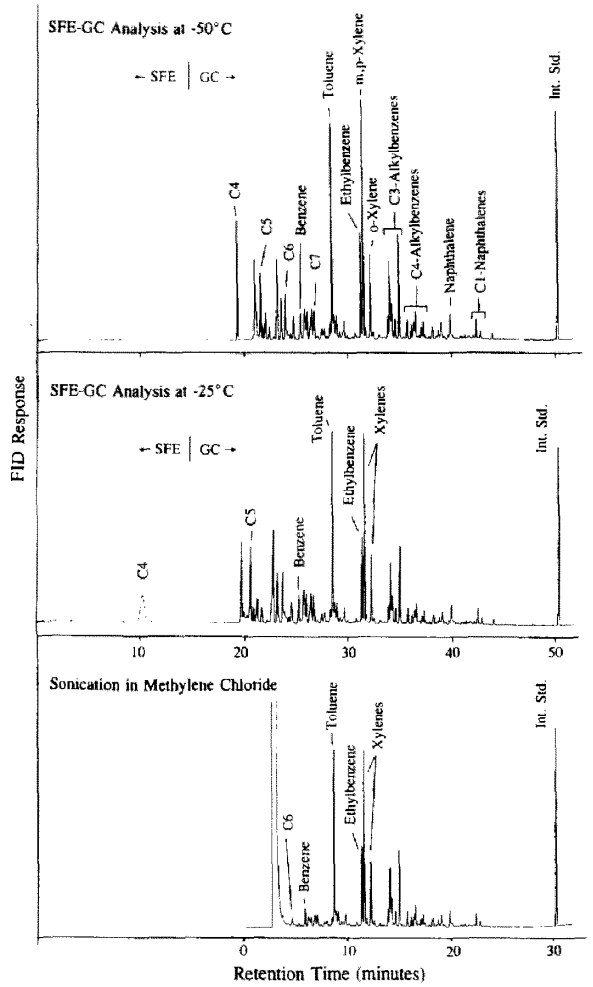

Fig. 1. Analysis of a 1-g soil sample spiked with 1-μl of neat gasoline using split SFE–GC–FID (split ratio ca. 1:100) and sonication in methylene chloride. The contaminated sample and a piece of filter paper spiked with the internal standard octahydroanthracene were placed on a bed of drying agent (molecular sieve 3A) inside an extraction cell and extracted for 15 min with 400 atm, 60°C, CO_2 at 0.6 ml/min. The extracted analytes were trapped onto a thick-film (5 μm) 30 m × 320 μm I.D. DB-1 capillary column at either −50 or −25°C (see top and middle chromatogram). After each extraction, the GC oven was heated at ca. 50°C/min to 40°C then at 8°C/min to 300°C. For comparison, the contaminated sample was also sonicated in 10-ml methylene chloride for 14 h (see lower chromatogram).

the peak width at half-height for both the volatile (pentane) and semivolatile (methylnaphthalene) analytes generated by the SFE–GC analysis were comparable to a conventional injection of the solvent extract. Raising the cryogenic temperature of the column from −50 to −25°C during SFE–GC analysis decreased the trapping efficiency of the column, as butane was eluted as a broad peak during the SFE step (Fig. 1). However, all the analytes could still be chromatographically resolved and quantified. Conversely, sonicating the sample in methylene chloride caused chromatographic problems as some of the volatile analytes (e.g., butane and pentane) could not be resolved from the solvent (Fig. 1) and, therefore, could not be quantified.

The extraction and recovery efficiencies obtained using the coupled SFE–GC techniques are shown in Table 1. The SFE–GC recovery of the gasoline was essentially quantitative at both the −50 and −25°C column trapping temperatures, except for the very volatile species (e.g., butane, pentane, hexane and benzene) which had recoveries as low as ca. 74%. The low recoveries are probably due to volatilization losses that occurred during the spiking of the soil, since SFE–GC yielded quantitative recovery of all of these species when gasoline range organics were extracted from Tenax-TA and XAD-2 sorbent resins [21]. To further ensure that quantitative recoveries were achieved the spiked soil sample was either re-extracted by SFE–GC or sonicated in methylene chloride. Both extraction techniques failed to recover additional analytes from the sample, confirming a quantitative recovery.

For comparison, the spiked soil was also analyzed by a conventional extraction method, namely sonication in methylene chloride (Table 1). Using the organic extraction method a non-quantitative or partial recovery of the gasoline was obtained. In this instance analyte losses

Table 1
Recovery of spiked gasoline from soil using split SFE–GC and sonication in methylene chloride

Analyte	Recovery (%) (R.S.D., %)[a]		
	Sonication[b]	SFE–GC (−50°C)[c]	SFE–GC (−25°C)[d]
Butane	ND	85 (13)	93 (12)
Pentane	ND	75 (12)	77 (9)
Hexane	11 (33)	74 (11)	85 (9)
Benzene	46 (26)	77 (10)	81 (12)
Heptane	39 (18)	89 (11)	94 (10)
Toluene	101 (8)	97 (9)	98 (8)
Ethylbenzene	103 (8)	102 (8)	104 (8)
m-, *p*-Xylene	103 (9)	102 (8)	104 (7)
o-Xylene	99 (8)	107 (8)	107 (9)
C_3-Alkylbenzene	107 (9)	107 (7)	106 (5)
C_3-Alkylbenzene	112 (11)	109 (7)	111 (3)
Naphthalene	103 (6)	115 (7)	109 (5)
C_1-Naphthalene	104 (7)	111 (8)	115 (6)
Total petroleum hydrocarbon	63 (10)	95 (9)	103 (6)

See Fig. 1 for chromatographic results. ND = Not detected.
[a] Recovery relative to values obtained from a neat injection of the gasoline spike. Values in parentheses are the relative standard deviations (%) of triplicate extractions and GC analyses.
[b] Spiked 1-g sample sonicated in 10-ml methylene chloride for 14 h.
[c] Spiked 1-g sample analyzed by SFE–GC–FID, the column temperature during the extraction was −50°C.
[d] Spiked 1-g sample analyzed by SFE–GC–FID, the column temperature during the extraction was −25°C.

occurred due to the sample handling, which included the sonication, centrifugation and evaporation of the extract from 10 to 1 ml (note that the methylene chloride extracts were never evaporated lower than 1 ml). These losses were most severe for the volatile analytes (e.g., *n*-butane to *n*-heptane) which were either not detected (as the organic solvent co-eluted with the analyte, Fig. 1) or had very low recoveries of 11 to 46% (Table 1). The loss of the volatiles during the extraction had a significant impact on the overall recovery of the gasoline, which was only in the region of ca. 63%. Sonication was, therefore, an unsuitable extraction method for gasoline analysis because of the loss of volatiles.

The reproducibility of both extraction techniques is indicated by the relative standard deviation which ranged from 6 to 33% for sonication extraction and from 3 to 13% for the SFE–GC analysis (Table 1). As expected, the recovery of the volatile analytes was more reproducible by the SFE–GC technique than by the sonication method as the coupled technique had far fewer sample handling steps. Furthermore, the online technique only required approximately 80 min analysis time, including sample weighing and loading the SFE cell, extraction, analyte collection and GC separation, compared to 18 h for the sonication analysis.

The analysis of such a relatively wet sample (16%, w/w, for the spiked soil) by SFE–GC can be a problem, as water is not very amenable to GC analysis since it causes band broadening [24]. Furthermore, the extracted water may freeze and plug in the column during the extraction and cryogenic trapping step of the SFE–GC analysis [16,25]; thus, preventing any additional analytes being introduced into the column (i.e., all analytes extracted after column plugging go out the split vent). Wet samples have previously been analyzed by SFE–GC by maintaining the GC column cryogenic trapping temperature above 0°C [25]. However, this approach was unsuitable for the analysis of gasoline range organics as volatile analytes in the C_4–C_6 range can not be efficiently retained on the column at this temperature [21]. In this study, column plugging by frozen water was avoided by placing the sample on a bed of drying agent (molecular sieve 3A) situated inside the extraction cell. Molecular sieve 3A is one of the most effective drying agents for SFE analysis [26] and proved ideally suited for the SFE–GC technique as a constant flow was maintained through the cryogenically cooled (−50°C) column during the entire extraction of the wet (16%, w/w, water) sample. Furthermore, the molecular sieve 3A selectively retained only the water during the extraction step, as demonstrated by the quantitative recoveries in Table 1 (except for the very volatile species lost during spiking), as well as the fact that no petroleum hydrocarbons were recovered by sonicating the drying agent in methylene chloride after the SFE–GC analysis.

Besides water, matrix components (e.g., non-volatile organics present in the soil samples) may potentially be co-extracted with the target analytes of interest and may cause a degradation of the chromatographic column performance. However, by using a split injection port with a high split ratio (100:1), the amount of non-"GC-able" components transferred into the chromatographic column was greatly reduced as the majority of these co-extracted compounds were deposited on the injection port liner. The use of molecular sieve 3A with the sample may also help reduce column contamination, as the drying agent can retain high-molecular-mass polar compounds. Therefore, the drying agent was used for all of the samples analyzed by SFE–GC, regardless of water or organic content.

3.2. SFE–GC detection limit

Coupled SFE–GC is often perceived as a technique that is limited to very small sample sizes typically in the order of < 100 mg [16,19]. While this is an advantage when the sample is difficult to collect in large quantities (e.g., air particulates or some samples collected at the scene of a crime), some analyses may require the use of larger sample sizes in order to ensure adequate sensitivity or sample homogeneity. In an attempt to work with a more realistic sample size, 1-g samples were used in this study. The final sensitivity of the SFE–GC method then

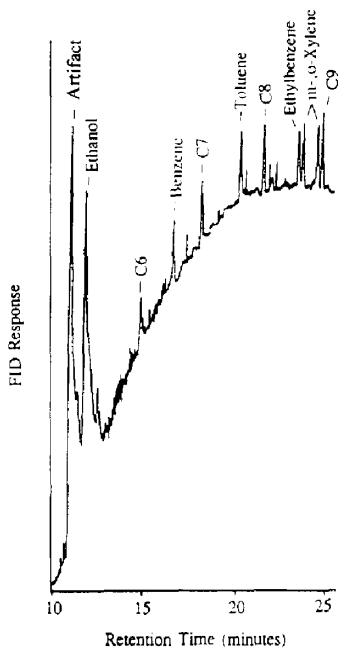

Fig. 2. Detection limit of the split SFE–GC–FID system. Approximately 9 ng each of the *n*-alkane and BTEX analytes were spiked onto Tenax-TA sorbent resin, and analyzed by SFE–GC at a split ratio of 1:100.

depends on the split ratio used during SFE and the FID detection limit. Selection of the split ratio depends on several factors. As previously described, higher split ratios during the SFE step allow faster extraction flow rates without causing distortion of the chromatographic peaks [21]; however, a higher split ratio also reduces the sensitivity of the analysis. In addition, many real-world samples are highly contaminated, so a relatively high split ratio is desirable to avoid overloading the GC column stationary phase. The goal of this study was to develop SFE–GC conditions that yielded low ppb (ng/g soil) detection limits for individual fuel components, while also being able to accommodate 1-g samples that were contaminated at widely varying concentrations. Therefore, a split ratio of 100:1 and a SFE extraction flow of 0.6 ml/min were chosen as standard conditions.

The detection limit of these SFE–GC conditions was determined using a hydrocarbon calibration standard spiked onto Tenax-TA [21] as described in the Experimental section. The resultant chromatogram for a spike of 9 ng each

Table 2
Comparison of split SFE–GC and sonication in methylene chloride for the quantitation of petroleum hydrocarbons in a fuel-contaminated sediment from an oil refinery

Analyte	Concentration (μg/g) (R.S.D., %)[a]			
	Sonication[b]	SFE–GC (−50°C)[c]	SFE–GC (−25°C)[d]	SFE residue[e]
n-Nonane	7.6 (1)	6.6 (7)	7.3 (6)	ND
n-Decane	34 (6)	29 (4)	31 (5)	1.3 (19)
n-Undecane	68 (5)	55 (3)	67 (4)	2.4 (15)
n-Dodecane	107 (3)	87 (3)	95 (4)	2.7 (13)
C_1-Naphthalene	91 (2)	73 (3)	87 (3)	ND
C_1-Naphthalene	53 (2)	45 (4)	51 (4)	ND
Naphthalene	36 (2)	32 (2)	35 (7)	ND
C_2-Naphthalene	20 (0)	17 (2)	18 (7)	ND
Phenanthrene	12 (3)	15 (3)	16 (5)	ND
Total petroleum hydrocarbon	1429 (6)	1700 (10)	1582 (14)	7.1 (17)

See Fig. 3 for chromatographic results. ND = Not detected.
[a] Values in parentheses are the relative standard deviations (%) of triplicate extractions and GC analyses.
[b] Sample sonicated in 10-ml methylene chloride for 14 h.
[c] Sample extracted with 400 atm 60°C CO_2 for 15 min, the column temperature during the extraction was −50°C.
[d] Sample extracted with 400 atm 60°C CO_2 for 15 min, the column temperature during the extraction was −25°C.
[e] SFE–GC sample residue re-extracted by sonicating in 10-ml methylene chloride for 14 h.

of BTEX compounds and *n*-alkanes ranging from *n*-hexane to *n*-nonane is shown in Fig. 2. Each of the fuel components showed a signal-to-noise ratio of > 5:1, demonstrating that very low ppb detection limits were achieved, even with the 100:1 split ratio used during the SFE step. Note also that artifacts from the Tenax-TA resin were very low compared to the low ppb quantities of the test analytes.

3.3. SFE–GC analysis of real-world environmental samples

With quantitative SFE–GC collection recoveries having been established and the coupled SFE–GC having sufficient sensitivity, five real-world samples were investigated. The ability of SFE–GC to yield reproducible quantitative results from real-world samples (1 g) was assessed by comparing the SFE–GC petroleum hydrocarbon recoveries to those obtained by a conventional organic solvent extraction. Table 2 shows the hydrocarbon recoveries from a fuel-contaminated sediment obtained from an oil refinery using SFE–GC and sonication in methylene chloride. The 15-min SFE–GC extraction was able to achieve similar quantitative recoveries as the 14 h sonication extraction, yet it did not need any of the intervening sample handling steps required by the organic extraction method. The SFE–GC technique also showed good reproducibilities with relative standard deviations for the individual species ranging from 2 to 7%, thus demonstrating the ability of the technique to yield both rapid and reproducible determinations of the extractable petroleum hydrocarbons. The low relative standard deviations also suggest that the 1-g sample is representative of the bulk sample.

To ensure that quantitative recoveries were

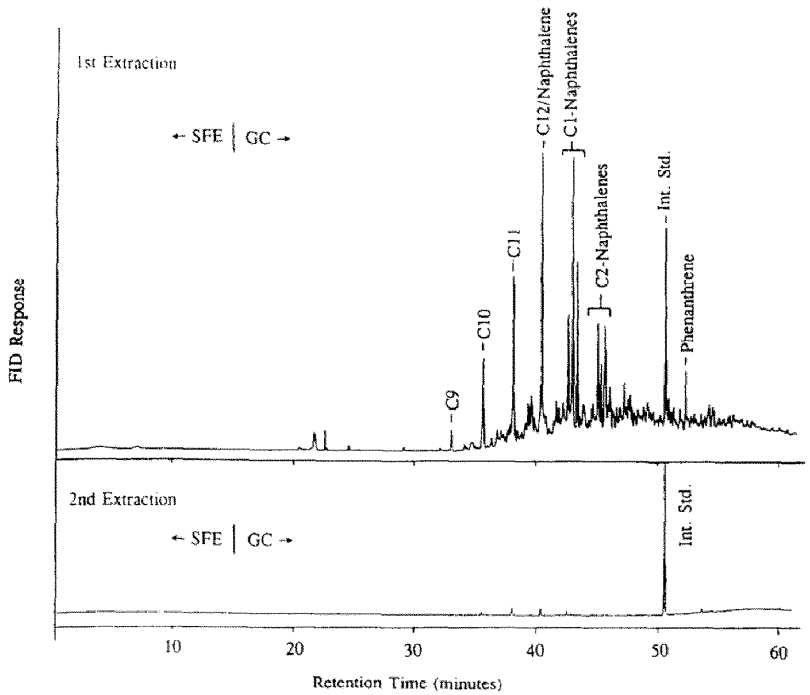

Fig. 3. Analysis of fuel-contaminated sediment from an oil refinery using split SFE–GC–FID analysis (split ratio ca. 1:100). A 1-g sample and a piece of filter paper spiked with the internal standard octahydroanthracene were placed on a bed of drying agent (molecular sieve 3A) inside an extraction cell and extracted for 15 min with 400 atm, 60°C, CO_2 at 0.6 ml/min. The extracted analytes were trapped onto a thick-film (5 μm) 30 m × 320 μm I.D. DB-1 capillary column at −25°C. After the extraction, the GC oven was heated at ca. 50°C/min to 40°C, then at 8°C/min to 300°C (top chromatogram). The sample was then extracted a second time under identical conditions as the first extraction (lower chromatogram).

obtained by SFE–GC the sample residue was either re-extracted by SFE–GC (Fig. 3) or sonicated in methylene chloride (Table 2). A second independent extraction method (e.g. sonication) was used as previous work had shown that simply re-extracting a real world sample under the same conditions as the first SFE extraction often failed to recover the more strongly bound analytes [27]. However, both extraction methods recovered less than 1% of the total hydrocarbon content from the SFE residues, indicating that the 15-min SFE was sufficient to quantitatively extract the fuel from the sediment. The SFE–GC quantitative recoveries also confirmed that the 0.6 ml/min CO_2 extraction flow-rate used during this study was an appropriate flow, both in terms of the requirements of the extraction (i.e., adequate flow to sweep the void volume and solubilize the analytes) and of the chromatography (i.e., produced Gaussian chromatographic peak shapes).

The quality of the SFE–GC chromatograms generated with a cryogenic trapping temperature of −50 or −25°C compared favorably with those generated by using the conventional split injection of the methylene chloride extract. Both trapping temperatures were suitable for the efficient retention of the extracted analytes on the column during the SFE step, as the recoveries at −50 and −25°C were similar (Table 2). Furthermore, no deterioration in the column performance or chromatographic peak shape was observed from analyzing the environmental sample in its native state [e.g., 5.0% (w/w) water and 0.8% (w/w) organic matter] demonstrating the effectiveness of using a high 100:1 split ratio and a drying agent in the SFE–GC analysis.

A second fuel-contaminated sediment obtained from an aquifer near underground fuel storage tanks contained analytes in the gasoline to kerosene range (Fig. 4). Two samples were collected, a water logged sediment from a poorly drained area (ca. 25%, w/w, water) and a wet sediment from a well drained area (ca. 17%, w/w, water). Both samples were placed on a bed of drying agent and analyzed by SFE–GC, but the recoveries obtained were significantly different (Tables 3 and 4). For the well drained

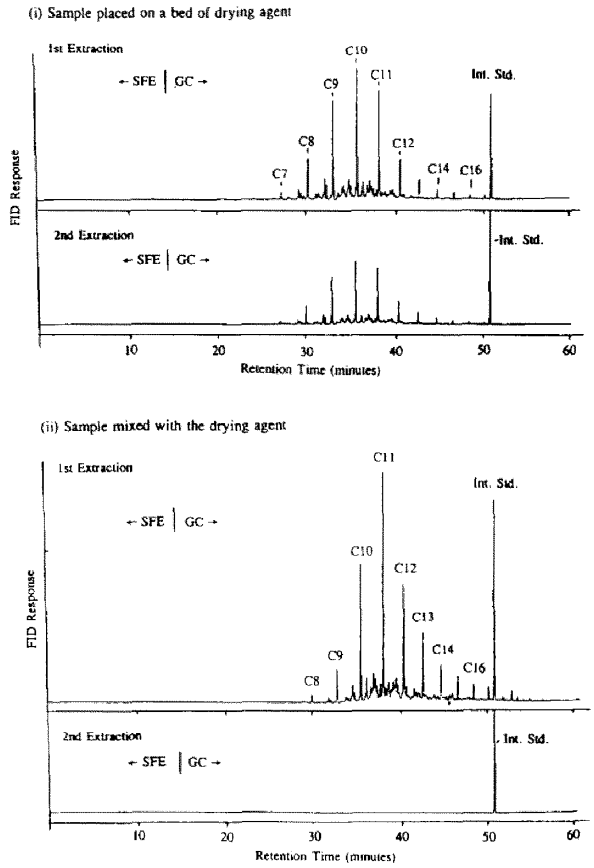

Fig. 4. Analysis of contaminated sediment near underground fuel storage tanks using split SFE–GC–FID (split ratio ca. 1:100). The water logged (25%, w/w, water) 1-g sample and a piece of filter paper spiked with the internal standard octahydroanthracene were either (i) placed on a bed of drying agent (molecular sieve 3A) inside the extraction cell or (ii) mixed with the dying agent (molecular sieve 3A) and then placed inside the extraction cell. The sediment, drying agent and internal standard were extracted for 15 min with 400 atm, 60°C, CO_2 at 0.6 ml/min. The extracted analytes were trapped onto a thick-film (5 μm) 30 m × 320 μm I.D. DB-1 capillary column at −25°C. After the extraction, the GC oven was heated at ca. 50°C/min to 40°C, then at 8°C/min to 300°C. The samples were then extracted a second time under identical conditions as the first extract.

sediment (17%, w/w, water) quantitative fuel recoveries were possible using the SFE–GC technique, as the hydrocarbon recoveries from the 15-min SFE–GC extraction were comparable to those obtained by sonicating the sediment in methylene chloride for 14 h (Table 3) whether the cryogenic trapping temperature was −25 or

Table 3
Comparison of split SFE–GC and sonication in methylene chloride for the quantitation of petroleum hydrocarbons in a contaminated sediment near underground storage tanks: wet sample (17%, w/w, water) placed on a bed of drying agent

Analyte	Concentration (μg/g) (R.S.D., %)[a]		
	Sonication[b]	SFE–GC[c]	SFE residue[d]
n-Hexane (C_6)	ND	26 (18)	ND
n-Heptane (C_7)	73 (15)	134 (12)	1.4 (32)
n-Octane (C_8)	306 (12)	297 (8)	10 (43)
n-Nonane (C_9)	505 (9)	428 (4)	24 (50)
n-Decane (C_{10})	486 (7)	422 (3)	31 (43)
n-Undecane (C_{11})	354 (6)	280 (4)	34 (38)
n-Dodecane (C_{12})	110 (5)	92 (3)	16 (35)
n-Tridecane (C_{13})	50 (7)	42 (4)	8.4 (34)
n-Tetradecane (C_{14})	24 (5)	21 (4)	4.4 (35)
n-Pentadecane (C_{15})	18 (7)	15 (4)	2.8 (35)
n-Hexadecane (C_{16})	12 (5)	10 (2)	1.8 (31)
n-Heptadecane (C_{17})	10 (5)	7.7 (5)	1.3 (26)
Total petroleum hydrocarbon	4415 (8)	4071 (5)	116 (2)

[a] Values in parentheses are the relative standard deviations (%) of triplicate extractions and GC analyses.
[b] Sample sonicated in 10-ml methylene chloride for 14 h; ND = not detected.
[c] Sample and bed of drying agent (molecular sieve 3A) extracted with 400 atm 60°C CO_2 for 15 min, the column temperature during the extraction was −25°C.
[d] SFE–GC sample residue re-extracted by sonicating in 10-ml methylene chloride for 14 h.

−50°C. The drying agent also efficiently retained the water from the 17% (w/w) sample as a continuous CO_2 flow was maintained through the cryogenically cooled column during the entire SFE step.

For the 25% (w/w) water sediment SFE–GC recovered only ca. 60% of the fuel in a 15-min extraction [Table 4, Fig. 4 (i)]. As the only measurable difference between the wet (17%, w/w, water) and water logged sediments (25%, w/w, water) was the water content, it appeared that the presence of a large amount of water was interfering with the SFE–GC analysis. There were two potential reasons for the low recoveries from the water logged sample, namely: (i) the water was inhibiting the column trapping efficiency despite the fact that a bed of drying agent was present; or (ii) the large amount of water present in the sediment was inhibiting the extraction, a similar phenomenon having been reported for the SFE analysis of a wet petroleum waste sludge [28]. To determine which hypothesis was correct the SFE–GC sample residue was re-extracted by sonicating in methylene chloride (Table 4). The combined recoveries of the SFE–GC and sonication extraction were comparable to the conventional extraction method of sonicating the sediment in methylene chloride, demonstrating that the low recoveries obtained from the 15-min SFE step were due to the slow extraction rate of the hydrocarbons from the 25% (w/w) water sample rather than due to poor trapping. Mixing the sample with the drying agent was partially successful in that all the extractable hydrocarbons present in the sample could be recovered by a 15-min SFE–GC extraction [Fig. 4 (ii)]. No additional fuel was recovered either by a second SFE–GC extraction or by re-extracting the sample with methylene chloride (Table 4). However, the sample–drying agent mixture approach also failed since significant volatile analyte losses (C_6–C_{12} n-alkanes) occurred during the mixing process because the molecular sieve 3A is an exothermic drying agent

Table 4
Comparison of split SFE–GC and sonication in methylene chloride for the quantitation of petroleum hydrocarbons in a contaminated sediment near underground storage tanks: water logged sample (25%, w/w, water) placed on a bed of drying agent or mixed with the drying agent

Analyte	Concentration (μg/g) (R.S.D., %)[a]				
	Sonication[b]	Sample on a bed of drying agent[c]		Sample mixed with a drying agent[d]	
		SFE–GC	SFE residue	SFE–GC	SFE residue
n-Hexane (C_6)	ND	2.2 (13)	ND	ND	ND
n-Heptane (C_7)	13 (31)	18 (19)	2.3 (34)	2.1 (43)	ND
n-Octane (C_8)	93 (19)	73 (9)	24 (15)	13 (37)	ND
n-Nonane (C_9)	218 (13)	148 (4)	67 (8)	46 (35)	ND
n-Decane (C_{10})	275 (10)	170 (2)	91 (9)	116 (24)	ND
n-Undecane (C_{11})	248 (7)	140 (1)	91 (12)	162 (12)	ND
n-Dodecane (C_{12})	88 (6)	47 (1)	34 (10)	63 (6)	ND
n-Tridecane (C_{13})	41 (3)	24 (7)	15 (8)	37 (9)	ND
n-Tetradecane (C_{14})	20 (4)	12 (0)	7.0 (9)	18 (5)	ND
n-Pentadecane (C_{15})	12 (0)	8.1 (1)	4.5 (5)	12 (7)	ND
n-Hexadecane (C_{16})	8.1 (6)	5.4 (2)	2.8 (5)	8.7 (7)	ND
n-Heptadecane (C_{17})	6.0 (3)	4.5 (10)	2.1 (4)	6.4 (5)	ND
Total petroleum hydrocarbon	2686 (11)	1551 (9)	1089 (8)	1109 (12)	ND

See Fig. 4 for chromatographic results. ND = Not detected.
[a] Values in parentheses are the relative standard deviations (%) of triplicate extractions and GC analyses.
[b] Sample sonicated in 10-ml methylene chloride for 14 h.
[c] Sample placed on a bed of drying agent (molecular sieve 3A) inside an extraction cell and extracted with 400 atm 60°C CO_2 for 15 min. Column temperature during the extraction was −25°C.
[d] Sample and drying agent (molecular sieve 3A) mixed together and then placed inside the extraction cell and extracted with 400 atm 60°C CO_2 for 15 min. Column temperature during the extraction was −25°C.

and produces heat upon hydration (Table 4). Similar losses have previously been reported for other wet samples mixed directly with drying agents [26].

SFE–GC analysis of the soil contaminated with diesel-range organics was quantitative as no additional hydrocarbons were recovered from either re-extracting the sample by SFE–GC (Fig. 5) or sonicating the sample residue in methylene chloride (Table 5). The 15-min SFE–GC extraction gave good quantitative agreement with the 14-h sonication extraction and both extraction methods had low relative standard deviations of replicate extractions in the region of 1 to 8%. The exception was the *n*-decane recovery by sonication, which had a lower recovery than that achieved by SFE–GC, which is a result of volatilization losses occurring during the sonication extraction process. The previous samples contained gasoline to kerosene range organics which could be analyzed by SFE–GC using a column cryogenic trapping temperature of −50 or −25°C. However, the −50°C column trapping temperature was unsuitable for the diesel-contaminated sample as the supercritical flow through the column quickly decreased upon commencing the extraction and within 5 min the GC column had plugged. The column plugging did not appear to be related to the water content of the soil as the sample only contained ca. 1.0% (w/w) water. Furthermore, the drying agent had previously enabled much wetter samples (e.g., spiked gasoline sample with 16%, w/w, water) to be analyzed at the −50°C cryogenic trapping

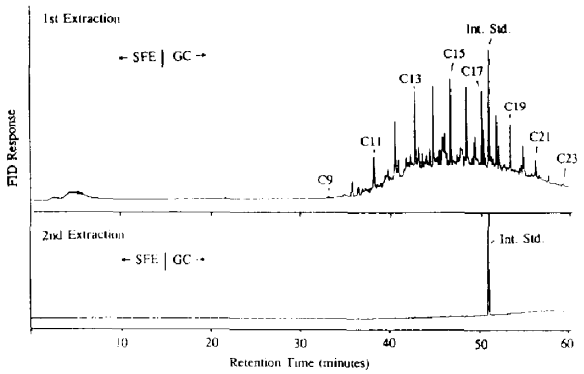

Fig. 5. Analysis of diesel contaminated soil using split SFE–GC–FID (split ratio ca. 1:100). A 1-g sample and a piece of filter paper spiked with the internal standard octahydroanthracene were placed on a bed of drying agent (molecular sieve 3A) inside an extraction cell and extracted for 15 min with 400 atm, 60°C, CO_2 at 0.6 ml/min. The extracted analytes were trapped onto a thick-film (5 μm) 30 m × 320 μm I.D. DB-1 capillary column at −25°C. After the extraction, the GC oven was heated at ca. 50°C/min to 40°C, then at 8°C/min to 300°C (top chromatogram). The sample was then extracted a second time under identical conditions as the first extract (lower chromatogram).

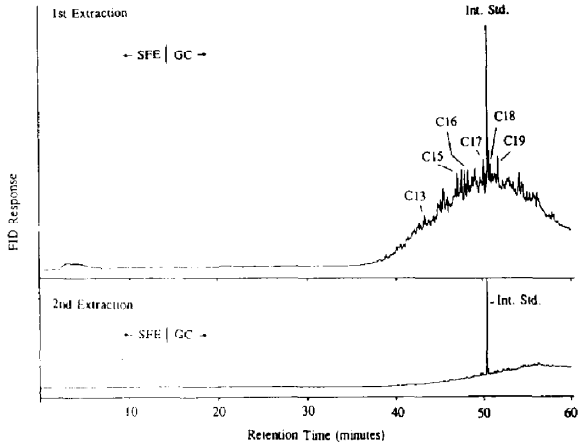

Fig. 6. Analysis of motor oil-contaminated soil from railroad embankment using split SFE–GC–FID (split ratio ca. 1:100). A 1-g sample and a piece of filter paper spiked with the internal standard octahydroanthracene were placed on a bed of drying agent (molecular sieve 3A) inside an extraction cell and extracted for 15 min with 400 atm, 60°C, CO_2 at 0.6 ml/min. The extracted analytes were trapped onto a thick-film (5 μm) 30 m × 320 μm I.D. DB-1 capillary column at −25°C. After the extraction, the GC oven was heated at ca. 50°C/min to 40°C, then at 8°C/min to 300°C (top chromatogram). The sample was then extracted a second time under identical conditions as the first extract (lower chromatogram).

temperature. It was, therefore, envisaged that the problem was related to the nature of the extracted hydrocarbons, the diesel extract having a "waxy" consistency at −50°C which caused the column to become plugged. However, when the diesel extract was analyzed at the −25°C trapping temperature a continuous supercritical flow was obtained through the column during the entire SFE step, enabling quantitative recoveries (Table 5) and good chromatographic analysis (Fig. 5) to be achieved. As shown in Tables 1–5, using the −25°C column trapping temperature would enable both gasoline- and diesel-range organics to be extracted and analyzed by SFE–GC.

To assess the range of petroleum hydrocarbons which could be analyzed by the SFE–GC technique a motor oil-contaminated sample was also analyzed. SFE–GC gave good quantitative agreement with sonicating the sample in methylene chloride for 14 h (Table 6). This sample (like the diesel sample) had to be analyzed with a cryogenic trapping temperature of −25°C to avoid column plugging, but this did not affect the chromatographic peak shapes, as the chromatograms generated by the SFE–GC (Fig. 6) were comparable to those generated by using a split injection of the methylene chloride extract. However, not all the analytes extracted from the soil by either SFE or by sonication in methylene chloride could be easily eluted from the 5-μm thick-film capillary column, as the less volatile analytes had a tendency to accumulate on the column to produce a shift in the baseline during the GC analysis (Fig. 6, second extraction). The motor oil components could have been fully eluted using a 0.25-μm film column but this would result in lower trapping efficiency of volatile components [21]. Fortunately, the gradual degradation of the thick-film column's chromatographic performance could easily be rectified by simply trimming off ca. 15 cm of the injection end of the column. The thick-film capillary column was, therefore, the appropriate column to use for the analysis of gasoline- and diesel-contaminated soils, and the motor oil

Table 5
Comparison of split SFE–GC and sonication in methylene chloride for the quantitation of petroleum hydrocarbons in a diesel-contaminated soil

Analyte	Concentration (μg/g) (R.S.D., %)[a]		
	Sonication[b]	SFE–GC[c]	SFE residue[d]
n-Decane (C_{10})	41 (19)	91 (2)	ND
n-Undecane (C_{11})	151 (2)	190 (4)	ND
n-Dodecane (C_{12})	288 (2)	294 (3)	ND
n-Tridecane (C_{13})	318 (2)	277 (1)	ND
n-Tetradecane (C_{14})	311 (1)	301 (1)	ND
n-Pentadecane (C_{15})	313 (2)	319 (2)	ND
n-Hexadecane (C_{16})	339 (1)	252 (5)	ND
n-Heptadecane (C_{17})	249 (5)	261 (3)	ND
n-Octadecane (C_{18})	172 (0)	187 (4)	ND
n-Nonadecane (C_{19})	160 (2)	150 (5)	ND
n-Eicosane (C_{20})	85 (1)	98 (7)	ND
n-Heneicosane (C_{21})	59 (2)	64 (8)	ND
n-Docosane (C_{22})	31 (1)	30 (3)	ND
Total petroleum hydrocarbon	24 319 (2)	26544 (1)	ND

See Fig. 5 for chromatographic results.
[a] Values in parentheses are the relative standard deviations (%) of triplicate extractions and GC analyses.
[b] Sample sonicated in 10-ml methylene chloride for 14 h.
[c] Sample extracted with 400 atm 60°C CO_2 for 15 min, the column temperature during the extraction was −25°C.
[d] SFE–GC sample residue re-extracted by sonicating in 10-ml methylene chloride for 14 h; ND = not detected.

Table 6
Comparison of split SFE–GC and sonication in methylene chloride for the quantitation of petroleum hydrocarbons in a motor oil-contaminated soil

Analyte	Concentration (μg/g) (R.S.D., %)[a]		
	Sonication[b]	SFE–GC[c]	SFE residue[d]
n-Tridecane (C_{13})	13 (13)	13 (18)	ND
n-Pentadecane (C_{15})	23 (11)	23 (14)	ND
n-Hexadecane (C_{16})	37 (4)	34 (14)	ND
n-Heptadecane (C_{17})	30 (6)	30 (6)	ND
n-Octadecane (C_{18})	14 (6)	16 (6)	ND
n-Nonadecane (C_{19})	25 (28)	30 (12)	ND
Total petroleum hydrocarbon	9747 (10)	10413 (7)	173 (4)

See Fig. 6 for chromatographic results.
[a] Values in parentheses are the relative standard deviations (%) of triplicate extractions and GC analyses.
[b] Sample sonicated in 10-ml methylene chloride for 14 h.
[c] Sample extracted with 400 atm 60°C CO_2 for 15 min, the column temperature during the extraction was −25°C.
[d] SFE–GC sample residue re-extracted by sonicating in 10-ml methylene chloride for 14 h; ND = not detected.

sample was realistically the limit of the petroleum hydrocarbon range that could be analyzed using this column.

The final real-world sample was a gasoline-contaminated charcoal filter obtained from a 1974 Chevette automobile. Since this sample was contaminated with ca. 17% extractable hydrocarbons, the sample size had to be reduced to 50 mg to avoid gross overloading of the GC column stationary phase. The 15-min SFE–GC extraction again yielded recoveries comparable to those obtained by sonicating the sample in methylene chloride for 14 h (Table 7), though the SFE–GC recoveries of naphthalene and methylnaphthalene were slightly lower than the values obtained by the sonication method. However, by re-extracting the sample for an additional 15 min by SFE–GC (Fig. 7), or sonicating the sample residue in methylene chloride (Table 7), quantitative polynuclear aromatic hydrocarbon recoveries were achieved. Both the SFE–GC and sonication extraction methods were reproducible (e.g., relative standard deviations from ca. 1 to 7%) demonstrating that the small 50-mg sample size was representative of the bulk sample.

4. Conclusions

Split SFE–GC is a rapidly developing technique which can quickly and quantitatively extract and analyze petroleum hydrocarbons from real-world environmental samples. SFE–GC analysis typically requires less than 80 min per sample to perform since no concentration and sample handling procedures are needed between the SFE and GC steps. The SFE–GC hydrocarbon recoveries are comparable to those obtained by a conventional organic extraction method which requires ca. 18 h to perform including the extraction, centrifugation, evaporation and GC analysis. A simple and reliable method has been developed to analyze the petroleum-contaminated samples in their native state (without any pre-preparation such as air drying) by using split SFE–GC operated at a high split ratio (e.g., 100:1) to avoid overloading

Table 7
Comparison of split SFE–GC and sonication in methylene chloride for the quantitation of petroleum hydrocarbons in a charcoal filter from a vehicle gasoline tank

Analyte	Concentration (mg/g) (R.S.D., %)[a]		
	Sonication[b]	SFE–GC[c]	SFE residue[d]
Toluene	1.2 (6.9)	1.2 (4.9)	ND
Ethylbenzene	4.8 (5.3)	4.4 (6.3)	ND
m-, *p*-Xylene	22.6 (5.9)	24.0 (2.2)	0.2 (41)
o-Xylene	12.2 (6.5)	12.2 (1.6)	0.2 (29)
C_3-Alkylbenzene	16.6 (5.0)	17.1 (2.0)	0.2 (7.1)
C_3-Alkylbenzene	23.8 (4.6)	25.5 (2.4)	0.6 (10)
C_3-Alkylbenzene	6.7 (4.0)	6.2 (4.2)	0.3 (9.3)
C_4-Alkylbenzene	5.8 (4.3)	5.6 (2.3)	0.2 (19)
Naphthalene	3.5 (3.9)	2.8 (2.8)	0.7 (11)
C_1-Naphthalene	2.2 (6.3)	1.2 (5.7)	0.9 (15)
Total petroleum hydrocarbon	169.7 (3.6)	167.9 (2.6)	6.0 (6.1)

See Fig. 7 for chromatographic results.
[a] Values in parentheses are the relative standard deviations (%) of triplicate extractions and GC analyses.
[b] Sample sonicated in 10-ml methylene chloride for 14 h.
[c] Sample extracted with 400 atm 60°C CO_2 for 15 min, the column temperature during the extraction was −25°C.
[d] SFE–GC sample residue re-extracted by sonicating in 10-ml methylene chloride for 14 h; ND = not detected.

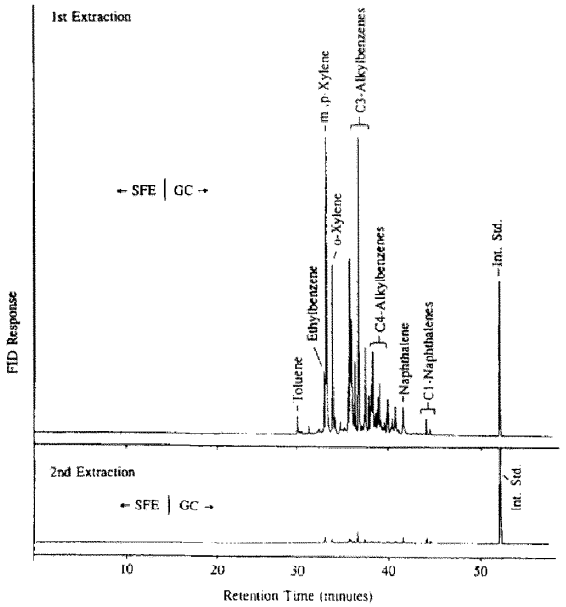

Fig. 7. Split SFE–GC–FID analysis of a gasoline-contaminated charcoal filter from a 1974 Chevette automobile. A 50-mg sample and a piece of filter paper spiked with the internal standard octahydroanthracene were placed on a bed of drying agent (molecular sieve 3A) inside an extraction cell and extracted for 15 min with 400 atm, 60°C, CO_2 at 0.6 ml/min. The extracted analytes were trapped onto a thick-film (5 μm) 30 m × 320 μm I.D. DB-1 capillary column at −25°C. After the extraction, the GC oven was heated to ca. 50°C/min to 40°C, then at 8°C/min to 300°C (top chromatogram). To ensure quantitative recoveries the sample was then extracted a second time under identical conditions as the first extract (lower chromatogram).

the GC column, and by using a drying agent to retain the extracted water from the sample so that column plugging could be eliminated. Furthermore, by using a thick-film (5 μm) column with a cryogenic trapping temperature of −25°C gasoline- to diesel-range organics can be determined by SFE–GC analysis using the same extraction and chromatography conditions with detection limits for individual compounds in the low ppb range. Good quantitative reproducibilities (R.S.D.s typically <5%) demonstrate that the SFE–GC technique is reproducible and that 1-g samples are representative of the bulk samples.

Acknowledgements

The financial support of the American Petroleum Institute, the US Department of Energy and the US Environmental Protection Agency (EMSL, Las Vegas), are gratefully acknowledged, as are instrument loans from ISCO.

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