

Determination of Petroleum Hydrocarbons in Contaminated Soils Using Solid-Phase Microextraction with Gas Chromatography–Mass Spectrometry

D. Cam* and S. Gagni

Montecatini Environmental Research Center, Via Ciro Menotti 48, 48023 Marina di Ravenna (RA), Italy

Abstract

Manual solid-phase microextraction (SPME) coupled with gas chromatography–mass spectrometry is investigated as a possible alternative for the determination of petroleum hydrocarbons in soils. Spiked onto an agricultural soil is a commercial diesel fuel (DF) with the following composition by weight: 12% linear alkanes, 52% saturated hydrocarbons (branched and cyclic), 21% alkylated aromatic hydrocarbons, 6% polycyclic aromatic hydrocarbons, and 9% unidentified compounds. The spiked soil samples are aged three days at room temperature before analysis. The optimal conditions for the SPME of DF from soils are examined and maximum sensitivity is obtained using a 100- μm polydimethylsiloxane fiber at a sampling temperature of 47°C by sonication both in the headspace and directly through a water medium. The reproducibility of the whole technique showed a relative standard deviation of 10%. The parameters that can influence the recovery of DF (such as the time of SPME extraction, the presence of organic solvent and water, and the matrix) are investigated. The linearity is verified in the range of 40 to 1200 mg/L for the direct injection of DF, 0.1 to 1 mg/L for the SPME of DF from water, and 1 to 50 mg/Kg of dry soil for the SPME of DF from soils. The detection limits are respectively 0.5 mg/L, 0.02 mg/L, and 0.1 mg/Kg of dry soil. The method is corroborated by comparing the results with those obtained by the traditional way.

Introduction

Soil and groundwater contamination resulting from petroleum hydrocarbon leaks pose a strong environmental hazard. As a result of many transport accidents over several decades, petroleum hydrocarbons have become a very common pollutant in the environment. The analysis of these compounds in solid matrices (such as soils, sediments, sludges, and hazardous wastes) traditionally requires several steps of extraction and preconcentration for the analytes and clean-up procedures. Moreover, these extraction methods need expensive and hazardous solvents that are undesirable for health and disposal rea-

sons. The Environmental Protection Agency (EPA) and other environmental organizations are attempting to find alternative extraction methods that minimize the use of solvents. Solid-phase microextraction (SPME) has been introduced as an alternative to traditional extraction techniques (1). It is a rapid, inexpensive, and solventless technique for the extraction of organic compounds from gaseous, liquid, and solid samples. An SPME fiber enables sampling and preconcentration in a single step, and then the adsorbed analytes are thermally desorbed from the polymeric fiber in a gas chromatograph (GC) injector. Many studies have supported the extremely appropriate capacity of the SPME–capillary GC system in the determination of general organic contaminant classes in environmental matrices such as air (2,3), water (4–8), and soil (9–13). However, the determination of organic contaminants in soils and sludges using SPME is not as widely studied as they are in air or water. In this study, the analytical system of SPME–capillary GC–mass spectrometry (MS) were used in the determination of a commercial diesel fuel (DF) in contaminated soil. SPME parameters were optimized in water and then used to determine contaminated soil by direct and headspace sampling modes. The optimal SPME conditions and equilibration times were defined using a 100- μm polydimethylsiloxane (PDMS) fiber and sonication at 47°C. The calibration was effectuated for the direct injection of DF, the direct and headspace sampling modes for DF from water, and headspace sampling modes for DFs from soils. The corresponding detection limits were estimated. Results obtained from applying the optimized SPME method on the determination of DF in soils were validated by comparing them with those obtained by traditional extraction.

Experimental

Materials

Standard DF (purchased from a petrol station) was dissolved in acetone and used for the preparation of standard solutions. For the direct injection of DF, the calibration ranged from 40 to 1200 mg/L. For the SPME of DF from distilled water the calibration

* Email: dcam@cramont.it.

range was from 0.1 to 1 mg/L, and for the SPME of DF from soil through distilled water the range was from 1 to 60 mg/Kg for dry soil. In order to prepare standard solutions of DF in water, a noted amount of standard solution in acetone was injected through a Hamilton (Bonaduz, Switzerland) syringe into the capped vial containing 13 mL of water. Standard samples of DF in soils were prepared by spiking a noted amount of standard solution in acetone into a dry agricultural soil.

Sample preparation

Soil matrix

An uncontaminated agricultural soil sample was collected in a

Table I. Summary of K_{fw} Data for Linear Alkanes, Pristane, and Phytane Obtained by Using a 100- μ m PDMS Fiber

Alkane	K_{fw}
C ₉	966
C ₁₀	779
C ₁₁	637
C ₁₂	830
C ₁₃	1061
C ₁₄	1034
C ₁₅	2211
C ₁₆	2880
C ₁₇	3078
Pristane	2688
C ₁₈	3314
Phytane	3392
C ₁₉	3644
C ₂₀	4045
C ₂₁	4029
C ₂₂	4369
C ₂₃	4270
C ₂₄	4817
C ₂₅	4874
C ₂₆	4628

field nearby Ravenna, Italy. This sample was controlled to contain no solvent-extractable organic matter (total organic matter was 1.56% \pm 0.05% and its moisture 6% \pm 1%) by thermogravimetry (TGA7, PerkinElmer, Norwalk, CT). Tests for impurities by extraction with SPME was carried out on this blank soil sample.

Diesel fuel

The contaminant diesel fuel (purchased at a gas station) underwent analysis and reported the following results relative to the organic carbon content: 12% linear alkanes from C₉ to C₂₅, 52% saturated hydrocarbons (branched and cyclic), 21% alkylated aromatic hydrocarbons, 6% polycyclic aromatic hydrocarbons, and 9% unidentified organic compounds.

Spiked soil samples

A suitable amount of the blank soil (approximately 100 g in total) was placed layer by layer (approximately 10 g per layer) alternating with the spiking operation (drop by drop of the pure DF standard per layer) in a 100-mL container with an open-top screw cap and Teflon-faced silicon septum. The container was capped immediately and hand shaken after each layer spiking. The same procedure was used to prepare spiked samples with a different concentration of DF.

Real soil samples

An agricultural soil was contaminated artificially by DF and introduced in a home-made pilot plant designated to a modelling study of the bioremediation process (COLOMBO-UE project) (14), and the real soil samples originated from an actual contaminated site.

SPME procedures

The manual SPME device and PDMS fiber (with different thicknesses of 7, 30, and 100 μ m) were purchased from Supelco (Bellefonte, PA). A definite amount of sample (from 0.1 to 1 g of spiked soil) was weighed in a 20-mL or 14-mL vial (or both), and then 13 mL of distilled water was added. The vial was immediately capped with a crimp-top septum silicon polytetrafluoroethylene-aluminum combination. The dimensions of the septum-sealed cylindrical vial were approximately 2 cm in diameter by 7 cm in height for the 20-mL vial that was used for headspace SPME and 2.5 cm in height for the 14-mL vial that was used for SPME direct extraction in water. The vial was then immersed in an ultrasonic bath at 47°C, and the entire fiber (which was fresh from thermal desorption) was immersed in the solution or exposed in the headspace (or both) for a selected time. A fresh sample was used for each measurement. Upon completion of exposure, the compounds-laden fiber was rapidly transferred to the GC, and a manual injection was effectuated. The same SPME fiber was used for the duration of the study; if a new SPME fiber was necessary, it was recalibrated.

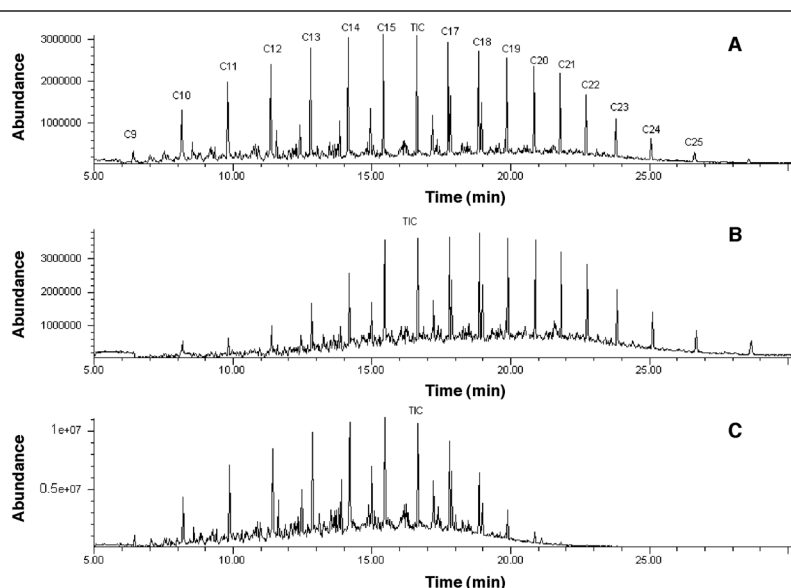


Figure 1. Distribution of diesel fuel by (A) the direct injection of the standard solution in acetone, (B) SPME direct extraction, and (C) headspace SPME of DF from water using a 100- μ m PDMS fiber.

GC-MS analysis

An HP (Palo Alto, CA) Model 5890 GC equipped with a Model 5970 mass selective detector was used. A ZEBRON (Phenomenex, Torrance, CA) column (30-m \times 0.25-mm i.d., 0.5- μ m film thickness) (95% methyl-5% phenyl polysiloxane) was used. A splitless mode was used for both the SPME and direct injection with the purge valve closed for 3 min. The inlet temperature was set at 280°C and 300°C (for SPME and direct injection, respectively) and for the detector chamber it was 300°C (for both SPME and direct injection). For thermal desorption, the

SPME fiber was left in the injector for 3 min. For direct injection, 2 μ L of the sample solution was injected manually. The column temperature was held initially at 50°C for 2 min, increased to 250°C at 10°C/min, and then held for 8 min. The quantitation of DF was based on the total GC-detectable hydrocarbons (defined as the sum of the resolved plus the unresolved aliphatic and aromatic hydrocarbons) that were quantitated with the external method using the base-line-correlated total area of the chromatogram. The crude reference DF over the entire analytical range was used as the response factor (RF) for the determination

of the total GC-detectable hydrocarbons. The RFs of the ion at m/z 85 for the C_9 - C_{25} linear alkanes were used for the determination of n -alkanes, and the average RF of ion 85 for pristane and phytane was used for the determination of branched alkanes.

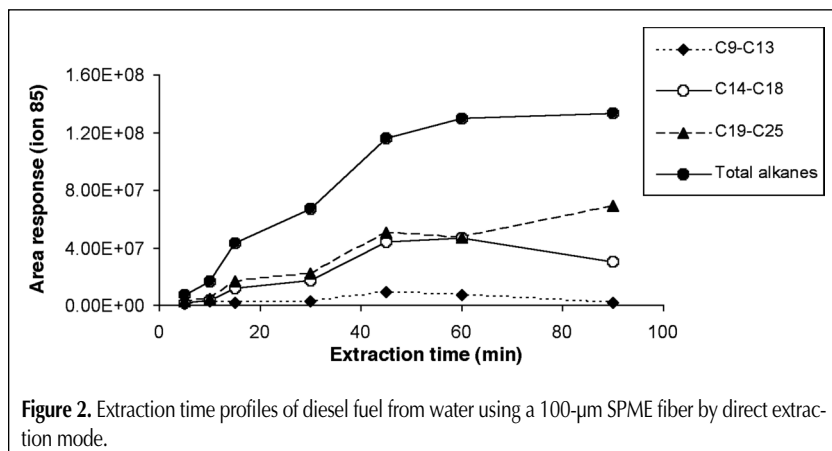


Figure 2. Extraction time profiles of diesel fuel from water using a 100- μ m SPME fiber by direct extraction mode.

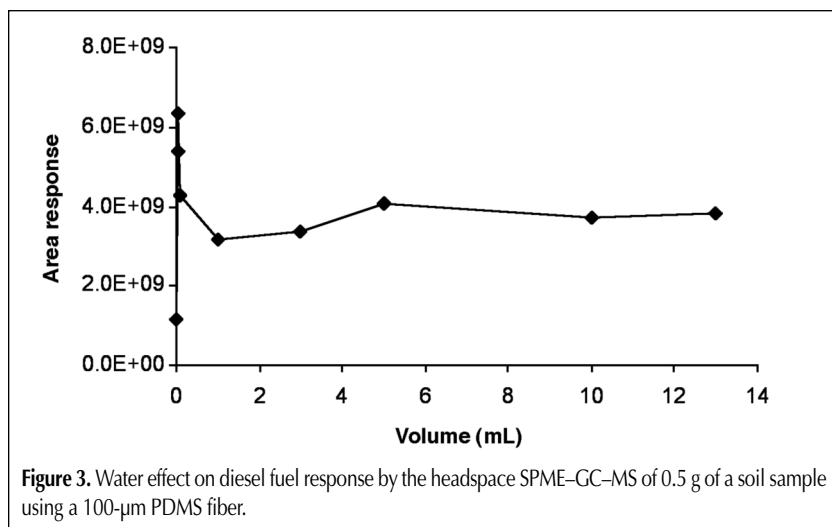


Figure 3. Water effect on diesel fuel response by the headspace SPME-GC-MS of 0.5 g of a soil sample using a 100- μ m PDMS fiber.

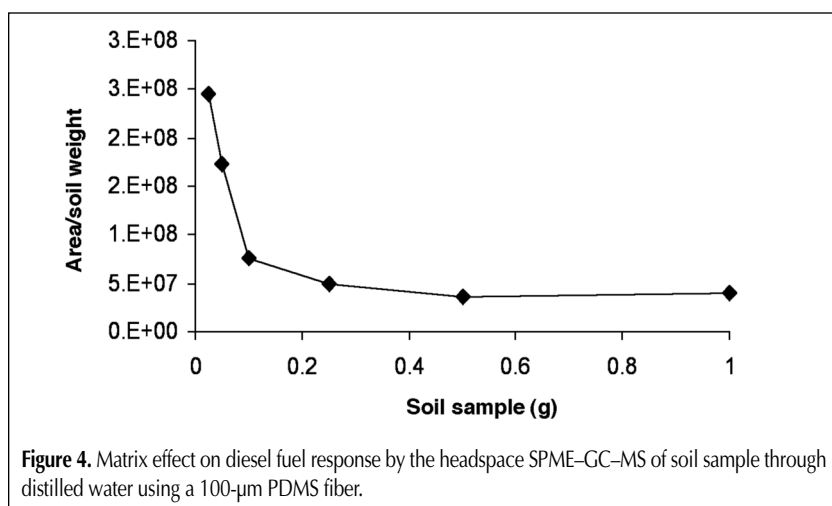


Figure 4. Matrix effect on diesel fuel response by the headspace SPME-GC-MS of soil sample through distilled water using a 100- μ m PDMS fiber.

Results and Discussion

Comparison of DF distribution by direct injection and the direct and headspace SPME of DF from water

Different SPME methods were developed in order to optimize the extraction of DF from soils. A PDMS fiber of 100- μ m thickness demonstrated the best extraction yield by sonication at 47°C. Figure 1 shows the comparison of DF distribution obtained by direct injection and the SPME direct and headspace extraction of DF from water. From the distribution of DF in Figure 1, it can be noticed that the direct extraction of DF from water is very suitable for the determination of mixtures of hydrocarbons from C_{15} to C_{26} , compared with the headspace sampling mode for mixtures of more volatile compounds ($< C_{15}$). However, the headspace SPME of DF from water is generally more sensitive than the direct sampling mode.

Influence of the extraction time by the direct SPME of DF from water

Figure 2 shows the extraction yield of total alkanes as well as the three principal fractions (C_9 - C_{13} , C_{14} - C_{18} , and C_{19} - C_{25}) as a function of the extraction time. The relative standard deviation of this method was 10% (calculated on 10 replicates). The time required to reach equilibrium was between 45 and 50 min for all the alkanes. For longer extraction times, an antagonistic phenomenon of absorption onto the PDMS fiber favoring high molecular-weight hydrocarbons can be noticed.

Calculation of the distribution constant

Table I reports the fiber-water distribution constant (K_{fw}) for the linear alkanes, pristane, and

phytane obtained by the direct extraction mode (45 min) of DF with SPME-PDMS. The K_{fw} calculation was based on the equation:

$$K_{fw} = nV_s/V_f(C_oV_s - n) \quad \text{Eq. 1}$$

Table II. Organic Solvent Effect on Diesel Fuel Response by Headspace SPME-GC-MS

Added solvent	Dielectric constant of added solvent	Diesel fuel absorbed on fiber (μg)	Diesel fuel absorbed on the fiber when no solvent was added
–	–	1.74	100
Acetone	20.7	2.11	121
Methanol	32.7	2.39	137
H ₂ O ₂	84.2	2.87	164

Table III. Summary of the Calibration Parameters Using the Total Ion Current Area for the Total DF, the Ion 85 Area for the Alkanes, and the Detection Limits* by GC-MS

GC-MS analysis mode				Total ion current area			Ion 85 area Detection limit
	Slope (10 ⁻⁶)	Intercept (10 ⁻⁶)	r ²	Slope (10 ⁻⁶)	Intercept (10 ⁻⁶)	r ²	
A [†]	6.9	-219	0.993	0.25	-3.5	0.999	3 mg/L
B [‡]	3880	-162	0.987	91.4	-10.2	0.991	0.04 mg/L
C [§]	8336	714	0.997	30.0	5.0	0.995	0.01 mg/L
D ^{**}	103	665	1	1.7	22.3	1	0.1 mg/Kg

* Defined as the concentration of analytes that cause a peak with a signal-to-noise ratio of 3.

[†] Direct injection of diesel fuel standard solutions in acetone.

[‡] SPME direct sampling mode from water.

[§] SPME headspace sampling mode from water.

** SPME headspace sampling mode of diesel fuel.

where n is the amount of each linear alkane partitioned into the coating, C_o is the initial concentration of analytes, V_s (equal to 13 mL) is the water sample volume, and V_f (equal to 0.65 μL) is the fiber volume (15). The K_{fw} value for the total considered DF was estimated to be equal to 3854. From Table I, it can be observed that the K_{fw} value of the individual DF component increased with the increasing molecular weight of the corresponding homologues. This observation adequately explained the antagonistic absorption behavior noted in Figure 2, because long time extractions favor the diffusion that is also of high molecular weight analytes towards the fiber, thus their absorption at expense of lower molecular weight hydrocarbons.

Effect of water on the extraction yield of DF from soils

Figure 3 reports the water influence on the DF response by headspace SPME-GC-MS. The addition of small amounts of water to the soil can facilitate the desorption and vaporization of analytes (16) because of the release of volatile organic compounds from their absorption sites in the soil by the polar water molecules. Figure 3 shows DF responses as a function of increasing the volume of added water into 0.5 g of dry soil sample using a headspace SPME-GC-MS procedure. An important increase in the responses for all the compounds can be observed with the addition of 30–70 μL of water. These results agreed with those obtained for the analysis of chlorobenzenes in spiked soil (12). A decrease and a stabilization in the responses were observed for volumes higher than 100 μL , although an improvement in sensitivity against the dry sample occurred (improvement by a factor of two when a volume of water that was 5 mL was added). Thus for the SPME of DF from soils, water was preferably used as the carrier medium. Moreover, the headspace sampling mode was necessary because direct extraction provoked damages on the polymeric fiber. This problem should be overcome using a membrane-protected SPME (7).

Effect of soil matrix on the extraction yield of DF from soils

The SPME of DF from soil samples was effected in the headspace through a water medium. Figure 4 reports the decrease of the extracted amount of DF onto the PDMS coating fiber when the amount of the soil sample is increased. It can be noticed that the yield of extraction decreased significantly (approximately 10 times) passing from 0.1 to 1 g of soil sample. However, no significant variation was observed when the added soil amount was over 0.5 g, probably because of the saturation of the water medium by soluble salts or organic matters present in the considered matrix. Therefore, the optimal SPME of DF from the considered soil matrix was established by using approximately 0.5 g of soil sample.

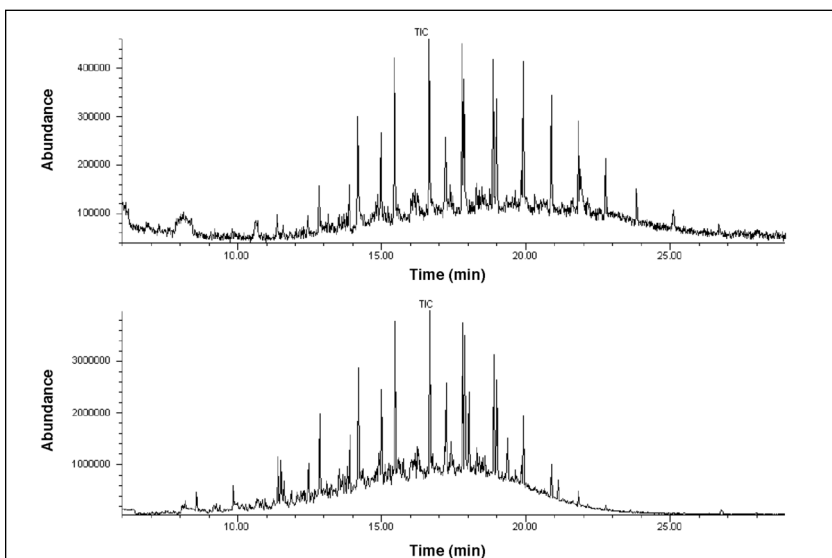


Figure 5. Distribution of a mixture of petroleum hydrocarbons by (A) the direct injection of the extract from a real soil sample by traditional extraction mode and (B) the headspace SPME of 0.5 g of the same sample through a water-acetone (12:1) medium.

Effect of organic solvent on the extraction yield of DF from soils

The SPME of DF from soil samples was effectuated in the headspace through a water medium in the presence of 8% (by weight) organic solvent. Table II reports the increase of the extracted amount of DF in the PDMS fiber coating when acetone, methanol, and hydrogen dioxide is added. The effect of organic solvents having a different dielectric constant such as acetone, methanol, and hydrogen peroxide was investigated for the optimized SPME method for the extraction of DF from soils through water. From Table II, it can be noticed that sensitivity increases for DF when solvent with an increasing dielectric constant is added. In fact, it is known that compounds have affinity for a phase of similar polarity, because the dielectric constant of water is very high ($\epsilon_{\text{H}_2\text{O}} = 78$). Thus, this should have more affinity with acetone, methanol, and H_2O_2 than with common organic compounds whose dielectric constants are very low and similar to that of PDMS (from 2.6 to 2.8 depending on the polymer molecular weight) (17). Therefore, the increase in the headspace SPME responses when adding solvent with a high dielectric constant should be a result of the fact that solvent molecules can help to liberate the analytes from the active sites on the soil and thus drag them from the matrix into the gas phase.

Calibrations and the detection limits

Table III reports the slopes, intercepts, and the detection limits of the calibration curves of DF by direct injection, SPME direct sampling from water, SPME headspace sampling from water, and SPME headspace sampling from soils. Linearity was verified in all considered concentration ranges. The headspace SPME of DF from soils demonstrated linearity in the concentration range from 1 to 50 g/Kg through a carrier medium composed of water–acetone (12:1 by volume).

Headspace SPME of petroleum hydrocarbons from real soil samples through water–acetone

Figure 5 shows the distribution of an unknown petroleum hydrocarbon extracted from a real soil sample (an adaptation of EPA Method 3550 optimized in our laboratory) (14) by direct injection and by the headspace SPME of the same sample through a water–acetone medium. It compared the distribution of petroleum hydrocarbons obtained by the traditional and new analytical method for real contaminated soil. Quantitative results gave 200 and 215 mg/Kg for dry soil, respectively. It should be noted that the sample was diluted five times with blank soil matrix in order to apply the previously mentioned optimized SPME method. The reproducibility of the optimized SPME of DF from soils was 10% calculated on four replicates.

Conclusion

SPME–GC–MS has been proven to be reliable in the determination of petroleum hydrocarbons both in water and soils. The procedure has been optimized using 100- μm polydimethyl siloxane by sonication. For solid matrices, water is preferably used as a carrier medium. The addition of some organic solvents

with a high dielectric constant to the matrix before extraction led to an increase in the sensitivity of headspace SPME. Good reproducibility of the method was obtained (relative standard deviation = 10%). The optimized method was applied to the analysis of a real soil sample giving good reproducibility and consistency with respect to the results obtained traditionally.

Optimized SPME can be proposed as an alternative method of analysis, which gives remarkable advantages because it consists of a fast, inexpensive, and solvent-free method of analysis. For every kind of contaminant or matrix, it is obviously necessary to use a methodical investigation in order to optimize the sampling conditions and identify the most suitable SPME fiber.

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