APPLICATION OF SOLID PHASE MICROEXTRACTION (SPME) IN PROFILING HYDROCARBONS IN OIL SPILL CASES

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Abstract.

In environmental forensic, it is extremely important to have a fast and reliable method in identifying sources of spilled oil and petroleum products. In this study, solid phase microextraction (SPME) method coupled to gas chromatography-mass spectrometry was developed for the analysis of hydrocarbons in diesel and petroleum contaminated soil samples. Optimization of SPME parameters such as extraction time, extraction temperature and desorption time, was performed using 100-µm polydimethylsiloxane (PDMS) fiber. These parameters were studied at three levels by means of a central composite experimental design and the optimum experimental conditions were determined using response surface method. The developed SPME method was applied to determine the profiles of hydrocarbons in several oil contaminated soil sample. The SPME method was also used to study the effects of weathering on the profiles of hydrocarbons in unleaded gasoline, diesel and kerosene contaminated soil samples. After several days, significant losses of the lighter hydrocarbons were observed compared to the heavier ones. From these data, SPME method can be used to differentiate possible candidate sources in oil spill cases.

Introduction

Gasoline, diesel and kerosene are all created from crude oil by a variety of refining and distillation processes. Each product is produced by the combination of multiple individual hydrocarbon compounds all of which have slightly different vaporization and boiling temperatures. Gasoline is the combination of many lower boiling range compounds while the middle boiling range compounds are used in differing proportions to create kerosene and diesel. The profile of hydrocarbons in oil may hence be used to characterize the oil. This enables the identification of the candidate source of oil spill cases. In forensic chemistry, ability to identify the sources of an oil spill is very important and hydrocarbon fingerprinting method is now realized as one of the fastest and reliable method for identifying the origin of oil spill cases.

In this study, a solid phase microextraction (SPME) method coupled to gas chromatography with mass spectrometry detector (GC-MSD) was developed for analyzing the profile of several types of oils. The simplicity of operation, sensitivity, selectivity, portability, and the solvent-free nature of the SPME method makes it a powerful tool for sample introduction method for gas chromatographic analyses of organic chemicals [1]. It is based on the enrichment of analytes on a polymer or adsorbent-coated fused-silica fiber either directly to the sample or its headspace. The extraction efficiency of SPME technique is dependent on several experimental parameters such as the extraction time, extraction temperature and desorption time [2,3]. These operating parameters were optimized using an experimental design approach that consisted of three stages; identifying the factors which may affect the result of an experiment, designing the experiment so that the effects of uncontrolled factors are minimized, and using statistical analysis to separate and evaluate the effects of the various factors involved. The optimized SPME method was used to analyze the effect of weathering on three types of oils: unleaded gasoline, diesel and kerosene.

EXPERIMENTAL

Preparation of spiked sample

Three types of oil (unleaded gasoline, diesel and kerosene) were used in this study. About 1 L of each type of oil was poured into three separate plots of soil. After 2 weeks, the contaminated soil for each plot was mixed thoroughly, sieved and stored in an amber bottle at -4 ˚C until analysed for optimizing the experimental conditions.

For the weathering study, three plots of soil measuring 2’ x 1.5’ each were chosen for three types of oil (unleaded gasoline, diesel and kerosene). Each plot was divided into 20 small sections. About 1 L of oil sample was poured into each dedicated plot. For each analysis, 100 g of two small sections of soil were thoroughly mixed and a 5 g sample was placed in a headspace vial (10 mL volume) and capped for SPME analysis. Soil was analysed 1 day, 2 days, 1 week, 2 weeks and 1 month after oil spillage.

Solid phase microextraction (SPME)

A 100-µm polydimethylsiloxane (PDMS) fiber (Supelco, Bellafonte, Pennsylvania, USA) was conditioned in a hot GC injection port at 250 °C for 30-60 min prior to sample extraction. In the optimization study, the SPME needle was inserted through the septum of the vial and the fiber was released and exposed to the headspace of the sample at a specified temperature (maintained using a water bath) for a specified extraction time. The fiber was then withdrawn, SPME needle was removed from the headspace and immediately injected into the gas chromatography (GC) with a desorption time of 35 sec. For the weathering study, the sample was extracted at 90 °C for 45 min. The compounds were then transferred into the GC with desorption time of 35 sec.

Experimental design

Statistical software package Design-Expert 6.0.6, an expert system for the design and analysis of experiments was purchased from Stat-Ease Inc., Minneapolis. Preliminary work on the optimization of SPME for the extraction of hydrocarbons in soil using three experimental variables (extraction temperature, extraction time and desorption time) showed that the desorption time was not significant within the range 20 to 50 seconds and from the response surface analysis, optimum extraction was achieved at desorption time of 35 sec. Optimization using central composite design was then focused on two experimental variables, namely extraction temperature and extraction time. The response variables selected were the GC area count for several common compounds of unleaded gasoline, diesel and kerosene. The response variables selected were the gas chromatograph area count for tridecane, hexadecane, and octadecane. The design matrix of the central composite design is shown in Table 1. The order of these experiments was randomized to remove any systematic error.

GC-MS analysis

GC-MS were performed on Agilent Technologies 6890 Network GC System with Agilent Technologies 5973 inert Mass Selective Detector. The flow rates of gases were set to manufacturer’s specifications. The column used was a HP-5MS fused silica capillary column, 30.0 m x 250 µm I.D and 0.25 µm capillary thickness. Injections were made in the splitless mode. The temperature programmed was set at an initial 60 °C for 2 min, followed by an increase of 10 °C min^{-1} to 200 °C and held for 15 min. Both the injector temperature and the detector temperature were set at 250 °C. Compounds were identified by matching their mass spectra with the NIST spectral library with a resemblance percentage above 90%.

Table 1: Central composite design of the optimization experiment

Run Order	Extraction Time (min)	Extraction Temperature (°C)
1	50.0	60.0
2	80.0	60.0
3	50.0	90.0
4	80.0	90.0
5	65.0	75.0
6	65.0	75.0
7	43.8	75.0
8	86.2	75.0
9	65.0	53.8
10	65.0	96.2
11	65.0	46.0
12	65.0	40.0

Results And Discussion

Optimization of SPME conditions

The results from the central composite design were fitted to a quadratic model. Analysis of variance (ANOVA) was performed on the design in order to determine which variables (A:extraction time and B:extraction temperature), if any, had a significant effect on the recovery of each compound. From the statistical analysis of the experimental design, it was found that extraction temperature was the important factor influencing the amount of hexadecane and octadecane extracted from soil. The influence of temperature on the extracted amount of hexadecane and octadecane was further studied using spiked sample with SPME extraction time of 45 min and desorption time of 35 sec. It was found that in both cases, the amount extracted increases as the extraction temperature increases, but at temperature more than 90 °C the amount of hexadecane and octadecane extracted decreases. Based on these analyses, the optimum operating conditions for SPME were: extraction time 45 min, extraction temperature 90 °C and desorption time 35 sec.

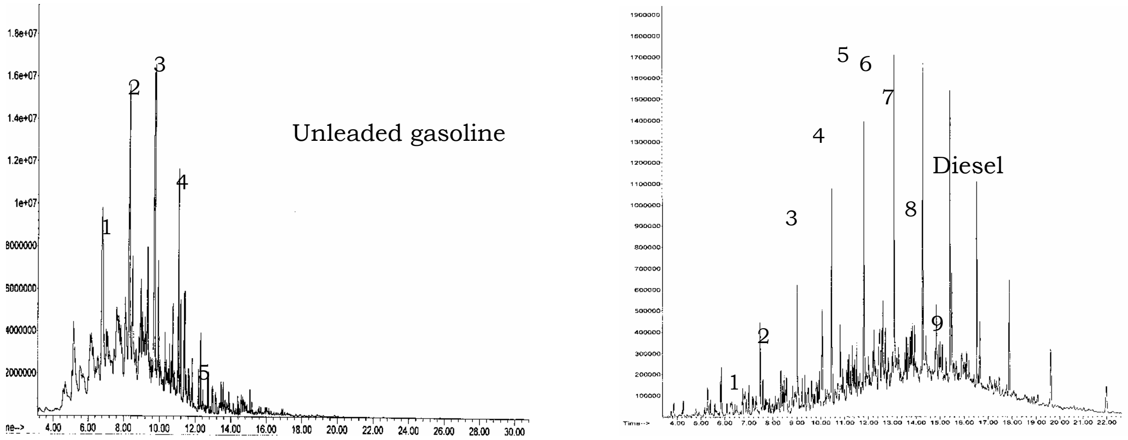
Profile of hydrocarbons in spiked sample

The optimized SPME method was applied in the extraction of unleaded gasoline, diesel and kerosene from spiked soil samples.

Gasoline is a complex mixture of hydrocarbons compounds predominantly in the range of $C_3 - C_{12}$. It is the light distillate product of petroleum containing more lower molecular weight hydrocarbons but higher fraction of both light hydrocarbons and aromatics. It contains about 41% alkanes with undecane, dodecane, tridecane and tetradecane as major compounds. In the profile of hydrocarbons in gasoline [Figure 1(a)], the hydrocarbons were eluted in the range between 5.50 min to 12.00 min.

Kerosene is a light end middle distillate of petroleum. It is composed of hydrocarbons mostly in the range of $C_9 - C_{16}$. It contains 50.5% aliphatic hydrocarbons and 30.9% naphthenes, the rest being aromatics hydrocarbons. Major compounds in kerosene are dodecane, tridecane, tetradecane and pentadecane. The hydrocarbons of kerosene were eluted in the range of 7.00 min to 13.50 min [Figure 1(b)].

iesel is a higher boiling point fraction composed of essentially C_{10} to C_{25} aliphatic hydrocarbons. It has a wide range of polyaromatic hydrocarbons such as naphthalenes and phenanthrenes. Diesel contains 55% paraffins, 24% aromatics, 12% naphthenes, and 5% olefins. It is similar in chemical composition to kerosene with the exception of additives. As shown in Figure 1, the hydrocarbon profile of diesel [Figure 1(b)] is quite similar to that of kerosene [Figure 1(c)], with additional compounds eluted up to 18.00 min.



(a) (b)

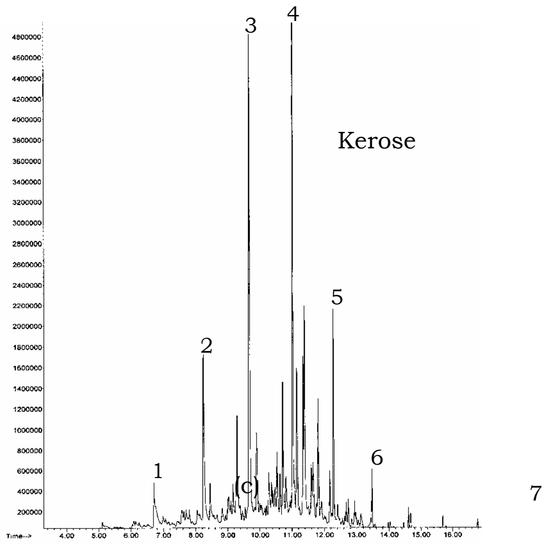


Figure 1. GC-MS total ion chromatogram of
(a) unleaded gasoline (b) diesel and (c) kerosene recovered from spiked soil sample.
Identification of compounds:
1: undecane 2: dodecane 3: tridecane
4: tetradecane 5: pentadecane 6: hexadecane 7: heptadecane 8: octadecane 9: nonadecane

Effects of weathering on oil hydrocarbon fingerprinting

When oil or petroleum products are accidentally released to the environment, they are immediately subjected to a wide variety of weathering process that can affect their chemical properties [4]. In the short term after a spill (hours to days), evaporation is the single most important and dominant weathering process, in particular for the light petroleum products. The lower boiling points components tend to volatilize more rapidly than the components of higher boiling points. The hydrocarbon profile of the spiked soil was obtained using SPME method using the optimized conditions. Figure 2 shows the profile of unleaded gasoline in soil after differing levels of weathering. It was found that after 1 week, the more volatile compounds, dodecane and tetradecane were reduced by 46% and 44% respectively while naphthalene 1, 6, 7-trimethyl was reduced by less than 1%. After 2 weeks, dodecane and tetradecane were reduced by 98% while naphthalene 1, 6, 7-trimethyl was reduced by 96% and after one month the more volatile compounds (dodecane and tetradecane) were undetected while the amount of naphthalene 1, 6, 7-trimethyl was further reduced by 96%.

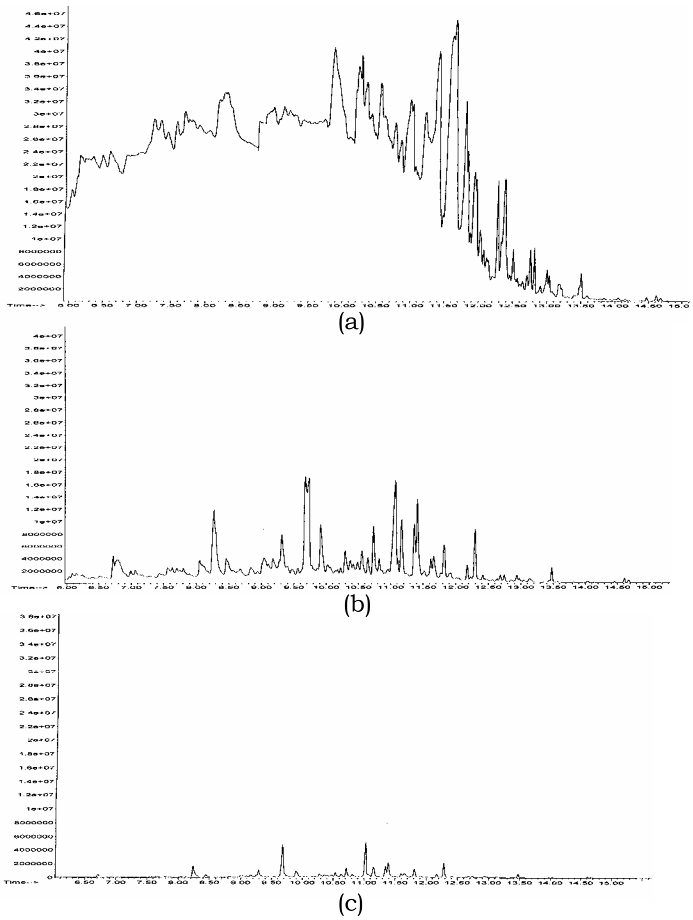


Figure 2. Hydrocarbon fingerprint of unleaded gasoline in soil sampled (a) 2 days, (b) 1 week and (c) 2 weeks after spillage.

Figure 3 shows the profile of diesel in soil after differing levels of weathering. These chromatograms clearly showed a decreased in peak intensity due to volatilization. It was found that after 2 weeks, the most volatile compound (dodecane) was not detected while tridecane, pentadecane and heptadecane were reduced by 93%, 92% and 88% respectively. However, after one month most compounds were reduced by 99%.

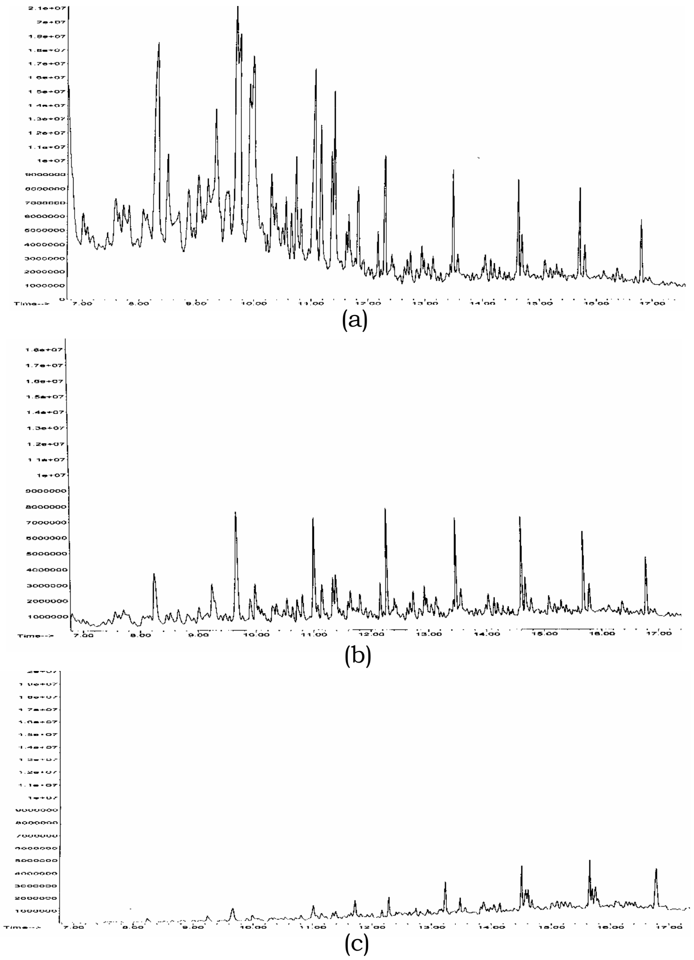
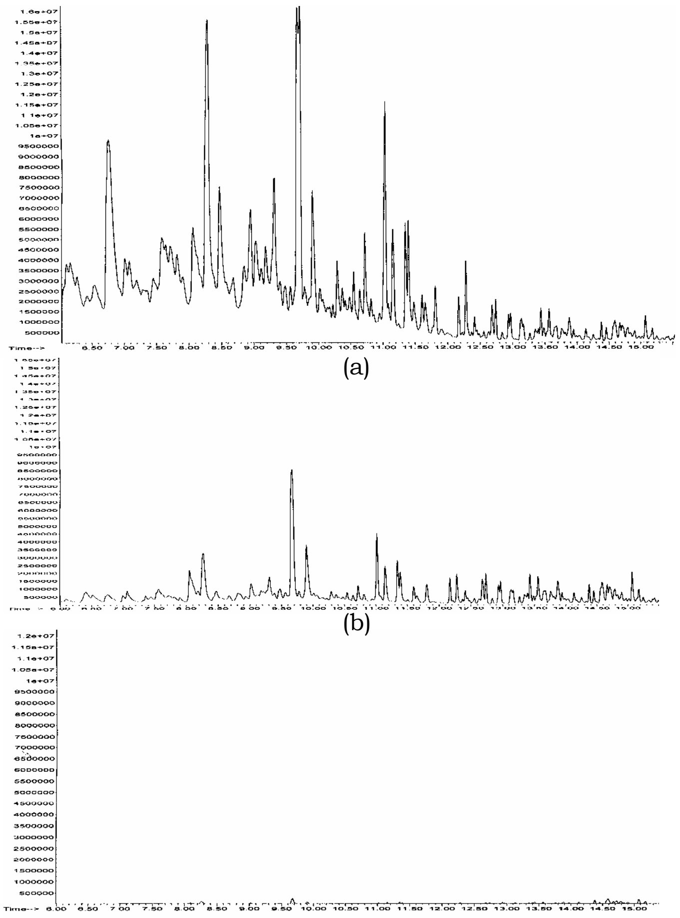


Figure 3. Hydrocarbon fingerprint of diesel in soil sampled (a) 2 days, (b) 1 week and (c) 2 weeks after spillage.

Figure 4 shows the profile of kerosene in soil after differing levels of weathering. After 2 weeks, most of the compounds in kerosene had almost disappeared. Tetradecane and pentadecane had disappeared by 96% while heptadecane had 86% evaporated. After 1 month these compounds were almost insignificant in the soil sample analysed.

CONCLUSIONS

The use of SPME-GC-MSD provides a reliable method for hydrocarbon fingerprinting of oil from soil. SPME technique, which enables the simultaneous extraction and pre-concentration steps, has been the method of choice for the analysis of these compounds in soil because it is fast, solvent-less extraction method, inexpensive and can handle the matrix sample directly. Therefore, it reduces analysis time (allowing processing a higher number of samples) and avoids loss of analytes. Study of weathered oils of spiked soil samples using SPME was able to show the change in the profiles of their chemical properties.



(a)

(b)

(c)

Figure 4. Hydrocarbon fingerprint of kerosene in soil sampled (a) 2 days, (b) 1 week and (c) 2 weeks after spillage.

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