The Simultaneous Analysis of Benzene, Toluene, Ethylbenzene, *o,m,p*-Xylenes and Total Petroleum Hydrocarbons in Soil by GC-FID after Ultra-Sonication

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A simultaneous determination method of BTEX (benzene, toluene, ethylbenzene, o,m,p-xylene) and TPH (kerosene, diesel, jet fuel and bunker C) in soil with gas chromatography/flame ionization detection (GC-FID) was described. The effects of extraction method, extraction solvent, solvent volume and extraction time on the extraction performance were studied. A sonication method was simpler and more efficient than Soxhlet or shaking methods. Sonication with 10 mL of acetone/methylene chloride (1 : 1, v/v) for 10 min was found to be optimal extraction conditions for 20 g of soil. Peak shapes and quantification of BTEX and TPH were excellent, with linear calibration curves over a wide range of 1-500 mg/L for BTEX and 10-5000 mg/L for TPH. Good reproducibilities by sonication were obtained, with the RSD values below 10%. By using about 20 g of soil, detection limits were 0.8 mg/L for BTEX and 10 mg/L for TPH. The advantages of this procedure are the use of simple and common equipment, reduced volumes of organic solvents, rapid extraction periods of less than 20 min, and simultaneous analysis of volatile and semivolatile compounds.

Introduction

In 1996, Korean government enforced the Soil Environment Conservation Act. The purpose of this Act is to appropriately maintain and preserve the soil and, thereby, to provide a healthy and agreeable life for the general public by preventing harm resulting from the soil contamination, to the general public and the environment.[1] Petroleum is complex soil contamination substance, which is originated from a variety of sources, including leakage of fuel storage tank, crude oil spills, and production of waste products.

Identifying and quantifying the contaminants spilled in the underground are of primary importance in providing a better regulation to petroleum contamination in soil. There have been many studies concerned with hydrocarbon pollutants in soil environments.[2-9] The most common approach to the monitoring of a spilled oil relies on analyses by gas chromatography. But the procedures used until now to extract petroleum hydrocarbons from soil have several potential disadvantages.

Soxhlet extraction has been accepted for extraction of semivolatile and nonvolatile organic compounds from soil matrices.[1,10] However, this method has the disadvantages that high volatile compounds in soil samples may increase variability in the analysis and large volumes of solvent are used. Moreover, the Soxhlet extraction requires up to 8 h of extraction and specialized apparatus, which may be inappropriate for large numbers of samples. A mechanical shaking method may be used interchangeably with Soxhlet and has been tested for soils.[1,11] This method limits the contact between solvent and soil micropores, thus giving poor extraction efficiency. Eckert-Tilotta *et al.*[12] used a supercritical fluid extraction (SFE) method to extract petroleum hydrocarbons in soil. This method is more rapid than Soxhlet and eliminates the use of organic solvents. Unfortunately, SFE instrumentation is expensive, and may be subject to low accuracy and high variability when used to extract natural soil samples.[13] Accelerated solvent extraction, involving higher temperatures and pressures, was found to be generally equivalent to the Soxhlet extraction[14] but also requires specialized and expensive equipment.

Sonication methods have been tested for the extraction of pollutants in soils.[15-17] The methods until now consume large quantities of solvent, are labor intensive, and require special equipment. A rapid and reliable extraction method is needed to accurately analyze a large number of soil samples.

The overall objective of this study is to evaluate a sonication method for the rapid and simultaneous extraction of volatile and semivolatile petroleum hydrocarbons from soils. Optimum extraction time, extraction solvent and solvent volume were determined for the better extraction efficiency.

Experimental Section

Materials. Benzene, toluene, ethylbenzene, *o,m,p*-xylene and fluorobenzene (internal standard) were obtained from Sigma (St. Louis, MO, USA). Total petroleum hydrocarbons (gasoline, diesel, jet fuel and bunker C) were kinedly presented from commertial tanks. Analytical grade of sodium sulfate, methanol, methylene chloride and acetone (E. Merck, Darmstadt, F.R.G.) was used as reagents and solvents.

Soil samples. Noncontaminated soils that were amended with petroleum hydrocarbons were obtained in the vicinity of Kongju National University, Kongju, Korea. For the test of solvents on soils with different textures, soils were chosen based on sand and clay content. The contents of total organic compounds and moisture in clay were about 3% and 9%, and those of sand were < 1.0% and 5%, respectively. The

spiking procedure was follows: Briefly, 500 g of dried uncontaminated soil was mixed in a porcelain dish in ice bath with a solution containing BTEX or TPH in acetone.

Contaminated soils were selected from two sites based on the type of contaminant. Soil 1 was from the underground contaminated by gasoline and kerosene in the vicinity of the tank in Songnam, Kyunggi and soil 2 from the underground contaminated by Bunker-C in the vicinity of the oil tank in Suwan, Kyunggi.

Extraction by Soxhlet. Twenty grams of each soil was mixed with 10 g of anhydrous sodium sulfate and extracted using 100 mL of methylene chloride for 8 h. The extraction solutions were concentrated in a Kuderna-Danish (K-D) concentrator to 20 mL and sealed in glass vials. A 2 μL aliquot of the final solution was injected in a GC.

Extraction by shaking. In a 50 mL glass vial, was placed 20 g of the soil and 10 g of sodium sulfate. Twenty milliliters of methylene chloride and 100 μL of flourobenzene (4000 mg/L in methanol) were added to the solution and mixed by mechanical shaking for 20 min at room temperature. The two phases were separated by centrifugation (5 min at 1500 × g) and the organic phase was transferred into a 20 mL glass test tube and a 2 μL aliquot of the final solution was injected in a GC.

Extraction by sonication. The extraction was carried out using common ultra-sonicator (BRANSON 5210 R-DTH, USA). The extraction solvents were methanol, acetone, methylene chloride or their optimal compositions. In a 50 mL glass vial, was placed about 20 g of the soil and 100 μL of flourobenzene (4000 mg/L in MeOH) as an internal standard was added to the solution, and the sample was sonicated with various volume of methylene chloride for 5-40 min. The two phases were separated by standing for several minutes and the organic phase was transferred into a 20 mL glass test tube and a 2 μL aliquot of the final solution was injected in a GC.

Gas chromatography. All GC experiments were performed with a Yeong Lin 800 M (YL) gas chromatography with a flame ionization detector (FID). A fused-silica capillary column (50 mL × 0.25 mm I.D.× 0.25 μL F.T.) coated with cross-linked 5% phenylmethylsilicone, was attached to the injection port. The flow rate of carrier gas (helium) was 1.1 mL/min, that of detector make-up gas (helium) was 25 mL/min and that of detector air and hydrogen were 300 and 35 mL/min, respectively. The injection port temperature was 330 °C, the detector temperature 330 °C, and the oven temperature was programmed from 40 (2 min) to 330 °C at 8 °C/min (holding for 5 min). A 2 μL aliquot of the final solution was injected in the GC (split ratio; 1 : 15).

Calibration graph and quantitation. Calibration graphs for benzene, toluene, ethylbenzene and o,m,p-xylene were established by extraction after adding 20, 50, 100, 250, 500, 1000 and 2500 μg of each standards and 400 μg of internal standard (flourobenzene) in 20 g of soil. The ratios of the peak area of standards to that of internal standard were used in the quantification of the compounds. Those of gasoline, diesel, jet fuel and bunker C were established by extraction after adding 0.2, 0.5, 1.0, 2.5, 5.0 10.0 and 20.0 mg of each standard in 20 g of soil. The peak areas of standards were used in the quantification of these compounds.

Results and Discussion

Chromatogram. The GC chromatogram of total dissolved BTEX (benzene, toluene, ethylbenzene, *o,m,p*-xylene) and TPH (kerosene, diesel and bunker C) in methylene chloride is shown in Figure 1. The peaks except for those of *m*- and *p*-xylene were well separated and showed typical GC-FID response of petroleum hydrocarbons. When acetone or methylene chloride was used as the dissolving solvent, solvent peaks were not overlapped with those of volatile compounds such as benzene and toluene. But methanol was tailed to the peak of benzene at the operating condition, therefore its use as extraction solvent may make a problem in exact quantitation of volatile compounds.

The extraction performance by shaking, soxhlet and sonication. The extraction yield was investigated in three different extraction methods of soxhlet, shaking and sonication. The procedures described here were applied to soil samples taken from two contaminated areas. For quantitation of BTEX, internal standard (fluorobenzene) were added to the soil samples prior to the procedure.

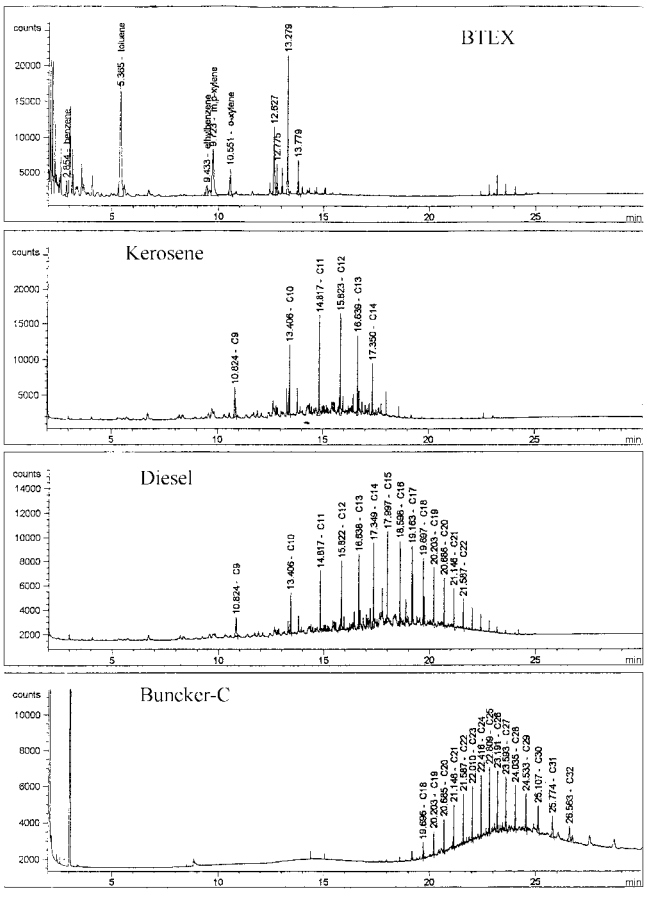

Figure 1. GC chromatogram of total dissolved BTEX (benzene, toluene, ethylbenzene, *o,m,p*-xylene) and TPH (kerosene, diesel and bunker C) in methylene chloride.

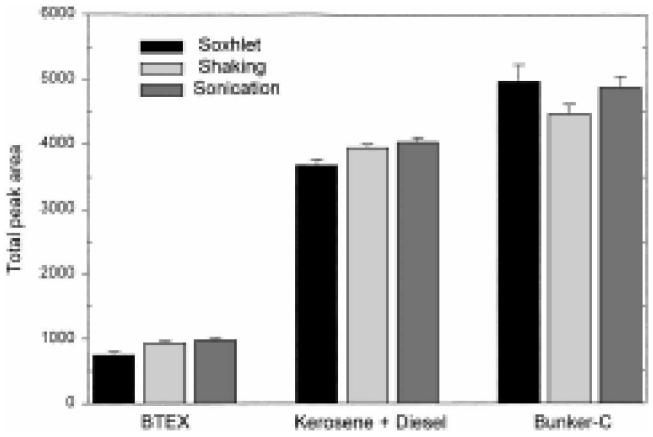

Figure 2. The extraction performance by soxhlet, shaking and sonication.

The results of the analysis are shown in Figure 2. As shown in Figure 2, most of the values resulting from the sonication extraction were almost same as or slightly higher than those resulting from the Soxhlet or shaking. The loss of volatile compounds was made during application of Soxhlet extraction since solvent evaporation occurs at some stage during sample recovery. But during extraction by shaking and sonication, volatile compounds such as BTEX remain in solvent, and quantitatively retaining the compounds. The results indicate that sonication has the advantage of retaining volatile compounds during recovery of aliphatic hydrocarbons and is more effective extraction method for the soil than the other two methods.

The development of extraction method by sonication. Sonication extraction using different organic solvent or solvent mixtures is a well-established technique for the efficient extraction of a variety of organic pollutants from soil samples. However, the simultaneous analysis of volatile and semivolatile hydrocarbons, and the minimum use of extraction solvent has not been reported as far as we know. We studied here the effect of various extraction solvents, solvent volume and extraction time on the extraction performance of BTEX and TPH.

The effect of various extraction solvents and time on the extraction performance. The purpose of this experiment was to assess the extraction ability of several solvents by the sonication method. The choice of solvent is critical in developing an extraction protocol. Strongly adsorbed compounds will be affected by the soil texture and moisture content. As extraction solvents, we tested methanol, acetone, methylene chloride, methanol/methylene chloride (1 : 1, v/v) and acetone/methylene chloride (1 : 1, v/v). The soils used here were those taken from two contaminated areas as described in Experimental. The solvent volume and sonication time were applied with 20 mL and 10 min for all sample extraction in this experiment, respectively.

The results of the analysis are given in Figure 3. Methanol or acetone extracts the BTEX more effectively from the soil matrix than methylene chloride, but methylene chloride provides more effective extractability to heavy hydrocarbons.

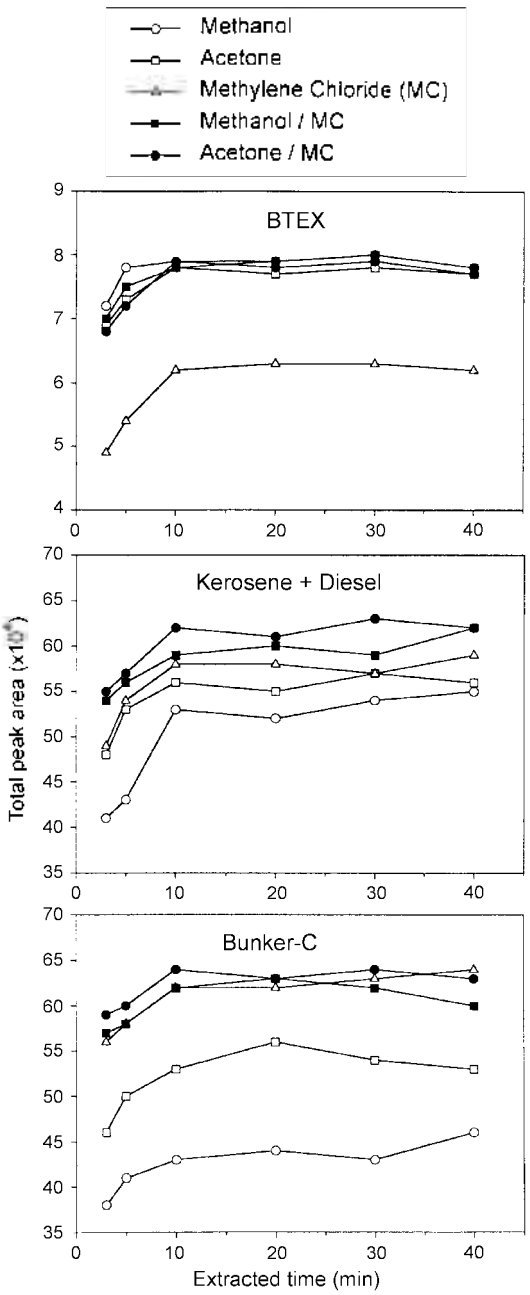

Figure 3. The effect of extraction solvents and time on the extraction performance of BTEX, kerosene + diesel and bunker-C.

The use of methylene chloride mixture with methanol or acetone significantly improved the extractability of the BTEX and TPH from soil compared to the use of a single solvent. An interesting advantage about the use of acetone/methylene chloride (1 : 1, v/v) is that solvent peak of methylene chloride or acetone is not overapped with that of benzene. Therefore, we selected a mixture of acetone/methylene chloride (1 : 1, v/v) as extraction solvent.

The extraction time was varied in the range from 3 to 40 min. When 20 g of the sample and 10 mL of the acetone/methylene chloride (1 : 1, v/v) as extraction solvent were used, amounts extracted for 10 min were appeared as maximum. Therefore, it can be concluded that the described soni-

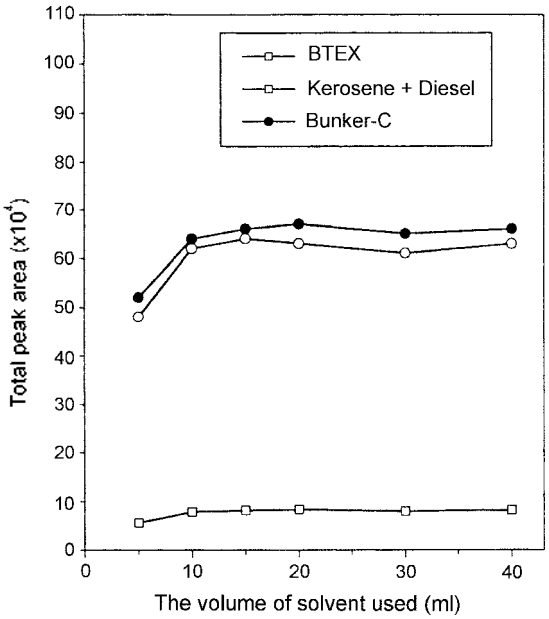

Figure 4. The effect of solvent volume on the extraction performance. (Total peak area was calculated by the peak area × solvent volume to correct the dilution effect by the volume of solvent used)

cation method is required less time to be taken for extraction compared to other two methods.

The effect of solvent volume on the extraction performance. On the basis of the results from the assessment of the extraction ability of several solvents, we selected acetone/methylene chloride (1 : 1, v/v) as extraction solvent. In this experiment, the extractability of BTEX and TPH from soil was evaluated as affected by solvent volume. In this experiment was used 20 g of soil taken from two contaminated areas and the sonication was performed for 10 min. As shown in Figure 4, amounts extracted with more than 10 mL of the solvent volume were appeared consistantly as maximum. But amounts extracted with 5 mL of the solvent volume were significantly decreased. Therefore, we conclude that the minimum volume of solvent for 20 g of soil is 10 mL.

Quality control of the described procedure. The parameters of various extraction solvents, solvent volume and extraction time on the extraction performance of BTEX and TPH were determined. Sonication with 10 mL of acetone/methylene chloride (1 : 1, v/v) for 10 min was found to be optimal extraction conditions for 20 g of soil. We performed here the validation of the procedure at the conditions described before.

Linearity. Examination of typical standard curves by computing a regression line of peak area ratios of BTEX to internal standard on concentration using a least-squares fit demonstrated a linear relationship with correlation coefficients being consistently greater than 0.9999. Standard curves of TPH were made by computing a regression line of peak area of TPH on concentration using a least-squares method. The lines of best fit for these compounds are shown in Table 1.

Table 1. Typical standard curves by computing a regression line of BTEX and TPH

Group	Compounds	Linear regression	Correlation coefficient
BTEX	Benzene	y = 0.0271x + 0.0710	0.9999
	Toluene	y = 0.0273x + 0.0608	0.9999
	Ethylbenzene	y = 0.0323x + 0.0651	1.000
	m,p-Xylene	y = 0.0196x + 0.0561	1.000
	o-Xylene	y = 0.0092x + 0.0550	0.9999
TPH	Kerosene	y = 0.478x + 0.713	0.9999
	Diesel	y = 0.460x - 0.600	0.9989
	Jet Oil	y = 0.468x - 0.783	0.9994
	Bunker-C	y = 0.458x + 0.065	0.9998

Table 2. Recovery of BTEX and TPH from soil by sonication (n=5)

Compounds	Recovery (%) SD		
	Clay	Clay + Sand	Sand
BTEX	88.9 ± 3.2	92.4 ± 4.3	98.3 ± 4.5
Kerosene+Diesel	87.8 ± 3.6	91.3 ± 4.4	98.9 ± 5.2
Bunker-C	86.5 ± 4.9	90.5 ± 4.1	95.5 ± 6.2

SD = standard deviation

Recovery. Several soil samples of various composition were prepared and the relative recovery was calculated by percentage of BTEX and TPH recovered (Table 2). Adsorbed compounds were affected by the soil texture. Generally, clay adsorbed more strongly the hydrocarbons than sand, thus it results in the decrease of extraction yield. High molecule hydrocarbons such as Bunker-C were adsorbed

Table 3. Within-run and Day-to-Day precision and accuracy of BTEX and TPH

Compounds	Added (mg/kg)	Found (mg/kg), Mean ± SD (RSD)	
		Within-run (n=10)	Day-to-Day (n=5)
BTEX	35.0	33.9 ± 2.1 (6.1%)	38.7 ± 3.6 (9.2%)
Kerosene+Diesel	570	588 ± 40 (6.9%)	552 ± 54 (9.8%)
Bunker-C	400	393 ± 22 (5.6%)	390 ± 33 (8.3%)

SD = standard deviation; RSD = relative standard deviation

Table 4. Method detection limits (MDL) of BTEX and TPH

Group	Hydrocarbons	MDL (mg/kg)	
		Each	Total
BTEX	Benzene	0.1	0.8
	Toluene	0.1	
	Ethylbenzene	0.1	
	m,p-Xylene	0.3	
	o-Xylene	0.2	
TPH	Kerosene	2.0	10.0
	Diesel	2.0	
	Jet	2.0	
	Bunker-C	4.0	

more strongly in clay than BTEX, because of their low polarity and high lipophilicity. The mean recoveries were about 93% at the concentration of 35 mg/L of BTEX and about 90% at the concentration of 400 mg/L of Bunker-C.

Precision and accuracy. The reproducibility of the assay was very good, as shown in Table 3. For five independent determinations at the concentration of 35 mg/L of BTEX and of about 500 mg/L of TPH, the coefficient of variation was less than 10%.

Method detection limit. Method detection limits were 0.8 mg/L for BTEX and 10 mg/L for TPH based upon an assayed soil weight of 10 g (Table 4). Method detection limits were defined by a minimum signal-to-noise ratio of 8 and coefficients of variation for replicate determinations (n=5) of 15% or less.

Conclusions

For the rapid and simultaneous extraction of volatile and semivolatile petroleum hydrocarbons from soils, a sonication method was used. Sonication with 10 mL of acetone/methylene chloride (1 : 1, v/v) for 10 min was found to be the optimal extraction conditions for 20 g of soil. The increasing extraction efficiency may be due to more complete contact with the soil micropores. In conclusion, the advantages of this procedure are the use of simple and common equipment, reduced volumes of organic solvents, rapid extraction periods of less than 20 min, and simultaneous analysis of volatile and semivolatile compounds. Therefore, we recommend this method to be used as an analytical method of BTEX and TPH in the Soil Environment Conservation Act.

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