

Extraction Characteristics and Quantitational Methods for Total Petroleum Hydrocarbons in Soil

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Quantitation methods of total petroleum hydrocarbons to determinate oil contaminated level in soil were discussed. Extraction characteristics of several pretreatment methods and practical detection limit and reappearances in gas chromatography/mass spectrometry with each pretreatment method were investigated. The obtained results showed that the newly adopted quantitation method and mechanical shaking extraction method using methanol with extraction solvent are more practical and applicable to real sample than the conventional methods. In applying these methods to gasoline, kerosene, fuel oil which are major source of soil contamination, the practical quantitation limit and % relative standard deviation was able to determine with range of 2.5 - 10 ppm, 5 - 7 %.

Key words : Soil contamination, Total petroleum hydrocarbon(TPH), Extraction of TPH, Quantitation of TPH

1. Introduction

Throughout the 20th century there has been a rapid increase in contamination of soil with oil and its derivatives, due to petroleum spills, industrial wastes, and transport and storage accidents¹⁻³). Among the environmental influences known to affect biodegradation of soil petroleum hydrocarbons, temperature and nutrient availability are two of the more important, particularly in cold-region soils⁵). Hydrocarbon pollution of the subsurface, especially in unsaturated soils, has become a big problem with the development of the petrochemical industry and installation of numerous petrol stations and underground pipes⁴).

Physical, chemical and biological technologies have been developed to remove hydrocarbon pollutants from soils and restore environmental quality. However, costs are high, and many techniques are difficult to use for in-situ remediation. It still remains necessary to study the natural attenuation of hydrocarbons in soil and to develop simple cost-effective techniques for

enhanced remediation⁴). The TPH method is extraction, quantitation method of oil-contaminated level from soil, highly divided into gasoline range organics (GRO) and diesel range organics (DRO). A gasoline comprises low molecular weight alkanes (C5-C10). A large proportion of gasoline is made up of BTEX (benzene, toluene, ethylbenzene, and m-, o- and p-xylene) components, which are relatively soluble and would degrade readily under the right environmental conditions⁵). If more than one TPH weight fraction (gasoline, diesel, residual) may be present at the site, multiple analyses will be required, resulting in high analytical costs that are further increased by the rapid turnaround times often needed to insure timely decision making during the sample event⁶). A number of studies have reported SFE (supercritical fluid extraction) methods for extraction of TPH and PCBs from soil⁷). Generally, GC-ECD results for SFE extracts and GC-ECD results for Soxhlet extracts are compared. In addition to these research reports, the US environmental Protection Agency (EPA) has published a SFE method for extraction of TPH and PCBs from solid matrices⁷⁻⁸).

In this paper, quantitation methods of total petroleum hydrocarbons to determinate oil level in soil were discussed. Extraction characteristics of several pretreatment methods and practical

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detection limit and reappearances in gas chromatography/mass spectrometry with each pretreatment method were investigated.

2. Experimental Methods

2.1 Reagents and Materials

The material used for this study include standard solution and sample that contaminated level has digestion process with an average detention time of between 3 and 20 years. Standard solution used for reference solution that no organic compounds was detected. For the test, standard solution used for normal-alkane stock standard solution, which purchased from alltech, gasoline, kerosene and fuel oil. Methanol used for solvent was, Methylene chloride were HPLC grade and purchased from Fisher.

2.2 Instrumentation

GC-MSD measurements were made on a Hewlett Packard (Model No. 5890) gas chromatography with a Hewlett Packard MSD (Model No. 5971) serving as the detector. Then, the chromatography column for all analyses was 30 m x 0.25 mm ID (0.25 μm film thickness)DB5-MS column (5% phenyl methyl polysiloxane crosslinking moiety, J&W). A sonic dismembrator (model no. 550, Fisher) was employed for ultrasonic extraction. Zymark TurboVap II model was employed for enrichment.

2.3 Analytical Procedure

Solvent extraction. sample and extraction solvent added to vials. Shaking process was performed at 5 cm of amplitude for 20 times per minute using physically stirrer. After 30 minutes of settlement, the upper phase was collected.

Soxhlet extraction. 20 g of soil samples stored at filter of thimble type, poured to 200 ml of solvent, was extracted for 16 hours after circulate from 4 rotations to 6 rotations, then the extraction solution was enriched of 1 ml.

Ultrasonic extraction. The soil did kept to in beaker, poured to solvent of 10 times, extracted for 3 minute at an interval of 3 seconds, poured again to solvent after filter to extraction solvent. The process was repeated two times.

3. Results and Discussion

3.1 Extraction characteristics of the TPH as affected by the extraction solvent and pretreatment method

In this experiment, extraction characteristic as GRO and DRO and extraction characteristic of DRO as Ultrasonic extraction and Soxhlet extraction was compared. Table 1 shows recovery as detected concentration after add to 50 ~ 1000 $\mu\text{g/g}$ of gasoline, kerosene, fuel oil by stages. Gasoline compared to extraction results as a kind of solvent from solvent extraction, however, as a result of extraction, the solvent extraction and soxhlet extraction did not apply to gasoline because extensive volatile gasoline loss a considerable amounts, therefore this methods did not considered. The kerosene, fuel oil did applicable all on three kinds of method. In solvent extraction, the methanol used for extraction solvent compared with methylene chloride, when methanol used for extraction solvent, gasoline take the high recovery at range from 10 % to 20 %, Kerosene is take the high recovery at range from 5 % to 10 %, there was no difference under such fuel oil. The soxhlet extraction did take a lower recovery in contrast to two kinds of extraction method. The necessary time when use of soxhlet, use of much solvent and the trouble of use, this method won't be appropriate for the extraction method about oils. The mean recovery, standard deviation and % RSD (% relative standard deviation) from obtained values as concentration showed relatively the high recovery and reproducibility, showed relatively the lower recovery and reproducibility about the soxhlet extraction. As such result, the ultrasonic extraction and soxhlet extraction generally used for extraction method of the kerosene and fuel oil, but three kinds of oil is detectable by the simple solvent extraction. Equally, the soxhlet extraction of wide application by generally extraction method can appear not to present to reliable results.

3.2 Discussions as the extraction efficiency and quantitation method by extrac tion solvent and extraction method

Table 1. Recovery and standard deviation dependent on extraction methods.

Spiked amount(ug/g)	Percent recovery											
	Solvent Extraction						Sonication			Soxhlet		
	MeOH			MC ^a			MeOH		MC		MC	
	G ^b	K ^c	D ^d	G	K	D	K	D	K	D	K	D
50	88	86	80	63	60	71	91	89	86	85	47	69
50	90	78	75	58	54	63	87	90	80	76	58	63
50	78	77	87	55	49	59	75	88	77	87	28	58
500	83	82	68	70	68	66	90	81	89	79	39	50
500	79	84	83	65	57	75	86	92	75	91	26	54
1000	91	76	72	68	64	73	76	85	70	75	44	66
1000	87	77	70	71	66	77	85	75	86	88	39	61
Mean recovery	85	80	76	64	60	69	84	88	80	83	36	60
Standard deviation	5.1	4.0	6.6	5.9	6.8	6.7	6.4	5.9	6.9	6.3	8.2	6.7
% RSD ^e	6.0	5.0	8.7	9.2	11.3	9.7	7.6	6.7	8.6	7.6	22.8	11.2

^a: Methylene chloride, ^b: gasoline, ^c: kerosene, ^d: diesel oil, ^e: percent relative standard deviation

Table 2. GC area percent of each marker in commercial gasoline, kerosene and diesel oil.

Area (%) ^a	Gasoline	B	T	E	X	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₅	C ₁₆	C ₁₇	C ₁₈
		Kerosene	0.01	0.2	0.14	0.6	5.5	5.1	5.2	4.4	2.2	0.4	0.1
Diesel oil	0.01	0.2	0.12	0.6	1.5	1.4	1.8	2.2	2.6	3.0	5.0	2.8	
Total area % Of markers		Gasoline				Kerosene				Diesel oil			
Relative Area(%) ^b	Gasoline	25.0	100	35.1	106.4	-	-	-	-	-	-	-	-
	Kerosene	0.2	3.5	7.9	31.7	100	93.0	95.2	80.2	40.6	7.2	1.4	-
	Diesel oil	0.25	3.9	2.8	12.5	30.1	27.9	35.2	44.0	51.1	58.9	100	55.0

^a: GC area count of each marker/total GC area count. ^b: Relative area percent of each marker to the T(G), C₁₁(K), C₁₇(D)

Table 3. Detection limit and standard deviation of target markers by using solvent extraction and GC/MS

	MeOH extraction												MC Extraction												
	Gasoline				Kerosene				Diesel oil				Gasoline				Kerosene				Diesel oil				
	B	T	E	X	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₅	C ₁₆	C ₁₇	C ₁₈	B	T	E	X	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₅	C ₁₆	C ₁₇	C ₁₈	
MDL ^a	0.05	0.06	0.04	0.04	0.04	0.03	0.05	0.05	0.04	0.04	0.05	0.07	0.05	0.07	0.05	0.05	0.05	0.04	0.05	0.05	0.07	0.05	0.05	0.05	0.1
PQL ^b	0.25	0.3	0.2	0.2	0.2	0.15	0.2	0.2	0.2	0.2	0.25	0.35	0.3	0.35	0.25	0.25	0.25	0.2	0.3	0.3	0.35	0.3	0.3	0.5	
%RSD ^c	6.6	5.7	6.0	5.5	5.5	5.3	4.7	5.7	5.5	6.0	6.2	6.6	7.2	6.8	5.8	6.0	6.2	7.0	7.5	7.2	5.7	5.3	6.7	6.5	
Reduced	2.5				3.8				8.3				3.0				5.3				12.1				

^a: Method detection limit, $S \times (t_{n-1, 1-\alpha} - 0.95)$ (S: standard deviation, t: student's t value for the 95% confidence level with n-1 degree of freedom), ^b: practical quantitation limit, MDL x 10, ^c: percent relative standard deviation, S/X 100 (s: standard deviation, X: mean value of measured amount of seven replicates).

Table 4. Detection limits and standard deviation of kerosene & diesel oil target markers by using ultrasonication and soxhlet extraction and GC/MS.

	Ultrasonication												Soxhlet																							
	MeOH						MC						Kerosene						Diesel oil																	
	Kerosene			Diesel oil			Kerosene			Diesel oil			Kerosene			Diesel oil			Kerosene			Diesel oil														
	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₅	C ₁₆	C ₁₇	C ₁₈	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₅	C ₁₆	C ₁₇	C ₁₈	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₅	C ₁₆	C ₁₇	C ₁₈	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₅	C ₁₆	C ₁₇	C ₁₈				
MDL	0.04	0.03	0.04	0.04	0.04	0.04	0.04	0.05	0.05	0.04	0.05	0.05	0.05	0.04	0.04	0.05	0.3	0.2	0.2	0.4	0.2	0.15	0.15	0.3	0.2	0.15	0.15	0.15	0.15	0.15	0.15					
PQL	0.2	0.15	0.2	0.2	0.2	0.2	0.25	0.25	0.2	0.2	0.25	0.25	0.2	0.2	0.3	1.5	1.0	1.0	2.0	1.0	0.75	0.75	1.5	1.0	0.75	0.75	0.75	0.75	0.75	0.75						
%RSD	5.8	6.5	5.0	6.6	7.0	6.7	5.9	7.2	8.1	7.7	8.9	9.3	7.6	8.7	8.8	6.9	27.5	21.3	18.7	16.8	19.3	12.4	15.5	10.9	15.5	10.9	10.9	10.9	10.9	10.9						
Reduced	3.7						7.1						4.5						7.9						27.5						33.3					

The purpose of this study finds out method of relatively a simple and a high application about detection method of total TPH after collect a primary typical compound. The typical compound

as a species of another oil represented the greatest intensity in gas chromatogram, collected in four species no distributed with different species; BTEX, n-C₁₀, n-C₁₁, n-C₁₂, n-C₁₃ and n-C₁₅, n-C₁₆,

n-C₁₇, n-C₁₈ about gasoline, kerosene, and fuel oil, relatively. Table 2 shows a relatively distribution ratio of the total typical compound. This value is the sum of area of total peaks into the sum of area of typical compound peaks. The relative ratio as typical compound is the relative ratio when toluene of gasoline, n-undecane of kerosene, and n-heptadecane of fuel oil represented the greatest intensity in species of each soil was 100. The peak area ratio of typical compounds take possession of 44.8 %(gasoline), 20.2 %(kerosene) and 13.4 % (fuel oil).

3.3 The accuracy, precision and detection limit by extraction method

The purpose of this study look for obtained parameters by a repeat experiment for acquire reproducibility and detection limit extraction method. Table 3 shows method detection limit (MDL), practical quantitation limit (PQL) and % relative standard deviation (% RSD) about different kinds of typical compound in extraction method that methanol and methylene chloride used for extraction solvent. Table 4 shows detection limit and reproducibility of ultrasonic extraction and soxhlet extraction. As results to extraction using methanol in solvent extraction, this results was not particularly high as compared with methylene chloride. The detection limit and reproducibility is some below. When consider with extraction efficiency of Table 1, Methanol can represent good results than methylene chloride. In the results of Table 3 and 4, detection limit of different specie of oils can detect ranges from 2.5 to 3.0 ppm (gasoline) in solvent extraction, 3.7 - 5.3 ppm (kerosene) in solvent extraction and ultrasonic extraction, 27.5 ppm in soxhlet extraction using methylene chloride, 7.1 - 12.1 ppm (fuel oil) in solvent extraction and ultrasonic extraction and 33.3 ppm in soxhlet extraction.

4. Conclusions

In this study, quantitation methods of total petroleum hydrocarbons to determinate oil contaminated level in soil were discussed. Extraction characteristics of several pretreatment methods and practical detection limit and reappearances in gas chromatography/mass

spectrometry with each pretreatment method were investigated. The proposed method is the newly adopted quantitation method and mechanical shaking extraction method using methanol with extraction solvent are more practical and applicable to real sample than the conventional methods. In applying these methods to gasoline, kerosene, fuel oil that are major source of soil contamination, the practical quantitation limit and % relative standard deviation was able to determine with range of 2.5 - 10 ppm, 5 - 7 %.

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