

오염토양내 석유계 총탄화수소 분석을 위한 추출방법의 비교

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Comparison of Extraction Methods for the Analysis of Total Petroleum Hydrocarbons in Contaminated Soil

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ABSTRACT

Two extraction methods for total petroleum hydrocarbon (TPH) from contaminated soil were evaluated. The soil used for this study was sandy loam. Diesel oil was selected as representative petroleum hydrocarbons and was spiked at 100, 10,000, 50,000mg TPH/kg dry soil. Percentage recovery of TPH by shaking method was higher compared to Soxhlet extraction. At extraction time of 2 hours and sample to solvent ratio of 1 : 5, the highest percentage recovery was obtained. In this condition, percentage recovery of TPH in soil contaminated with 100mg/kg and 50,000mg/kg as TPH was 95.9% and 95.5%, respectively. The volume of solvent lost by volatilization in shaking method was relatively small compared to Soxhlet extraction.

Key words : Percentage recovery, TPH, Soxhlet extraction, Shaking extraction

1. 요약 문

본 연구에서는 오염토양내 석유계 총탄화수소를 분석하기 위한 추출방법을 비교하였다. 사용된 토양은 사질양토였으며 석유계 총탄화수소로는 디젤오일을 선정하였다. 토양내 디젤오일의 오염농도는 건조질량기준으로 100, 10,000, 50,000mgTPH/kg이었다. 오염토양내 석유계 총탄화수소를 추출하는데 있어서 진탕교반에 의한 추출법이 속시렛장치를 이용한 추출법보다 전반적으로 높은 회수율을 보였다. 진탕교반추출법에서 시료와 용매의 비율을 1:5(w/v)로 하여 2시간 동안 진탕교반하였을 때 석유계 총탄화수소의 회수율이 가장 높았다. 동일조건에서 100mg/kg과 50,000mg/kg으로 오염된 토양을 진탕교반추출한 경우 각각 95.9%와 95.5%의 회수율을 보였다. 사용된 용매의 손실량을 측정해 본 결과 진탕추출법이 속시렛추출법에서 보다 손실량이 적었다.

주제어 : 회수율, 석유계 총탄화수소, 속시렛추출, 교반추출

1. INTRODUCTION

Fuel oils such as diesel, gasoline, and kerosene consist of various petroleum hydrocarbons having different boiling points. The diversity and complexity of fuel oil components require an analytical approach that measures the mixture as a whole^(1, 2). The general name for these techniques is Total Petroleum Hydrocarbon (TPH) analysis. Several methods have been developed for measuring TPH. Three common techniques are currently used: gravimetric method, infrared spectrophotometric method, and gas chromatography.

Both the gravimetric method and infrared method are fast, relatively simple methods to perform. However, these do not provide valuable qualitative contaminant information, and identification of the individual chemical constituents of the fuel

oils^(1, 2, 3). Capillary gas chromatography is an alternative to the gravimetric method and infrared method, and is well established. The method of component detection can be a simple conventional detector, flame ionization detector (FID), or, when considerable qualitative information is needed, a mass spectrometer. Gas chromatography can also help determine whether a fuel oil sample has been biologically weathered, which is done by comparing the ratio of certain straight chain alkanes (C17 and C18) with specific branched alkanes (pristane and phytane). At present, this is known as the most universal method for the analysis of TPH.

Extraction procedure of TPH in contaminated soil and groundwater should be carried out to analyse TPH. Methods for extracting organic compounds in soil or other solid-phase materials include Soxhlet extraction, sonication, and shaking

extraction. Soxhlet extraction and sonication are extraction methods which are mandated in Korea Soil Conservation Act. Soxhlet extraction is a powerful method which has been used universally as the extraction method of organic compounds in soil⁽⁴⁾. But, this method is time-consuming and the high ratio of sample to solvent is needed. Ultrasonic extraction is not as rigorous method as the other extraction methods for soil/solids⁽⁵⁾. This means it is very critical that the method be followed explicitly to achieve percentage recovery which approaches that of Soxhlet extraction. Shaking extraction method can reduce extraction time and solvent volume. This method also has advantages that can extract many samples at the same time and thimble filter which used in Soxhlet extraction is not needed.

In this study, TPH recovery efficiencies by shaking extraction procedure were tested and compared to those of Soxhlet extraction.

2. MATERIALS AND METHODS

2.1 Materials

The soil was collected from the top 15 cm of the soil surface in the campus of Konkuk University. The collected soil was air-dried and passed a 2 mm sieve. The portion of sand, silt, and clay in the soil was 59.5%, 23.0%, and 17.5%, respectively. Moisture content of soil was adjusted to 70% of field

capacity. Target contaminant of this study was diesel oil. Fresh diesel oil was spiked at 100 mg/kg, 10,000 mg/kg, and 50,000 mg/kg on the dry basis.

2.2 Extraction

The solvent used in TPH extraction was methylene chloride. All glassware used for GC analysis was washed with soap and water, rinsed with acetone, and dried in oven where temperature was maintained at $100 \pm 5^\circ\text{C}$.

Soxhlet extraction procedure was followed in accordance with the method modified by Namkoong⁽⁴⁾ except concentration step. Ten grams of sample were extracted for 4 hours, 8 hours, and 16 hours using 300 mL of methylene chloride in a Soxhlet extraction apparatus. The sample extract was filtered through 0.45 μm PTFE filter paper. The filtered extract was passed through anhydrous sodium sulfate (Na_2SO_4) column in order to remove water in extract. Water removed-extract was used for GC analysis to measure percentage recovery.

Extraction time and the ratio of sample to solvent mainly influence the shaking extraction procedure. First, 10 g of sample and approximately 10g of sodium sulfate were added into the extraction bottle of 100 mL volume^(6, 7, 8). Sodium sulfate was added to remove water in samples. Methylene chloride was added to achieve the ratios of sample to solvent 1:1, 1:5, and 1:10, respectively. Extraction times were 1 hour,

2 hours, and 4 hours. The extract was filtered through 0.45 μm PTFE filter paper and used for GC analysis to determine percentage recovery.

2.3 GC analysis

A 1 μL sample of the extract was injected into a gas chromatograph (Hewlett Packard Model 5890 Series II) equipped with an integrator (Hewlett Packard Model 3395) and a flame ionization detector. Methylene chloride was used for the preparation of both stock standard solutions and working standard solutions in order to eliminate any possible effect from different solvents on the chromatographic output. Stock standard solutions for TPH were prepared from commercial diesel fuel. A total of five TPH standards were prepared for the calibration curve, respectively. The chromatographic system was calibrated using the external standard technique. TPH concentration was obtained from calibration curve by comparing peak area of sample with that of standard.

Table 1 presents the operating conditions of the gas chromatograph. A column used for GC analysis was HP-1 (25 m length \times 0.32 mm internal diameter \times 0.52 μm film thickness). The initial temperature and temperature progress rate were selected based on the retention time of the spiked compounds. The initial temperature was kept at 50 $^{\circ}\text{C}$ for 1 minute, increased at 25 $^{\circ}\text{C}$ /min to 300 $^{\circ}\text{C}$ of final temperature, and

maintained at that temperature for 1 minute in order to ensure that the column was clean. The injection port and detector temperature were 250 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$, respectively. Hydrogen gas and air flow rate for the flame ionization detector was 33 mL/min and 330 mL/min, respectively. Nitrogen carrier gas was delivered at a rate of 28 mL/min.

3. RESULTS AND DISCUSSION

The standard calibration curve for TPH presented in Fig. 1 indicates that the curve is linear. The correlation coefficient of calibration curve produced by direct injection technique used in this study was 0.9994. TPH standard of 1,000mg/L was prepared and injected 10 times to evaluate the variation in GC output because sample volume (1 μL) introduced to the GC can effect on the GC output. The relative standard deviation for TPH was 1.5% (data was not presented).

At each day the analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly⁽⁹⁾. When comparing daily response of a given analyte versus the initial response, percent difference should be below 15%. If the response for any analyte varies from the predicted response by more than 15%, a new calibration curve must be prepared for that analyte. In this study, when standard solutions were injected again

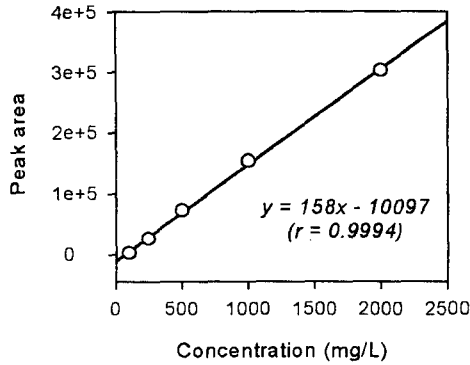


Fig. 1. The standard calibration curve for TPH

after calibration curve was obtained, relative standard deviations(RSD) of these were in the range of 4.1% to 5.8%(Table 2). This means that calibration curve obtained from this study can be used usefully to estimate sample concentration.

Table 3 shows percentage recovery of TPH in soil contaminated with 10,000 mgTPH/kg using Soxhlet extraction procedure. When the sample was extracted

for 16 hours, recovery efficiencies were in the range of 91% to 94% (Table 3). This indicates that TPH recovery is the highest in the extraction time of 16 hours. In case of 4 hour and 8 hour extraction, recovery efficiencies were relatively lower than those of 16-hour extraction.

Table 4 shows an percentage recovery of TPH in soil contaminated with 10,000 mgTPH/kg using shaking extraction procedure. When shaking time was 1 hour, percentage recovery was somewhat lower than those of 2 hours and 4 hours shaking, regardless of sample to solvent ratios. Therefore, it may be desirable to select shaking time of over 2 hours. The highest percentage recovery was obtained in the ratio of sample to solvent of 1 : 5 and extraction time of 2 hours (98.7 %). This value is relatively high compared to Soxhlet extraction.

Pyo *et al*⁽¹⁰⁾. suggested that if the percentage recovery of target contaminant is

Table 1. Operating conditions for the gas chromatographic analysis

	Initial time	1 minute
	Initial temperature (°C)	50°C
	Progress rate (°C/min)	25°C/min
	Final temperature (°C)	300°C
	Final time	1 minute
Temperature(°C)	Injection port temperature (°C)	250°C
	Detector temperature (°C)	300°C
Detector	Flame ionization	
Gas	Hydrogen gas	33 mL/min
	Air	330 mL/min
	Nitrogen (carrier gas)	28 mL/min

Table 2. Reliability test of working calibration curve

Injected concentration (mg/L)	Concentration calculated by calibration curve (mg/L)	Average \pm Standard Deviation (mg/L)	Relative Standard Deviation (%)
100	103, 97, 105	101.7 \pm 4.2	4.1
500	452, 503, 498	484.3 \pm 28.1	5.8
1000	1054, 1018, 959	1010.3 \pm 48.0	4.7

Table 3. Percentage recovery of TPH by Soxhlet extraction procedure

Extraction method	Extraction time (hrs)	Recovery (%)
Soxhlet extraction	4	87-91 (89.2) ¹⁾
	8	88-90 (89.4)
	16	91-94 (92.8)

1) A value in the bracket implies average.

over 60% and relative standard deviation for reproducibility is below 10%. this can be used for quantitative analysis in the concentration of part per million. Recovery efficiencies from Soxhlet extraction procedure and shaking extraction procedure in this study were much higher than this value. Sawyer⁽¹¹⁾ reported that percentage recoveries for DRO (Diesel Range Organics) in soils using sonication extraction procedure were 71 to 90%. This value is relatively low compared to the results of Soxhlet extraction and shaking extraction tested in this study. Even the direct comparison with this result was not feasible, high recovery of shaking extraction showed that this method was as effective for TPH extraction as sonication and Soxhlet extraction.

When extraction methods for

contaminated samples are developed, one of the most important considerations is consistent recovery of analyte despite variation of analyte concentration. To evaluate consistency of recovery, minimum five samples should be analyzed in the low concentration near detection limit and high concentration, respectively⁽¹⁰⁾. In this study, TPH recoveries for low concentration (100mg/kg) and high concentration (50,000mg/kg) were tested under the shaking extraction condition of sample to solvent ratio of 1 : 5.

Fig. 2 shows percentage recovery for TPH according to the variation of spiked concentrations. In low concentration (100mg/kg), percentage recoveries for TPH were 92.9 to 100.2% (average 95.9%). Percentage recoveries for TPH in high

Table 4. Percentage recovery of TPH by shaking extraction procedure

Extraction method	Extraction time (hrs)	Sample : Solvent (g : mL)	Recovery (%)
Shaking extraction	1	1 : 1	85-88 (86.3) ¹⁾
		1 : 5	83-87 (85.3)
		1 : 10	85-91 (88.1)
	2	1 : 1	89-94 (91.1)
		1 : 5	97-101 (98.7)
		1 : 10	86-103 (95.3)
	4	1 : 1	91-94 (92.7)
		1 : 5	93-96 (94.3)
		1 : 10	92-95 (93.1)

1) A value in the bracket implies average.

concentration (50,000mg/kg) were in the range of 86.2 to 104.6% having an average of 95.5%. As such, shaking extraction showed high recovery regardless of TPH concentration even slight fluctuation of percentage recovery was observed.

The volume of solvent lost by

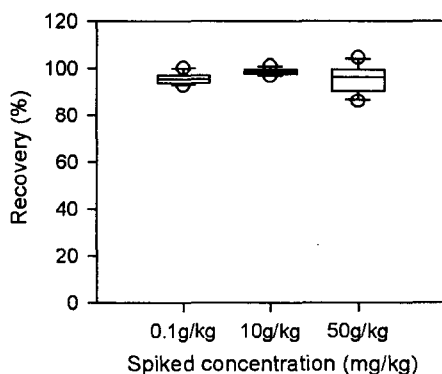


Fig. 2. Comparison of TPH recovery depending on the spiked concentrations.

volatilization in shaking method was about 3% of initial volume (data was not presented). While volatilization loss of solvent in Soxhlet extraction was about 10%. Shaking method showed a higher percentage recovery and a smaller volatilization loss of solvent compared to Soxhlet extraction. One of the major drawbacks of Soxhlet extraction is large amount of solvent used in sample extraction procedure. In Soxhlet extraction, about 300mL of solvent per sample is required, which indicates that volume of waste solvent generated for extraction is relatively large compared to shaking extraction. Therefore, shaking extraction is an effective alternative to achieve waste minimization while achieving the desired results. Shaking extraction can also reduce the time required to perform a sample analysis. In this study, this method could reduce the sample

extraction time by up to a factor of 2 to 8 over that necessary by Soxhlet extraction. In addition to, shaking extraction procedure also has advantages that special equipment for extraction is not needed and a lot of samples can be extracted at the same time. These advantages indicate indirectly that shaking extraction procedure can be used as extraction method for TPH analysis in fuel oil-contaminated soil.

4. CONCLUSIONS

In this study, two extraction methods were evaluated under certain extraction conditions. Percentage recovery of TPH by shaking method was higher than that of Soxhlet extraction. The volume of solvent lost by volatilization in shaking method was relatively small compared to that of Soxhlet extraction. In extraction time of 2 hours and sample to solvent ratio of 1 : 5, the highest percentage recovery was obtained. From these results, authors suggest that shaking extraction method can be used as extraction method for TPH analysis in fuel oil contaminated soil even though more research is needed to develop a specific extraction method.

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