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DIESEL FUEL EXTRACTION FROM SOIL

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Abstract. This study investigated the influence of five factors on the degree of extraction of a petroleum pollutant from a soil matrix using a Soxhlet apparatus. In order to determine the optimal combination of the five factors, that is, the number of cycles per hour, extraction time, solvent type, the amount of drying agent, and the amount of water added, a Taguchi experimental design was used: five variables (with four levels each) in an L'16 orthogonal array. Optimum extraction conditions were found to be as follows: 50.0 mL of dichloromethane, 2 h extraction time, 7 cycles, 1.0 mL of water added/5.0 g of soil, and 1.5 g of sodium sulfate/5.0 g of sample. Using the presented method, more than 90% of the diesel fuel introduced into the model matrix was extracted. This indicates that the procedure is reliable and should be applied for environmental monitoring.

Key words: diesel fuel, Taguchi method, Soxhlet extractor, extraction, orthogonal experiment

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a major group of organic soil contaminants. These compounds are mainly derived from anthropogenic sources due to, e.g., the combustion of diesel fuel and leaks from old gasworks [Kanaly and Harayama 2000, Juhasz and Naidu 2000, Meckenstock et al. 2004, Johnsen et al. 2005], and are often associated with the production of gas, coke, and petroleum products [Meckenstock et al. 2004].

Prior to choosing a method of soil and groundwater remediation, samples of the studied matrix should be tested for the concentration of hydrocarbons to determine the degree of contamination of the environment [Fatemi and Baher 2009, Sen and Chakrabarti 2009].

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The basic techniques of environmental pollutant identification for monitoring purposes are methods that allow for selective separation of chemical elements from complex mixtures, thus enabling both qualitative and quantitative assessment of pollution [Wood et al. 1990, El-Shoubary and Woodmansee 1996, Khodadoust et al. 1999].

Techniques of analyte separation include solvent extraction, extraction by supercritical fluid, and solid-phase, and single-drop extraction or microextraction. Additionally, these processes may be supported by ultrasonic energy, microwaves, or high pressure [Khodadoust et al. 2005, 2008, Subramanian et al. 2010].

The selection of an extraction technique primarily depends on the type of matrix, the properties and concentration of the analyte, and the properties and concentration of other substances present in the matrix [Luque de Castro et al. 1994, Luque de Castro and Priego--Capote 2010].

The extraction of diesel fuel from contaminated soil was carried out in a Soxhlet apparatus and the influence of five factors (solvent type, extraction time, the number of cycles per hour, water content, and the amount of drying agent in the sample) on the extraction rate (%) was examined.

In order to assess the reliability and usefulness of this procedure in environmental matrices for analytical purposes, soil samples with a certain amount of petroleum compounds were prepared.

The process parameters were optimized using the Taguchi method, which allowed for simultaneous assessment of the impact of all the studied input factors.

MATERIALS AND METHODS

Materials

Diesel fuel (PKN Orlen, Poland), dichloromethane (reagent grade, Chempur), hexane (reagent grade, Chempur), hexane for GC analysis (Chempur), acetone (reagent grade, Chempur), isopropanol (reagent grade, Chempur), anhydrous sodium sulfate (Chempur) hexatriacontane 98% (Aldrich).

Soil

The soil sample was collected in the municipality of Opoczno, Lodz Province, Poland (51°22’0” N, 20°15’19” E). The basic physical and chemical properties of the sample are presented in table 1.

Table 1. Basic physical and chemical properties of the fresh soil sample

Texture, %			Moisture, %	OM, %	pH
Sand	Silt	Clay			
73	12	15	25	1.66	6.14
Main elements, %					
Ca	Mg	Fe	P	K	N
0.06	0.05	0.042	0.038	0.06	0.08

Soil matrix model

First, 22,400.0 mg of diesel fuel dissolved in acetone (250.0 mL) was added to the soil matrix (2,500.0 g dry weight), which was then mixed multiple times. Subsequently, the solvent was evaporated and 5.0 g samples containing 44.8 mg of contaminants were taken for experiments.

Extraction of hydrocarbons

Water (0.0 to 1.5 mL) and anhydrous sodium sulfate (0.0 to 5.0 g) were added to the soil samples (5.0 g). Samples prepared in this way were introduced into 22 × 80 mm cellulose thimbles (Whatman) and placed in a four-position Soxhlet apparatus (Behr). For each extraction, 50.0 mL of solvent was used (table 2).

Samples for chromatographic analysis (GC)

An extract sample was concentrated under reduced pressure (IKA · RV 10) to a volume of 1.0 mL, then 0.5 mL of an internal standard (2.0 mg hexatriacontane in 1 mL of hexane) was added, and subsequently the container was filled to a volume of 2.0 mL with hexane.

Control sample

Fist, 44.8 mg of diesel fuel was added to 1.0 mL of hexane; subsequently, 0.5 mL of hexatriacontane was introduced, and the containers with samples were filled to 2.0 mL with the same solvent.

The extraction rate (%) of hydrocarbons from the matrix was defined as the ratio of the peak area of the test sample to the peak area of the control sample (GC analysis) × 100%.

Gas chromatography

A 5980 Hewlett-Packard gas chromatograph was used with a ZB–1XT SimDist capillary column (5 m × 0.53 × 0.15 μm), the carrier gas was helium, the injector temperature 300°C, the temperature program was 100°C/6°C per 1 min increment/230°C/15°C per 1 min increment/350°C – 10 min, FID detector temperature – 300°C.

Experimental design

Petroleum pollutant extraction from soil was optimized according to the Taguchi experimental design by simultaneously assessing the impact of all the input factors studied [Cukor et al. 2011, Benito-Román et al. 2011, Venkata et al. 2009]. The application of the Taguchi method significantly reduces the cost and duration of experiments. An L'16 orthogonal array composed of 16 experimental setups was used with five factors (having four levels each): solvent type (dichloromethane, hexane, hexane : acetone (1 : 1), isopropanol), extraction time (2 h, 4 h, 8 h, 12 h), the number of cycles per hour (7, 5, 3, 1), the amount of water added (0 mL, 0.5 mL, 1 mL, 1.5 mL/5 g of sample), and the amount of drying agent (0.0 g, 1.5 g, 3.0 g, 5.0 g/5.0 g of sample).

The aim of optimization was to select such levels of input factors that would ensure the highest degree of extraction (%), and therefore the response of the system was defined as the amount (%) of extracted diesel fuel. In order to avoid systematic errors, the sequence of experiments was randomized, and experiments were repeated four times for each setup. The signal-to-noise ratio (S/N, Eta), which was used in variation calculus, was computed from experimental data on the basis of a quality loss function. Parameters with the highest desired value were adopted and the S/N ratio (controllable factors/confounding factors, Eta) was calculated using the relationship described by the formula:

$$(S/N)_{HB} = -10 \log \left[\left(\frac{1}{n} \right) \sum \left(1 / y_i^2 \right) \right]$$

where y_i is the experimental response and n is the number of tests in a trial [Antony and Antony 2001, Hsieh et al. 2005, Tansel et al. 2011, StatSoft electronic manual 2012]. The theoretical amount of petroleum compounds extracted from the contaminated soil matrix under optimum conditions was determined based on the expected S/N ratio from equation (1).

RESULTS

The results of experiments are presented in table 2.

Table 2. Optimization of diesel fuel extraction from contaminated soil according to the Taguchi method (L'16 orthogonal array) – levels of input variables with corresponding averaged output variables (5.0 g of soil, 50.0 mL of solvent)

Stand. run	Number of cycles per hour	Extraction time h	Solvent	Amount of water added ml	Amount of the drying agent g	Extraction rate %	S/N ratio Eta
12	3	4	hexane	1.5	3.0	43.97	114.37
16	5	12	dichloromethane	0.5	3.0	60.50	117.1062
13	3	4	dichloromethane	0.5	5.0	70.00	118.39
15	5	8	hexane	0.5	5.0	55.54	116.37
6	7	4	hexane : acetone (1 : 1)	0.0	5.0	61.00	117.21
8	5	2	hexane : acetone (1 : 1)	1.5	1.5	61.46	117.24
10	1	12	isopropanol	1.5	5.0	0.00	0.0000
1	1	2	hexane	0.0	0.0	70.15	118.38
4	3	2	dichloromethane	1.0	5.0	79.90	119.53
3	7	2	isopropanol	0.5	3.0	0.00	0.00

Table 2. cont.

Stand. run	Number of cycles per hour	Extraction time h	Solvent	Amount of water added ml	Amount of the drying agent g	Extraction rate %	S/N ratio Eta
9	1	12	hexane	1.0	1.5	70.96	118.5
7	7	8	isopropanol	0.0	1.5	0.00	0.00
11	5	4	isopropanol	1.0	0.0	0.00	0.00
14	3	12	hexane : acetone (1 : 1)	0.5	0.0	40.73	113.64
2	1	8	hexane : acetone (1 : 1)	1.0	3.0	58.61	116.86
5	7	8	dichloromethane	1.5	1.5	47.75	115.06

The results were analysed statistically using ANOVA. All parameters of the extraction process were found to affect the efficiency of diesel fuel extraction from the soil matrix at the adopted significance level of $p = 0.05$. The most important parameter was solvent type (table 3).

Table 3. Analysis of variance for the main effects of the factors

Factors	Sum of squares SS	Fisher criterion F	p-Value	Contribution* %
Number of cycles per hour	18.5	9.04	0.000075	0.01
Extraction time, h	28.2	13.76	0.000001	0.01
Solvent type	163987.0	80074.79	0.000000	99.92
Amount of water added, mL	43.4	21.19	0.000000	0.04
Amount of drying agent, g	36.6	17.85	0.000000	0.02

* Contribution is defined as 100 × (pooled sum of squares/total sum of squares)

The effect of the mean values of the input parameters on mean Eta is shown in Fig. 1.

The optimum levels of the input parameters are: 50.0 mL of dichloromethane, 2 h extraction time, 7 cycles, 1.0 mL of water added/5.0 g of soil, and 1.5 g of sodium sulfate/5.0 g of sample.

After determining the optimal process conditions, the theoretical amount of diesel fuel extracted from the soil was calculated on the basis of the expected S/N ratio.

The S/N value under optimal conditions is 121.23, hence $y_i = 96.56$ from equation (1).

A verification experiment was conducted (four repetitions) under the optimum conditions to give 94.45 ± 2.59% extraction of the compounds introduced to the soil matrix.

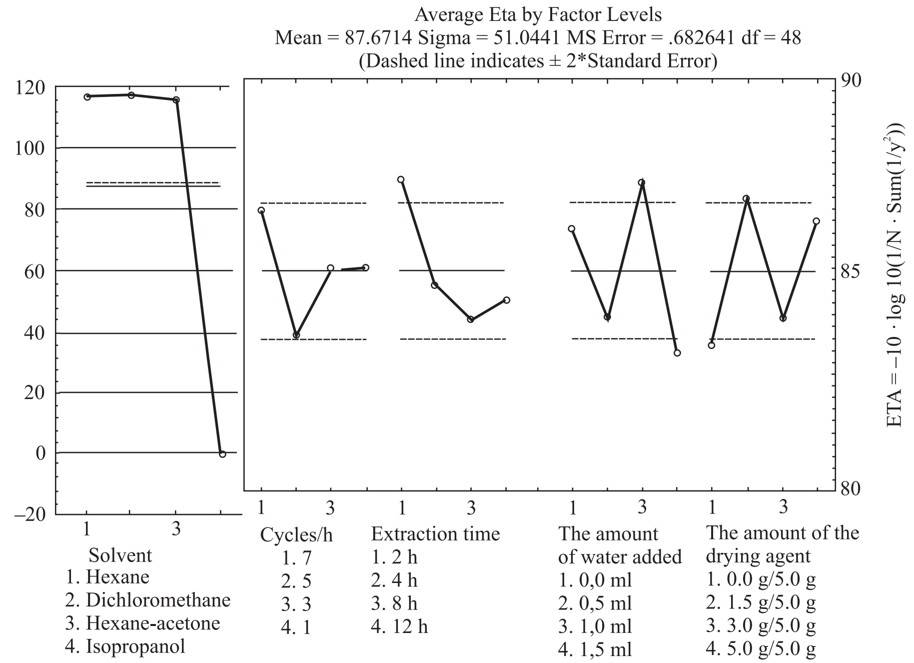

Fig 1. The effect of input factors on the S/N ratio for diesel fuel extraction from a contaminated soil matrix in a Soxhlet apparatus

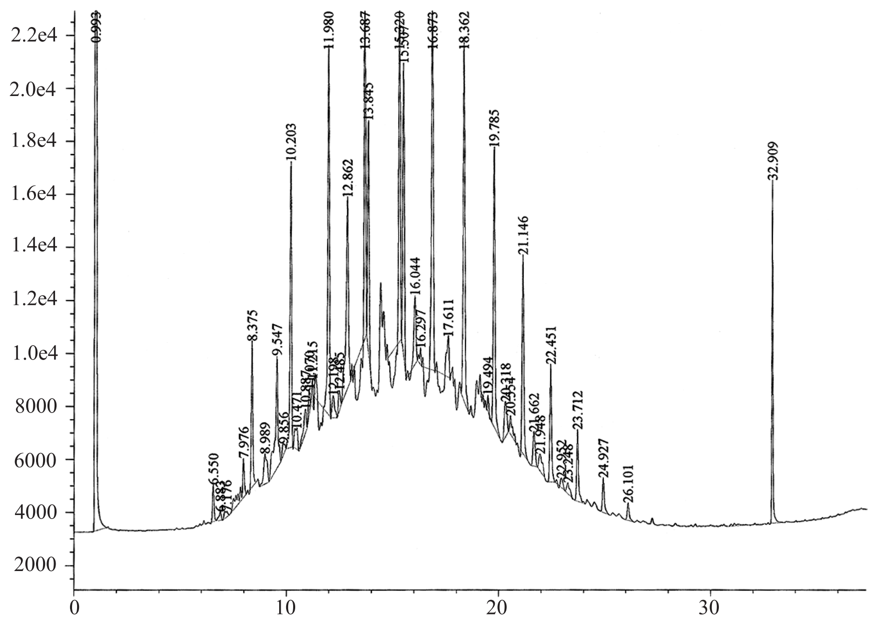

Fig 2. GC – extraction of diesel fuel from a blank sample

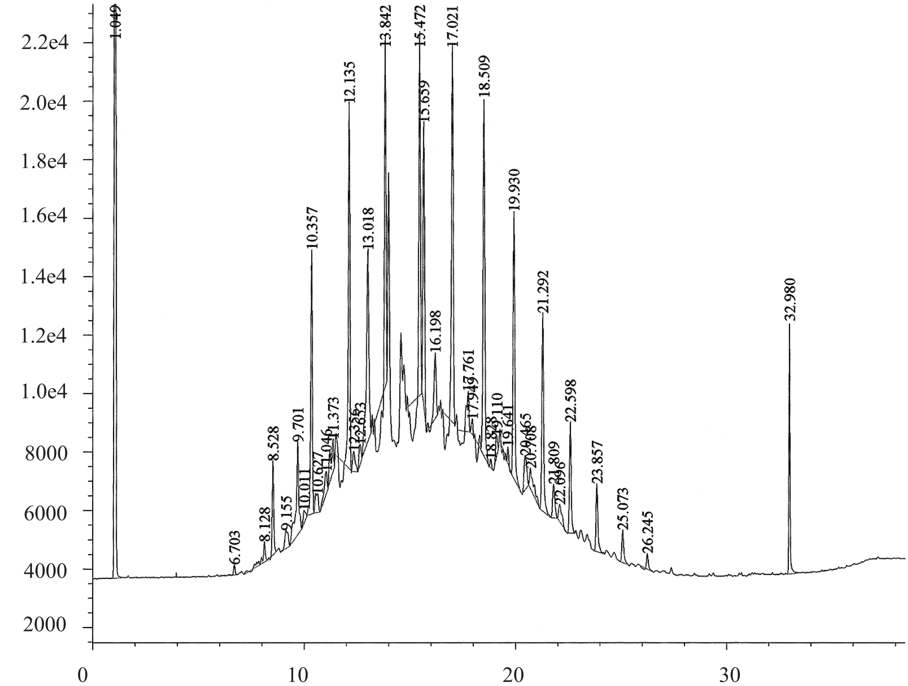

Fig 3. GC – extraction of diesel fuel from the soil matrix (5.0 g) was carried out under optimum conditions (50.0 mL of dichloromethane, 2 h, 7 cycles, 1.0 mL of water added/5.0 g of soil and 1.5 g of sodium sulfate/5.0 g of sample)

CONCLUSIONS

It has been shown that the most important parameter affecting the efficiency of diesel fuel extraction from a soil matrix is the type of extractant (solvent) used. Extraction with dichloromethane, carried out in a Soxhlet apparatus under optimum conditions: 50.0 mL of dichloromethane, 2 h, 7 cycles, 1.0 mL of water added/5.0 g of soil and 1.5 g of sodium sulfate/5.0 g of sample results in an extraction rate higher than 90%. This indicates that the procedure is reliable, meets the criteria of good analytical practice, and should be used for environmental monitoring.

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EKSTRAKCJA OLEJU NAPĘDOWEGO Z GLEBY

Streszczenie. Przeprowadzone badania miały na celu zbadanie wpływu pięciu czynników na stopień ekstrakcji zanieczyszczeń ropopochodnych z gleby z wykorzystaniem aparatu Soxhleta. W celu określenia optymalnej kombinacji tych czynników: liczby cykli na godzinę, czasu ekstrakcji, rodzaju rozpuszczalnika, ilości dodanego środka suszącego oraz ilości dodanej wody, wykorzystano projektowanie doświadczeń metodą Taguchi. Metoda ta uwzględniała pięć zmiennych (na czterech poziomach każdy), w postaci tablicy ortogonalnej L'16. Optymalne warunki ekstrakcji otrzymano dla danych wartości: 50,0 ml chlorku metylenu, czas ekstrakcji 2 godziny, 7 cykli, 1,0 ml wody na 5,0 g próby oraz 1,5 g siarczanu sodu na 5 g próby. Przedstawiona metoda pozwoliła na wyekstrahowanie ponad 90 % oleju napędowego wprowadzonego do matrycy modelowej. Procedura ta okazała się niezawodna i powinna być stosowana do monitorowania środowiska.

Słowa kluczowe: olej napędowy, metoda Taguchi, aparat Soxhleta, ekstrakcja, tablice ortogonalne

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