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## Abstract

Present paper describes optimization of the method of quantitative determination of total petroleum hydrocarbons in soil samples using headspace solid - phase microextraction (SPME) in combination with gas chromatography - mass spectrometry (GC-MS). Effects of moisture content and solvent additives were studied. It was established that an increase of the moisture content in soil leads to an increase of the response of petroleum hydrocarbons reaching its maximum at 15-20% depending on the soil type and concentration of total petroleum hydrocarbons followed by its gradual decrease. For the same concentration of petroleum hydrocarbons, an increase of moisture content in soil from 0 to 20% may lead to a 15x increase of total petroleum hydrocarbons response by solid - phase microextraction. Determination of total petroleum hydrocarbons in soils by SPME -GC-MS without moisture control of samples may lead to large errors, especially at low concentrations. It was established that addition of the solvent to a soil-water mixture allows dissolution of an oil film on the water surface and provides better extraction of hydrocarbons from soil to water phase. To avoid effect of moisture content on the extraction efficiency and more precise analysis of the real samples, addition of the excess distilled water must be done. Addition of the polar organic solvent to a soil-water mixture (10% isopropanol) allows dissolution of an oil film on the water surface and provides linear dependence of extraction efficiency vs total petroleum hydrocarbons content in soil. Testing of the optimized method on model soil samples provided quantitative data, results being in 30-120% range from the real values.

## Keywords

2, 4-dichlorophenoxyacetic acid, Raman scattering, bentonite clay, carbon nanotubes

## Disciplines

Bioresource and Agricultural Engineering | Environmental Health and Protection | Environmental Indicators and Impact Assessment

## Comments

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## Effects of Moisture Content and Solvent Additive on Headspace Solid-Phase Microextraction of Total Petroleum Hydrocarbons from Soil

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### Abstract

Present paper describes optimization of the method of quantitative determination of total petroleum hydrocarbons in soil samples using headspace solid - phase microextraction (SPME) in combination with gas chromatography - mass spectrometry (GC-MS). Effects of moisture content and solvent additives were studied. It was established that an increase of the moisture content in soil leads to an increase of the response of petroleum hydrocarbons reaching its maximum at 15-20% depending on the soil type and concentration of total petroleum hydrocarbons followed by its gradual decrease. For the same concentration of petroleum hydrocarbons, an increase of moisture content in soil from 0 to 20% may lead to a 15x increase of total petroleum hydrocarbons response by solid - phase microextraction. Determination of total petroleum hydrocarbons in soils by SPME -GC-MS without moisture control of samples may lead to large errors, especially at low concentrations. It was established that addition of the solvent to a soil-water mixture allows dissolution of an oil film on the water surface and provides better extraction of hydrocarbons from soil to water phase. To avoid effect of moisture content on the extraction efficiency and more precise analysis of the real samples, addition of the excess distilled water must be done. Addition of the polar organic solvent to a soil-water mixture (10% isopropanol) allows dissolution of an oil film on the water surface and provides linear dependence of extraction efficiency vs total petroleum hydrocarbons content in soil. Testing of the optimized method on model soil samples provided quantitative data, results being in 30-120% range from the real values.

### Introduction

Soil contamination resulting from petroleum hydrocarbon leaks pose a strong and widespread environmental hazard in Kazakhstan. In consequence of many transport accidents over several decades, petroleum hydrocarbons have become a very common pollutant in the environment. The analysis of these compounds in solid matrices traditionally requires several steps of extraction and preconcentration for the analytes and clean-up procedures. Besides, these extraction methods require expensive and hazardous solvents that are undesirable for health and disposal reasons. The environmental laboratories are attempting to find alternative extraction methods that will minimize the use of solvents. Solid

phase microextraction (SPME) has been introduced as an alternative to traditional extraction techniques [1]. SPME has become very popular in the last 10 years, especially in environmental analysis [2-6]. It is a rapid, inexpensive, and solventless technique for the extraction of organic compounds from gaseous, liquid, and solid samples. SPME provides sampling and preconcentration in a single step, and then the extracted analytes are thermally desorbed from the polymeric coating in gas chromatograph (GC) inlet. Many studies have supported the extremely appropriate capacity of the SPME-GC system in the determination of general organic contaminant classes in environmental matrices such as water [7-9] and soil [10-12]. However, quantitative determination of organic contaminants in soils and sludges using SPME is not as widely studied as it is for air or water. Quantitative determination of total

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petroleum hydrocarbons (TPH) in soil samples using headspace SPME is complicated due to variations in properties and chemical composition of different soil samples leading to unpredictable equilibrium shift in soil-headspace system.

The goal of this work was to study effects of moisture content and solvent additive on solid-phase microextraction of total petroleum hydrocarbons from soil samples.

## Experimental

### *Reagents and Materials*

SPME fiber 100  $\mu\text{m}$  polydimethylsiloxane (PDMS) was purchased from Supelco (Bellefonte, PA, USA). Fiber was conditioned in the hot injector port of the gas chromatograph according to recommendations of the manufacturer. Twenty mL vials with magnetic caps and PTFE/silicone septa (CTC Analytics AG, Switzerland) were used for extraction of TPH from soil. Prior to analyses, vials and septa were conditioned in a desiccator at a temperature of 150°C for 2 hrs. Chemically pure acetone and isopropanol were obtained from Sigma-Aldrich (USA). Crude oil was taken from Koschagyl oil field located in Atyrau oblast of Kazakhstan.

### *Parameters of SPME*

The mass of soil sample was 2 g. The optimal SPME conditions and equilibration times were determined using a 100- $\mu\text{m}$  (PDMS) fiber that was found to be optimal for extraction of TPH from aqueous samples [13]. The SPME parameters for extracting petroleum hydrocarbons from soil: pre-incubation time 1800 s, extraction time 60 s, extraction temperature 95°C, desorption time 3 min.

### *Parameters of GC-MS*

Analyses by GC-MS were carried out using 6890/5973N (Agilent, USA) system equipped with a Combi-PAL autosampler (CTC Analytics AG, Switzerland). The autosampler was equipped with a 32-position 10/20 mL tray, 10/20 mL agitator, SPME fiber holder and a conditioning station. The GC was equipped with a split/splitless inlet working in splitless mode to a 30 m  $\times$  0.250 mm DB-1MS column with a 0.25  $\mu\text{m}$  film thickness (Agilent, USA). Helium was used as carrier with a constant flow rate of 1 mL/min.

GC oven temperature program: 40°C (held for 10 min), heating to 240°C at 20°C/min (held for 20

min), the temperature of the MS interface was kept at 240°C. MS detection was conducted in the mode of scanning ions in the range of  $m/z$  34-600.

### *Effect of Moisture Content and Soil Type on SPME Extraction TPH from Soil*

Samples of soils of different particle size: marl, clay and loam, were taken to study the effect of moisture and soil type on the solid phase microextraction of petroleum hydrocarbons from soil. After that, 3 fractions weighing 15 grams each were sampled from soil of each type. Before the experiment, all the soils were dried in oven to constant weight at 105°C (for 4 hours). Each soil sample was spiked with crude oil from Koschagyl deposit, so that concentrations were 1.0 g/kg and 30 g/kg. Then samples were left in sealed vessels for 2 days to establish equilibrium between solid and gas phases. Soil samples of 2 g were weighed into 20-mL vials. Before analysis, soil samples were wetted with distilled water so that the moisture content was 0, 5, 10, 15, 20 and 25%, and analyzed by SPME-GC-MS.

### *Effect of Addition of Different Solvents on SPME of TPH from Soil*

To study the effect of addition of solvents on the solid phase microextraction of petroleum hydrocarbons from soil, three solvents were selected: distilled water, 10% acetone and 10% isopropanol.

Ten grams of dried soil was contaminated by petroleum from Koschagyl deposit ( $C_{\text{TPH}} = 1$  g/kg). Then 2 g of the prepared sample was placed into four 20-mL vials. Three samples were wetted with 5 mL of solvents and one sample was left dry. The experiment was performed in duplicate.

### *Preparation of Calibration Samples*

To obtain calibration plot, seven standard solutions of TPH in methylene chloride having a volume 5.0 mL and concentrations 0.5, 2.5, 5.0, 25.0, 50.0, 150 and 250 mg/L were prepared from a working solution of TPH with a concentration of 10 mg/mL. The working solution of 10 mg/mL was prepared in methylene chloride gravimetrically. Each of the prepared solutions was spiked in the volume of 100  $\mu\text{L}$  to the vials with 2.00 g soil sample. Then vials were left open under the fume hood for 30 min for evaporation of methylene chloride. The concentration of TPH in the calibration soil samples made up 0.01, 0.05, 0.1, 0.5, 1.0, 3.0 and

5.0 g/kg, respectively. Samples were analyzed by SPME-GC-MS at the optimized parameters. Analysis of each sample was performed in duplicate.

## Results and Discussion

Obtained results showed that the increase of the moisture content in marl and clay loam leads to the increase of the response of petroleum hydrocarbons (Figs. 1 and 2), which may be caused by the displacement of petroleum hydrocarbons from soil by water because of the greater affinity of the soil to water and low concentration of natural organic matter in the soil.

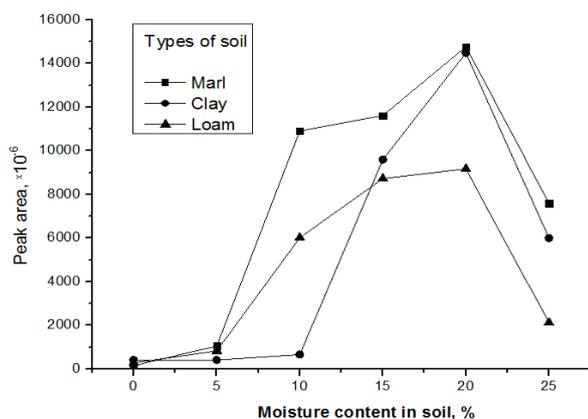


Fig. 1. Relationship between peak area of petroleum hydrocarbons and moisture content for different soil types at C(TPH) = 1 g/kg.

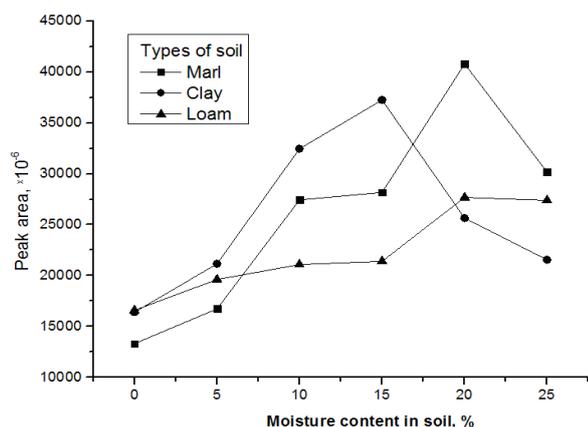


Fig. 2. Relationship between peak area of petroleum hydrocarbons and moisture content for different soil types at C(TPH) = 30 g/kg.

It was established that at the concentration of petroleum hydrocarbons of 30 g/kg, an increase of the moisture content in clay leads to an increase of the response of petroleum hydrocarbons reaching its maximum at 15-20% depending on the soil type

followed by its gradual decrease. At the concentration of petroleum hydrocarbons of 1 g/kg, the maximum response was observed at the moisture content 20% followed by its gradual decrease. The decrease of the response can be caused by saturation of soil with water leading to formation of a flat water surface above the soil. It provides a decrease of a surface area on the sample-headspace interface followed by a slower evaporation of hydrocarbons.

The experimental results showed that for the same concentration of petroleum hydrocarbons, an increase of moisture content in soil from 0 to 20% can lead to a 15x increase of TPH response by SPME. This effect is particularly pronounced at lowest concentrations of petroleum hydrocarbons.

### *Effect of addition of different solvents on SPME of TPH from soil*

Determination of the total content of petroleum hydrocarbons in soils by SPME-GC-MS without humidity control of samples may lead to large variations in results and errors, especially at low concentrations. To minimize the effect of moisture content, excess water can be added immediately prior to analysis with careful shaking of the vial during the extraction, which will also effectively displace petroleum hydrocarbons from soil and increase the extraction efficiency. To avoid effect of moisture content on the response, it was decided to add 5.0 mL of distilled water to 20-mL vial containing 2.0 g of soil sample. The main drawback of this method is possible formation of the oil film on the surface of the water thus complicating quantitation of petroleum hydrocarbons. Experiments confirmed this hypothesis: increase of TPH in soil over 100 mg/kg did not lead to the increase of TPH response by SPME-GC-MS. The oil film was visually observed at TPH content in soil over 10 g/kg.

To avoid this problem it was suggested to add organic solvent to a soil-water mixture. It will provide better solubility of hydrocarbons in water.

The objective of the next experiment was to establish the effect of addition of acetone and isopropanol on SPME of TPH from soil-water mixtures. Both solvents are well soluble in water and can provide better dissolution of the fine oil film.

Collected data (Fig. 3) showed that the addition of acetone and isopropanol leads to the decrease of TPH response that was expected before because of the better dissolution of oil in water and inhibiting evaporation of hydrocarbons. Isopropanol is more hydrophobic ( $\log K_{ow} = 0.05$ ) than acetone ( $\log K_{ow} = -0.24$ )

and it should provide better dissolution of hydrocarbons in water. In spite of that fact, addition of isopropanol provided higher response of TPH compared to acetone. It may be caused by more efficient extraction of hydrocarbons from soil by more hydrophobic solvent.

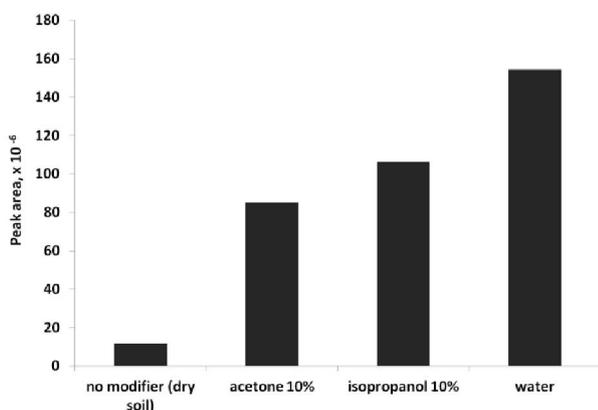


Fig. 3. The influence of the addition of different polar solvents to the soil on the response of TPH.

At the next stage, the effect of addition of the various amounts of isopropanol to the soil-water mixture was studied (Fig. 4). It was established that an increase of isopropanol concentration leads to a gradual increase of TPH response followed by a maximum achieved at 10%. The increase of the response can be explained by more efficient extraction of hydrocarbons from soil.

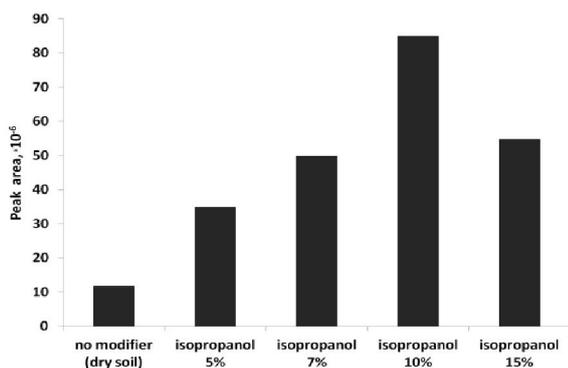


Fig. 4. Effect of isopropanol concentration on SPME of TPH from soil-water mixtures.

Thus, it was established that the addition of solvent to the soil-water mixture allows dissolution of the oil film on the water surface and provides better extraction of hydrocarbons from soil to water phase. Isopropanol was found to be the most efficient solvent for this purpose. Its optimal concentration was found to be 10%.

### Calibration plot

To check the optimized parameters, calibration plot of TPH SPME-GC-MS peak area vs its concentration in soil was obtained. The calibration plot was found to be linear in the range from 0.01 to 1.0 g/kg (Fig. 5). At concentrations higher than 1.0 g/kg calibration curve becomes curved most probably due to saturation of the fiber coating.

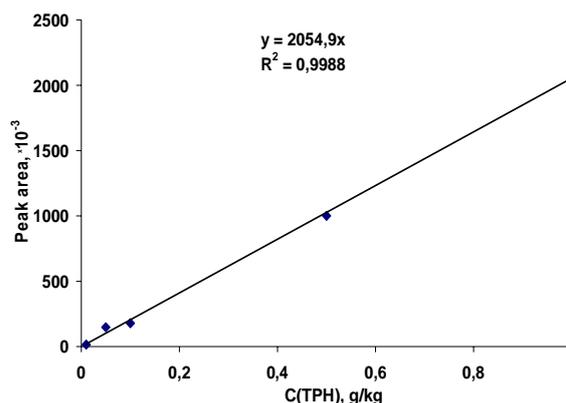


Fig. 5. Calibration curves of TPH by SPME-GC-MS from soil.

Thus, the obtained linear calibration plot showed the efficiency of the optimized extraction parameters. The optimized method was applied for quantitative determination of petroleum hydrocarbons in soil samples taken from Koschagyl deposit contaminated with known concentrations of TPH. Obtained recovery values were in 30-120% range. To achieve better precision of the method, it requires further optimization including parameters like extraction temperature and time, fiber coating and calibration by internal standard or standard addition methods.

### Conclusions

Thus, in a present work, effects of moisture content and solvent additive on solid-phase microextraction of total petroleum hydrocarbons from soil samples were studied. It was established that an increase of the moisture content in soil leads to the increase of the response of petroleum hydrocarbons reaching its maximum at 15-20% depending on the soil type and concentration of TPH followed by its gradual decrease. For the same concentration of petroleum hydrocarbons the increase of moisture content in soil from 0 to 20% may lead to the 15x increase of TPH response by SPME. Determination of TPH in soils by SPME-GC-MS

without humidity control of samples may lead to large errors, especially at low concentrations. To minimize the effect of moisture content, excess water (5.0 mL) can be added before analysis.

Addition of solvent to a soil-water mixture allows dissolution of the oil film on the water surface and provides better extraction of hydrocarbons from soil to water phase. Isopropanol was found to be the most efficient solvent for this purpose. Its optimal concentration was found to be 10%.

At the optimized parameters, linear calibration plot was obtained. Testing of the optimized method on model soil samples provided quantitative data, results being in 30-120% range from the real values.

The method requires further optimization including parameters like extraction temperature and time, fiber coating and calibration by the methods of internal standard or standard addition.

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