

Rapid Screening Method for the Total Petroleum Hydrocarbons in Water Samples by Solid-Phase Microextraction and GC-MS

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Abstract

Determination of total petroleum hydrocarbons (TPH) in water is an important tool for monitoring of contamination due to oil spills or leaking storage tanks. In this study, a screening method for the quantification of total petroleum hydrocarbons in water based on solid phase microextraction (SPME) in combination with gas chromatography – mass spectrometry (GC-MS) is presented. Extraction of hydrocarbons from water samples were conducted by SPME fiber coating placed into the headspace above water. Petroleum hydrocarbons were desorbed from the fiber coating in the injection port of gas chromatograph. The effect of the following parameters affecting the distribution of the analytes between three phases on the response of TPH were studied: SPME fiber coating type and dimensions, extraction temperature, extraction time and pH. The optimized method uses 100 μm polydimethylsiloxane fiber coating, extraction time 600 s, extraction temperature 80°C, without addition of salt at basic pH. The developed method was successfully applied for detection of total petroleum hydrocarbons in water taken from Koschagyl oil fields and Koschagyl village.

Introduction

As contaminants, petroleum and petroleum products pose a threat to the environment and its inhabitants. Covering vast areas of water surface with a thin film, petroleum is harmful to many living organisms and adversely affects all parts of the biological chain. Not only petroleum films on the water surface of the seas and oceans can disrupt the exchanges of energy, heat, moisture and gases between the atmosphere and water body; affect the physical and chemical processes, but petroleum settled on the bottom for a long time also can hurt all living things: the accumulation of petroleum can appear in the food chain of the simplest and higher animals. Aquatic toxicity is manifested at the concentration of more than 1 mg/L. Sources of TPH in the environment are diverse: oil spills at oil production, transportation and storage of fuel, oil

pipelines and oil storage breakthrough; process disturbances and lack of wastewater treatment refineries, refueling engines, as well as emissions into the air of unburned fuel components from the internal combustion engine [1]. In surface water and groundwater, most petroleum products are the result of the transportation of oil from wastewater enterprises for domestic and municipal water [2]. Over time, the concentration of petroleum in the water under the influence of evaporation of the more volatile components, dissolution, oxidation, biodegradation, and emulsification is reduced. Oxidized residues of petroleum settle to the bottom of reservoirs [1].

Determination of petroleum products in the environment is quite complex task since the latter do not represent one particular substance, but the complex mixture of many different compounds, besides not having a constant composition. For analysis of TPH in water samples, methods based on different physical properties of petroleum

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products are used: gravimetric, IR spectrophotometric, fluorescence and chromatographic. Sample preparation is the most time-consuming and "dirty" stage of the analysis, which includes an extraction by organic solvent, cleanup and concentration.

Solid-phase microextraction has appeared recently, but immediately became one of the most popular "state-of-the-art" sampling/sample preparation methods due to its simplicity, speed and efficient extraction of toxic substances from various matrices. It became standard technique for many analytical tasks. SPME is based on extraction of analytes by a thin polymeric film coated to a thin quartz rod (fiber). SPME has been applied to the analysis of different petroleum-originated water pollutants including petroleum fuel contamination [3], polycyclic-aromatic and aliphatic hydrocarbons [4, 5], bioavailable petroleum hydrocarbons [6] and gasoline range hydrocarbons [7].

The goal of this study was to develop a method of rapid screening of total petroleum hydrocarbons in water samples using GC-MS in combination with SPME.

Experimental

Reagents and materials

Four SPME fibers, such as 100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane/divinylbenzen (PDMS/DVB), 85 μm carboxen/polydimethylsiloxane (CAR/PDMS), 7 μm PDMS were purchased from Supelco (Bellefonte, PA, USA). All fibers were 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) were used for extraction of TPH from water. Prior analyses, vials and septa were conditioned in a desiccator at a temperature of 150°C for 2 hrs. Chemically pure isopropanol and sodium chloride were obtained from Laborpharma LLC (Almaty, Kazakhstan). Helium (99.995 % purity) was obtained from Tehgaz (Orenburg, Russia). Crude oil was taken from Koschagyl oil field located in Atyrau oblast of Kazakhstan.

Parameters of SPME

The volume of water sample was 2 mL. SPME was done at a periodic shaking. The optimal SPME

parameters for extracting petroleum hydrocarbons from water (fiber coating, extraction temperature and time, salt additive and pH) were determined experimentally.

Study of the effect of fiber coating was conducted under the following SPME parameters: extraction time 180 s, extraction temperature 80°C.

Study of the effect of extraction temperature was conducted under the following SPME parameters: fiber coating 100 μm PDMS, extraction time 60 s.

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 split/splitless inlet working in splitless mode to a 30 m x 0.250 mm DB-1MS column with a 0.25 μm 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.

Preparation of solutions of petroleum hydrocarbons in water

All the experiments were conducted on model water samples contaminated with crude oil taken from the Koschagyl oil field.

Distilled water was used for preparation of experimental samples. Distilled water was always checked for the presence of hydrocarbons by SPME-GC-MS before experiments, its pH was measured to be 6.0.

To prepare a standard solution of TPH (C = 10 mg/L), 6 μL of crude oil ($\rho = 0,878 \text{ g/mL}$) was added to 500 mL of water. For better dissolution of crude oil, water was preheated close to its boiling point.

Results and Discussion

Selection of the optimal extraction coating

SPME coating significantly affects the selectivity of SPME for organic compounds from

the samples and the final method sensitivity. The obtained results (Fig. 1) showed that 100 μm PDMS fiber coating provided highest MS response of TPH and, thus, was used as optimal at subsequent method development.

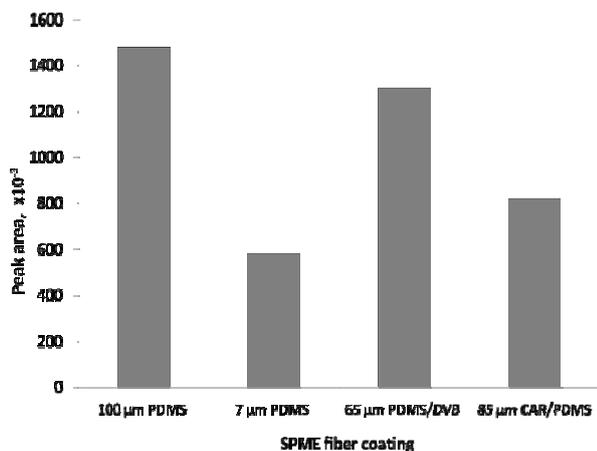


Fig. 1. Effect of fiber coating on efficiency of extraction of TPH from water.

Determination of optimal extraction temperature

Temperature has a significant impact on SPME of organic compounds from the headspace above the water. To determine the optimal extraction temperature, solutions of crude oil, fraction 1 (boiling point 330-340) and fraction 2 (boiling point 350-360) in water with concentrations of 10 mg/L were extracted at temperatures of 50, 60, 70 and 80°C and analyzed by GC-MS. Extraction from water at higher temperatures is technically impossible due to a significant increase in pressure inside vials and its possible destruction.

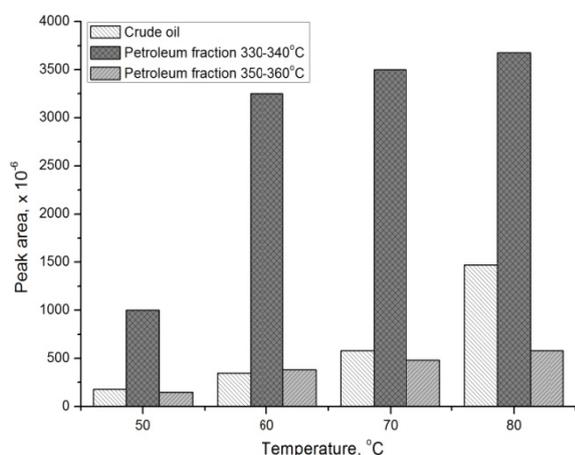


Fig. 2. Effect of SPME extraction temperature on TPH peak area.

The experimental results (Fig. 2) showed that the increase of the extraction temperature in the selected range leads to an increase in the response of TPH for all the studied samples, which is undoubtedly due to an increase in vapor pressure of the hydrocarbons above the aqueous phase. In addition, a comparison of chromatograms obtained by extraction at different temperatures (Fig. 3) shows that the increase of temperature leads to extraction of a wider range of hydrocarbons due to the increased volatility of heavy petroleum fractions.

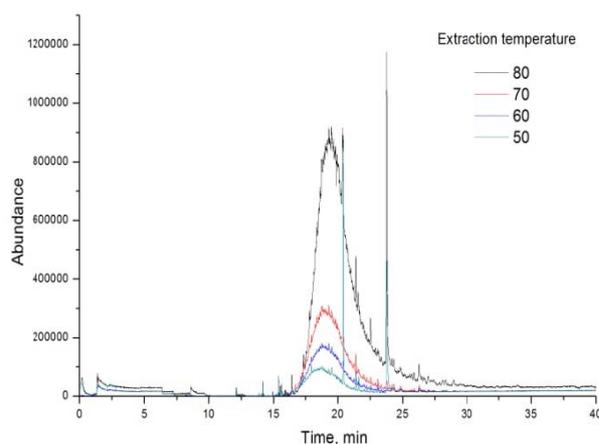


Fig. 3. Effect of temperature on the extraction of petroleum hydrocarbons from water.

Thus, the optimal extraction temperature, providing the highest response of TPH is 80°C. Further experiments were carried out at this extraction temperature.

Determination of the optimal extraction time

To obtain the highest response using SPME, extraction must be conducted when equilibrium between water, headspace and fiber coating is reached. To establish equilibration time, water samples contaminated by crude oil and 2 different oil fractions were analyzed using extraction time 10, 30, 60, 120, 300, 600, 1200 and 1800 s. The results are presented in Figure 4.

From Figure 4, it is seen that for all the studied samples, equilibrium is reached after 600 s extraction.

Due to the fact that a further increase in extraction time does not allow increasing the TPH response, extraction time of 600 s was chosen as an optimal. Subsequent experiments were performed using this value of extraction time.

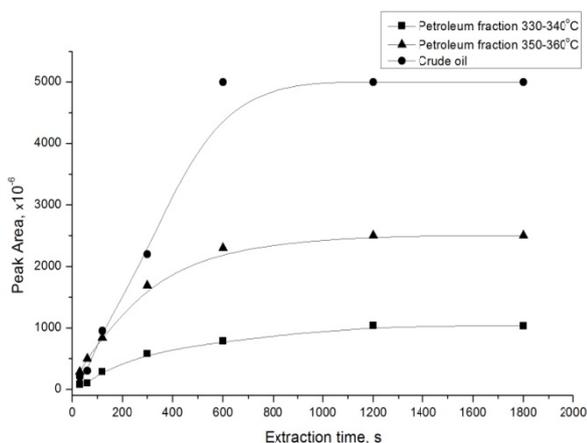


Fig. 4. Effect of extraction time on the peak area of petroleum hydrocarbons.

Effect of ionic strength

Another method used to enhance extraction of organic analytes from water samples is addition of strong electrolyte that increases ionic strength of a solution. This is so-called “salting out” effect.

To determine the effect of ionic strength on the response of TPH, 0.25, 0.40, 0.55, 0.70 g of sodium chloride was added to 2 mL of aqueous solution of crude oil and 2 different oil fractions followed by SPME-GC-MS analysis. The experimental results are presented in Figure 5.

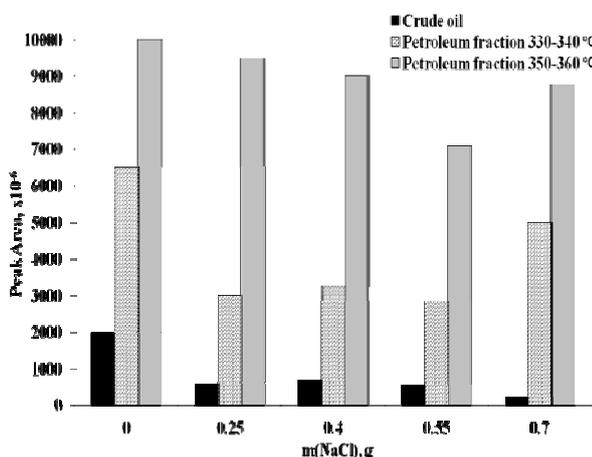


Fig. 5. Effect of ionic strength on the peak area of petroleum hydrocarbons.

The experimental results showed that the increase of sodium chloride concentration lead to a decrease of the response of TPH for the most of the samples. The highest response was registered in the analysis of petroleum samples containing no sodium chloride. It could be caused by a reduced

solubility of hydrocarbons in water forming a third phase in the system. This phase has no contact with the gas phase followed by an obstructed process of extraction of hydrocarbons from the headspace above the water samples.

Thus, it is the most advisable to carry out headspace SPME of petroleum hydrocarbons from water without addition of salt. In the case of analyzing water samples containing significant amounts of dissolved salts, it will be necessary to adjust the quantitative method using standard addition or an internal standard method.

Effect of pH

pH can have a significant impact on extraction of ionic compounds from aqueous samples. Typically, the extraction efficiency of bases is higher at high pH, for acids – at low pH, caused by a higher water solubility of ions than the corresponding neutral molecules. To establish the effect of pH on the efficiency of SPME of petroleum hydrocarbons from distilled water, 10 μ L of 1M HCl or NaOH were added to 2 μ L to solutions of crude oil (10 mg/L) and analyzed by SPME-GC-MS under the previously determined optimal parameters.

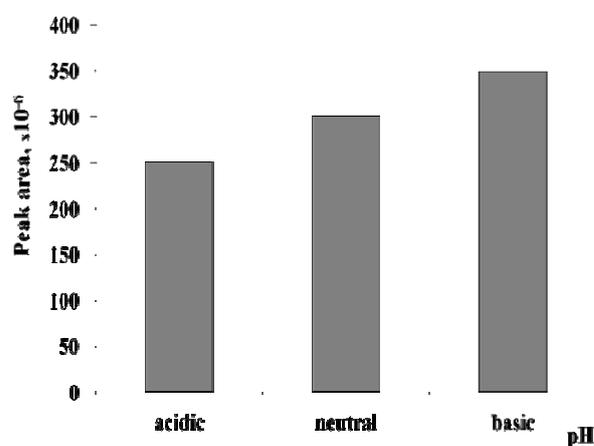


Fig. 6. Effect of pH on the peak area of petroleum hydrocarbons.

The experimental results (Fig. 6) showed that the increase of pH of a sample leads to an increase in the response of petroleum hydrocarbons, which is probably caused by a predominance of weakly basic compounds in the petroleum, which is a complex mixture of hydrocarbons of various classes and their derivatives. The difference between the results of analyzes of acidic and basic

solutions of petroleum was less than 30%, but for other samples, the difference may be greater, and should be determined by the concentration of ionizable compounds in them.

Application of the developed method

To verify the developed method, it was applied for the analysis of water samples taken from Koschagyl oil fields and Koschagyl village.

In Koschagyl oil fields, contamination is represented by a pure crude oil located inside old natural lakes and oil storage pits. In fall and spring, rain and ice water covers surface of oil contamination (Fig. 7) followed by a partial dissolution of hydrocarbons causing health risks for neighboring population and local animals represented by several small species and camels.

Analysis of water taken from Koschagyl oil fields using SPME-GC-MS showed the presence of TPH in all the studied samples. Quantitative analyses performed by standard method [8] showed TPH concentrations of up to 500 mg/L.

Analysis of utility water taken from Koschagyl village showed presence of TPH while standard GC and FTIR based methods did not provide sufficient sensitivity for detection of such levels of TPH.



Fig. 7. Water in Koschagyl oil fields in June, 2011.

Conclusions

Thus, in the present work, a new optimized method for screening of total petroleum hydrocarbons in samples of water was developed using gas chromatography–mass spectrometry in combination with solid phase microextraction. The method sensitivity was optimized for water samples contaminated by crude oil from Koschagyl oil

fields, the following optimum parameters were established: fiber coating 100 μm polydimethylsiloxane, extraction temperature 80°C, extraction time 600 s, no addition of salt, basic pH. The developed method was successfully applied for detection of TPH in water taken from Koschagyl oil fields and Koschagyl village.

The goal of the next stage will be development of SPME-GC-MS based method for quantitative determination of TPH in water samples.

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