

A STATIONARY PHASE FOR SOLID-PHASE EXTRACTION BASED ON NATURAL NANOMATERIAL SHUNGITE

Dr. Mereke Alimzhanova

Anel Kapar

Erlan Adilbekov

Kazhybek Ashimuly

Center of Physical Chemical Methods of Research and Analysis, **Republic of Kazakhstan**

al-Farabi Kazakh National University, **Republic of Kazakhstan**

ABSTRACT

This work describes an analytical procedure for determination of petroleum hydrocarbons in petroleum-contaminated water. The method involves a solid-phase extraction method with stationary phase sorbent from natural raw material shungite. Method development was performed on model samples of water samples contaminated by petroleum from Tengiz deposit. The use of natural raw nanomaterial shungite as stationary phase solves the problems concerned with industry wastes, since this nanomaterial is waste of gold mining plant in Eastern Kazakhstan from dumps of the polymetallic Bakyrchik deposit. The proposed method provides a rapid, environmentally friendly and accurate method for identification and quantification of the petroleum hydrocarbons contaminating water resources of Western Kazakhstan. This work describes application of the developed methodology for analysis of petroleum hydrocarbons in the water resources of Western Kazakhstan. It was investigated that 5 g of sorbent was the optimal mass for solid-phase extraction of petroleum with concentration to 3000 mg/L. In addition, it was established that 5% hexane solution extracted petroleum more effectively from water samples. The most advanced stage of sorption of a sorbent occurs at 0.8 mm of a sorbent particles size. The optimum solvent for elution was chloroform, that allows to elute the greatest amount of petroleum hydrocarbons. Also, it was proved that an activated shungite has the highest sorption ability comparing to non activated (extraction recovery at concentration of 100 mg/L is equal about 90 and 40% for activated and non activated sorbents, respectively).

Keywords: shungite, solid-phase extraction, sorbent, petroleum hydrocarbons, carbon nanotubes.

INTRODUCTION

At the present time, economic stability of many countries of the world depends on the amount of petroleum. Petroleum seeps in certain regions of the world Oceans, such as in the Gulf of Mexico, contribute substantial amounts of petroleum to nature environments that are comparable to large-scale accidental spills due to transport or drilling activities [1]. However, although the reserves may be roughly equivalent, rates are not. The case of the Exxon Valdez in Alaska or the Erika recently in South Brittany (France), are vivid examples of how anthropogenic influences impact coastal environments at a hurried pace.

Kazakhstan, with its considerable reserves of petroleum and gas (Figure 1), looks for increase in production of these minerals every year. However, it leads to serious environmental problems in zones of production and petroleum refining, in particular, about the Caspian Sea. Pollution of water of the Caspian Sea is one of the most serious problems of environmental protection for Kazakhstan today. Therefore, government should be directed on the using of new technologies and purification of water in mining areas. Precise quantification of natural or obtained hydrocarbon slicks floating on water is essential to reduce the effects on safety environment [2].



Figure 1. Spreading of petroleum and gas in Kazakhstan

As it is demonstrated in Figure 1, there are a lot of petroleum deposits near Caspian sea, consequently there is increased risk of pollution by petroleum. Determination of total petroleum hydrocarbons (TPH) in water samples is the analysis, which is carried out in many ecological laboratories. Total petroleum hydrocarbons is an any mixture of hydrocarbons that are found in crude petroleum. Traditional methodologies, as a rule, include manual liquid - liquid extraction (LLE) of samples of water with immiscible solvent, such as n-hexane or dichloromethane. Subsequently, extraction is dried up, using especially prepared the anhydrous sodium sulfate, concentrated through an evaporation step, which can include the dissolving exchange and is analyzed by gas chromatography with flame-ionization detector (GC-FID) using usual split. In contemporary ecological laboratories for analyzing TPH solid-phase extraction is used [3].

Now, scientists even more often pay much attention on the use of a method of solid-phase extraction (SPE). SPE – is an extraction method which includes cleaning of sample from impurities [4]. This method is effective for cleaning of the coastal bases affected by petroleum spills [5]. Solid phase extraction is a rapid method of sample preparation in which a sorbent (a solid motionless phase) is applied to concentrate and separate target components with the subsequent eluting (washing away) by suitable solvent [6]. In the SPE method the most significant thing is sorbent, that provides the adsorption of analytes. Developing this method, scientists develop more effective sorbents based on natural raw materials which provide high extraction recoveries of extremely small quantities of pollutants.

At the present time in analytical practice determination of organic pollutants in various objects is one of the most complex analyses, so when the highest sensitivity and selectivity of definition in most cases is required. For development of approaches of

green analytical chemistry, there was the purpose to develop a stationary phase for solid-phase extraction based on natural material shungite which is an available carbon sorbent.

The extraction recovery depends mainly on properties of a sorbent. That is why it is necessary to select the most corresponding sorbent for given application [7]. Alternative materials for sorbents of solid-phase extraction carbonaceous materials such as carbon nanotubes, a decanter and absorbent carbon are most often used. Selection of an appropriate analytical method and conditions of extraction allows to reach the expected selectivity of analytical procedure [8]. New perspective raw material for development of stationary phase for SPE can be shungite breeds of which are found in large volumes in Kazakhstan. Shungite is the material, based on polymers of carbon. Shungite and absorbent carbon possess has very similar sorption properties. In the majority of scientific researches, shungite was used as a sorbent for cleaning water from impurities, and also in production of rubber and construction materials. Researches on studying of properties of a shungite as adsorbent have been conducted, however shungite so far was not applied as a stationary phase for solid-phase extraction [9].

The following research had the aim to develop a method of solid-phase extraction procedure coupled to a gas chromatography with a mass-spectrometry (GC-MS) based on the natural nanomaterial shungite. To determine TPH in petroleum-contaminated water samples, parameters of solid-phase extraction with stationary phase based on nanomaterial shungite were optimized. Application of a shungite in the form of nano powder for extraction of pollutants allows to considerably reduce the cost of analysis and increases efficiency of solid-phase extraction method.

EXPERIMENTAL PART

Reagents and Chemicals

Chloroform (> 99.8 %), hexane (> 99.5 %) were obtained from Sigma-Aldrich (Germany). Shungite was obtained from (dumps of the polymetallic Bakyrchik deposit) Zharminsky district, Eastern Kazakhstan. Petroleum was obtained from Tengiz deposit, Atyrau region, Western Kazakhstan.

GS-MS parameters

This analysis was performed using CTC-Combi-PAL autosampler (Agilent, USA) installed on a 7890N/5975C gas chromatography-mass-spectrometry (Agilent, USA) system equipped with a split/splitless injector. The sample with volume of 1.0 μ L was injected into the inlet heated to 280°C in splitless mode. Separation was conducted on a 60 m x 0.25 mm (0.50 μ m film) DB-WAX etr column at a constant flow rate of helium (> 99.995 %) of 1.0 mL/min. The oven temperature was programmed from 50°C (held for 5 min) to 280°C (held for 30 min) at a heating rate of 50°C/min. Temperatures of MS source, quadrupole and interface were set to 230, 150 and 280°C, respectively. Detection was performed in scan mode (m/z 34-400). Total run time was 25 min.

Influence of a sorbent mass on petroleum solid-phase extraction

For determination of optimal mass of the sorbent for SPE were used 5 and 10 g of a shungite. Three petroleum-contaminated water samples till concentrations – 30, 300,

3000 mg/L have been studied. Condensation was carried out by 10 mL of 5% water solution of hexane and elution was carried out by 15 mL of chloroform.

Influence of a solvent type on condensation at solid-phase petroleum extraction

Activation and efficiency of the sorbent are determined by time using a stage of condensation of pure organic solvents and water solutions of organic solvents. The stage of condensation brings a sorbent into an active state and improves interaction with a sample. Independent variable of the experiment was concentration of hexane. The selection of suitable solution for condensation of a sorbent was carried out with use of hexane and its 5% solution.

Influence of particles size on solid-phase extraction recovery

Shungite samples were sifted through a sieves of 0.8 mm and 0.3 mm in size. Independent variable of the experiment was sorbent particle size.

Selection of optimum solvent for elution of petroleum hydrocarbons

Eluent is one of important parameters of solid-phase extraction. Petroleum nature directly affects its solubility in various organic solvents. Therefore, it is necessary to select the eluent for washing of SPE cartridge, considering solubility of petroleum in different solvents. For eluent selection 2 solvents were used: hexane and chloroform, because petroleum Tengiz is highly soluble in these solvents.

The comparison of sorption abilities of activated and not activated sorbents

The sorbent based on a shungite is received by carbonization and further activation. In this experiment, extent of sorption of hydrocarbons of petroleum by activated and not activated sorbents based on a shungite was studied. During carbonization process, the raw materials are burned in oxygen-free space at 750-800°C. Activation of a sorbent was carried out by the gas-vapor method, the sorbent is treated by water vapor. At activation of a sorbent nanopores increase, micro- and meso- pores open, while not activated sorbent has a macropores.

Quantitative analysis of TPH

For creation of calibration dependences as standards petroleum solutions which are selected from Tengiz deposit with concentration of 100, 300, 500, 700 and 10000 mg/L were used. Working solution with concentration of 10000 mg/L, was prepared by a gravimetric method: on analytical scales 0.100 g of oil was weighed and dissolved in 10 mL of chloroform. Further calibration solutions were prepared by dissolving of working solution in chloroform with corresponding ratios. Selected 1 mL of prepared solutions and carried out Determination of petroleum hydrocarbons was carried out analyzing 1 mL of prepared solutions by GC-MS.

By results of experiment, calibration curve of petroleum hydrocarbons is linear in the range of concentrations 100-10000 mg/L ($R^2 = 0,9996$). Using developed SPE method in combination with external calibration approach, it is possible to quantify petroleum hydrocarbons in petroleum-contaminated water.

Comparison of solid-phase extraction and liquid-liquid extraction of petroleum hydrocarbons from water samples

To conduct comparative tests of SPE and liquid-liquid extraction (LLE), four petro polluted water samples were chosen (A, B, C and D - model samples with various

unknown concentration) and were extracted by solid-phase and liquid-liquid extraction. Dependent variable of the experiment was measured by gas chromatography-mass spectrometry. Quantitative determination of hydrocarbons of petroleum was performed by external standard method.

Liquid-liquid extraction was carried out as follows: 50 mL of petro polluted water sample and 50 mL of chloroform were placed in a funnel of 150 mL and extracted within 20 min and left for 10 min for division of organic and water phases. For analysis of hydrocarbons of petroleum, 1 mL of an organic phase was collected.

RESULTS AND DISCUSSION

According to obtained results (Figure 2A), 10 g of a sorbent extract target analytes less efficiently (1.3 times) in comparison with 5 g of a sorbent for concentration 3000 mg/L. For concentrations 30 and 300 mg/L insignificant difference in analytes responses was observed. It can be concluded that with increase in mass of a sorbent, it is necessary to increase eluent volume.

Figure 2B demonstrates that 5% water solution of hexane extracted analytes more efficiently for concentrations 3 and 300 mg/L (2 and 3 times, respectively). It may be caused by stationary phase activation by water solution, due to affinity of a matrix of the analyzed solution and subsequently, the eluent quickly pass through a sorbent.

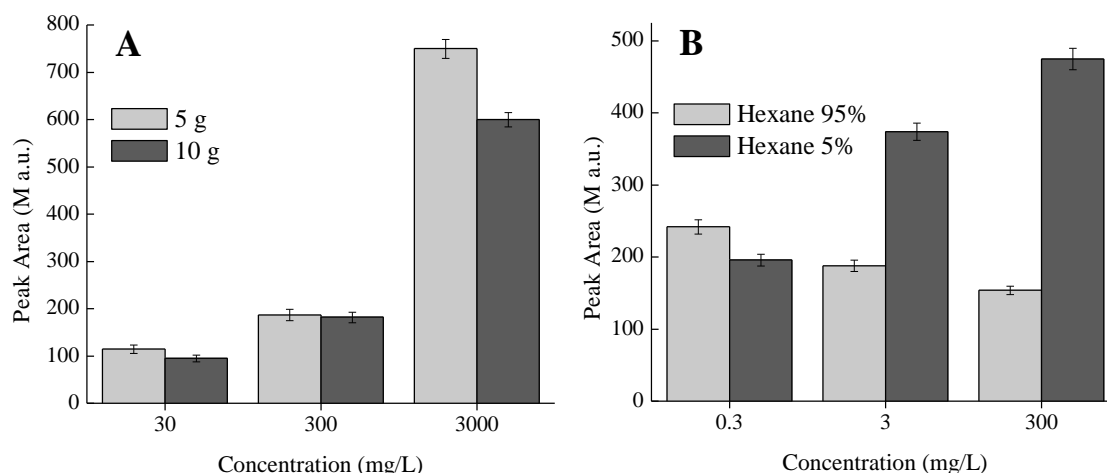


Figure 2. Effect of a sorbent mass on responses of total petroleum hydrocarbons (A) and effect of concentration of eluent on responses of total petroleum hydrocarbons (B)

It was established that sorbent with macro- particles size (0.8 mm) showed better results, than with a meso- and nano- size (0.3 mm). Extraction recovery by the sorbent with 0.8 mm was twice higher than with particles size 0.4 mm. Thus, the large particles size of a sorbent is necessary for higher extraction recovery of petroleum hydrocarbons from water samples (Figure 3A).

According to obtained results, response of TPH was 1.5 times higher for concentration of 300 mg/L with chloroform as eluent than hexane. Responses of analytes remained almost unchanged for concentration of 0.3 mg/L (Figure 3B).

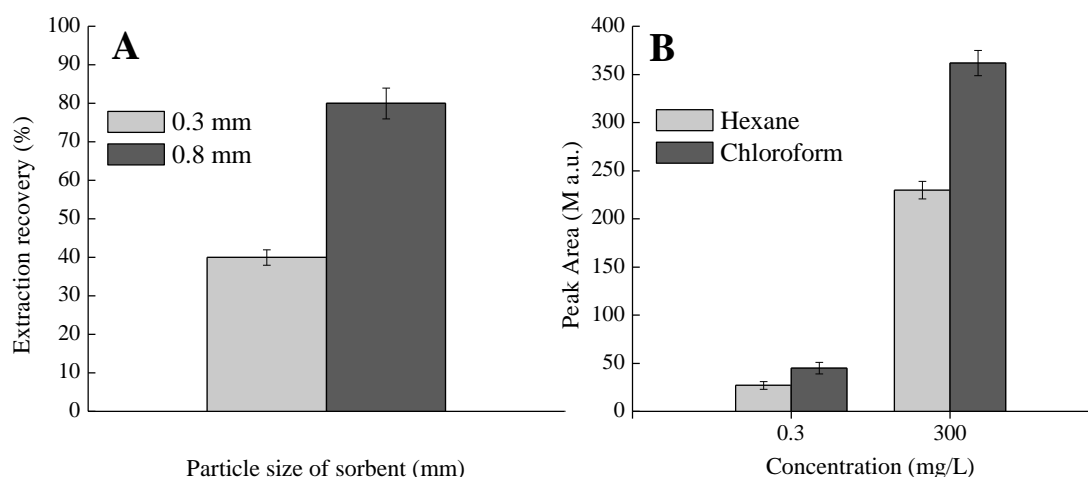


Figure 3. Effect of particle size of sorbent on analytes responses (A) and histogram of eluents comparison (B)

By results of experiment, it was quantitatively proved that sorption ability of the activated shungite is twice higher, than not activated sorbent. Petroleum hydrocarbons occluded to macro- and mesopores of sorbent, desorb effectively to solvent and therefore, high sorption efficiency is provided (Figure 4A).

The results of comparison of extraction types showed that petroleum extraction by solid-phase extraction method with a stationary phase shungite is not inferior in efficiency to a classical method of extraction of petroleum products from water samples (Figure 4B). Concentration extracted by SPE method was almost similar to LLE method for the samples A, B, C and D insignificantly lower (1.2 times). At high concentration of petroleum (over 3000 mg/L) in water efficiency of solid-phase extraction decreased that can be caused by reduction of sorption capacity of a sorbent. For analysis of strongly polluted samples of water it is necessary to increase the mass of a sorbent twice. For achievement of effective solid-phase extraction or for economy of a sorbent it is possible to dilute water sample several times.

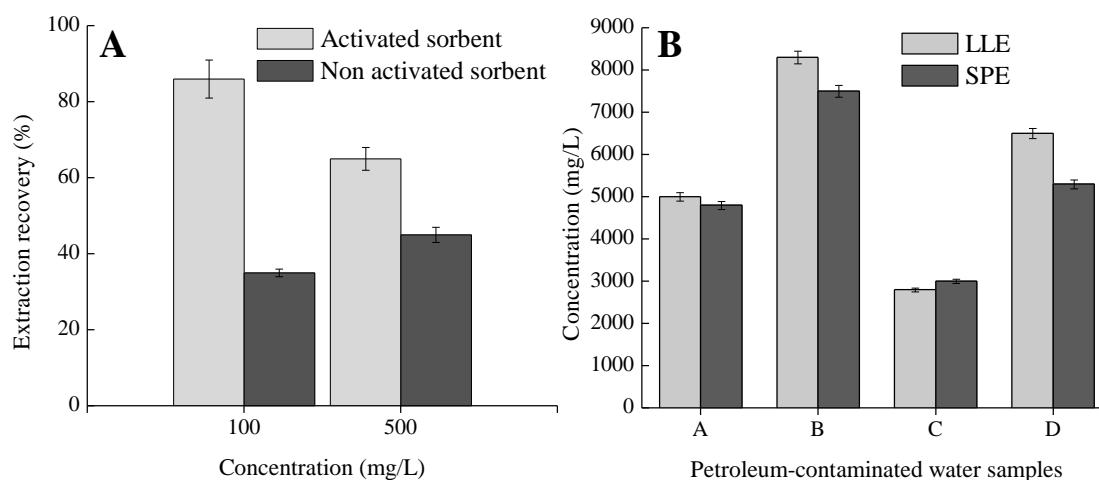


Figure 4. Histogram of comparison of sorption ability for activated and not activated sorbents (A) and histogram of comparison of extraction types for petroleum hydrocarbons in water samples (B)

Thus, on the example of use of a shungite as a stationary phase for petroleum SPE from water objects it was established that shungite is quite competitive sorbent allowing to extract effectively investigated substances. The scheme of sample preparation with use of shungite is presented in Figure 5.

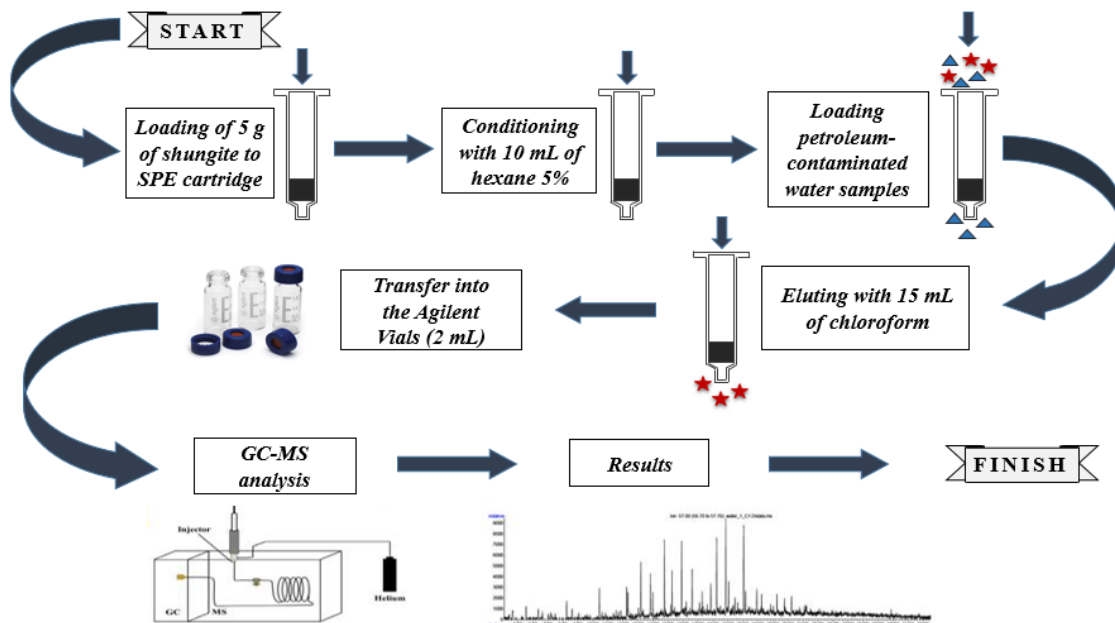


Figure 5. Scheme of sample preparation by developed solid-phase extraction method for determination of TPH in petroleum-contaminated water

CONCLUSION

This paper demonstrates the successful application of shungite as a stationary phase for SPE analysis of TPH in petroleum-contaminated water samples. It was investigated that 5 g of sorbent was the optimal mass for solid-phase extraction of petroleum with concentration 3000 mg/L. In addition, it was established that 5% hexane solution extracted petroleum more effectively than pure hexane from water samples. The most advanced stage of sorption of a sorbent occurred at 0.8 mm of a sorbent particles size. The optimum solvent for elution was chloroform, that allows to elute the greatest amount of petroleum hydrocarbons (1.5 times higher for concentration of 300 mg/L than hexane). Also, it was proved that an activated shungite has the highest sorption ability (extraction recovery at concentration of 100 mg/L is equal to 90%). Shungite is quite competitive sorbent for TPH. Sorbents based on a shungite are ecological and economic favorable. Therefore, sorbents based on shungite can be alternative stationary phase for SPE for determination of various environmental pollutants.

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