



Automated IR determination of petroleum products in water based on sequential injection analysis



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ABSTRACT

The simple and easy performed automated method for the IR determination of petroleum products (PP) in water using extraction-chromatographic cartridges has been developed. The method assumes two stages: on-site extraction of PP during a sampling by using extraction-chromatographic cartridges and subsequent determination of the extracted PP using sequential injection analysis (SIA) with IR detection. The appropriate experimental conditions for extraction of the dissolved in water PP and for automated SIA procedure were investigated. The calibration plot constructed using the developed procedure was linear in the range of 3–200 $\mu\text{g L}^{-1}$. The limit of detection (LOD), calculated from a blank test based on 3σ was 1 $\mu\text{g L}^{-1}$. The sample volume was 1 L. The system throughput was found to be 12 h^{-1} .

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1. Introduction

Petroleum products inevitably are released into the environment and contaminate surface water bodies particularly near production or storage sites, but also escape accidentally during handling, transport or processing [1]. As it is well known [2,3], the petroleum products are very complex mixtures that contain primarily aliphatic and aromatic hydrocarbons and heterocycles. Currently, World Health Organization regulates the PP content (dissolved/emulsions) in water, which cannot exceed levels higher than 300 $\mu\text{g L}^{-1}$ to provide a conservative level of protection [4]. Thus, one of the most important analytical tasks of environmental monitoring is the PP determination in the natural waters to assess levels of environmental pollution.

The four most commonly used PP testing methods include gas chromatography (GC) [5–10], infrared absorption (IR) [11], spectrofluorimetry (SFL) [12] and gravimetric analysis (GA) [13,14] (Table 1). GC-based methods detect a broad range of hydrocarbons, provide both sensitivity and selectivity, and can be used for petroleum hydrocarbon identification as well as quantification. However, there are difficulties in the automation of whole procedures and determination of total PP content in water. The main advantage of the IR method is the insignificant dependence of absorption on the type of petroleum hydrocarbons, mainly

containing in water samples. However, the IR method assumes the delivery of large volume of water sample in laboratory (up to 1 L per determination). The SFL is the most sensitive method for the determination of aromatic hydrocarbons and heterocycles, but the emission of hydrocarbons depends on their structure [15]. GA methods may be useful for water samples with a high PP concentration.

Generally GC, IR, SFL, and GA methods include conventional liquid-liquid extraction (LLE) of PP from the water samples to another water-immiscible solvent. Commonly used solvents for extraction are carbon tetrachloride, tetrachlorethylene, trifluorotrichloroethane and hexane. Although LLE is relatively simple and inexpensive, it has many drawbacks, among them the need to use large quantities of solvents. In order to achieve the desired enrichment factor, the excess solvent requires removal by evaporation, and extract cleanup may also be necessary. Also the solid-phase (SPME) [7], headspace solid-phase microextraction (HS-SPME) [8] and flow solid-phase (FSPME) [9] microextraction techniques are proposed to the hydrocarbons determination in water by GC. The SPME is based on the extraction of hydrocarbons from the water using a microsyringe equipped by poly(dimethylsiloxane) fiber in a needle. In the case of HS-SPME fiber with a poly(dimethylsiloxane) coating is placed in a headspace of a water sample. For the FSPME water is passed through a syringe steel needle filled with the Tenax GR sorbent at the rate of 2 mL min^{-1} . The double solid-phase extraction (SPE) is suggested for the determination of aliphatic and aromatic hydrocarbons in

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Table 1
Comparison of the methods for determination of PP.

Detection technique	Analyte	Sample	Sample volume, mL	Sample preparation	LOD	Reference
GC-FID	C ₁₀ –C ₄₀ Hydrocarbons	Surface and wastewater	900	Extraction (50 mL hexane), solvent evaporation (to 1 mL)	0.1 mg L ⁻¹	[5]
GC-FID	Hydrocarbons	Water and wastewater	2	Solid-phase microextraction (poly(dimethylsiloxane) fiber)	0.03–1 µg L ⁻¹	[7]
GC-FID	C ₆ –C ₂₀ Hydrocarbons	Water	2	Headspace solid-phase microextraction (poly(dimethylsiloxane) fiber)	2.0–13 µg L ⁻¹	[8]
GC-FID	Hydrocarbons	Water	5	Flow solid-phase microextraction (Tenax GR sorbent)	1–5 µg L ⁻¹	[9]
GC-FID	Hydrocarbons	Groundwater	100	Double solid-phase extraction (Sep-Pak C18 cartridges)	5 µg L ⁻¹	[10]
IR	Aliphatic and aromatic hydrocarbons and heterocycles	Surface and saline waters, industrial and domestic wastes	1000	Extraction (30 × 2 mL trifluorotrichloroethane), interferences adsorption (silica gel)	1 mg L ⁻¹	[11]
SFL	Aromatic hydrocarbons and heterocycles	Surface and wastewater	100	Extraction (10 mL hexane), interferences adsorption (aluminum oxide)	5 µg L ⁻¹	[12]
GA	Oil	Surface and saline waters, industrial and domestic wastes	1000	Extraction (30 mL hexane), interferences adsorption (silica gel)	1.4 mg L ⁻¹	[13]
FIA-SFL	Aromatic hydrocarbons and heterocycles	Natural water	20	On-line extraction-chromatographic preconcentration (PTFE column), elution (0.5 mL hexane) and chromatomembrane phase separation	1 µg L ⁻¹	[15]
FIA-IR	Aliphatic and aromatic hydrocarbons and heterocycles	Water	6.5	On-line extraction (4 mL 1,2,3,4-tetrachloro-1,1,2,3,4,4-hexafluorobutane) and membrane phase separation	0.1 mg L ⁻¹	[16]
SIA IR	Aliphatic and aromatic hydrocarbons and heterocycles	Water	1000	On-site extraction (PTFE cartridge), elution (1 mL trifluorotrichloroethane) and interferences adsorption (silica gel)	1 µg L ⁻¹	This work

IR – infrared absorption; GC-FID – gas chromatography-flame-ionization detector; SFL – spectrofluorimetry; GA – gravimetric analysis; FIA-SFL – flow injection analysis with SFL detection; FIA-IR – flow injection analysis with IR detection; SIA IR – sequential injection analysis with IR detection.

groundwater [10]. By using the first SPE (reverse phase), the hydrocarbons are extracted from groundwater sample, meanwhile the second SPE is accomplished for fractionating hydrocarbons into aliphatic and aromatic hydrocarbons. Finally SPME and SPE devices are introduced into the injection port of gas chromatograph to thermal desorption of hydrocarbons.

The important and rapidly growing trend in modern analytical chemistry is the automation of analysis. Currently, the automation of analytical procedures based on flow analysis is intensively developing. To the best of our knowledge, only two articles have been devoted to the PP determination in water based on flow system [15,16].

The developed flow-injection method with IR detection assumes the mixing carbon tetrachloride with an aqueous carrier containing the sample into an extraction coil. Finally the two phases are separated into a membrane separator and the organic phase is transferred to the detection cell for absorbance measurement [16]. The main disadvantage of this flow method is low sensitivity (0.1 mg L⁻¹) because it is impossible to increase water and organic segments volume ratio to PP preconcentration. In the case of FIA fluorimetric determination of aromatic hydrocarbons and heterocycles in water [15], the on-line preconcentration of analytes is carried out into the extraction-chromatographic column. The extract is eluted by hexane with the following separation of extract from aqueous phase in chromatomembrane cell and aromatic hydrocarbons and heterocycles are detected, wherein all saturated hydrocarbons are ignored. This fact leads to the essential underestimation of the results in the determination of PP by this detection method when the sample contents, for example, petrol, kerosene and other same fractions.

The aim of this work was to develop an automated method for IR determination of total PP content (aliphatic and aromatic hydrocarbons and heterocycles) in water. To increase the sensitivity and exclude the mentioned disadvantages of LLE the special extraction-chromatographic cartridges have been developed and used for on-site extraction of PP during a sampling.

2. Experimental

2.1. Chemicals

Analytical grade chemicals and distilled water were used throughout the experiments. Carbon tetrachloride, tetrachlorethylene, trifluorotrichloroethane, hexane, isooctane, hexadecane, benzene, isopropyl alcohol, aluminum oxide and silica gel for chromatography (01–0.25 mm) were purchased from Sigma-Aldrich. Different types of PP (gasoline, diesel, transformer, industrial and vaseline oils) were obtained from the co-operation partner (Gasprom, Russia).

The 0.5 g L⁻¹ stock solutions of PP in a water-soluble matrix were prepared by dissolving PP in isopropyl alcohol. The working water solutions/emulsions of PP were prepared by dissolving the corresponding aliquots of 0.5 g L⁻¹ stock solutions in water and adjusting the volume up to 1 L by adding distilled water, and then flask contents were carefully mixed and immediately analyzed.

The calibration solutions were prepared by mixing isooctane, hexadecane and benzene at the volume ratio of 1.5:1.5:1 (OCB standard solution) and dissolution of this mixture in trifluorotrichloroethane, and stored in a sealed container to avoid evaporative loss.

2.2. Apparatus

2.2.1. Sampling and sample preparation setup

Extraction-chromatographic cartridges (polytetrafluoroethylene (PTFE)) (height – 20 mm, 5 mm i.d.) using for PP extraction were filled

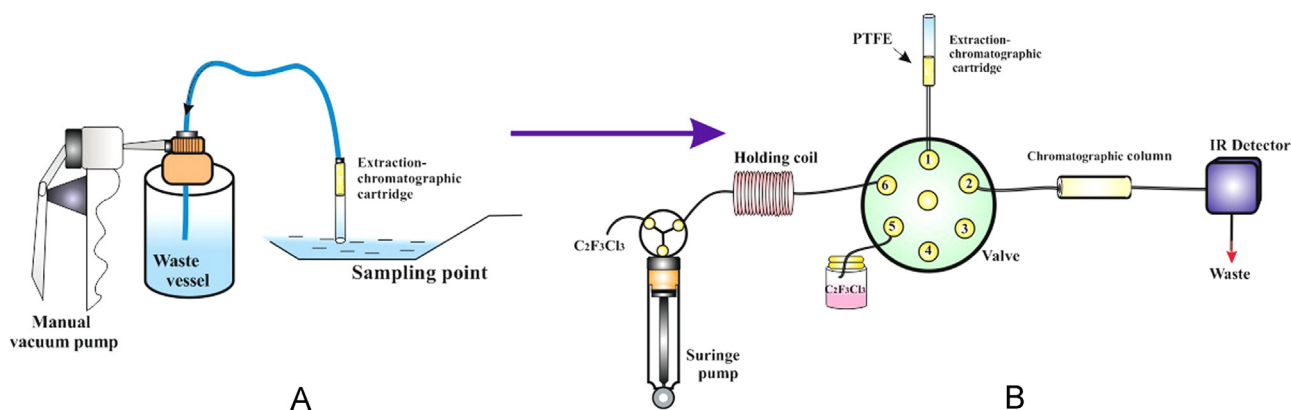


Fig. 1. (A) The scheme of sampling and extraction. (B) The SIA manifold for the IR determination of PP in water.

with block porous PTFE. The PTFE powder (Fluoroplast-4) was sintered at a temperature of 380 °C for 5 h in metal form ($20 \times 50 \times 50 \text{ mm}^3$) to prepare a block porous PTFE. Then the PTFE block was crushed in a blender, and the fraction size of PTFE powder from 0.5 to 0.9 mm was selected. Cylindrical form (height – 10 mm, diameter – 5 mm) was filled with prepared fraction and PTFE powder was re-sintered at a temperature of 380 °C for 1.5 h.

0.5 mL of trifluorotrichloroethane was passed through the prepared cartridge for its activation. After that the cartridge was washed with 2 mL of the distilled water to remove the excess of trifluorotrichloroethane.

Aluminum oxide and silica gel chromatographic columns were used for the separation of polar components from extracts (height – 2 mm, 1.5 mm i.d.). Aluminum oxide was preliminary dried at 600 °C for 4 h.

The manual vacuum pump with manometer «SM 16673» (Sartorius, Germany) was used for the sampling. The column was connected to the vacuum pump by using a silicone tube (Fig. 1A).

2.2.2. Sequential injection setup

The sequential injection manifold (Fig. 1B) for the determination of PP in water was based on a flow analyzer (Rosanalit, Russia). It included a syringe pump (SP) ensuring the reverse flow with 5 mL capacity, a 6-position solenoid valve (Cole-Parmer, Inc., USA), tubes for communications (PTFE, 0.5 mm of i.d.). The 2000 cm length holding coil (HC) from PTFE with 0.5 mm of i.d. was connected to the central port of the solenoid valve. The manifold was connected with an IR-spectrometer with a 40 mm path-length flow cell (Emi, Russia), an extraction-chromatographic cartridge and a silica gel chromatographic column (Section 2.2.1). Absorption registration was carried out in the $2700\text{--}3200 \text{ cm}^{-1}$ spectral region. The analyzer was operated automatically by means of a computer.

2.2.3. Batch experiments

An RF-5301PC Spectrofluorophotometer (Shimadzu Scientific Instruments, Japan) was employed for batch spectrofluorimetric measurements.

2.3. Sampling/extraction

The extraction-chromatographic cartridge was immersed in water (depth – 0.5 m), and 1 L of the water sample was directly pumped from the sampling place using a vacuum pump at the rate of 60 mL min^{-1} through the extraction-chromatographic cartridge (Fig. 1A). After extraction the extraction-chromatographic cartridges could be stored for a day in a refrigerator.

2.4. SIA operational protocol

After on-site extraction of PP the extraction-chromatographic cartridge was included into the SIA manifold (valve position 1) (Fig. 1B). The procedure started with the aspiration of 1 mL of trifluorotrichloroethane from the reservoir flask (valve position 5) to the HC by movement of the SP. Trifluorotrichloroethane was then directed to the extraction-chromatographic cartridge (valve position 1) by the SP at the rate of 2 mL min^{-1} . Afterwards, the obtained extract was aspirated to the HC and moderately pushed into the silica gel chromatographic column (valve position 2), where adsorption of polar components took place. After that, the PP extract was delivered from chromatographic column into the flow cell for IR detection, and the signal was measured under stopped-flow conditions for 20 s. Subsequently, the solution was sent to the waste. The tubes and the flow cell were cleaned with trifluorotrichloroethane to prevent any cross-contamination.

2.5. SFL operational protocol

The 100 mL of $100 \mu\text{g L}^{-1}$ water solution of PP was placed into a separatory funnel and 10 mL of hexane was added. The mixture was shaken for 5 min. After separation of the phases, the extract was separated, and then SFL determination of PP was performed at an excitation wavelength of 270 nm and fluorescence recording wavelength of 310 nm [12].

3. Results and discussion

3.1. Preconcentration and SIA conditions

For on-site preconcentration of PP from water the extraction-chromatographic cartridge with immersed block PTFE was used. In the pores of block PTFE various solvents (carbon tetrachloride, tetrachlorethylene and trifluorotrichloroethane) were used as a stationary phase. Criterion for the choice of solvent was the absence of IR radiation absorption in the $2700\text{--}3200 \text{ cm}^{-1}$ spectral region, where the absorption by PP, caused by the stretching vibrations of CH_3 and CH_2 groups of aliphatic, alicyclic compounds and side chains of aromatic hydrocarbons, as well as aromatic CH-bonds, was observed. In addition, the solvent should be well fastened in the pores of block PTFE immersed in the extraction-chromatographic cartridge. Different volumes of $200 \mu\text{g L}^{-1}$ water solution of transformer oil were passed through the cartridge at the sampling rate under 50 mL min^{-1} . It was found that by using carbon tetrachloride, tetrachlorethylene or trifluorotrichloroethane as the stationary phase, PP extraction efficiency has been determined to be equal to 95% by passing up to 10 L of PP water solution. In this case the

concentration factor equal to 6×10^3 could be achieved, this fact allowed to significantly increase the sensitivity of PP detection. The removal of the organic phase from the block PTFE occurred, when the volume of passing aqueous sample was increased. For further studies trifluorotrichloroethane was chosen as a more environmentally friendly solvent.

The effect of the PTFE powder fractions size on the reproducibility of the analytical signal was investigated. The minimum RSD (1%) was observed, using block PTFE, obtained from 0.5 to 0.9 mm PTFE fraction. By using the 1–2 mm PTFE fraction the stationary phase was removed during passing water and efficient extraction of PP did not occur. While using the 0.1–0.4 mm PTFE fraction the hydrodynamic resistance was increased and the RSD also increased to 7%.

Furthermore the efficiency of PP extraction at various sampling rates of PP water solution was investigated. For this purpose, 1 L of $200 \mu\text{g L}^{-1}$ water solution of transformer oil was passed through the extraction-chromatographic cartridge. The univariate optimization method was applied, while the sampling rate was changed from 20 to 100 mL min^{-1} . The results showed (Fig. 2A) that the satisfactory PP extraction was obtained at the sampling rate under 60 mL min^{-1} , which was chosen for further experiments. At the next stage, the optimal volume of trifluorotrichloroethane required for the elution of PP under SIA conditions was chosen (Fig. 2B). Based on the obtained results, the optimal eluent volume was 1 mL.

It has been further found that filtration rate could be increased to 300 mL min^{-1} by three-fold increase of the cartridge size (height – 60 mm, 15 mm i.d.). However, 8 mL of the solvent was required for the elution of PP; it was not justified due to the significant organic waste generation.

3.2. Study of interferences

The effect of different polar components encountered in water was investigated using model samples. Adequate recovery was taken to be an analytical response with a signal deviation up to $\pm 5\%$. The results showed that the polar components such as glyceryl tristearate, phenol, alkylated phenols, organic acids (stearic, palmitic acid, etc.), naphthenic acids interfere at up to 2-fold excess. Due to the polar components can interfere to the IR-determination of PP, the efficiency of their extraction was evaluated by moving of trifluorotrichloroethane through the aluminum oxide and silica gel columns. The effect of the polar components was investigated using the 100 mg L^{-1} solutions of mentioned polar components in trifluorotrichloroethane. The highest efficiency of polar components sorption was achieved by using silica gel as a sorbent, which was chosen for further studies. Therefore, it can be assumed that the developed procedure should be applicable for the determination of PP in water.

3.3. Analytical performance

The calibration plot constructed using OCB standard solutions in the SIA setup was linear in the range of $3\text{--}200 \mu\text{g L}^{-1}$ with correlation coefficients (r^2) of 0.999 while the sample volume equals 1 L. The limit of detection (LOD), calculated as three-times the standard deviation (3 s), and limit of quantification (LOQ), calculated as 10-times the standard deviation (10 s) of the blank test ($n=10$), were assessed as $1 \mu\text{g L}^{-1}$ and $3 \mu\text{g L}^{-1}$, respectively. The suggested method showed satisfactory repeatability of the analytical response by evaluation of the relative standard deviation (RSD) from 10 replicate measurements of the PP in real samples, with a value from 1.4% to 4.6%. The system throughput, assessed as the sampling frequency, was found to be 12 h^{-1} .

3.4. Analysis of model and real samples

The developed method has been verified on the $100 \mu\text{g L}^{-1}$ water solutions of different types of PP. Moreover determination of PP in model solutions was performed by the SFL method, described in Section 2.5. In the case of IR detection (see Section 2.4.) added and found amounts of PP were almost identical (Fig. 3). A significant understating of results (Fig. 3) was observed in the determination of PP by the SFL method for gasoline and diesel samples, since they were mainly composed of aliphatic hydrocarbons, and the content of aromatic hydrocarbons and heterocycles was negligible in these PP.

The developed procedure was applied for the analysis of real samples: natural water from rivers and lakes. Samples were collected from 4 sample points in St. Petersburg (Russia). The water samples were directly pumped through the extraction-chromatographic cartridge using a vacuum pump at the rate of 60 mL min^{-1} . To carry out the recovery study, the water samples (1 L) were collected into the glass flasks by using bathometer and spiked with 0.5 and 1 mL of 10 mg L^{-1} solution of transformer oil in isopropyl alcohol and then flask contents were carefully mixed and immediately pumped through the extraction-chromatographic cartridges. After sampling the extraction-chromatographic cartridges were stored for a day in a refrigerator at the temperature $5 \text{ }^\circ\text{C}$. Analytical results measured by the proposed automated method are presented in Table 2. The recoveries obtained for each of the water samples were within of 96.1–103.2% range which is considered to be accept for this type of samples. The RSD does not exceed 5%.

4. Conclusion

The new simple and easy performed automated method for the IR determination of total PP content in water has been developed. The developed procedure is based on the on-site extraction of PP

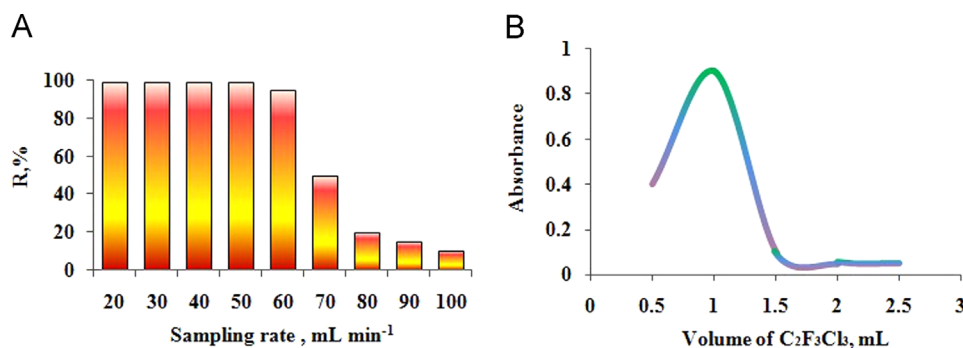


Fig. 2. The investigation of optimal parameters of the analysis. (A) Effect of the sampling rate (transformer oil concentration – $200 \mu\text{g L}^{-1}$). (B) Effect of $\text{C}_2\text{F}_3\text{Cl}_3$ volume.

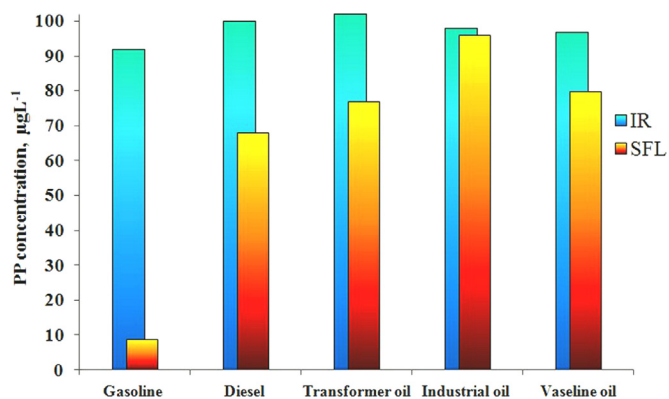


Fig. 3. The results of the PP determination in the model water solutions using IR and SFL detection ($n=3$, $P=0.95$).

Table 2

The results of the PP determination in the natural waters ($n=3$, $P=0.95$).

Sample	Added, $\mu\text{g L}^{-1}$	Found, $\mu\text{g L}^{-1}$	Recovery
River I	0	111 ± 10	–
	5	115 ± 8	99.1
	10	122 ± 5	100.8
River II	0	21 ± 2	–
	5	25 ± 4	96.1
	10	32 ± 2	103.2
Lake I	0	55 ± 5	–
	5	60 ± 4	100.0
	10	64 ± 5	98.4
Lake II	0	73 ± 6	–
	5	79 ± 8	101.3
	10	81 ± 7	97.6

during a sampling by using the extraction-chromatographic cartridges and subsequent sequential injection determination with IR detection. This method is more advantageous than the previously developed FIA methods because it is more sensitive and allows determining the total PP content (aliphatic and aromatic hydrocarbons and heterocycles).

Novelty statement

The first sequential injection IR method for the determination of total petroleum products (PP) in water has been presented. The extraction-chromatographic cartridges for the on-site sampling of PP have been proposed. New method is more advantageous than

the previously developed flow methods because it is more sensitive and allows determining the total PP content (aliphatic and aromatic hydrocarbons and heterocycles).

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