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SPECTROPHOTOMETRIC METHOD OF DETERMINING THE QUANTITY OF OIL PRODUCTS IN NATURAL AND WASTEWATER

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ARTICLE INFO	ABSTRACT
<p>Article history Received:2025-02-05 Received in revised form:2025-02-13 Accepted:2025-04-11 Available online</p>	<p>Oil products are the strongest toxic substances on the earth's surface, and their permissible levels in water bodies are 0.1 mg/dm³. However, until now, insufficient attention has been paid to determining the amount of oil products in natural and waste water. The article presents the results of spectrophotometric determination of the amount of oil products in water samples taken from lakes in the Absheron Peninsula and compares them with the existing gravimetric method. Extractants were selected to determine oil products, and the improved spectrophotometric method was applied to real objects under optimized conditions. The aim of this work was to select an organic extractant for the extraction of petroleum products from natural and waste waters and to apply an improved spectrophotometric method to natural objects. The aim of this work was to select an organic extractant for the extraction of petroleum products from natural and waste waters and to apply an improved spectrophotometric method to natural objects. The waters taken from the lakes of Gu and Girmizy on the territory of the Absheron Peninsula were selected as objects of the study. Spectrophotometric, gravimetric and chromatographic methods of analysis were used in the study. A mixture of organic reagents was selected to determine oil products in the waters of the lakes. Using the selected organic reagent, the oil products contained in the objects of study were isolated and analyzed using the GX-MS method. A new improved separation method using a mixture of organic reagents was proposed for the spectrophotometric determination of oil products. An improved spectrophotometric method for determining oil products in natural waters was developed. Optimal conditions for the extraction of oil products were found and the extraction method using a new organic reagent was optimized. The proposed method was tested on natural waters.</p>
<p>Keywords: "oil products" "waste water" "spectrophotometry" "approved standard" "extractants" "lake Gu"</p>	

Introduction

The development of the production of oil and gas products, unfortunately, leads to the problem of processing or disposal of the waste of these industries. Currently, the most common pollutants in the hydrosphere are oil and its products. A monomolecular layer of oil reduces gas permeability by 50%, pollution of the atmosphere and hydrosphere with oil products causes

disruption of normal gas and heat exchange. The result of these disturbances can lead to uncontrollable changes in our planet's climate, as well as the mass extinction of phytoplankton, which produces about 70% of the oxygen, [1] causing serious imbalances in the Earth's oxygen balance. Therefore, the development of modern, highly sensitive chemical analysis methods for controlling and determining the amount of oil products is one of the urgent problems in Uzbekistan. Oil and its products are the most common and dangerous substances that pollute natural waters. Oil and its products consist of a complex and diverse mixture of organic substances, and the concept of "petroleum products" in hydrochemistry is conventionally understood as a hydrocarbon fraction consisting of non-polar and low-polar aliphatic, aromatic, alicyclic hydrocarbons that can be extracted from water [2].

The results of man-made accidents in the process of extraction, processing and processing of oil products are considered the main factors that pollute the hydrosphere and atmosphere. Contamination of water with oil products makes it unsuitable not only for consumption, but also for various household needs. Currently, the most common polluting petroleum products include fuel oil, kerosene, gasoline, and petroleum oils. These oil products are extremely dangerous not only for the human body, but also for the environment [1, 4].

One ton of oil can form a film on the surface of 12 km² of water. When petroleum products enter water, they are mostly in a coarse dispersion and easily float to the surface of the water to form a floating film. Low molecular weight components evaporate easily. Depending on the type of oil products, it can evaporate from 10% to 75% [3]. Such atmospheric processes increase the density of the remaining oil products and cause the oil products to lose their ability to remain on the water surface. Under the influence of sunlight, oil products are oxidized, and oil products that have formed a thin layer on the water surface are oxidized more easily and faster. Water flow and vibrations cause oil emulsions to form. Emulsions formed on the surface of water remain stable for a long time.

The main sources of oil products entering natural waters include:

- oil warehouses;
- oil bases;
- oil processing enterprises;
- enterprises engaged in transportation of oil and its products.

The amount of petroleum products in water is 0.5 mg/dm³ and the amount of petroleum acid is 0.01 mg/dm³, which has a sharp effect on the smell and taste of water [4]. The presence of oil products in water of 100-500 mg/dm³ causes a sharp change in the chemical effect of water. The oil layer formed on the water surface disrupts the gas exchange between the water and the atmospheric layer, slows down the aeration rate, and removes carbon dioxide formed from oil oxidation. If the layer of oil products is 4.1 mm in water and the amount is 17 mg/dm³, the amount of dissolved oxygen will decrease by 40% in 20-25 days [5].

To control the amount of oil and its products in water, periodic water sampling and chemical analyzes are required. Chemical analyzes [6-14] are performed based on one of the methods listed in Table 1.

Table 1. Comparative table of modern methods of determining oil products

Method	Description	Measuring tools and equipment	Chemical reagents	Sampling and storage	Test execution process
Spectrophotometry method [9,11,14].	The amount of oil products is determined by spectral analysis of the separated oil extract. The analysis is based on the absorption intensity of S-N bonds in the infrared region of the spectrum. The measurement range is from 0.02 to 2.0 mg/dm ³	Spectrophotometer, photometer, volumetric flasks, pipettes, drying cabinet, muffle furnace, solvent drive, glass cooler, glass slide, indicator paper	Carbon tetrachloride, aluminum oxide, sodium sulfate, sulfuric acid, distilled water	The sample is taken in a glass container. It can be stored for 6 hours at a temperature of 15-25 C and 24 hours at a temperature of 6 C. A preserved sample can be stored at 15-25 C for 5 days, at 6C for 1 month	Extraction; Purification of the extract; Taking measurements; Calculation of results;
Gravimetric method [6,12,13].	It is based on separation of oil products using an organic solvent, purification of polar compounds using a column chromatography column, and determination of the amount of oil products by gravimetric method. The measurement range is from 0.3 to 50.0 mg/dm ³	Analytical balance, thermometer, glass cooler, magnetic stirrer, funnel, cylinder, beaker, measuring cups	Hexane, chloroform, aluminum oxide, sodium sulfate, sulfuric acid, glass wool, distilled water	The sample is taken in a glass container. If it is not possible to perform the analysis on the same day, the sample is preserved.	Extraction; Purification of the extract; Solvent evaporation; Residue measurement; Calculation of results;
Fluorimetry method [7,10].	The amount of extracted oil products is based on the measurement of fluorescence intensity using a liquid analyzer. The measurement range is from 0.005 to 50.0 mg/dm ³	Liquid analyzer "Fluorate-02", measuring flasks, pipettes, drying cabinet, magnetic stirrer, desiccator, indicator paper, glass cooler	Hexane, hydrochloric acid, nitric hydroxide, distilled water	The sample is taken in a glass container. The analysis should be done on the day of sampling. If it is not possible to perform the analysis on the day of sampling, the sample can be extracted and the analysis can be continued during the week.	Extraction; Purification of the extract; Taking measurements; Calculation of results;
Gas chromatography method [8].	Extraction of oil products, purification of the extracted extract from polar compounds and analysis of the purified eluate in a gas chromatograph. The measurement range is from 0.01 to 2.0 mg/dm ³	Gas chromatograph (MS, FID), volumetric flasks, pipettes, drying cabinet, glass cooler, chromatographic column	n-hexane, n-octane, eicosane, tetracontane, sorbent (magnesium silicate), sodium sulfate, hydrochloric acid, stearyl stearate, distilled water	The sample is taken in a glass container. Can be stored in a tightly closed container for 1 day, and a preserved sample for 1 month.	Extraction Purification of the extract from polar compounds Taking measurements Calculation of results

The correct performance of laboratory analysis also depends on the environmental factors necessary for conducting the analysis, and it is important to create the necessary environmental conditions for performing the tests based on the methods discussed above [6-16]. Table 2 presents a comparative table of environmental conditions (temperature, humidity and atmospheric pressure) required for quantitative analysis of oil products in water bodies.

Table 2. Environmental requirements

Methodology	Room temperature ^o C	Air humidity, %	Atmospheric pressure, kPa	Literature
RD 118.3897485.13-92, Fluorimetry	20±5	80±5	84,0-106,7	[10]
O'z O'U 0697:2015, Gravimetry	20±5	not specified		[6]
O'z O'U 0791:2019, Gravimetry	20±5	80±5	84,0-106,7	[16]
HDPE F 14.1:2:4.5-95, Infrared-spectrometry	20±5	<80	84,0-106,7	[9]
HDPE F 14.1:2.116-97, Gravimetry	20±5	80±5	84,0-106,7	[12]
State standard 4.1.1013-01, Infrared-spectrometry	20±5	<80	84,0-106,7	[15]
State standard of Russia 51797-2001, Infrared-spectrometry	not specified			[14]
State standard 31953-2012, Gas chromatography	not specified			[8]
HDPE F 16.1.41-04, Gravimetry	20±5	25 °C да <80	97,3-104,6	[13]

1. Research method and research

Equipment. The accuracy of the solutions to determine the hydrogen index was measured in MI-150 ionomer at 0.01 units. Chromatographic column for separating the oil layer from water, UF-spectrophotometer SPECORD 210 PLUS providing measurements at a wavelength of 3.42 microns with an absorbent layer thickness of at least 40 mm, Agilent 7872A gas chromatograph for determining the purity of standard samples, 0.0001 g for gravimetric analysis of oil products. precision analytical balance VL-224 and laboratory glassware according to GOST 25336-82 were used.

The following conditions must be observed when performing the test.

- ambient temperature (20 ± 5) °C;
- air humidity should not exceed 80% at 25 °C;
- atmospheric pressure from 84.00 to 106.70 kPa;

To measure the amount of petroleum products in water using the IR-spectrophotometric method, it is based on extracting the amount of petroleum products from water using an organic solvent extraction method and purifying the extracted extract using an aluminum oxide filter.

2. Discussion of research method and its results

For analysis, water samples taken from existing effluent and monitoring boreholes in the territory of Fergana Oil Refinery (FORP) were used. The collected water samples were first chemically analyzed for pH value and mineral content. Based on the obtained results, it can be seen that the amount of minerals and other chemical parameters in oil-polluted waters are higher than the permissible standards. Table 3 shows a comparative analysis of the water sample by chemical parameters.

Water samples taken from Absheron lakes were also used for the analysis. The collected water samples were first subjected to chemical analysis for pH and mineral content. Based on the results obtained, it is evident that the amount of minerals and other chemical indicators in oil-polluted waters exceed permissible standards. Table 4 presents a comparative analysis of the water sample by chemical indicators[17-19].

Table 3. Results of chemical analysis of water sample

Sampling location (well)	Hydrogen index (pH)	Total hardness (mg*eq/dm ³)	Amount of total minerals (g/dm ³)	Note [17,18]
Monitoring borehole No. 121	6.80	8.12	0.62	The chemical composition of the water is within the permitted standards
Monitoring borehole No. 121 № 0.14	7.38	7.80	0.78	
Treated wastewater	7.82	6.20	2.24	
The outlet of the wastewater from the plant	6.96	29.60	4.62	The total mineral content and hardness of the water is above normal
Wastewater pool	7.38	29.20	4.28	

Table 4. Results of chemical analysis of the water sample

Water sample	Hydrogen index (pH)	dissolved O ₂ (mgO ₂ /l)	COD	BOD	salinity (mg/l)
Girmizy lake	7.81	12,6	72	43	1580
Gu lake	7.2	0.7	60	38	3152

The chemical composition of the lakes water is within the permitted standards, the total mineral content and hardness of the lakes water is above normal[17-19].

Preparation of chromatographic column. Chromatographic column - washed thoroughly first in chromium mixture and then in water. It is then rinsed in the organic solvent used for analysis. 6 g of aluminum oxide dried in a drying cabinet at a temperature of 100-110 °C for 2 hours is placed in a 50 cm³ beaker. A suspension is formed by adding 5-6 cm³ of organic solvent on top. Passing the resulting suspension through a filter, a layer containing 1 g of sodium sulfate is formed on the remaining aluminum oxide, which is dried in a drying cabinet at a temperature of 100-110 °C for 2 hours.

Choose a pure organic extractant. The main analytical process for the determination of oil products in water is the extraction of oil products from water. Therefore, the choice of organic reagent for extraction is important. Chloroform, hexane and carbon tetrachloride were selected as the most used organic solvents as organic reagents. Solvents were checked for purity by gas chromatography before starting the analytical procedures. Table 5 shows the percentages of purity specified in the regulatory documents for the production of extractants and the results of real analysis of extractants.

Table 5. Table for determination of purity level of organic reagents

Solvent name and production regulatory document number	Purity level of solvents specified in regulatory documents, %	Results obtained in the analysis, %
Chloroform GOST 20015-88	≥99,60	99,60
Hexane GOST 4517-2016	≥99,00	97,60
Carbon tetrachloride GOST 20288-74	≥99,00	96,20
Petroleum ether TC 2631-074-44493179-01	>40,00	60,00
Isohexane GOST 24676-2017	≥94,00	90,50
Pentane T ES TC COMP 1-178-10	≥85,00	86,00

Based on the results of the analysis, three extractants, chloroform, hexane and carbon tetrachloride, were selected for extracting the samples. Figures 1, 2, 3 show chromatograms of selected extracts.

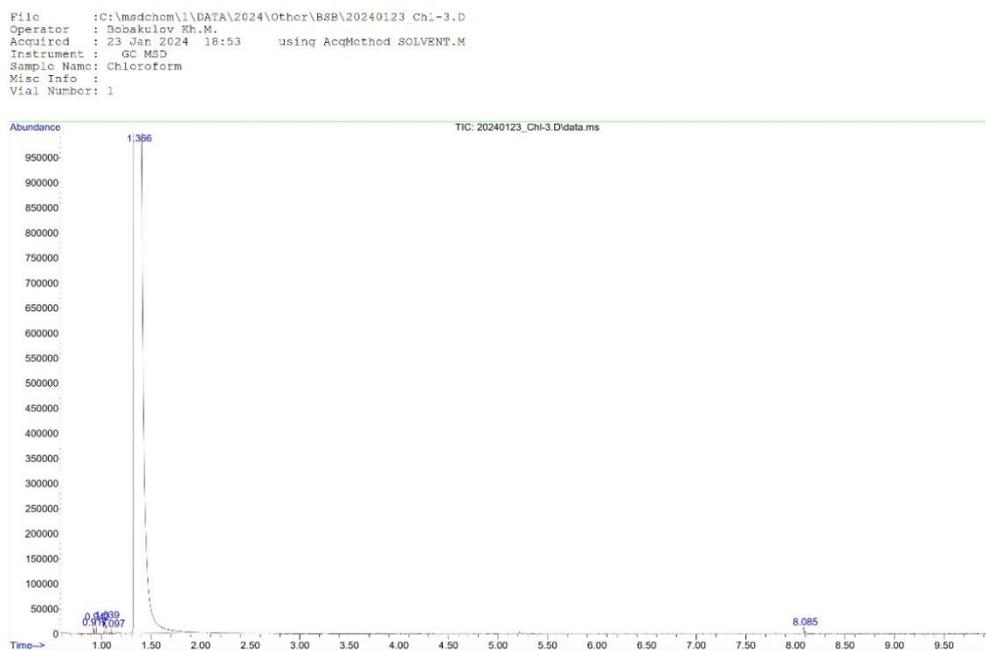


Fig 1. Chromatogram of chloroform obtained for extraction



Fig 2. Chromatogram of hexane obtained for extraction

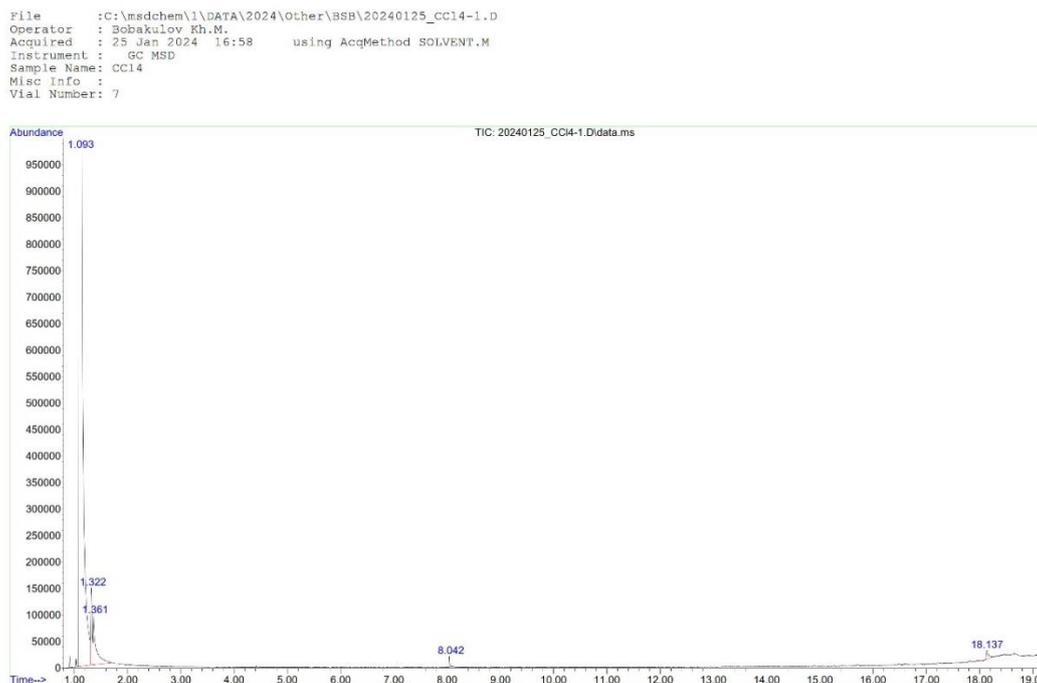


Fig 3. Chromatogram of carbon tetrachloride obtained for extraction

The extractant should not contain impurities adsorbed on aluminum oxide. If the extractant does not meet the requirements, it must be cleaned.

Purification of the extractant. Add 2 g of aluminum oxide to 200 ml of organic solvent and shake for 5 minutes. After the aluminum oxide is completely precipitated, the liquid is decanted and driven at normal pressure using a bottle cooler. Fractions driven at 46-47 oS or 76-77 oS are collected during the driving process. When driving, 1.0-1.5 g of activated carbon is added to 100 ml of organic solvent.

Creating a graduated graph. A standard sample consisting of a mixture of hydrocarbons with a mass content of 50 mg/dm³ is used to make a graduated graph.

Primary standard sample preparation. To prepare a standard sample with a mass of 1.00 mg/dm³, 1 cm³ of the standard sample is taken into a clean 50 cm³ volumetric flask and the volume is brought up to 50 cm³ using an organic solvent.

Preparation of working solution. To prepare a standard sample with a mass content of 0.100 mg/dm³, 5 cm³ of the primary standard sample is measured using a pipette and placed in a 50 cm³ volumetric flask and made up to 50 cm³ using an organic solvent.

0.025 to 25 cm³ volumetric flasks using 1 and 5 cm³ pipettes; 0.50; 1.00; 2.50; 5.00; 10.00; 15.00 cm³ of the working solution is added and mixed with an organic solvent until the volume is 25 cm³. The number of hydrocarbons is 0.0001 by volume; 0.002; 0.004; 0.01; 0.02; 0.04; It is 0.06 mg/cm³. A standard sample of 0.10 mg/cm³ can be used for the final graduated solution.

100-500 ml of the samples brought for analysis are measured in a glass flask, 20 ml of organic solvent is added and mixed by shaking well. The walls of the glass container are rinsed with an organic solvent. The well-mixed sample is placed in a separatory funnel, and the organic layer is separated from the aqueous phase in a 50 cm³ glass beaker with a tightly closed mouth. The remaining sample is reextracted with another 20 ml of organic solvent, and the organic layer is separated again into the glass beaker from which it was first extracted. The resulting eluate is passed through a filter prepared with aluminum oxide and placed in a test tube. Measurements are made after rinsing the spectrophotometer cuvettes with an organic solvent. In order to confirm the accuracy of our results, an artificial mixture of organic compounds was prepared in pure distilled water. The amount of oil products in the artificial mixture is 8.00-8.50 mg/dm³.

Table 8. The results obtained when extracting the amount of petroleum products in the sample in three different organic solvents

Location of taken sample	Total mineral content of the sample, mg/dm ³	Hydrogen indicator of the sample, (pH)	The result of chloroform extracted sample, mg/dm ³	The result of hexane-extracted sample, mg/dm ³	The result of carbon tetrachloride extracted sample, mg/dm ³
Observation well № 131	0.56	7.08	0.10	0.05	0.06
Observation well № 014	0.84	7.12	0.12	0.10	0.08
Waste water (discharge point in the pond)	3.44	5.54	14.50	10.10	11.60
Sewage pool	3.64	5.40	16.20	12.20	14.40
Waste water after treatment	1.20	6.86	1.64	1.10	1.24
Artificial mixture	-	-	8.40	8.38	8.34

According to the results of the analysis, it can be seen that chloroform is the strongest separator as an organic reagent in the spectrophotometric determination of oil products (in the case of the Fergana oil refinery).

Table 9. The results obtained when extracting the amount of petroleum products in the lakes waters samples in three different organic solvents

Location of taken sample	Total mineral content of the sample, mg/dm ³	Hydrogen indicator of the sample, (pH)	The result of chloroform extracted sample, mg/dm ³	The result of hexane-extracted sample, mg/dm ³	The result of carbon tetrachloride extracted sample, mg/dm ³
Girmizy lake	0.56	7.81	0.14	0.07	0.08
Gu lake	0.84	7.2	0.16	0.10	0.09

As can be seen from Table 9, the results of the analysis show that chloroform is the strongest separator as an organic reagent in the spectrophotometric determination of petroleum products in water samples from Lakes Gu and Girmizy [20-21].

In order to confirm spectrophotometric results, oil products were analyzed gravimetrically. Tables 10 and 11 shows the results of spectrophotometric and gravimetric analysis.

Table 10. Results of spectrophotometric and gravimetric analysis of oil products

Location of taken sample	Total mineral content of the sample, mg/dm ³	Hydrogen indicator of the sample, (pH)	The results of spectrophotometric analysis, mg/dm ³	The results of gravimetric analysis, mg/dm ³
Observation well № 131	0.56	7.08	0.11	<0.3
Observation well № 014	0.84	7.12	0.14	<0.3
Waste water (discharge point in the pond)	3.44	5.54	14.54	14.30
Sewage pool	3.64	5.40	16.80	16.54
Waste water after treatment	1.20	6.86	1.70	1.62
Artificial mixture	-	-	8.44	8.34

Table 11. Results of spectrophotometric and gravimetric analysis of oil products

Location of taken sample	Total mineral content of the sample, mg/dm ³	Hydrogen indicator of the sample, (pH)	The results of spectrophotometric analysis, mg/dm ³	The results of gravimetric analysis, mg/dm ³
Girmizy lake	0.56	7.81	0.15	0.13
Gu lake	0.84	7.2	0.18	0.2

Conclusion

In the course of scientific research, the chemical and biological impact of petroleum products in the hydrosphere and atmosphere, exceeding permissible levels on the human body, toxicological properties, quantitative analysis of petroleum products in water from various lakes of the Absheron Peninsula, as well as the development (verification) of the spectrophotometric method in laboratory conditions were studied, taking into account the results of the analysis, the following conclusions were made:

- since the gravimetric method of analysis of oil products currently used in our country does not allow to determine the presence of oil products in small amounts (<0.3 mg/dm³), it is not possible to analyze oil products in samples taken from monitoring wells and water facilities using the method;
- spectrophotometric method - accurate quantitative analysis, fast and high sensitivity, low sample requirement, the possibility of detecting large and very small amounts of the method, low time consumption, taking into account the small error rate, the minimum amount of oil products in the sample (>0, 05 mg/dm³) that it is also possible to determine;
- based on the analysis results, it can be concluded that hexane is the strongest separator as an organic solvent (extractant) by spectrophotometric method (in the case of the Fergana oil refinery facility).

For the quantitative analysis of the water samples taken for analysis, the quantitative analysis of petroleum products in water using the spectrophotometric method was carried out for the first time in the "Geoecologist-chemistry" laboratory of the "Institute of Hydrogeology and Engineering Geology" State Institution and the method was verified. Based on the obtained results, it is proposed to use spectrophotometric methods in the analysis of oil products in the waters of "Hydrochemistry" laboratories in Uzbekistan Republic in the future.

Also for the quantitative analysis of water samples from lakes Gu and Girmizy taken for analysis, the laboratory of the Ministry of Ecology and Natural Resources of the Republic of

Azerbaijan conducted for the first time a quantitative analysis of oil products in water using a spectrophotometric method, and the method was tested on real objects (in water samples from lakes Gu and Girmizy). Based on the results obtained, it is proposed to use spectrophotometric methods in the future when analyzing oil products in other natural waters.

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