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## Scheme for Analytical Control of Oil and Biogenic Hydrocarbons in Bottom Sediments Using Gas Chromatography/Mass Spectrometry Technique

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### Abstract

The paper is devoted to the development of an efficient scheme for analytical control of biogenic and oil hydrocarbons in bottom sediments using gas chromatography/mass spectrometry technique (GC/MS) without using toxic, expensive compounds and internal standards to acquire data of the depth of penetration of anthropogenic oil pollution and total contents of oil hydrocarbons (OHC). This testing scheme was performed for real objects with different environmental loads. Bottom sediment samples were taken in the Nizhnevartovsk district 30 km north-east from Nizhnevartovsk city. The study area is a series of lakes located in the territory of the Samotlor oil field in the West Siberian oil and gas province. The deposit is the largest in Russia. Survey results of 28 oil-polluted water bodies allowed forming the scheme for carrying out analytical monitoring of hydrocarbons in bottom sediments, and also identifying a set of analytical parameters by which one can authenticate pollution of bottom sediments with oil and OHC, assess its level and composition characteristics, which in turn enables to receive specific data on the depth of penetration of technogenic oil pollution and the total content of hydrocarbons in bottom sediments.

**Keywords:** bottom sediments, oil, oil products, oil hydrocarbons, gas chromatography, mass spectrometry, analytical control

### INTRODUCTION

The problems of pollution with oil and oil products of environmental objects, effects of the background of biogenic hydrocarbons in bottom sediments when determining contents of oil hydrocarbons, identification of pollutants and their quantitative determination are relevant for one of the largest oil-producing regions of the country, *i.e.* the Khanty-Mansiisk Autonomous District (KhMAD-Yugra). The peculiarity of water bodies of this territory is the presence of a substantial fraction of

biogenic hydrocarbons (BH) and opportunities of their effect on a specified level of oil pollution of bottom deposits [1, 2]. The used standard indicator (SI), such as oil products does not allow assessing the actual extent of technogenic load and probable pollution sources. Study acuity of oil pollution of bottom sediments in the territory of KhMAD is substantiated by insignificant rate of bacterial decomposition of truly anthropogenic oil hydrocarbons (oil products) at a low temperature of the surrounding water. Thus, chemical composition analysis under conditions of the slowdown

of biodegradation of oil and oil products is relevant. The indicator, such as technogenic pollution hydrocarbons is an alternative of the indicator, such as oil products. The identification of markers will allow reliably determining types of hydrocarbons and objectively assessing the pollution level of water bodies in the territory, forming recommendations on the planned recultivation activities.

Optical methods for determination (IR, UV, spectrophotometric, and luminescent) that have higher sensitivities (to 0.02 mg/dm<sup>3</sup>), expressness, and simplicity of analysis compared to gas chromatography are more efficient to use when assessing the total content of oil products. The properties that are the basis of these methods (adsorption in IR, UV spectral regions and luminescence) are different for hydrocarbons of different classes. Therefore, a change in the composition of oil products usually affects significantly these properties. The IR spectrophotometric method takes into account aliphatic and naphthenic hydrocarbons (accounting for 70–90 % of total hydrocarbons) and is most universal. An opportunity to use artificial mixtures of hydrocarbons (HC) is an advantage of this method. The spectrophotometric method combined with thin-layer chromatography has the highest sensitivity (0.02 mg/dm<sup>3</sup>). The error of determination using this method may substantially increase with biochemical transforming oil products in water bodies. Aliphatic hydrocarbons are exposed to this in a larger extent. Infrared spectrometry is used to detect both main and specific functional groups in the initial stage of oil product identification [3–5].

Sample preparation used in analysis by HPLC method does not allow entirely extracting the majority of substances, especially those that are found in the sorbed condition and represent markers of technogenic origin of polyarenes in environmental objects. As a consequence, lowered contents of 5- and 6-membered compounds, anthracene and heavy polycyclic aromatic hydrocarbons (PAH), most important from the standpoint of solution of geoenvironmental challenges are being obtained by us resulting from analysis by this method.

The use of low-molecular-weight monoaromatic HC (ArHC or BTEX index) is

more efficient during oil-pollution monitoring. The lack of these compounds in natural geochemical background does not allow using them as markers of technogenic oil pollution. These compounds are characterised by high values of water solubility compared to aliphatic and naphthenic HC. However, it is certainly required to consider pollution remoteness, as these compounds may not be detected in water after 4–6 months [6–9].

The use of the phenol index as one of the identification criterium of OHC type is possible in oil pollution monitoring [10, 11]. The photometric determination method of the phenol index in aqueous media that assumes preliminary isolation of alkylphenols and their derivatives from water samples directly during sample preparation by filtration *via* tributyl phosphate extraction-chromatographic column as stationary phase followed by their determination under cyclic injection analysis conditions was elaborated in the paper [12]. A detection limit of 0.1 µg/L in terms of phenol was reached. However, the wide distribution of phenols in natural geosystems complicates unequivocal gradation for bio- and geo-phenols and requires even more complex analysis to determine their genesis.

Polycyclic aromatic hydrocarbons (PAH) occupy a special place in the monitoring system of oil pollution. Numerous compounds of this series are highly cancerogenic, however, normative documents do not control them. The MPC level for PAH, according to standards of Russia, has been found only for the content of benzo(a)pyrene in soil (0.02 mg/kg).

Currently, the gas chromatographic method (GS/MS) with mass spectrometric detection has obtained a wider application. Isomers with identical MM can be differentiated using the data obtained using this method [3, 13]. Unlike HPLC, it allows separating more complicated mixtures of components for a relatively short time when studying complex natural objects and providing qualitative and quantitative information on the composition of the sample under study with comparable availability level [13]. GS/MS is used to study polluted bottom sediments. This is confirmed by studies [14] on geoenvironmental assessment of pollution of the Gusinoye Lake. Analysis of bottom sediment

samples with the object to 19 individual PAH that was performed using GC/MS method was a part of the study area. To optimize conditions of extraction and determination of volatile organic compounds (VOC) in bottom sediments studies on the selection of optimum conditions to carry out static vapour-phase analysis combined with GC/MS were conducted. The considered study method [15, 16] provides for simultaneous determination of 51 VOC in concentrations ranging from 0.0004 to 2.5 mg/kg.

Proceeding from literature data [17, 18], the bitumen component of organic compounds (OC) can be regarded as the main efficient qualitative characteristic of oil pollution, the study of which allows acquiring a large array of analytical data. Luminescent-bitumen analysis (LBA) allows carrying out primary diagnostics of objects. Thin-layer chromatography (TLC) enables determining group composition. Methods of gas chromatography (GC) and gas-liquid chromatography (GLC) identify various compositions of benzene and its homologs, *n*-alkanes, and isoprenate varieties. Photometry determines phenols, nitrogen compounds, and surfactants. Infrared spectroscopy technique (IRT) identifies molecular structure in the composition of samples under study. Analysis of the bitumen component by GC/MS method allows determining individual hydrocarbon composition [19].

The difficulty of determining various substances in bottom sediments is related to a strong effect of matrix components (organic and mineral components) for extraction and accuracy of analyte determination, and also to the inhomogeneity of samples. Paper [20] compared the total content of hydrocarbons that a part of gasolines, kerosenes, aviation, diesel fuel and lubricating oils in soils using methods of GC-FID, and IR spectroscopy. Infrared spectroscopy technique yields the overstated content of hydrocarbons, which is related to measurements of the background signal of a matrix, as demonstrated on an example of real and standard samples. Additionally, this method allows determining only the total content of hydrocarbons. The GC-FID method allows determining volatile and semi volatile hydrocarbons and the total content of hydrocarbons without carrying out additional

concentrating beginning with 500 mg/kg. Despite a large number of papers devoted to determining hydrocarbons and various oil products in environmental objects, there is no universal method that meets availability requirements, high expressness and accuracy, and also allows determining hydrocarbon types. To date, there are a number of methodological obstacles impeding studies of oil hydrocarbons in bottom deposits. Modern standard analytical methods do not allow isolating technogenic oil hydrocarbons from natural oil-like hydrocarbons. The variability of both the quantitative and qualitative chemical composition of oil hydrocarbons (spottiness) is also high, which often leads to serious mistakes in interpreting analysis results.

The existing regulating documents on monitoring hydrocarbons in bottom sediments allow carrying out the determination of structural-group composition and origin of oil components by IR spectrophotometric, luminescent, and gas chromatographic methods, and also detection of the mass fraction of oil components in bottom sediments. The normative literature (RD 52.24.505–2010, RD 52.24.609–2013) presents a number of approaches and a range of markers that can identify the technogenic route of admission of hydrocarbons into environmental objects. This is both the ratios between the sums of the areas of *n*-alkanes with the uneven number of carbon atoms to even and the pristane/phytane ratio, a significant prevalence of *n*-alkanes with an even number of carbon atoms in gas chromatograms, etc. However, the peculiarity of using these normative documents consists in the fact that, in the absence of MPC and APC for bottom sediments, sampling to determine background concentrations of hydrocarbons is a mandatory procedure.

The purpose of the present work was elaboration of approaches towards analytical monitoring process of oil and oil-like hydrocarbons in bottom deposits using gas chromatography technique that is mass spectrometry without using internal standards and the need to determine background concentrations of hydrocarbons, toxic and expensive substances to obtain qualitative and quantitative data on the total OHC content

and the depth of penetration of technogenic oil pollution, and also testing this scheme on real objects with different environmental loads.

## EXPERIMENTAL

Bottom sediment samples were selected in the Nizhnevartovsk district of KhMAD-Yugra 30 km north-east from Nizhnevartovsk city. The study area is a series of lakes located in the territory of the Samotlor oil field in the West Siberian oil and gas province (bottom sediments for each of the lake were studied in 70–80 evenly distributed points at the 75–100 cm depth, with observance of stratification in increments of 25 cm, and also and at three points at the 3 m depth in accordance with GOST 17.1.5.01–80 by peat borer along the coastline and water-surface lake area).

Determining the mass fraction of oil products (OP) in bottom sediments was performed in accordance with the technique [21]: organic substances were isolated by extraction with carbon tetrachloride, the hydrocarbon fraction was purified from the accompanying polar compounds in the column with aluminum oxide of II degree of activity (by Brockmann). The measurements were carried out using an IKN-025 concentration meter.

Sample analysis by GC/MS method was carried out as follows: a part of the eluate (5 mL volume) of the HC fraction of each sample remaining after determining OP mass fraction was concentrated in a rotary evaporator to 1 mL volume and then under a nitrogen stream to 0.2 mL volume. Analysis of the composition of saturated and aromatic HC was performed using a Perkin-Elmer Clarus 500 MS mass spectrometer. Analysis conditions are an Elite-MS5 30 m × 0.25 mm × 0.25 μm capillary column; helium carrier gas; temperature programming of the thermostat from 100 to 310 °C with 10 °C/min heating rate, final temperature exposure of 20 min; ionization method – 70 eV electron impact energy, ionization chamber temperature of 190 °C; transferline temperature of 300 °C; injector temperature of 220 °C; split mode (1/20 flow division); manual sample entry in 5 μL volume, mass scanning range from 40 to 450 amu.

To process mass spectra TurboMassGold software with the NIST 98 mass spectra library was used. To identify components the initial chromatogram of complete ion current was reconstructed on  $m/z$  values of 57, 71, 85, 91, 92, 105, 106 (characteristic ions) typical for appropriate HC (alkylbenzenes and *n*-alkanes). The peaks with the given characteristic ions were found in the mass chromatogram, and the search was carried out according to the library data. The data (retention time and mass fragmentograms) obtained resulting from identifying chromatographic peaks of components of the samples of oil pollution (bitumen crust), that was detected during the inspection of the coastal line of the oil-polluted lakes under study was used to identify components in the composition of extracts of bottom sediment samples.

## RESULTS AND DISCUSSION

To select the most optimum analysis scheme preliminary experiments with bottom sediment samples from the territory of three oil-polluted lakes were carried out. A range of background concentrations of oil products for similar lake objects of KhMAD that is varied from 0.8 to 3.8 g/kg was determined during infrared spectral study of background samples of peat bottom sediments stratified by depth (in 3 layers *via* 25 cm) from various objects. This large variation of background values is mainly determined by the difference in the peat according to botanical composition and decomposition degree (both by occurrence depth and laterally). Considering the 25 % error of the IR spectral method for determining OP, the variation of the background range becomes even more significant – from 0.6 to 4.7 g/kg. The findings are consistent with literature data on the background content of OP for organogenic bottom sediments [22, 23]. A significant excess of maximum background concentration of OP is observed in the surface layer (depth of 0–25 cm), as established by infrared spectral analysis of bottom sediments. The OP concentrations are by an order of magnitude lower than in the surface layer. The OP concentrations in deeper layers of bottom

sediments (25–50 and 50–75 cm) are by an order of magnitude lower than in the surface layer. Herewith, the bulk of these layers falls within the range of varying the concentration of oil products (minimum and maximum values obtained from the analysis of background samples) for a given type of objects or close to it.

Thus, the findings of a series of bottom sediment samples enabled to conclude that all samples with concentrations of oil products (determined by the standard IR spectral method higher than maximum background established for objects, such as lakes of secondary origin with peat bottom sediments at a level of 4.7 g/kg (the upper boundary given the relative error is 25 rel. %). Herewith, if traces of technogenic oil pollution are not detected in the superstratum of bottom sediments, GC/MS analysis of the sublayer of bottom sediments in the same point is not required.

The carried out GC/MS studies of a series of bottom sediment samples allowed highlighting groups of substances, *i.e.* “indicators” of anthropogenic oil pollution:

1. Group – normal and methyl-substituted alkylbenzenes of the composition C14–C25 (identification in comparison with a sample of oil pollution detected/not detected). These components in similar compositions and distributions were identified in all bottom sediment samples (both organogenic and mineral type) with concentrations of oil products of higher than 4.7 g/kg. At the same time, GS/MS studies of bottom sediments of background objects demonstrated the absence of these components in samples. Oil product concentrations varied (1.3–3.3 g/kg, without a certain gradient of decreasing or increasing with depth) during analysis of deeper samples (from the depth to 3 m). At the same time, alkylbenzenes were not detected in these subsurface samples. Thus, identification of alkylbenzenes in bottom sediments was regarded by us as one of the main sign of oil technogenic pollution.

2. Group – C15–C17 alkylphenanthrenes (identification in comparison with a sample of oil pollution – discovered/not discovered). Identification of these compounds in samples, in our opinion, can act as additional supporting indicators of oil pollution.

3. Group – normal alkanes up to C34(35) (comparison with a sample of oil pollution of the calculated parameters of the composition of *n*-alkanes – the oddness index of odd *n*-alkanes, the ratio of high- and low-molecular-weight homologs). The oddness index of *n*-alkanes of background samples significantly differed from bottom sediment samples with the concentration of oil products higher than background maximum – from 8.6 to 12.6 g/kg for background samples and from 1.4 to 2.4 for samples with the concentration higher than 4.7 g/kg. Figure 1 presents the monitoring circuit of oil and oil-like hydrocarbons in bottom sediments using GC/MS method.

Afterwards, bottom sediment samples from 25 oil-polluted lakes of the study area were analysed according to the presented scheme. The total content of hydrocarbons in combined samples of lake bottom sediments varies within 1 to 65 g/kg, as established by IR spectrometry, and according to chromatographic determination – from 0.5 to over 50 g/kg.

The ranking order of lakes was determined by the level of technogenic pollution with oil products, which corresponded to their ranking by the total content of oil products in bottom sediments; the content of hydrocarbons for 6 lakes is found at a level of the background content of hydrocarbons of vegetable origin, and hydrocarbons of anthropogenic (oil) origin in sediments of other lakes are present in varying degrees with concentrations ranging from 0.0621 to 0.576 g/kg; herewith, hydrocarbons of anthropogenic (oil) origin in concentrations greater than 10 g/kg are contained in the sediments of 10 lakes. According to Infrared Spectroscopy finding, the mass fraction of oil products in surface water samples varies in the range of from 0.06 to 73 mg/dm<sup>3</sup>; the presence of a film of oil products in sampling sites on the water surface was found for 16 lakes.

## CONCLUSION

Research results of 28 oil-polluted water bodies in the territory of Nizhnevartovsk district of KhMAD-Yugra have allowed forming the scheme for carrying out analytical monitoring of hydrocarbons in bottom sediments and identifying a set of analytical parameters

(characteristics of the individual composition of hydrocarbons (HC), group composition of oil and oil products (OP), the presence of hydrocarbon indicators proving the anthropogenic origin of organic matter) that allow identifying pollution of bottom sediments with oil and oil hydrocarbons, assessing the level and characteristics of the composition, which in turn enable providing the opportunity to provide correct data on the total content of hydrocarbons and the depth of penetration of technogenic oil pollution into bottom sediments. Bottom sediments allow constructing a reliable spatial model of a layer of bottom sediments, assessing its volume and providing recommendations for recultivation and other reconstruction works of water bodies of the study area and regions with similar types of soil grounds. The carried out research broadens opportunities of using gas chromatography/mass spectrometric detection method for analytical monitoring of oil and oil-like hydrocarbons without using internal standards, the need of determining background concentrations of hydrocarbons, toxic and expensive compounds to obtain qualitative and quantitative information on the total content of oil hydrocarbons, and the depth of penetration of technogenic oil pollution in complex natural objects, such as bottom sediments. The proposed scheme allows carrying out on-line testing of analyzed objects with high reliability of conclusions.

## REFERENCES

- 1 Volkova S. S. Physical and chemical features of the formation of the organic matter and carbonate system in small lakes of West Siberia: Dis. ... Cand. Chem. Sciences: 02.00.04. Tyumen, 2015. 108 p.
- 2 Minaev N. D., Nekhorosheva A. V., Nekhoroshev S. V. Assessment of the state of bottom sediments of lakes at the present stage and a retrospective of the issue, *Ecological Systems and Devices*, 2016, No. 5, P. 34–40.
- 3 Litvinenko I. V. Features of distribution of polycyclic aromatic hydrocarbons in sediments of the Arctic seas: dis. ... Cand. geog. Sciences: 25.00.36. SPb., 2012. 127 p.
- 4 Nemirovskaya I. A. The hydrocarbons in the ocean (snow-ice-water-slurry-bottom sediments): dis. ... Doct. Geol.-Mineral. Sciences: 04.00.10. M., 2000. 323 p.
- 5 Rovinskii F. Y., Teplitskaya T. A., Alekseeva T. A. Baseline monitoring of polycyclic aromatic hydrocarbons. L.: Gidrometeoizdat, 1988. 224 p.
- 6 Nikanorov A. M., Stradomsky A. G. The problems of oil pollution of freshwater ecosystems. Rostov-on-Don: "NOC", 2008. 222 p.
- 7 Bakhtiari A. R., Zakaria M. P., Yaziz M. I., Hjlajis M. N., Mohamad Shafiee M. R., Sakari M. Distribution of PAH sand *n*-alkanes in Klang River Surface Sediments, Malaysia, *Pertanika J. Sci. & Technol.*, 2010, Vol. 18, No. 1, P. 167–179.
- 8 Martins C. C., Bicego M. C., Tanigushi S., Montone R. C. Aliphatic and polycyclic aromatic hydrocarbons in surface sediments in Admiralty Bay, King George Island, Antarctica, *Antarctic Science*, 2004, Vol. 16, No. 2, P. 117–122.
- 9 Nishigima Noboru F., Weber R. R., Marcia Bicego Caruso M. Aliphatic and aromatic hydrocarbons in sediments of Santosand Cananeia, SP, Brazil, *Marine Pollution Bulletin*, 2001, Vol. 42, No. 11, P. 1064–1072.
- 10 Magasumova A. T. Perfection of the system of ecoanalytical control and monitoring of phenol and its derivatives in water objects in the zone of influence of chemical and petrochemical enterprises: dis. ... Cand. Chem. Sciences: 03.02.08. Kazan, 2012. 168 p.
- 11 Safarov A. M. Assessment of the state of the environment and its protection against oil pollution in case of emergency situations (for example, a region with a high concentration of oil companies): dis. ... Doct. Tehn. Sciences: 03.02.08. Kazan, 2007. 457 p.
- 12 Bulatov A. V., Michailova E. A., Timofeeva I. I., Moskvina L., Moskvina L. N. Determination of the "phenolic index" in water by the method of cyclic injection analysis with autonomous extraction-chromatographic concentration, *Journal of Analytical Chemistry*, 2013, Vol. 68, No. 1, P. 18–21.
- 13 Filimonov V. D., Slepchenko G. B., Belyanin M. L., Nartov A. S., Determination of polycyclic aromatic hydrocarbons in soils using gas chromatography-mass spectrometry, *Analytics and control*, 2015, Vol. 19, No. 4, P. 310–315.
- 14 Shirapova G. S., Batoyev V. B., Vyalkov A. I., Morozov S. V., Geoeological assessment of pollution of Lake Gusinoy with persistent organic pollutants, *Bulletin of the Buryat State University*. 2012. Special issue B. P. 280–283.
- 15 Galaktionova E. B., Safarova V. I., Shaydulina G. F., Teplova G. I., Kudasheva F. H., Optimization of conditions for extraction and determination of volatile organic compounds in bottom sediments by the method of static vapor-phase analysis in combination with chromatography-mass spectrometry, *Bulletin of the Bashkir University*, 2009, Vol. 14, No. 1, P. 68–71.
- 16 Volkov K. S. Restoring the quality of surface waters polluted by accidental discharges of dissolved oil: Authoref. dis. ... Cand. Tehn. Sciences. 25.00.36. Ekaterinburg, 2006. 23 p.
- 17 Bikbulatov E. S., Bikbulatova E. M., Ershov Yu. V., Stepanova I. E., Anthropogenic and natural components of hydrocarbons in the water of the lake. Nero of the Yaroslavl Region, *Water resources*, 2004, Vol. 31, No. 1, P. 78.
- 18 Drugov Yu. S., Rodin A. A., Environmental analyzes for oil spills and petroleum products: practical guidance, M.: BINOM. Laboratory of Knowledge, 2007. 270 p.
- 19 Odintsova T. A. Development of technology for identification and monitoring of oil pollution: Authoref. dis. ... Cand. Tehn. Sciences. 25.00.36. M., 2010. 21 p.
- 20 Nadim F., Liu Sh., Hoag G., Chen J., Carley R., Zack P., A comparison of spectrophotometric and gas chromatographic measurements of heavy petroleum products in soil samples, *Water, Air, Soil Pollut.*, 2002, Vol. 134, P. 97–109.
- 21 HDPE F 16.1: 2.2.22–98. Method for performing measurements of the mass fraction of petroleum products in soils and bottom sediments by IR spectrometry. M., 1998 (Edition of 2005). 20 p.
- 22 Experience in assessing the condition of lakes subjected to oil pollution [Electronic resource]: official site of CJSC "Siberian Research and Design Institute of Rational Nature Management" / E. L. Shor [and others], URL: <http://www.sibnipirp>.

ru/?part=a&c=p5 (accessed May 22, 2017).

23 Status of bottom sediments within the boundaries of licensed areas [Electronic resource]: official site of the Service for control and supervision in the sphere of environmental protection, wildlife and forestry relations,

URL: <http://www.prirodnadzor.adhmao.ru/sostoyanie-okruzhayushchey-sredy/poverkhnostnye-vodnye-obekty/donnye-otlozheniya/131966/sostoyanie-donnykh-otlozheniy-v-granitsakh-litsenziyonnykh-uchastkov> (accessed May 22, 2017).