

Determination of petroleum compounds in bottom sediments

Oznaczanie związków ropopochodnych w osadach dennych

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Abstract: The following study was a theoretical base for selection, development and validation of the analytical procedure for determination of petroleum hydrocarbons in bottom sediments to be used in a commercial research laboratory. Crude oil and petroleum products belong to the group of pollutants that are easily accumulated in sediments. The process of accumulation of petroleum substances is due to the large sorption capacity. Having accumulated in sediments, the substances may constitute a secondary source of pollution which, despite being cut-off from the primary sources, may yet cause environmental pollution for a number of years. Recognition of the level of contamination in sediments, and monitoring of changes in the environment require employment of appropriate analytical procedures, which would ensure that the work is less laborious and time-consuming.

Keywords: petroleum hydrocarbons, sediment contamination.

Streszczenie: Niniejsza praca stanowiła podstawę teoretyczną do wyboru i opracowania właściwej procedury analitycznej oznaczania węglowodorów ropopochodnych w osadach dennych do zastosowania w komercyjnym laboratorium badawczym. Ropa naftowa i produkty ropopochodne należą do tych zanieczyszczeń, które mogą gromadzić się w osadach dennych. Proces kumulacji substancji ropopochodnych spowodowany jest dużą pojemnością sorpcyjną. Kumulując się w osadach substancje te mogą stanowić wtórne źródło zanieczyszczeń, które mimo odciążenia źródeł pierwotnych jeszcze długie lata będą przyczyną zanieczyszczenia środowiska. Poznanie stopnia skażenia osadów dennych jak i monitorowanie zmian w środowisku, wymaga posiadania odpowiednich procedur analitycznych, które zapewnią małą czaso- i pracochłonność.

Słowa kluczowe: węglowodory ropopochodne, zanieczyszczenia osadów dennych

Introduction

Bottom sediments are formed in the environment as a result of the process of sedimentation of particles from a layer of water. In the process, organic compounds are transmitted into the sediments together with the solid particles. It is an effect of hydrophobic organic substances getting absorbed on the particles of the suspension, and a reason why sediments are of very complex physico-chemical structure. Inside the sediments, there settles a chemical balance between the solid phase and the water contained in it. There occur various processes in them, such as precipitation, adsorption, biological degradation, biological absorption, and concentration of chemical compounds [3].

Bottom sediments are an important element of aquatic ecosystems. They constitute kind of ecological niches, where

benthic organisms, that is the animals and plants living at the bottom of the waters, develop, as well as they are a source of nourishment for the aquatic organisms, such as small invertebrates and protozoa.

Assessment of pollutants' influence on the life in water bodies requires that the levels of their concentrations, and sources of these pollutions are examined. In this respect, bottom sediments are a particularly useful research material, as they works like an absorption column, and provide a clear picture of what takes place in the water above them.

Thanks to their structure and well-developed surface, bottom sediments may be considered a natural sorbent, on which there occurs retention of various components, inter alia, the petroleum hydrocarbons. The substances undergo various

physical and chemical processes. By accumulating in the sediments, the substances may also constitute a secondary source of contamination, which despite being cut-off from the primary sources, may be a cause of water contamination for a number of years [10].

Aim of the work was selection and verification of the theoretical information on analytics of petroleum hydrocarbons in environmental samples for the purposes of choosing and developing the right analytical procedure for determination of petroleum hydrocarbons in the bottom sediments to be used in a commercial research laboratory.

Description and properties of the group of compounds under analysis

Crude oil is a combustible liquid of natural origin which is a basic raw material used in production of liquid fuels, and other petroleum products: lubricants, waxes, asphalts, and petrochemicals. A huge number of chemical compounds of different structures and compositions are components of crude oil. They may be grouped into petroleum hydrocarbons, and heteroorganic compounds.

In the group of petroleum hydrocarbons included are the following compounds:

- ◆ n-paraffinic compounds (n-alkanes) ($C_n H_{2n+2}$),
- ◆ isoparaffinic compounds (isoalkanes),
- ◆ naphthenic (cycloparaffins, cycloalkanes), mainly monocyclic ones with the chemical formula $C_n H_{2n}$, such as cyclopentane. There occur also bi- and more cyclic naphthenes (up to 10 rings) with alkyl substituents or without them. This is the largest group of hydrocarbons, and it constitutes about 50% m/m.
- ◆ aromatic – (ca. 15% m/m), the biggest groups among which constitute benzene and its methyl derivatives (BTEX – benzene, toluene, ethylbenzene, and xylenes), and alkylbenzenes containing up to 40 carbon atoms in substituents. In crude oil, there occur also Polycyclic Aromatic Hydrocarbons (PAHs) with 2 to 10 condensed rings,
- ◆ of mixed structures, containing aromatic as well as naphthenic rings (e.g. indene) [19].
- ◆ Heteroorganic compounds are non-hydrocarbon compounds (mainly of polar character), which contain sulfur, nitrogen, oxygen, chlorine, and metals. In this group, there may be distinguished:

- ◆ asphaltenes,
- ◆ resins [19].

In Table 1/Tabela 1 there are presented the basic oil products broken down by the boiling range, and the range of number of their carbon atoms in a molecule [4].

Hazards and effects of contamination of the aquatic environment (water, bottom sediments) by petroleum products

Increasing social awareness translates into growing importance of environmental analyses, especially the ones concerning petroleum products, which are one of the main contaminants of the aquatic environment (and thus, indirectly also of the bottom sediments). Depending on oil's quality, oil spills pollute water either by spreading over its surface in an oily layer, or by mixing with water and dissolving in it. Oil contaminations are very disruptive for the aquatic environment, as they are very persistent, and all that time they have multi-faceted effects. These processes are illustrated in Figure 1/Rysunek 1/.

Crude oil spilt over the water surface undergoes numerous processes, which have a considerable influence on distribution of oils' remnants in the aquatic environment. Immediately after the spillage, oil begins spreading over the surface of water. Irrespective of how thick the layer of oil spilt over the water surface is, it is subject to so-called weathering process. It comprises:

- ◆ evaporation of the lightest fractions,
- ◆ photolysis (i.e. decomposition of the heavy particles under the influence of ultraviolet light),
- ◆ dispersion of the water column resulting from the wave motion,
- ◆ formation of oil-in-water emulsions,
- ◆ formation of aerosols (suspension of microscopic drops in the air). [4, 5, 6].

While on the water surface, oil poses a danger to birds and seals, which get covered in a layer of it. This limits their chances of survival, as their mobility is impaired, or their skin or feathering are devoid of the isolating qualities. If the pollutant gets into the gastrointestinal tract, the birds suffer death from poisoning. Oil dispersed in the water column penetrates into the organisms of plants and animals together with their food, and when its concentration is high enough, it makes clams, fish, and seaweeds inedible. Oil contaminations destroy the habitat of numerous species of fauna and flora, as well as spawning grounds for fish [7]. Remains of the weathered oil are deposited by the sea waves on the beach, resulting in its contamination, or they sink. Oil sinkage is one of the substance's most dangerous effects, as decomposition of oil requires a lot of oxygen, which is most often deficient at the bottom. This causes a fast extension of the oxygen deficit in the bottom waters, which may, in extreme cases, lead to emergence of hydrogen sulphide [4].

Tab. 1. Characteristics of the basic petroleum products [4].

GROUPS OF PETROLEUM PRODUCTS	NUMBER OF CARBON ATOMS RANGE	BOILING RANGE [°C]
motor gasoline	C ₅ -C ₁₀	30-215°C
jet fuel	C ₉ -C ₁₆	150-250°C
diesel fuel	C ₉ -C ₂₄	163-370°C
lubricating oil (engine oil, spindle oil etc.)	C ₂₀ -C ₄₀	1-570°C

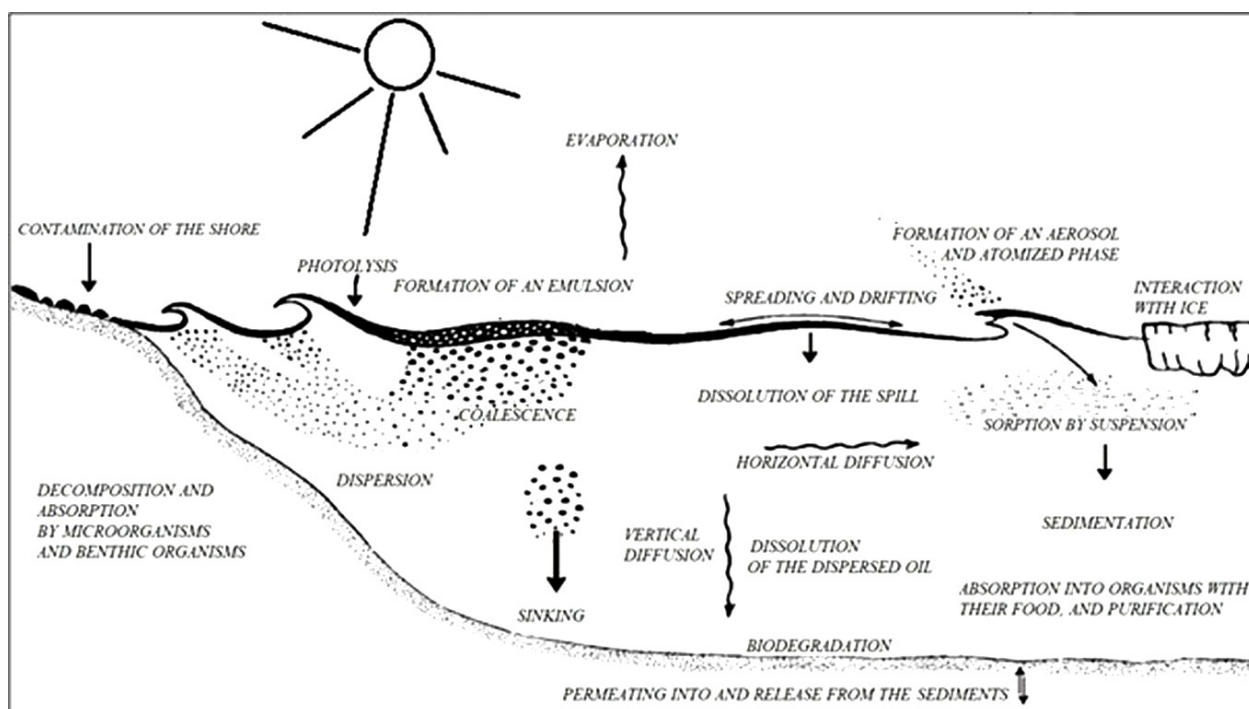


Fig. 1. Processes of transformation of crude oil after an oil spillage in an aquatic environment – a schematic presentation [5, 8].

Crude oil, and petroleum products belong to the group of contaminants that may be deposited in the bottom deposits. The process of petroleum products accumulation is a result of high sorption capacity of components of bottom sediments [1]. Length of the period of time throughout which the oil's components, and products of their degradation remain within the bottom sediments is dependent on numerous factors, such as: type of sediment, temperature, type of oil, nutrients content, pace of biological decomposition, etc. [12]. The power of sorption of hydrocarbons in the sediments changes depending on the hydrocarbon's type, and organic matter content in the sediment [15]. Figure 2/Rysunek 2 presents the basic processes taking place in the bottom sediments involving petroleum hydrocarbons.

Sources of petroleum products contamination

Oil-derivative pollution is a serious threat to the environment. Products of crude oil processing do not undergo spontaneous naturalization, and they get decomposed into simpler compounds only to a very limited degree. The biggest source of contamination caused by petroleum compounds from the urban areas is their runoff with the river water from the land. It is due to the polluted technological water from industrial plants, wash water from washing motor vehicles, and rinsing away the gasoline and oil spilt by cars on hard-surfaced roads and parking areas. The second significant source of petroleum products contamination is the normal (that is, trouble-free) operation of ships, including vessels used for sporting purposes. Accidents of oil tankers rank (on a global scale) as low as third. Only a little less serious are the oil contaminants in-

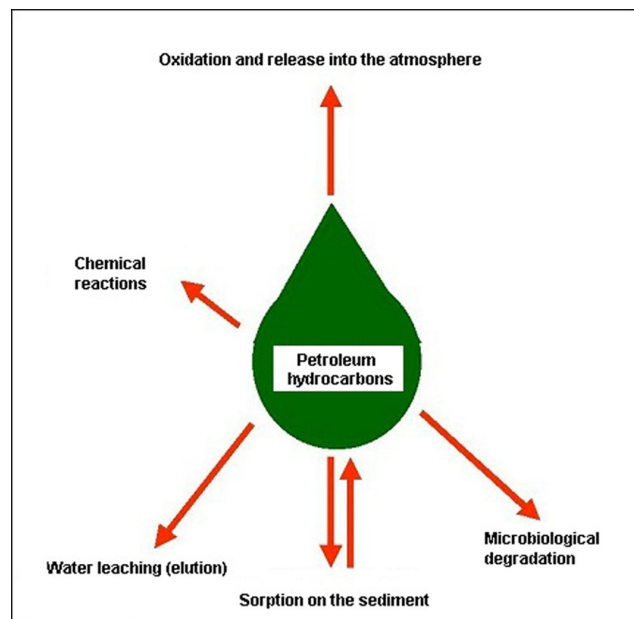


Fig. 2. Basic processes taking place in the bottom sediments involving petroleum hydrocarbons [15].

produced through the atmosphere. These are mainly effects of the incomplete combustion of diesel oils in engines, boiler-rooms, and CHP plants. Next place falls to the natural sources (escapes of oil through the fractures in the earth's crust, and its leaching through the permeable layers). The last in this ranking is the off-shore oil extraction, that is, activities of the exploration, and production platforms [9]. All these sources ultimately lead to accumulation of hydrocarbons in the bottom sediments of ponds, lakes, rivers and seas.

Methods of determining the oil-derived substances

Samples of bottom sediments are a typical example of environmental samples the physical state of which makes it impossible to determine the analytes directly with application of most of the methods in use. Because of their extremely complicated physical-chemical structure, the samples require use of several successive phases of treatment, in which there should be removed the compounds presence of which is undesirable during the analysis, such as:

- ◆ macromolecular compounds (e.g.: fats, waxes) of molecular weight within the 600-1500 g·mol⁻¹ range. The compounds are usually characterized by occurrence of polar groups which may form hydrogen bonds, high molecular weight, and low volatility;
- ◆ compounds of particle-size similar to that of the analytes (e.g. PAHs).

Determination of petroleum hydrocarbons in bottom sediments requires observance of the following stages of the proceeding:

- ◆ preliminary processing of the samples of bottom sediment (drying, grinding),
- ◆ isolation and enrichment, which consists of transfer of the analyte from the primary to the secondary matrix,
- ◆ purification and fractionation of the extracted material,
- ◆ identification and final determination of the selected group of analytes.

Storage and preliminary preparation of the samples before their analysis

The PN-EN 14039:2008 standard [13] recommends storing samples of bottom sediments in glass vessels made of the amber-colored glass, at a temperature of 4°C, for no longer than a week. Longer term storage is permissible at a temperature of -18°C [2].

Some analytical procedures provide for drying the samples until they achieve so-called air-dry state, by means of leaving a thin layer of the soil at 20–30°C. Because of the risk of losing the low-boiling components in the process of drying in driers (possible even at a temperature as high as 40°C), the determination should be carried out with use of raw samples, or samples dehydrated by means of chemically bonding the water with anhydrous Na₂SO₄ or MgSO₄ [17, 18]. The above mentioned standard recommends application of the drying phase only when the losses of hydrocarbons may be ruled out, and it advises in favor of the method of drying by lyophilization (freeze-drying). Another recommendation of the standard is in favor of sieving with preferred particle-size of <2 mm [2, 17].

Isolation and enrichment of analytes

The aim of the isolation and enrichment phase is to transfer the determined analytes into a matrix, where there can be conducted a chromatographic analysis, and if need be, also

enrichment up to the concentration enabling quantification. The methods of isolation (extraction) of analytes most often presented in the publications are primarily based on solvent extraction with use of mechanical shaking [16], solvent extraction in a Soxhlet extractor (involving heating) [11, 14, 16], and solvent extraction modified with ultrasounds (sonification) [2]. In all the listed above types of extraction there are most often used: pentane, hexane, heptane, light petroleum, toluene, methylene chloride, chloroform, methanol, and their mixtures [2, 14, 16, 17, 21].

Concentrations of analytes in the extracts of solvents are usually below the limit of quantification of the techniques used in the final determinations, and that is why it is necessary to allow the solvent to evaporate. In the process of evaporation of solvents (usually to the volume of few cm³), there is applied a Kuderna-Danisha apparatus, and a stream of gas (nitrogen or air) [18, 21].

Purification of the extracts

Most of the procedures of hydrocarbons determination allow for the phase of removing the polar compounds, which get transferred into the extract from the sediments. The total amount of extractable substances is defined as oils and fats, and only after it is purified from the polar substances, it is called TPH (Total Petroleum Hydrocarbons). In the purification process there are used such adsorbents as: silica gel, alumina, and Florisil. This phase of the analytical procedure may be conducted by means of:

- ◆ - adding a specific amount of an adsorbent to the extract, and next, decantation or filtration of the extract,
- ◆ - employing the column chromatography, with the listed above adsorbents serving as the filling [17, 18, 21].

Identification and quantitative analyses

The phase of final determinations encompasses identification and quantitative analysis of the contaminations. The main methods applied here are the gravimetric, IR [11, 16], and chromatographic ones. The most often used are gas chromatography with a flame ionization detector (GC-FID) [2, 14], and gas chromatography/mass spectrometry (GC/MS) [15]. The methods enable both identification of the hydrocarbons, and their quantitative analysis.

With use of the standard GC devices there may be determined the hydrocarbons which have up to 40 carbon atoms per molecule, which encompasses most of the compounds occurring in the crude oil and petroleum products. In the analyses of this kind, a lot of compounds occur in the form of isomers with similar boiling points, in concentrations below the limit of quantification. That lets a large part of the compounds not decompose, which is reflected in higher level of the baseline, or a “bump” in the chromatogram. The best decomposition and characteristic chromatographic profile of petroleum hydrocarbons are obtained on the capillary-columns with non-polar stationary phases by means of temperature programing

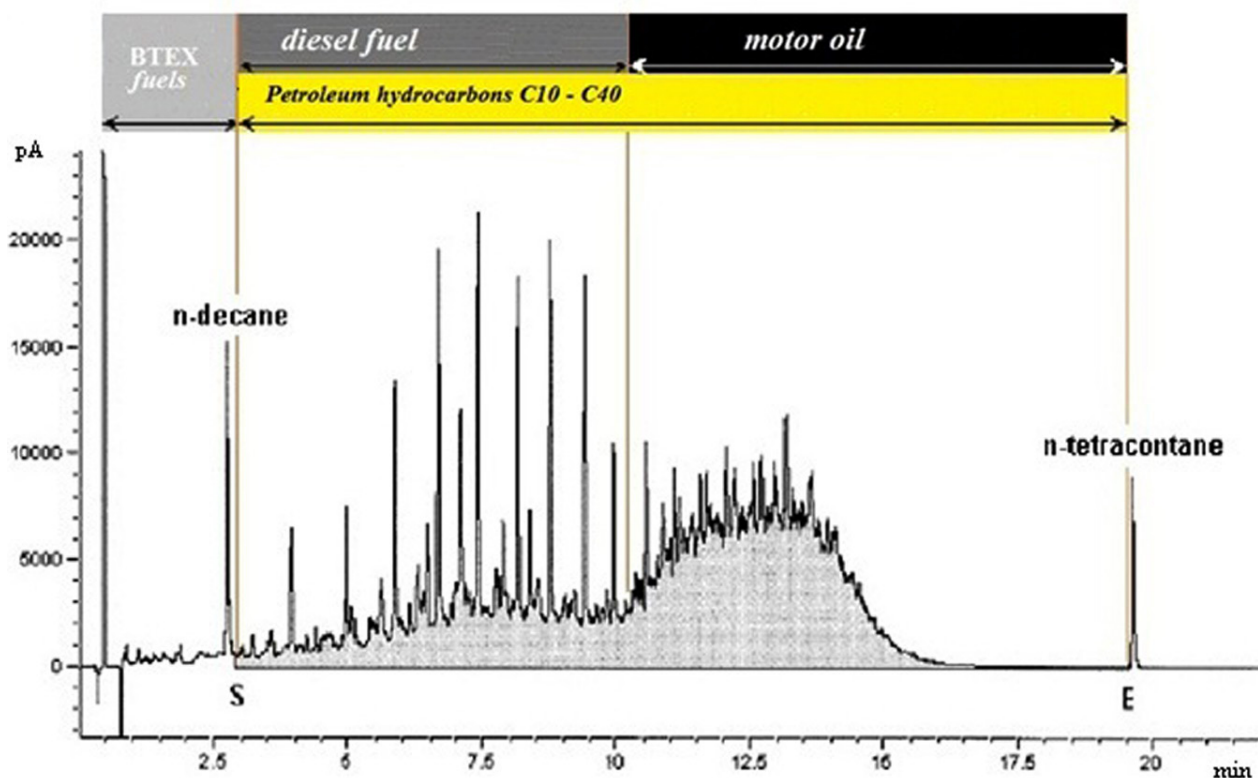


Fig. 3. Chromatogram of internal standard made of diesel fuel and motor (lubricating) oil [2, 15].

adequate for elution of the hydrocarbons with a rising number of carbon atoms in a molecule. Used most often is the flame ionization detector (FID), which demonstrates a high sensitivity, good repeatability, and a wide linearity range for various groups of hydrocarbons [21].

Identification (qualitative) analysis

The content of petroleum hydrocarbons is characterized with use of a sum parameter, namely the mineral oil index, which determines only the contents of hydrocarbons within the C_{10} to C_{40} range. In the Figure 3/Rysunek 3, there is presented a chromatogram of internal standard made of diesel fuel and engine (lubricating) oil, with the two groups of hydrocarbons set clearly apart.

In identification of the compounds there is used retention time. It is a constant amount for a given compound, if an analysis is performed under identical conditions. While conducting a qualitative analysis, determined are all the hydrocarbons eluting from the chromatography column placed between the n-decane's (C_{10}), and the n-tetracontane's (C_{40}) retention time.

Quantitative analysis

The basis of the quantitative analysis is the measurement of the area under chromatographic peak, which is proportional to the quantity of the component that is being determined. This proportionality is preserved in relation to the linearity of

the detector's indications. The basis for determining concentration of the analyzed compounds is a comparison of the area under their peaks with the area corresponding with the known volume of these compounds [18, 20, 22]. The case under discussion is specific both for the chromatographic analyses, as well as for the environmental ones, and it requires nearly entire area of the chromatogram to be calculated [15].

Recapitulation

Analyses connected with determination of substances occurring in the environment at a very diverse level of concentrations are of great importance. Analyzing the environmental protection is very complicated and complex a process, particularly because amounts of the surveyed pollutants are very small in comparison with the volume of all the other substances included in the complex matrix of bottom sediments. Selection of analytical method for conducting the routine determinations is an important part of the validation process in a research laboratory. Review of theoretical knowledge on the subject of analyzing petroleum hydrocarbons in environmental samples presented herein made it possible to work out a fast and effective method of determining the compounds in the bottom sediments to be used in the research laboratories. The method acquired certification from the Polish Centre of Accreditation (PCA), and is applied in the routine determinations in the Laboratory of Environmental Protection Department of the Maritime Institute in Gdańsk.

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