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APPLICATION OF FLUORESCENCE IN STUDIES OF MARINE PETROLEUM POLLUTANTS

The paper presents some information about fluorescence properties of mineral oils and the application of fluorescence spectroscopy for testing petroleum pollutants in marine environment. Detection of oil slicks on the water surface, determination of petroleum contaminants in seawater and determination of particular petroleum derivative compounds as well as identification of pollution sources – all of these are the main questions of petroleum presence in marine environment and these topics are described briefly in the paper. The paper also points on some prospects of fluorescence application in the near future.

INTRODUCTION

Petroleum oils are the earliest group of substances which have been stated as pollutants. It was in 1954 and since this time the word „oil" is a synonym of the term „petroleum pollutant" in regard to the sea. According to the MARPOL Convention, oil means any kind of crude oil and any petrochemical product (like fuel or grease oil) as well as a product of petroleum transformation in the marine environment [13, 18]. The Convention also imposes a duty to protect the environment and to monitor the level of oil contamination. Despite the constant development of protection systems, petroleum still belongs to the most common pollutants of the sea [8]. This fact exclaims researches of the oil pollutants and practical questions take significant place in these investigations. Especially intensive development of these investigations occurred in seventies of the last century. At this time also fluorescence properties of oils was utilized. In the later years interest in this subject decreased and many questions remained still open. Petroleum in the sea creates the large area of research and for application of fluorescence at the same time. The paper presents briefly application of fluorescence in the following topics:

- detection of petroleum pollutants,
- determination of oil in water concentration,
- determination of particular polycyclic aromatic compounds,
- identification of oil contaminants.

1. FLUORESCENCE

Fluorescence (photoluminescence) is the emission of light by a substance that has absorbed electromagnetic radiation. Fluorescence usually appears as visible light and occurs when the exciting radiation is in the ultraviolet or blue light region of the spectrum. The phenomenon occurs when an orbital electron of a molecule relaxes from its first excited state (S_1) to a ground state (S_0) by emitting a photon of light after being excited to any higher quantum state. Therefore in most cases, emitted light has lower energy than the absorbed and wavelength of fluorescence is longer then wavelength of exciting radiation (see Fig. 1).

Absorption of the radiation is a common phenomenon unlike fluorescence. Even in case of a fluorescent compound, an excited molecule can give back absorbed energy by various competing pathways. It can undergo nonradiative relaxation in which the excitation energy is dissipated as heat. The relaxation can also occur through interaction with a second molecule through fluorescence quenching. Thus, a luminophore give back only a part of absorbed energy in form of light. This fact is described by efficiency of fluorescence. Energetic efficiency (energetic yield) is the quotient of emitted energy and absorbed energy. Another value is a quantum yield defined as the ratio of the number of photons emitted to the number of photons absorbed.

Fluorescence decays immediately after stopping excitation. The fluorescence decay depends on average lifetime τ the molecule stays in its excited state before emitting a photon. Fluorescence typically follows the first-order kinetics and the concentration of molecules in an excited state decreases with time exponentially. Intensity of fluorescence I decreases with the time t:

$$I = I_0 \exp\left(-\frac{t}{\tau}\right), \tag{1}$$

where I_0 is the initial intensity. The lifetimes (τ) of most fluorescent compounds are of order of several or dozens nanoseconds.

Intensity of luminescence light is proportional to the intensity of exciting radiation. This dependence may be not true if exciting beam is very intensive like in case of pulse laser of high output power. Some devices measure the ratio of fluorescence light to the intensity of exciting radiation. These measurements allow to determine the internal energy efficiency of fluorescence w. This parameter describes real fluorescence at the point where this phenomenon occurs. The w is a function of two variables: the exciting radiation wavelength and the luminescence wavelength and represents a total spectrum of a luminophore. This function also represents an ordinary fluorescence spectrum. An emission spectrum is the wavelength distribution of an emission measured at a single constant excitation wavelength. Conversely, an excitation spectrum is the dependence of emission intensity, measured at a single emission wavelength, upon scanning the excitation wavelength [16].

Devices that measure fluorescence are called fluorimeters or fluorometers. The most versatile spectrofluorimeters have dual monochromators and a continuous excitation light source. With such devices it is possible to measure both excitation and emission spectra. In a spectrofluorimeter a narrow beam of radiation runs through a monochromator and then passes through the centre of a quartz glass cell. When the cell contains a luminophore, the passing radiation excites fluorescence. The fluorescent light is emitted in all directions, but the measured radiation came from the cell at right angles to the illuminating flux, runs through a monochromator and reaches a detector. Intensity of fluorescent light is a result of the measurement. Some fluorimeters measure directly the ratio of the luminescence intensity and the intensity of the exciting radiation. Some other devices measure fluorescence from the front. Such measurements are often done for turbid or opaque samples. Both types of measurements are carried out in testing petroleum pollutants of marine environment. Some devices are equipped with multichannel detectors. A multichannel detector measures the intensity at several wavelengths simultaneously, while a single-channel detector can only detect the intensity of one wavelength at a time. Some devices are equipped with lasers as sources of exciting radiation. A laser emits light of high irradiance and of one wavelength, which makes an excitation monochromator unnecessary. The disadvantage of this method is that the wavelength of a laser cannot be changed and a set can measure only a fluorescence spectrum. A pulse laser allows to measure time resolving fluorescence. Any contemporary instrument automatically records the results of measurements as digital data [16].

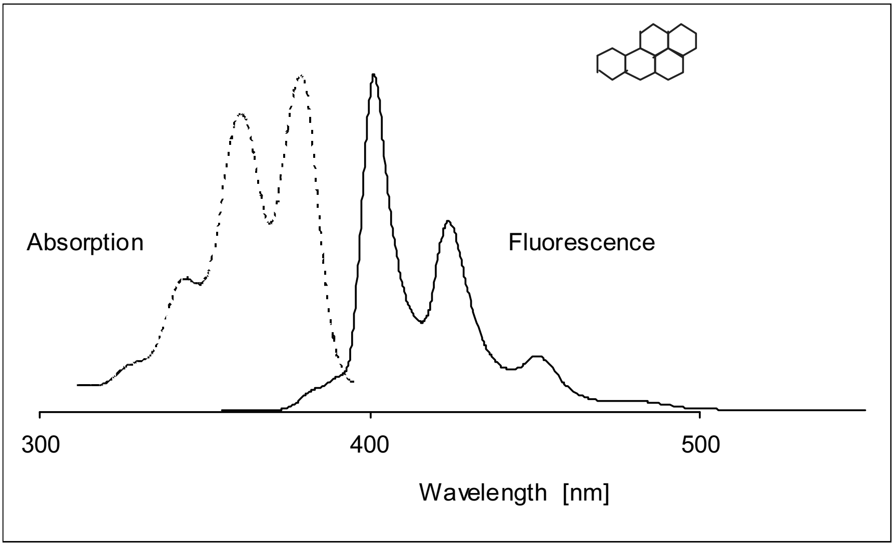

Fig. 1. Shapes of the absorption and fluorescence spectra of benzo(a)pyrene

2. FLUORESCENCE PROPERTIES OF PETROLEUM

Petroleum oils are extremely diverse class of substances. The oils – over thousand kinds of crude oils and countless of different petrochemical products – vary in their properties [16, 22] and any differences have their source in the diverse chemical constitution. Main components of any oil are hydrocarbons. The other components are primarily derivatives of hydrocarbons containing single atoms of sulfur, oxygen or nitrogen. Just hydrocarbons as the main components are a common feature of oils. Only a few of hydrocarbons fluoresce, while the major of them show no ability to luminescence. The content of compounds able to fluorescence rarely exceeds 10% of the oil mass. At the same time the petroleum strongly absorbs radiation, especially the ultraviolet and blue light. In spite of this petroleum is a luminescent medium and fluorescence is a phenomenon which allows testing oils.

Fluorescence of oils has wavelength over then 260 nm and covers a spectral area of ultraviolet and visible light. The phenomenon is most significant in the 270–400 nm range [27]. Fluorescence is greatest if it is excited by radiation of wavelength below 280 nm. If wavelength of exciting radiation is longer than 300 nm and further increases, then the fluorescence decreases and visible light causes luminescence relatively slight.

3. OIL SPILLS DETECTION

Fluorescence is used for detecting marine oil spills. A set for remote sensing by means of fluorescence is named fluorosensor. The first field trials of the airborne fluorosensor over marine oil spills were reported in eighties of the past century. Now some aircrafts are equipped with laser fluorosensors – among many other instruments – especially for remote detecting of oil covering seawater surface [2, 5, 6, 11, 18]. Such fluorosensor is a combined set like a lidar. The set is equipped with a pulse laser emitting ultraviolet radiation (usually 308 nm). The laser illuminates sea surface and the set records automatically spectrum of light coming from the below. In case of pollution, radiation coming from the laser excites fluorescence in the oil layer and the fluorosensor records the light emitted by the pollutant. This light differs significantly from the radiation coming from clean seawater.

Fluorescence is not completely selective phenomenon. In particular, some fats on water surface fluoresce like a petroleum (see Fig. 2) and detection of an oil pollution by means of fluorescence requires confirmation by other methods. Fats, like fish or vegetable oils, contain very small amounts of fluoresce compounds in comparison to petroleum. Hydrocarbons absorb radiation strongly, especially the ultraviolet and the blue light. Petroleum oils absorb both radiation exciting fluorescence and emitted light, so fluorescence is quenched in petroleum much more strongly then in fats. Some oils behave like a blackbody. In consequence, intensity of fluorescence observed above a petroleum pollutant could be similar to this of a fat layer. Despite of this fluorescence is useful in remote tracking at the sea. The natural oil slicks in the Gulf of St. Barbara are monitored in this way constantly [4]. Also the crude oil beds were localized along the northern coast of Australia. Flights of an aircraft equipped with a fluorosensor indicated some places where fluorescence was higher, although there were no oil spills in this area. Subsequent drillings have shown rich deposits of crude oil hidden in these places.

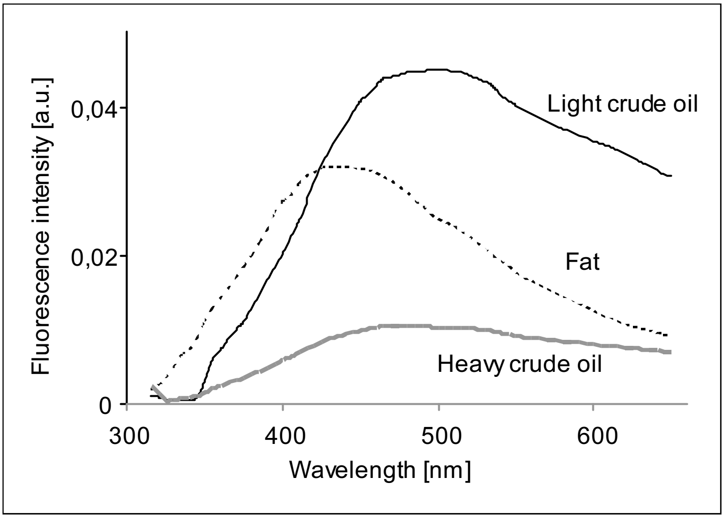

Fig. 2. Fluorescence spectra of petroleum oil layers and layer of vegetable oil excited by radiation of wavelength 300 nm

4. DETERMINATION OF PETROLEUM CONTENT IN SEAWATER

As was mentioned above, petroleum oils vary in their compositions and properties. Furthermore, the natural environment affects the oils and fluorescence reflects these changes. Despite their differences, oils constitute a single class among a variety of marine pollutants – this status arises from the MARPOL Convention [12]. The variability of petroleum is the reason for the difficulties in perfecting a method for determining the concentration of a petroleum pollutant in any compartment of the environment.

Determining the concentration of petroleum contaminants by means of fluorescence was developed back in the 1970s [11, 13]. In this method, a hexane extract of a water sample is obtained and the intensity of light emitted by the extract is measured. Then result of this measurement is compared with the intensity of luminescence of a pattern – solution of an artificially aged crude North Sea oil. Though still used in the 1980s, the method is no longer applied as it is not sufficiently accurate [8]. In this method, the wavelength of the exciting radiation is 310 nm and that of the fluorescence is 360 nm. The intensity of light emitted by solutions of different oils of the same concentration varies over a range of values in such conditions. In spite of this fluorescence method is only one reliable technique of monitoring small-scale oil pollution in seawater. Now the method is applied after its significant improving. The fluorescence is excited by radiation of 210 nm wavelength and intensity of emitted radiation of 295 nm wavelength is measured. Furthermore, absorption of the radiation is taken in consideration. The method allows estimating of petroleum concentration in water with relatively good uncertainty not exceeding 50% [25, 27].

5. DETERMINATION OF THE PAHS

Petroleum pollutions are the main (but not a single) source of hydrocarbons in marine environment. This is a reason that the state of petroleum pollution is determined from the measurements of the concentration of individual hydrocarbons in deep water or in sediments. Mainly polycyclic aromatic hydrocarbons (PAHs) are determined because of their very adverse impact on the environment. Most of the PAHs are also the fluorescent compounds. Analysis of fluorescence and absorption spectra allows to identify some individual compounds [22]. Such methods are not used now because of their limited accuracy. Particular hydrocarbons are determined by means of chromatography. High performance liquid chromatography (HPLC) is most common method of determination the PAHs. Fluorescence is applied in HPLC for detection of particular compounds.

The Shpolskii spectroscopy is an alternative method of PAHs determination. This method does not differ in its principles from the ordinary fluorescence spectroscopy. It consists on fluorescence measurement made at liquid nitrogen temperature (77 K) or even close to that of liquid helium (4.2 K). At such temperature any solvent is frozen and tested extract constitutes a system where aromatic molecules are embedded in a crystalline matrix. The fluorescent molecules have no rotation energy and their oscillation energy is the lowest, so the spectrum exhibits characteristic narrow lines instead of the broadened features. The Shpolskii method is applied exceptionally [1, 19].

6. POLLUTANTS IDENTIFICATION

The great diversity of oils manifests itself in the variety of their fluorescence properties. The differences concern intensity and spectral area of the fluorescence, the shapes of the spectra and the phenomenon lifetime. This fact has been known since the 1970-ties [7, 8, 15]. These differences are clear in case of different crude oils and various types of petroleum, but the problem deals with an answer to the following question: can any two oils be differentiated even if the oils are similar and belong to one kind of petroleum? This is a precondition of any objective method of identification of oils and determination the sources of petroleum pollutants by means of fluorescence.

Obviously, any differences in properties have their source in the diverse chemical constitution of petroleum. Therefore any system of identification of a pollutant bases on comparison the chemical composition of tested sample with the composition of suspected oil [9, 20]. The composition is determined by means of a gas chromatography and a mass spectrometry. Fluorescence was utilized in USA by the Environmental Protection Agency as an auxiliary method [28]. Despite the often high formalization, particularly in Europe, any current manner of pollutant identification is only an expertise based on determination of the similarities of respective chromatograms and spectrograms, but it is not an objective method allowing to state identity of two oils.

Total fluorescence spectrum is a function w of two variables: the wavelengths of the exciting radiation λ^{ex} and the luminescence λ^{f}. The value of the function w in any point (λ^{ex}, λ^{f}) represents fluorescence of defined wavelength $\lambda_{\mathrm{j}}^{\mathrm{f}}$ excited by the radiation of $\lambda_{\mathrm{i}}^{\mathrm{ex}}$ wavelength. The total spectrum is obtained from measurements of several emission spectra (as the functions of luminescence wavelength λ^{f}). Fluorescence of each spectrum is excited by radiation of different wavelengths $\lambda_{\mathrm{i}}^{\mathrm{ex}}$ and is measured for discrete set of luminescence wavelengths $\{\lambda_{\mathrm{j}}^{\mathrm{f}}\}$. Finally a matrix $[w_{\mathrm{ij}}]$ of values of the spectral function w results from these measurements. Such a matrix represents total spectrum of defined oil. The total spectra could be compared by comparison of respective matrices. Difference D between two spectra A and B could be presented by the sum of modules of relative differences between respective values of the two functions w in particular points:

$$D_{\mathrm{AB}} = \frac{\sum_{ij} \left| w_{\mathrm{ij}}^{\mathrm{A}} - w_{\mathrm{ij}}^{\mathrm{B}} \right|}{\sum_{ij} w_{\mathrm{ij}}^{\mathrm{A}}} \,. \tag{2}$$

This parameter is an objective measure of how much the total spectrum of an oil “B” is different from the spectrum of an oil “A”. If two oils are identical then $D = 0$.

7. PROSPECTS FOR THE FUTURE

Remote sensing is used in different areas of the earth sciences due to its possibility to collect continuous data from inaccessible places. Aircrafts and vessels equipped with optical instruments collect data, which provide information for monitoring marine environment, where petroleum is almost constant ingredient of seawater in some basins and there is no reason to expect that such situation will change. There are taken the efforts to work out an optical method for determination of an oil concentration and simultaneous identification of petroleum derivative compounds. Highly sensitive laser-induced spectrometry offers a fast method for the detection and distinction of hydrocarbons in water and it has a significant potential for a wide range of marine applications. A significant step on this way is an submarine fluorimeter, which has been worked out during the *ldquosubLIFrdquo* project [23]. This device measures time-resolved fluorescence and can be operated remotely from a vessel.

Another question – and at the same time a prospect of fluorescence application – is interaction between petroleum pollutants and marine environment. There has been a remarkable growth in the use of fluorescence in the natural sciences during the past twenty five years. Fluorescence spectroscopy and time-resolved fluorescence are considered to be primarily research tools and fluorescence is now a dominant methodology used extensively in biology and related sciences [16]. Fluorescence detection is simple and highly sensitive and there is no longer the need for the difficulties of analytical measurements. Fluorescence can be applied especially for testing the kinetic of pollutant degradation in particular compounds of the environment.

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WYKORZYSTANIE FLUORESCENCJI W BADANIACH ZANIECZYSZCZEŃ NAFTOWYCH MORZA

Streszczenie

W pracy przedstawiono właściwości fluorescencyjne olejów naftowych i omówiono zastosowanie fluorescencji w badaniach zanieczyszczeń naftowych środowiska morskiego. Fluorescencja jest wykorzystywana w wykrywaniu rozlewów olejowych na powierzchni morza, do oznaczania oleju w wodzie morskiej i do oznaczania wybranych związków ropopochodnych, a także do identyfikacji zanieczyszczeń olejowych. W zakończeniu wskazano na perspektywy rozwoju metod fluorescencyjnych jako szczególnie przydatnych w badaniach zanieczyszczeń naftowych morza.