SPECTROFLUORYMETRY IN APPLICATION TO OIL-IN-WATER EMULSION CHARACTERIZATION

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Abstract

The question of identifying the type of oil in exploitation of engine room is associated with both the quality of ship consumables (fuels and lubricants) and the composition and origin of oil in settling tanks or in dumping water. Related issue is the possibility of determining the origin of oil, which is detected in the marine environment. The key question is how oils vary in their ability to fluorescence, understood as the shapes of fluorescence spectra obtained for different wavelengths of light exciting fluorescence. In this paper we present spectra of fluorescence for six chosen oils. Those oils were previously dispersed (emulsified) in the seawater, then extracted into hexane. Fluorescence spectra were obtained using fluorescence spectrometer Perkin Elmer LS55, for excitation wavelengths in the range from 240 nm to 500 nm, and emission wavelengths from 300 nm to 790 nm. In this paper there is shown that in general both total intensity of fluorescence and shapes of spectra of fluorescence depend on the excitation wavelength and are differ for various kinds of oil. In order to visually show the differences in fluorescence abilities of various oils, the results of measurement were placed on a chart of fluorescence intensities in the function of both variables: the excitation wavelength and the emission wavelength (so called the total fluorescence spectra). Analyses of results of the described studies confirm that the different oils fluoresce differently and identification of type of oil is possible by fluorescence spectrophotometry.

Keywords: oil, fuels, lubricants, aquatic environment protection, fluorescence spectra

1. Introduction

Nowadays events of crude oil derivatives entering the marine environment are still frequent. Only in the Baltic Sea a number of documented oil spills reached several hundred cases yearly [1]. The reasons of discharges of oil are intentional (at the present the frequency of their occurrence decreases) or unintentional. Anyway, the need for new rapid and inexpensive methods for determining the type of oil in the water column or in vessel discharge waters is high. In the case of the seawater masses increase of likelihood of identification of the oil pollution perpetrator is valid. On the other hand in the case of discharge waters a chance of oil content efficient monitor is important.

Different types of oil substances - for exemplary oils from different phases of exploitive use or from various stages of degradation in natural water - are characterized by different chemical composition. Emerging differences in the relative amounts of individual components of oil, one can register using various methods of fluorescence. Phenomenon of fluorescence relies on light emission with a characteristic spectral composition stimulated by light of a specific wavelength.

The shape of the fluorescence spectrum depends on the competing processes of emission of light by certain components of oil (mainly aromatics) and the processes of light absorption by all the components of oil. Particularly useful for testing of samples containing more than one emitting spices are the tree-dimensional fluorescence spectra - so called "total spectra". Most of the spectral information about the type of oil is located in tree-dimensional spectra, in which intensity of fluorescence as a function of both wavelength of emitted light (emission wavelength) and excitation wavelength of light forcing fluorescence (excitation wavelength) [2].

The question arises whether one can distinguish between types of oils in the case when they previously were in contact with water. In this paper we report the study on fluorescence spectra of oils extracted from previously prepared oil-in-water emulsions, using three-dimensional excitation\emission fluorescence spectroscopy.

2. Materials and methods

Six types of oils were used: two types of fuel oil, two types of crude oil, hydraulic oil and transformer oil. All oils have been dispersed in seawater (salinity 8 PSU) using a stirrer (1 cm^3 of oil in 1dm^3 of water). The emulsion samples were left in bottles for a week in the dark. Next the samples were collected from the bottom of the bottle and were extracted into hexane. Three-dimensional fluorescence spectra for all extracts were measured in the spectrofluorimeter *Perkin Elmer LS55*. Spectral area of analysis covered range from 240 nm to 500 nm for excitation, and from 300 nm to 790 nm for emission.
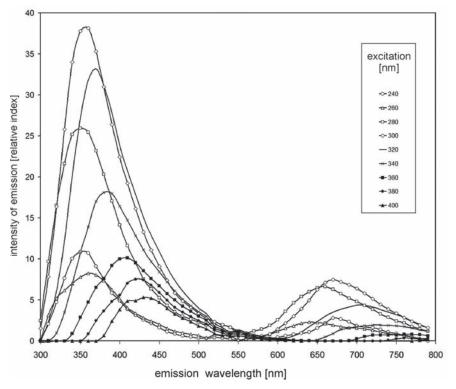
3. Results

Fig. 1. Emission spectra for various excitation wavelength

Spectral changes in fluorescence emission waveforms for different excitation wavelength (so called emission spectra) are shown in Fig. 1 (for crude oil extracted in the Polish Exclusive Economic Zone "Petrobaltic"), whereas in Fig. 2 fluorescence emission waveforms for different emission wavelength (so called excitation spectra) are plotted.
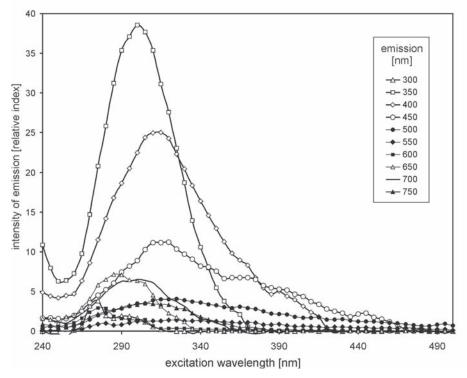
Fig. 2. Excitation spectra for various emission wavelength (for exemplary oil the same as in Fig. 1)
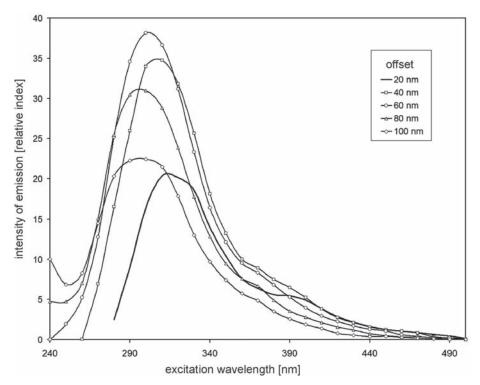

Fig. 3. Synchronous spectra for various offset for exemplary oil (the same as in Fig. 1)

For characterization of type of oil also so called synchronous spectra of are in use [3]. These are the spectral waveforms of intensity of fluorescence as the function of emission wavelength with synchronous changes of excitation wavelength, then the difference (offset) between the excitation wavelength and emission wavelength is fixed. In Fig. 3 synchronous spectra for various offsets are shown.
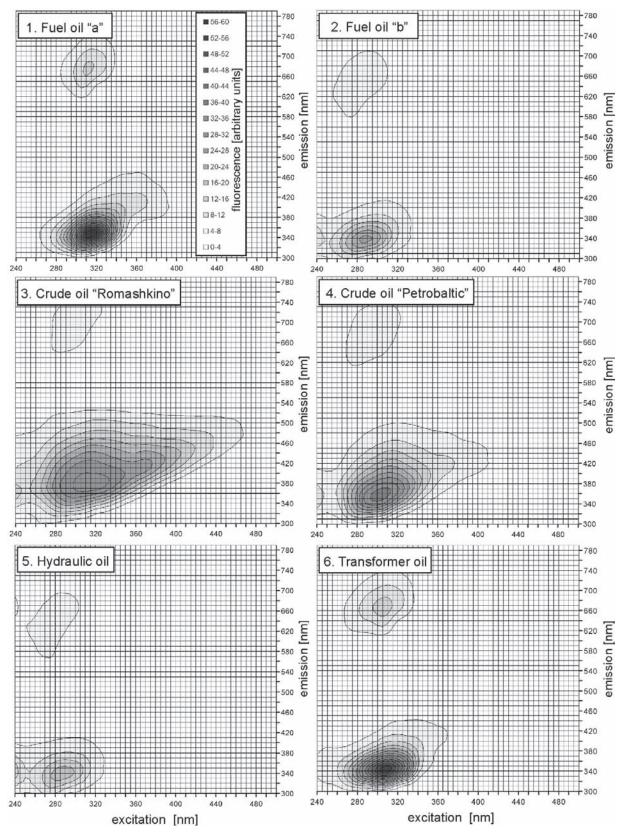
Fig. 4. Total fluorescence spectra for chosen oils

The entire results of fluorescence measurement (total fluorescence) is in array of fluorescence intensity, in which rows are values for subsequent fluorescence emission wavelengths, while the columns can be seen for different values of the fluorescence excitation wavelength. Such arrays

can be imaged as the function of two variables in the form of three-dimensional graph in a three-dimensional projection of an oblique (3D chart) or as a chart in the form of isolines of equal values of intensity of fluorescence (map/contour chart). In the Fig. 4 contour-charts of total fluorescence for various oil are shown.

4. Discussion

The knowledge that the shapes of fluorescence spectra of different types of oil are different is a phenomenon well known [4], although the surgery (such as sensors, testers, etc.) is as yet not used. In this article are presented the results of oil, which had previously been in direct contact with sea water (in this case as an emulsion oil-in-water).

Research has shown that the emission spectra take different shapes depending on the excitation wavelength. Similarly, the excitation spectrum. At the current stage of research would be difficult to decide which type would be most representative of the spectrum, as information about the type of oil. The shapes of emission spectra strongly depend on the excitation wavelength. By analogy with the shapes of excitation spectra depend on the emission wavelength. The best solution would be to determine the analytical form of functions that would be appropriate for a given course of spectral emission or excitation spectra. Then the parameters of this function (preferably a single parameter) could be an indicator of the type of oil, which would allow the objective (mathematical) way to determine the type of oil without the subjective factor, which is a visual assessment of similarity between the shapes of graphs. From the observation of synchronous spectra, one can suggest that the shapes of emission spectra in wavelengths in the range of 250-370 nm could be described by any of the bell curves. Unfortunately, this problem requires a separate longer-term studies.

Full spectral information corresponding to a particular type of oil is contained in the total-spectra. From visual observations of the spectra we can see that their view strongly depends on the type of oil. Fig. 4 presents total-spectra for extracts of six different oil. They are characterized by the presence of two peaks of varying intensity and extent. The shapes of the peaks strongly depend on the type of oil. This effect well promises the possibility of creating a representation of each type of oil in the form of two-dimensional array of numbers, then a mathematical algorithm can be created/chosen (for example the Principal Component Analysis) for an array automatically refer to specific type of oil.

Of course, a very interesting problem would be to compare the fluorescence spectra of oil before and after contact with water, and examine how the shape of fluorescence spectra evolves with the degree of degradation (wear and tear, chemical changes when exposed to light and living organisms). This problem will be the subject of our further investigations.

References

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