

## PROPERTIES OF THE BALTIC CRUDE OIL IN THE OIL-IN-WATER EMULSION FORM: EXCITATION-EMISSION SPECTRA

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### Abstract

Due to the fact that marine environment contamination by oil substances are not uncommon, it is necessary to improve the ability of determine their origin. Therefore, research on the possibility of recognizing the type of oil using its individual characteristic manifested in the processes of fluorescence excitation has been undertaken. Oil pollutants present in seawater mainly coming from ship drives, tankers, pipelines or sea bottom seeps, moreover oil leaks from offshore extraction equipment also are possible. For this reason, the crude oil extracted from the Baltic Sea deposit in the Polish Maritime Areas has been chosen for tests. Fluorescence properties of water containing small amounts of oil (concentrations from 5.59 to 55.4 ppm) in the form of oil-in-water emulsion were tested. Individual samples were assigned matrices of fluorescent values for different wavelengths, while excited by monochromatic light also for different wavelengths. The obtained matrices were visualized as a contour maps and 3D charts. For considered concentrations of crude oil dispersed in water, the wavelength-independent fluorescence maximum was determined. Obtained result indicates that in the studied wavelength range, the total fluorescence intensity is proportional to the oil concentration only for the lowest oil concentrations. The analysis of the objective parameter of the difference between the shapes of spectra indicates the similarity of the spectral shape for the lowest oil concentrations. These results are the methodological suggestion, that for the purpose of identifying the type of oil dispersed in water, spectra should be determined for sequences of different dilutions, until the excitation-emission spectra shapes become independent from the oil concentration.

**Keywords:** crude oil, excitation-emission spectra, fluorescence, seawater

### 1. Introduction

The paper is a part of the stream of research activities aimed at developing methodologies for detecting and identifying oil substances that can be found in the aquatic environment. The problem is difficult due to fluoresce of natural seawater components [4, 7]. Moreover, the overlapping of the spectra of oils and spectra of natural seawater components is observed.

In the seawater, various types of hydrocarbons can be found. They can come from various sources and further staying in the water in various forms. If heavy fuel enters to the marine environment, then the chemical composition of this substance changes slowly. However, if it is oil consisted of short carbon chains, for example light fuel; one should expect a quick evaporation of volatile hydrocarbons into the atmosphere [1, 5, 6]. However, the quickest transformation of the composition of oil takes place in crude oil.

The short-chain and monocyclic hydrocarbons penetrate between the water molecules. However, their solubility is low. In spite of this, in the seawater, at some distance from the polluted place, one can detect the dissolved components of the oil, which manifest themselves in the disturbance of the natural spectra of seawater fluorescence [3].

Typically, oil substances accumulate on the surface of the water. They are then relatively easy noticeable [8]. However, when the oil disperses and passes deeper into the water under the action

of wave motions or combating the spillage with the use of dispersants, then the observational methods fail. Therefore, methods to detect the presence of hydrocarbons located under the sea surface are needed. Fluorimetry seems promising in this case, as greatest oils contain compounds with fluorescent centres [2].

Referring to the situation when dispersed petroleum is present in the water, we performed measurements of the fluorescence intensity of the oil emulsion that is strongly diluted in water.

## 2. Material and methods

Crude oil coming from the mining fields of the southern Baltic Sea (named *Petrobaltic* crude oil) has been dispersed in demineralized water using a high-speed stirrer. The emulsion obtained was stored in the dark for one day to stabilize the suspension. Next, oily water was drawn from the bottom of the vessel to the oil content determine by the fluorimetric method. The method is based on the extraction of oil from the water into n-hexane and determining intensity of fluorescence of the extract. Fluorescence was measured at 295 nm, while at 210 nm fluorescence was excited. The oil from which the emulsion was previously made was applied to prepare calibration solutions. Tab. 1 presents the oil concentrations in the studied oil-in-water emulsion samples. Samples are marked from (a) to (d) (see Tab. 1), which are further used for markings on the drawings.

Tab. 1. Concentration of oil dispersed in water

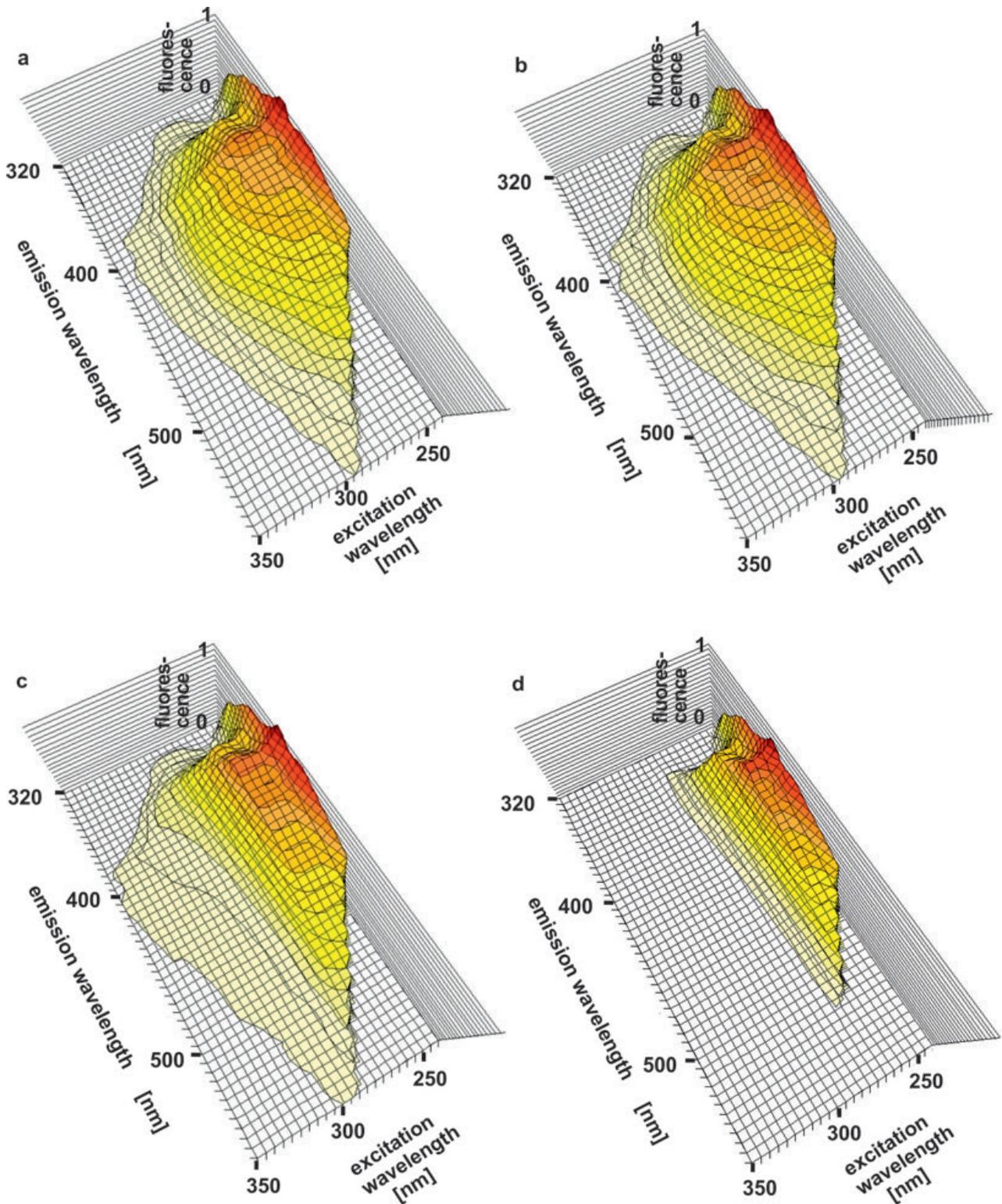
probe	concentration [ppm]
a	5.59
b	11.2
c	27.9
d	55.4

Spectrofluorometer *AqualogHoriba* was applied to determine the fluorescence spectra of oil samples. Determinations of spectra of oil for all solutions in 1×1 cm quartz cuvette were performed. During measurements, the following parameters were applied: excitation wavelength from 240 nm to 600 nm with a 5 nm sampling interval, emission wavelength from 212.75 nm to 622.97 nm with a 1.623 nm sampling interval, 5 nm excitation slit, 5 nm emission slit, and 1 s integration time. The measurements were made at stabilised temperature of 20° C.

## 3. Results

The result of the spectrofluorometric measurement is a two-dimensional digital table containing fluorescence intensity values for individual emission wavelengths obtained for each excitation wavelength. In order to visualize the results included in numerical tables, fluorescence intensity plots were prepared as a function of two variables: excitation wavelength (Ex) and emission wavelength (Em). In order to present the shape of individual spectra, they are presented after normalizing on the 3D chart (Fig. 1) and on the contour map (Fig. 2). Contour map allows determining the position of the spectral peaks – described by excitation and emission wavelength, which are coded in parameter – the wavelength-independent fluorescence maximum. Four peaks were determined:  $\lambda_{Ex} = 260$  nm and  $\lambda_{Em} = 380$  nm,  $\lambda_{Ex} = 240$  and  $\lambda_{Em} = 390$ ,  $\lambda_{Ex} = 260$  and  $\lambda_{Em} = 406$ ,  $\lambda_{Ex} = 240$  and  $\lambda_{Em} = 405$ . However, fluorescence maximum was detected for excitation wavelength  $\lambda_{Ex} = 240$  nm corresponds to the emission wavelength  $\lambda_{Em} = 390$  nm. Fluorescence occurs in the excitation range 260-340 nm, whereas emission decreases in the wavelength range from 320 nm to 555 nm. The shortest excitation wavelength for the device used is 240 nm. It is certain that the fluorescence excitation of the analysed oil also occurs for shorter wavelengths of ultraviolet radiation. The fluorescence range is narrowed at high concentration of oil suspension. It

turns out that for the oil concentration up to 28 ppm, the fluorescence spectrum changes to a small extent. However, for concentration 55.4 ppm, the spectrum differs significantly from the spectra at lower concentrations and the location of the spectral peaks does not change noticeably. Moreover, the shape of the spectrum is definitely steeper for the oil concentration 55.4 ppm than for lower concentrations. However, the tendency to increase steepness is already present for oil concentration 27.9 ppm.



*Fig. 1. Normalized Excitation-Emission spectra as 3D charts obtained for various concentration of oil in the water*

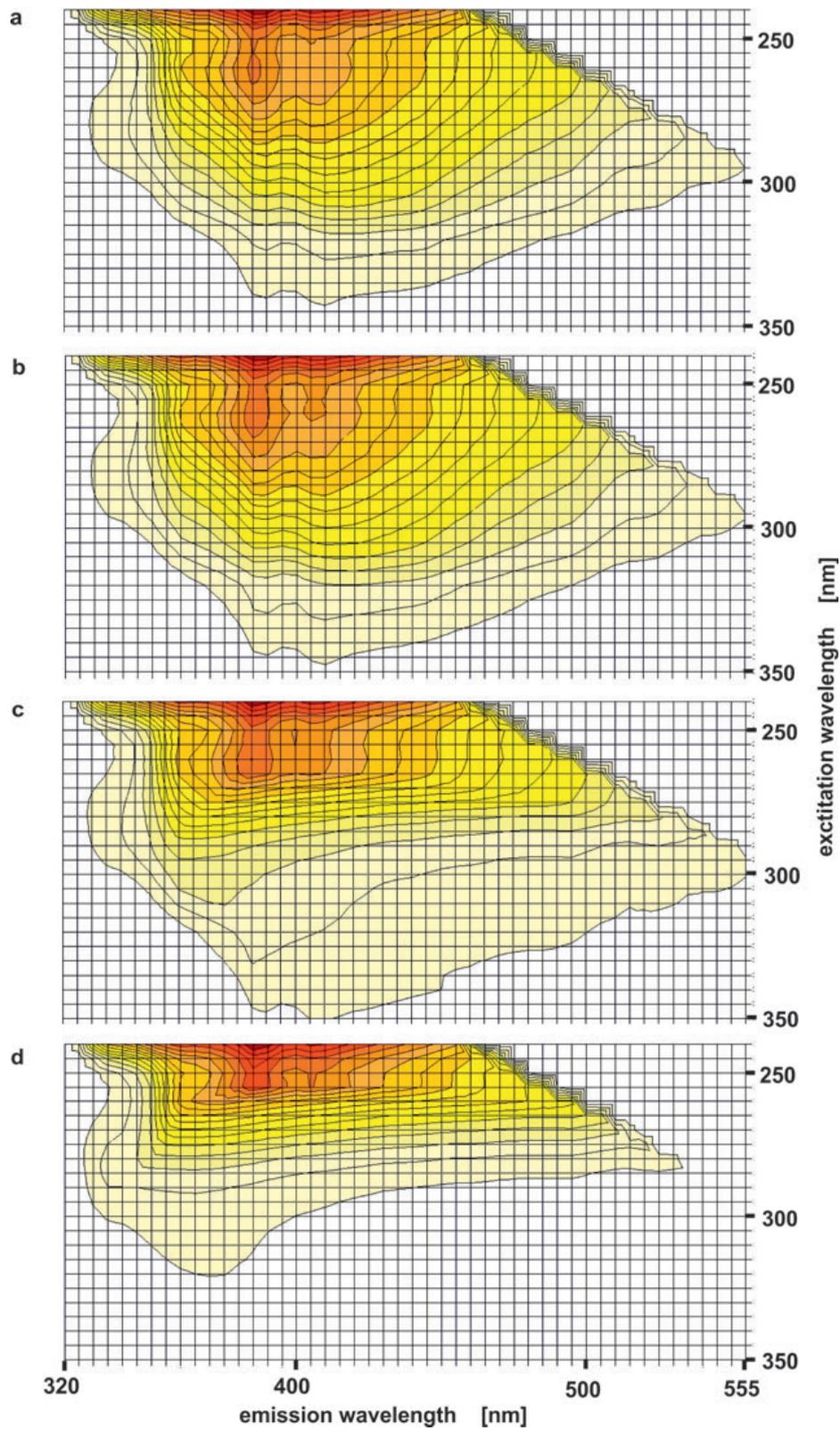


Fig. 2. Normalized Excitation-Emission spectra as contour maps obtained for various concentration of dispersed oil

#### 4. Discussion

The total fluorescence spectra – so-called Excitation-Emission spectra (EEMs) as 2D maps present in Fig. 2 correspond to the various concentrations of oil suspension in water. The spectra were normalized to the maximum value of fluorescence intensity; therefore, the fluorescence

intensity does not take into account. The shape of the spectrum is formed as a result of the overlap of the fluorescence emission process of the photons in the cuvette, their partial absorption and possible secondary emissions and absorptions.

The tested oil suspension samples contain very small amounts of oil – from several to several dozen ppm. Due to that, the amount of oil is really small the contaminated water is visually clear. However, the presence of this impurity, even in very low quantities, is measurable – additionally directly in the water (without chemical processing) – by a fluorimetric method.

For these research measurements, conditions are important. As mentioned above, in this work we describe fluorimetric measurements in a 1 x 1 cm quartz cuvette. Certainly, with a high concentration of dispersed oil, this method would fail because the fluorescence would occur at the wall of the cuvette from the excitation side of the light. In this case, the measuring technique should be based on reflection fluorescence.

In order to check the extent to which the intensity of the fluorescence being recorded depends on the concentration of the oil in the water placed in the spectrofluorometer cuvette, the fluorescence intensities for all excitation wavelength and all emission wavelengths are summed up. As can be seen in Fig. 3, it is not a linear relationship over the entire concentration range. Linearity occurs only up to a concentration of 11.2 ppm. Considering the nature of the line in Fig. 3, it should be assumed that the intensity of registered fluorescence would decrease for concentration above 100 ppm. Therefore, using a fluorimetric method for estimating the concentration of dispersed oil in water, measurements should be taken with increasing degree of dilution until a linear relationship between fluorescence and concentration is achieved. Similar nonlinearity is also observed for the relationship between the maximum value of fluorescence and the concentration of dispersed oil (Fig. 4).

Fluorimetric method for determining the content of dispersed oil in water would be fully effective (high accuracy would be achieved) when in a given region oil spill would be the same as used in the tests described in this paper, then the plots in Fig. 3 and 4 could be used as calibration lines. The similar calibrating problem occurs with all spectrophotometric methods for determining

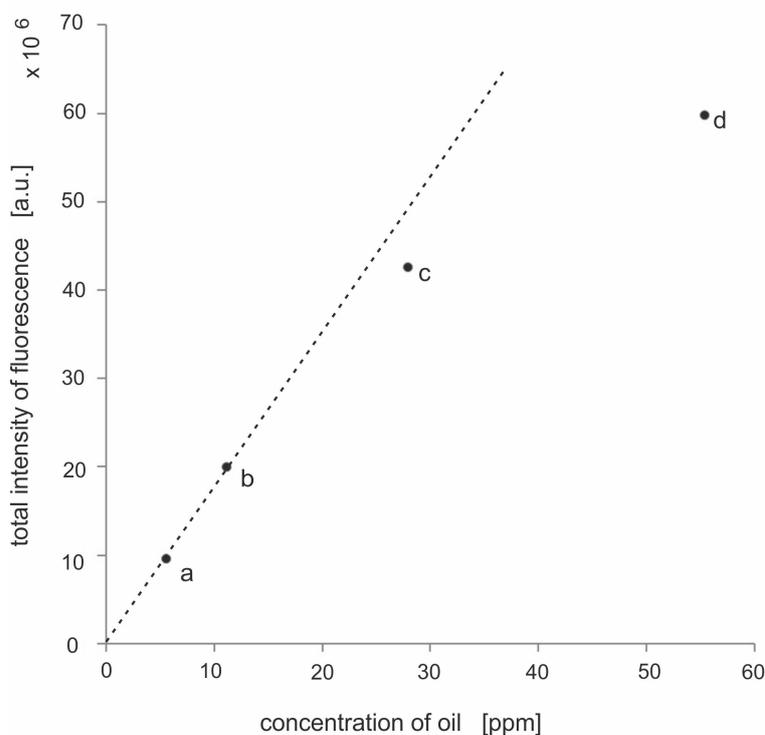


Fig. 3. Dependence of the whole fluorescence of water polluted with oil-in-water on concentration of oil (letters a..d refer to concentrations of oil according to the Tab. 1)

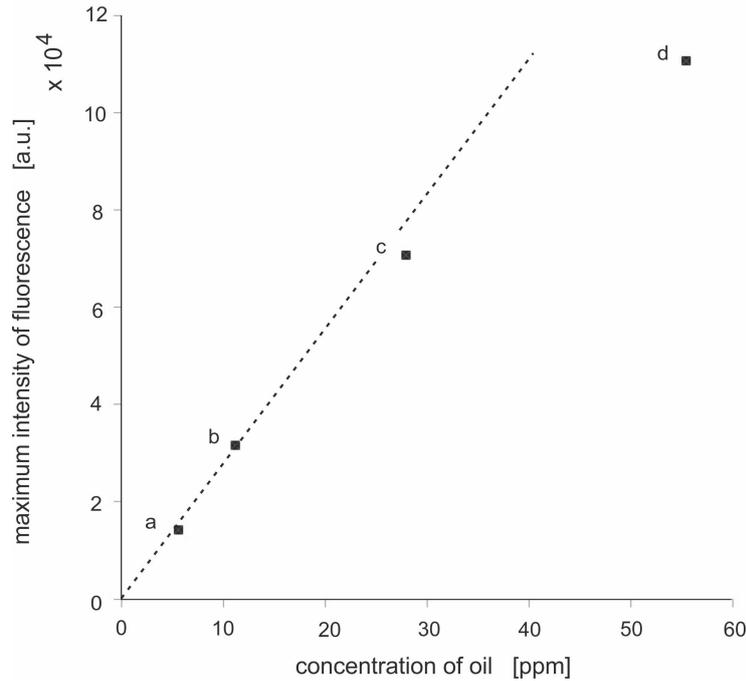


Fig. 4. Dependence of the maximal value of fluorescence of water polluted with oil-in-water on concentration of oil (letters a...d refer to concentrations of oil according to the Tab. 1)

determining the degree of water polluted with oil substances. In principle, a conventional oil substance (e.g. a specific type of petroleum) or the hydrocarbon chemical compound having fluorimetry centres in its structure is taken as the standard for the calibration of the method [9]. Although the measurement results are given in units typically used to determine the concentration ( $\mu\text{g dm}^{-3}$ , ppm), these results should be treated as a non-unit number. However, in the case when the kind of oil for contamination is known, and this type of oil has been prepared for the calibration relationship, then this number is a real concentration.

Another problem is the ability to identify the type of oil based on the analysis of the shape of the EEMs. In this case, the concentration of oil in the sample placed in the spectrofluorometer is of great importance. The analysis of the disparity of the shape of spectra obtained for different concentrations of crude oil was carried out. In this case, the sum of absolute differences between fluorescence intensities for specific excitation wavelengths and emission wavelengths (Expression 1) was taken as a measure of the difference between spectral shapes.

$$d_{x-y} = \sum_{mn} |w_{mn}^x - w_{mn}^y|, \quad (1)$$

where:

$d_{x-y}$  – difference between the spectrum x and the spectrum y,

$m, n$  – numbers of consecutive excitation wavelengths and emission wavelengths,

$w$  – values of registered fluorescence intensities.

A comparison between each spectrum with each ones of the four measured spectra was performed (see Fig. 5). The most important fact coming from these comparisons is that the difference between the spectra measured for the lowest oil concentration and the subsequent spectra for higher oil concentrations increases. Therefore, it is necessary to specify the oil concentration in the sample placed in the spectrofluorometer.

At the current stage of spectrofluorometric analysis for water contaminated with dispersed oil, it can be proposed that the fluorimetry of water contaminated with dispersed oil will be determined for samples diluted to such an extent that the fluorescence intensity is proportional to the oil concentration.

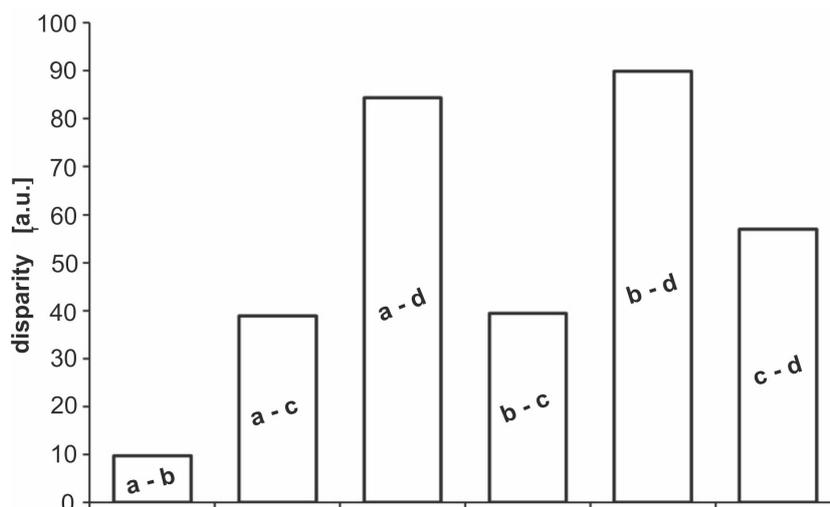


Fig. 5. Comparisons of spectra of water polluted with varying degrees of oil-in-water emulsion (letters a..d refer to concentrations of oil according to the Tab. 1)

## 5. Conclusions

Crude oil contains substances that, when dispersed into water, cause its fluorescence in the ultraviolet range. The fluorescence maximum occurs when it is excited by ultraviolet light with a light of the wavelength around 240 nm. The analysis indicates that the range of ultraviolet radiation wavelengths that are able to excite fluorescence depends on the concentration of oil in water, and widens the more when oil concentration is lower. It is a methodical proposition that the fluorescence spectra should be determined at a relatively low oil concentration, corresponding to a straight-line range of the relationship between the fluorescence intensity and the oil concentration.

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