

COMPARISON OF FLUOROMETRIC SIGNATURES OF OIL RESIDUES IN BOTH MARINE ENVIRONMENT AND IN ORGANIC DILUENT

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Abstract

The significant part of petroleum substances is transferred to the marine environment after technical activities (inevitable exploitive spills, illegal discharges). However a certain part of petroleum in seawater coming from the natural sources. Therefore, to develop the safety of natural marine environment it is necessary to track not only the anthropogenic pollutants but also the natural sources of petroleum. To distinguish both source of oil the fluorescence properties of oil can be used as the tools to oil identification. The aim of the study is to describe the optical properties of crude oil after it contact with aquatic environment based on fluorescence spectroscopy. For the study, crude oil 'Petrobaltic' type potentially found in marine environment due to coming from natural source was applied. To dissolve oil, two different solvent – hexane and Baltic seawater from the Gdynia coast were used. To measure the excitation-emission spectra (EEMs) of oil spectrofluorometer Hitachi F-7000 FL was applied. In the paper, we discuss the changes of oil EEMs in two cases for oil dissolved in n-hexane and for oil dissolved in seawater for various oil concentration. Obtained EEMs for oil dissolved in seawater indicate that EEMs spectrum contain the main peak – describing by the wavelength – independent fluorescence maximum, which was detected for oil dissolved in n-hexane (typical for this kind of oil). However, the intensity of oil fluorescence decreases after oil contact with seawater. This approach could allow expanding the description of complex mixtures of oils as a possible tool proposed for identification the type and origin of oil found in marine environment.

Keywords: oil pollution, seawater, excitation-emission spectra, fluorescence spectroscopy

1. Introduction

Institutions and organizations engaged in natural environment protection are still concerned about the permanent inflow of petroleum substances into the aquatic environment and their negative effects on biological processes. Because the marine transport is indicated as the main source of oil pollution in the sea areas, methods of detection of oil substances in both waters: discharging from vessel installations ones and in natural sea water – are the objects of specific attention.

To detect of oil in water by analysing the fluorometric signatures well knowledge about shaping of spectra is required. Mentioned spectra can be obtained directly in polluted water or in chemical extract [6, 7]. The second solution is been usually applied when concentration of tested substance in water is very low. As the extraction solvent, the substance well diluting oil must be used. At the same time, solvent should not show fluorescence.

In the paper the tests on two physicochemical systems are described, namely fluorescence of exemplary crude oil dissolved in the solvent (in low concentration) and fluorescence of natural seawater exposed to small amount of this oil. Obtained spectra are compared to detect characteristic differences in the spectra for two oil-systems tested.

2. Method

Crude oil *Petrobaltic* was used to prepare crude oil samples. Two different type of crude oil samples were prepared, respectively, crude oil samples were dissolved in n-hexane and crude oil

were dissolved in seawater. The difference of crude oil samples were described below and were presented in Fig. 1.

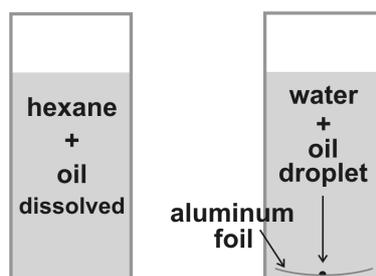


Fig. 1. Scheme of two oil systems with the same ratios of oil to water

2.1. Oil samples preparation in n-hexane

To prepare crude oil samples as a solvent n-hexane was used. Next, the stock solution of crude oil in n-hexane was prepared. Then based on dilution method two individual crude oil concentration 20 ppm and 50 ppm in n-hexane were prepared.

2.2. Oil samples preparation in seawater

Seawater from the Baltic Sea from Gdynia-Orłowo coast was used as a solvent to prepare crude oil samples. The pure seawater samples were taken in the middle of May. First, two individual samples of seawater were prepared. Next, two individual oil concentration in n-hexane were prepared. Then the hexane was evaporated to obtain the appropriate amount of oil. Next evaporated oil from each n-hexane sample was added to seawater sample. Finally, crude oil was diluted in seawater for each individual oil concentration (see Tab. 1).

Tab. 1. 'Petrobaltic' oil amount in seawater samples

Petrobaltic (P)	Ps1	Ps2
c [ppm]	20	50

2.3. Measurement

- EEM spectra of oil in n-hexane samples were obtained with an *Aqualog* Horiba spectrofluorometer [1, 2]. The EEMs for all solutions were measured in a 1x1 cm quartz cuvette. For EEMs measurements for crude oil dissolved in n-hexane, the following measurement 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 software package of the spectrofluorometer allows automatic removal of Raman and Rayleigh scattering [5], to yield a digital matrix of excitation-emission spectra.
- Excitation-emission spectra of crude oil *Petrobaltic* samples dissolved (after seawater was exposed to crude oil) in seawater in three-dimensional plane (3D) were measured using spectrofluorometer Hitachi F-7000 FL [3, 4]. EEMs for the solvent – pure seawater and for each concentrations of oil in seawater were measured in 1x1 cm quartz cuvette. To measure EEMs of pure seawater and oil seawater samples the following measurement parameters were applied: excitation wavelength from 240 nm to 340 nm with excitation sampling interval 5 nm, emission wavelength from 260 nm to 450 nm with emission sampling interval 5 nm, excitation slit 5 nm, emission slit 5 nm, integration time 0.5 s and photomultiplier tube voltage 400 V.

Firstly, EEM spectra for used solvent – pure seawater at a stabilised temperature 20°C were performed. Next, EEM spectra of seawater exposed to crude oil *Petrobaltic* for particular four oil’s concentrations were measured, also at a stabilised temperature 20°C.

Further, to obtain the real EEMs of crude oil after it contacts with seawater each data of measured oil samples diluted in seawater and particular four oil’s concentration were corrected by subtraction the spectra of pure seawater.

3. Results and discussion

To obtain information about the changes in EEM spectra of crude oil *Petrobaltic* after it contacts with water at first measurements of EEMs of crude oil in hexane were performed [2] and next EEM spectra of crude oil dissolved in seawater.

Figure 2 presents three-dimensional charts of EEMs for oil dissolved in hexane and the same oil added to seawater for oil concentration 20 ppm. In fluorescence process of oil in hexane takes part all components of oil, whereas only soluble in water oil components. Shapes of EEMs are different for oil-in-water and for oil-in-hexane. More evidences spectrum-shape effect is visible in Fig. 3.

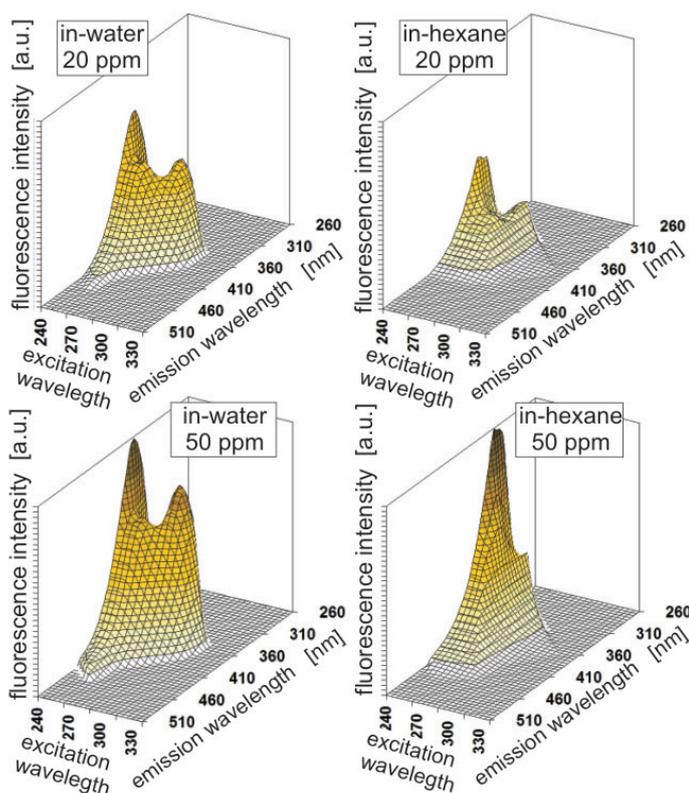


Fig. 2. Excitation-emission spectra (EEMs) of seawater exposed to oil pollution (left) and of hexane dilution of oil (right [2]) for ratio of oil to water: 20 ppm and 50 ppm

In Fig. 3 EEMs of the seawater exposed to oil pollution (left column) and of hexane dilution of oil (right column – published yet [2]) in two-dimensional plane for two ratios of oil to water: 20 ppm (upper row) and 50 ppm (lower row) are presented. In Fig. 3 is also visible that EEMs both for oil dissolved in n-hexane as well as for seawater exposed to oil change for excitation wavelengths starting from 240 nm to 340 nm and for emission wavelengths starting from 280 nm to 500 nm. In EEM spectra, different peaks are observed. To obtain the information about location of crude oil *Petrobaltic* EEMs peaks the normalization procedure of EEMs were performed for each crude oil sample.

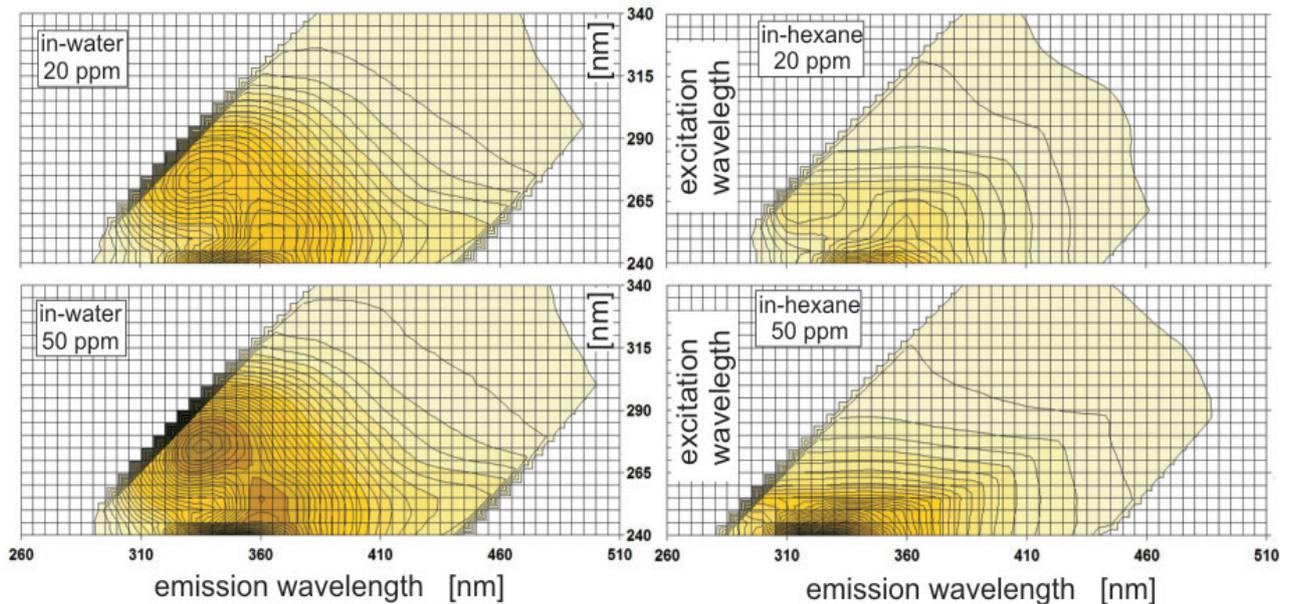


Fig. 3. Excitation-emission spectra (EEMs) of seawater exposed to oil pollution (left column) and of hexane dilution of oil (right column) for two ratios of oil to water: 20 ppm (upper row) and 50 ppm (lower row)

Normalized EEMs of the seawater exposed to oil pollution (left column) and of hexane dilution of oil (right column [2]) in two-dimensional plane for two ratios of oil to water: 20 ppm (upper row) and 50 ppm (lower row) are presented in Fig. 4. It allows precisely determining EEMs peaks of crude oil and describing by the wavelength-independent fluorescence maxima – the maximum of excitation wavelength correspond to the maximum of emission wavelength ($E_{X_{max}} / E_{M_{max}}$). The main peak is located at 240 nm for excitation wavelength and at 350 nm for emission wavelength for crude oil dissolved in n-hexane. Moreover, the same main peak at 240 nm excitation wavelength is observed for seawater exposed to crude oil EEMs for *Petrobaltic* in n-hexane is observed also for seawater exposed to crude oil. Moreover, for crude oil dissolved in n-hexane for oil concentration 20 ppm there is observed a second peak at 260 nm for excitation wavelength and at 320 nm for emission wavelength [2]. On the other hand, when we consider in detail EEMs peaks of seawater exposed to crude oil for oil concentration 20 ppm there is clearly visible also the second peak at excitation wavelength 275 nm and emission wavelength at 325 nm. Moreover in the EEMs for seawater exposed to crude oil is visible the third peak at 265 nm for excitation wavelength and at 255 nm for emission wavelength. Those three EEMs peaks determined for seawater exposed to crude oil for oil concentration 20 ppm are also observed for seawater exposed to crude oil for oil concentration 50 ppm.

4. Conclusions

Taking into account presented results for *Petrobaltic* crude oil based on excitation-emission spectroscopy both for crude oil dissolved in n-hexane and for the case when seawater is exposed to crude oil we indicate, that the most important information about *Petrobaltic* crude oil was fixed in the wavelength-independent fluorescence maximum ($E_{X_{max}} / E_{M_{max}}$), which characterised these spectra.

Obtained results allows to determine wavelength-independent fluorescence maximum for seawater exposed to crude oil for considered oil concentrations based on fluorescence peaks characteristic for oil dissolved in n-hexane. Summarising up obtained results precisely indicates, the main peak of crude oil *Petrobaltic* dissolved in n-hexane at 240 nm for excitation wavelength and at 350 nm for emission wavelength is observed also for the case when seawater is exposed to crude oil. Moreover, the second peak observed for oil dissolved in n-hexane peak at 260 nm for

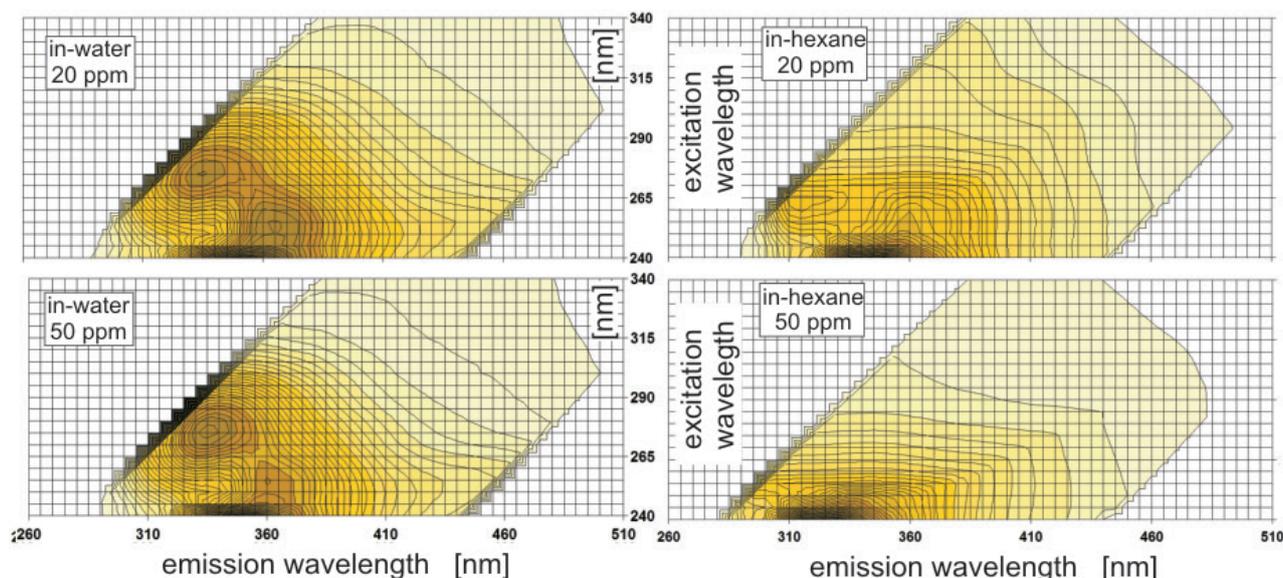


Fig. 4. Normalized excitation-emission spectra (EEMs) for objects like in Fig. 3

excitation wavelength and at 320 nm for emission wavelength could be detected also for seawater exposed to crude oil for excitation wavelength 275 nm and emission wavelength at 325 nm (there is observed shift toward longer wavelengths).

One can conclude that characteristic fluorescence peaks detected in EEMs spectra for oil dissolved in n-hexane allow to detected and probably identify type of oil potentially found in the vessel waste water directly in the seawater. On the other hand, further tests with natural seawater can improve information on possibility of detecting human made oil pollution directly in the bulk of water basing on fluorescence signatures.

Acknowledgements

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