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# LIGHT ABSORPTION PROPERTIES OF 'PETROBALTIC' OIL-IN-WATER EMULSION PRESENT IN SEAWATER

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***Abstract***

*In the article, the characteristic of crude oil 'Petrobaltic' potentially present in the Baltic Sea water masses is considered in relation to the protection of marine environment. The main spectroscopic method to characterize various oils (crudes and refinery products like fuels and lubricating oils) is fluorescence. However, the absorbance measurements of oils are necessary due to the partial overlapping the spectra of natural seawater components and oil substances. Therefore, properties of crude oil are considered to expand the basis of spectroscopic properties of oils – typical marine organic pollutants – based on absorption measurements. Oils potentially found in the marine environment are, in addition to surface forms, also in-depth ones as oil-in-water emulsion. Therefore, in the article crude oil as oil-in-water emulsion form is considered. As a solvent demineralised water with salinity, corresponding to Baltic Sea salinity was used. Several concentrations of dispersed crude oil were prepared. The absorbance spectra in the UV and visual range of the light in the range from 240 to 600 nm, for each prepared samples are discussed. Based on the Lambert-Beer law for each wavelength of excitation, in the range 240-600 nm, the specific parameter absorption coefficient was determined. Obtained results indicate the rapid decreasing of the absorbance for this kind of oil in the wavelength range from 240 nm to 420 nm. However, in the shape of absorbance spectra is observed the characteristic wide and flat peak located at 260 nm for excitation wavelength, which could be a specific point for this kind of oil.*

***Keywords:*** *crude oil, absorbance, absorption spectra of dispersed oil, absorption coefficient, oil-in-water emulsion*

## 1. Introduction

The growth of marine transport leads to increase of conflicts within maritime sectors and between human uses of maritime areas and the nature. Due to the balance between human needs and natural environmental ecosystem, it is necessary to track changes and occurrence of potential hazards especially oil pollutants in marine waters. It is a challenge for scientist to expand the knowledge about oil pollution and searching an effecting method to monitor of oil substances started from large oil leakage to the smallest oil amount in seawater both in costal and open waters.

The potential oil spill found in the marine environment usually comes from machines working on vessels, but also from containers of transported hydrocarbons and from the leak of submarine pipelines. After all, leakages cannot be ruled out when extracting oil on the continental shelf. Natural seepage of the seabed also appears [4]. Oil pollution at first appears as an oil film in the sea surface and is subjected to the action of wind force and waves. In time scale, oil exposed to natural factors partially evaporates, and a small percentage of oil may dissolve and disperse in the seawater in the oil-in-water system so-called oil emulsion [4, 5].

Petroleum consists of a complex mixture of hydrocarbons of various molecular weight contain specific organic compounds such as monocyclic (MAH) or polycyclic (PAH) aromatic compounds showing the ability to relatively strong fluorescence [6]. Moreover, petroleum consists of substance, which is responsible to absorb light. Absorption properties of petroleum derivatives such lubricate oils in oil-in-water emulsion form were discussed in our earlier paper [3]. Therefore, to expand the knowledge about the absorption properties of petroleum and its derivatives, the studies for petroleum in the oil-in-water emulsion form were undertaken.

In the article, description of studies on absorption properties of crude oil *Petrobaltic* dispersed in water – specific form of oil typically found in seawater – is presented in terms of broadening knowledge about oil pollutants could be detected in seawater.

## 2. Method

### 2.1. Dispersed oil samples

*Petrobaltic* type crude oil from mining fields in the Polish Exclusive Economic Zone was chosen for this study. This kind of crude oil is visually bright and relatively transparent in comparison with other types of crude oil.

At first, to disperse oil in the water sample a high-speed stirrer was used and oil-in-water sample was prepared. Next oil-in-water emulsion was seasoned for one week in order to stabilize the oil-water system. Further, a stock solution of oil-in-water emulsion sample was prepared and diluted in de-mineralised water. Next, based on the dilution method, four individual concentrations of oil-in-water emulsion samples for *Petrobaltic* crude oil were prepared. The individual concentrations for oil-in-water emulsion samples are presented in Tab. 1. The concentration of crude oil was determined by measuring the fluorescence intensity (excitation 210 nm, emission 295 nm) in relation to standard solutions.

*Tab. 1. Concentration (ppm by weight) of crude oil dispersed in water (oil-in-water emulsion) used for the study*

| *Petrobaltic* | | | | |
|---|---|---|---|---|
| | P1em | P2em | P3em | P4em |
| *c* [ppm] | 5.5 | 11 | 28 | 55 |

### 2.2. Measurement and apparatus

Spectrofluorometer *AqualogHoriba* was applied to determine the absorbance spectra of oil samples [1, 2, 7]. Measurements of absorbance spectra of crude oil for all solutions in 1×1 cm quartz cuvette were performed.

For measurements, the following parameters were applied: excitation wavelength from 240 nm to 600 nm with a 5 nm sampling interval, 5 nm slit and a 1 s integral time. Moreover, due to the technical features of the spectrophotometer, the absorbance spectra were measured from the longest to the lowest excitation wavelength. Absorbance measurements were made at stabilised temperature of 20ºC.

## 3. Results

Taking into account the Lambert-Beer law, absorbance spectra $A(\lambda)$ for water polluted with dispersed crude oil *Petrobaltic* at a particular given wavelength $\lambda$ were calculated by formula (1) [1, 3]:

$$A(\lambda) = -\log\left(\frac{I(\lambda,c)}{I_w(\lambda,c)}\right), \tag{1}$$

where:

$I_w(\lambda)$ – intensity of the light that has passed through the reference sample (de-mineralized water),

$I(\lambda)$ – intensity of the light that has passed through the dispersed oil sample, *c* – concentration index of the concentration of oil dispersed in water in kilograms of oil per one kilogram of oil-in-water emulsion (ppm by weight).

The absorbance spectra for several oil concentrations were registered in the range 240-600 nm. Determined absorbance spectra for each concentrations of oil in water are presented in Fig. 1.

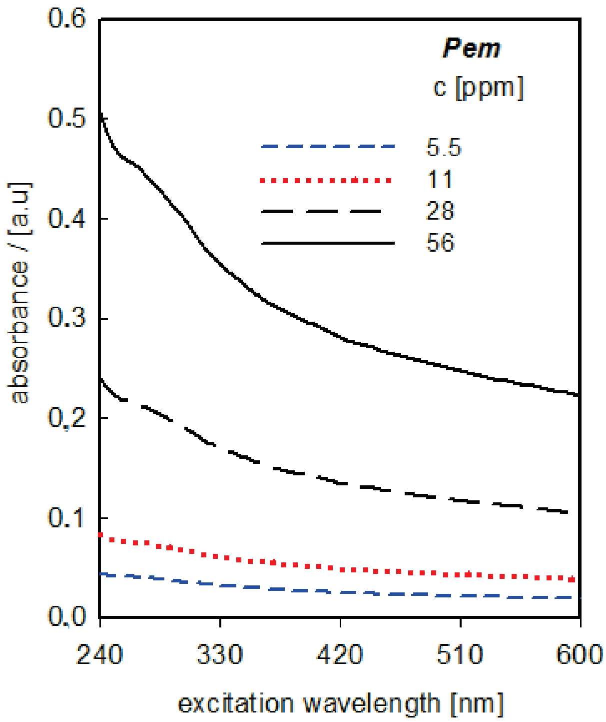


*Fig. 1. Absorption spectra for 'Petrobaltic' crude oil dispersed in de-mineralized water (oil-in-water emulsion) for various oil concentrations*

In Fig. 1 is visible that, the absorbance values of crude oil *Petrobaltic* dispersed in water decrease when the excitation wavelength increases. Moreover, strongly changes in the absorbance values is observed in the range from 240 nm to around 420 nm for excitation wavelength, while for the longer excitation wavelengths, the values of absorbance decrease minimally and remain constant in relation to the individual concentration. Moreover, in the absorption spectrum a small, flat, and wide peak is observed for excitation wavelength at 260 nm – quite clearly visible for the highest oil concentration 55 ppm. Additionally, in Fig. 1 it is clearly visible that, the values of absorbance and half-width of absorption spectra depend on the oil concentration. Absorbance spectra are stepper for higher oil concentration, while for the lowest oil concentration the absorbance values changes minimally in the whole excitation wavelength range. Moreover, the analysis of values of absorbance for particular dispersed oil concentration indicates that, when the oil concentration increases ten times then the absorbance values for oil concentration 55 ppm increases about ten times in comparison to the lowest oil concentration 5.5 ppm. Therefore, it is necessary to highlight that in considered oil concentration from 5.5 ppm to 55 ppm for crude oil *Petrobaltic* dispersed in water the absorbance values changes linearly with oil concentration. Moreover, the position of the detected peak at 260 nm does not shifted in excitation wavelength when the concentration of oil is changing.

## 4. Discussion

To monitor the natural seawater constituents, measurements of absorption spectra are performed. Based on measurements of absorption spectra the specific parameter could be determined – absorption coefficient $a(\lambda)$.

Absorption coefficient $a(\lambda)$ for each concentration of oil dispersed in de-mineralized water basing on Lambert-Beer law (2) was determined [8].

$$I(\lambda, c) = I(\lambda, c)\, e^{a(\lambda)\, d\, c}, \tag{2}$$

where:
$c$ – concentration index as in formula (1),
$d$ – cuvette length.

Taking into account the formula 1 and 2 the absorption coefficient $a(\lambda)$ which corresponds with individual excitation wavelength λ is recalculated as follows:

$$a(\lambda) = \frac{2.303 A(\lambda)}{c\, d}, \tag{3}$$

where:
$A(\lambda)$ – above-mentioned absorbance for individual excitation wavelength,
$c$ – concentration index of the concentration of crude oil dispersed in water in kilograms of oil per one kilogram of oil-in-water emulsion (ppm by weight),
$d$ – cuvette length.

The absorption coefficients $a(\lambda)$, expressed by formula (3), for dispersed in de-mineralized water *Petrobaltic* crude oil samples for each oil concentrations in the whole of excitation wavelengths range from 240 nm to 600 nm were determined. Fig. 2 presents the calculated absorption coefficients for dispersed in de-mineralized water *Petrobaltic* crude oil for particular oil concentrations. Fig. 2 shows that the absorption coefficient decreases when excitation wavelengths increase and depends on the concentration of oil dispersed in water. The values of absorption coefficients are changing in the excitation wavelength range from 240 nm to 420 nm and the same like in absorbance spectrum (see Fig. 1) a small, flat and wide peak for excitation wavelength at 260 nm was detected. The dependence of determined absorption coefficient from oil concentration for oil-in-water emulsion is caused by light scattering on oil droplets during the process of light attenuation in oil-in-water emulsion contained in the measuring cuvette.

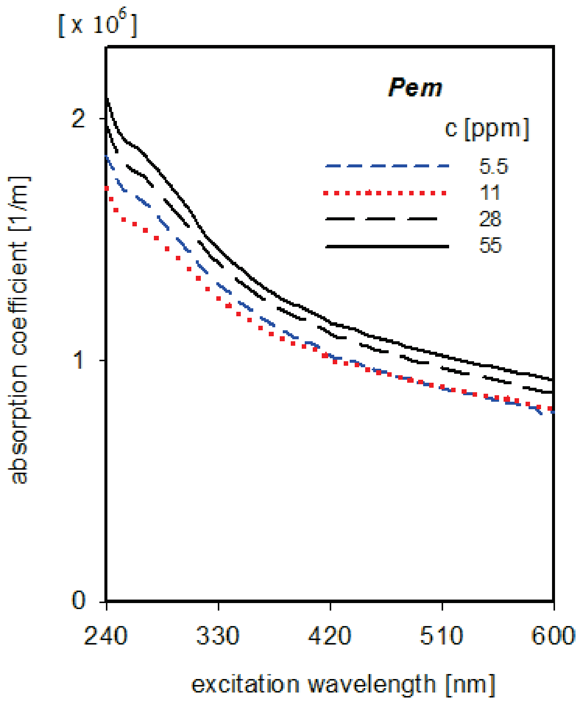


*Fig. 2. Absorption coefficient of 'Petrobaltic' crude oil dispersed in de-mineralized water (oil-in-water emulsion) for various oil concentrations (derived using formula (3) based on the data depicted in Fig. 1)*

Taking into account derivatives of petroleum such as lubricate oils the shape of absorption spectra for crude oil *Petrobaltic* dispersed in water in comparison with oils like *Marinol* and *Cyliten* dispersed in water belonging to the lubricate oils [1, 3] is similar. However, the values of absorbance decrease quickly for crude oil than for lubricate oils. Moreover, the position of the peak detected in these spectra is similar, while the peaks are broader for crude oil than for lubricate oils. The same dependence between crude oils and lubricate oils is observed for determined absorption coefficients.

## 4. Conclusions

To expand the base of spectroscopic properties about the oil pollutants in seawater absorbance properties of crude oil dispersed in water were described basing on absorbance measurements. To characterize the spectroscopic properties of analysed crude oil dispersed in water basing on absorbance spectra the specific indicator of absorption so-called absorption coefficient were determined for each excitation wavelength in the range from 240 nm to 600 nm. The absorbance spectra for dispersed in water crude oil were performed for several oil concentration in the range of concentration from 5.5 ppm to 55 ppm to check the impact of amount of oil on the shape of absorbance spectra.

Obtained results for crude oil dispersed in water indicate that the values of absorbance and absorption coefficients $a(\lambda)$ depend on the oil concentration. For all considered oil concentrations, the decreasing of the values of absorbance in the whole range of excitation wavelength is observed, while in the range from 240 nm to 420 nm strongly changes in the absorbance values were detected. Moreover, the characteristic point for this kind of oil-small, flat, and wide peak was detected for excitation wavelength at 260 nm both for absorbance spectra and for absorption coefficient. Moreover, the peak does not shifted in excitation wavelength when dispersed crude oil concentration is changing.

Summarizing up although the dependence of absorbance spectra as well as absorption coefficients from the oil concentration is observed the characteristic point–peak–in these spectra detected for 260 nm for excitation wavelength does not depend from the oil concentration and could be a useful point in the detection of crude oils in seawater.

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## References

[1] Baszanowska, E., Zielinski, O., Otremba, Z., Toczek, H., *Influence of oil-in-water emulsions on fluorescence properties as observed by excitation-emission spectra*, J. Europ. Opt. Soc. Rap. Public., Vol. 8, No. 13069, pp. 13069-1 – 13069-5, 2013.

[2] Baszanowska, E., Otremba, Z., *Spectral signatures of fluorescence and light absorption to identify crude oils found in the marine environment*, J. Europ. Opt. Soc. Rap. Public., Vol. 9, No. 14029, pp. 14029.1 – 14029.7, 2014.

[3] Baszanowska, E., Otremba, Z., *Spectrum of light absorption as the indicator of lubricate oil dispersed in the natural water*, Journal of KONES Powertrain and Transport, Poland, Vol. 23, No. 1, pp. 61-66, Warsaw 2016.

[4] Fingas, M., *Introduction and the Oil Spill Problem*, in: Oil Spill Science and Technology Prevention, Response, and Cleanup, pp. 3-46, Elsevier, 2011.

[5] Fingas, M., *Behaviour of Oil in the Environment and Spill Modeling*, Part IV, in: Oil Spill Science and Technology Prevention, Response, and Cleanup, pp.187-199, Elsevier, 2011.

[6] Geddes, C. D., Lakowicz, J. R., *Review in fluorescence*, Springer, 2005.

[7] Meier, D., Voß, D., Zielinski, O., Heuermann, R., Horn, M., Krause, S.-E., Machulik, U., Munderloh, K., Oest, J., Spitzy, A., *Development of an online detection system for determination and characterization of dissolved organic substances in water via fluorescence spectroscopy*, 3rd EOS Topical Meeting on Blue Photonics® – Optics in the Sea (Blue Photonics 3), Texel, 2013.

[8] Zieliński, W., Rajca, A., *Metody spektroskopowe i ich zastosowanie do identyfikacji związków organicznych*, Tom 1, pp. 19-20, WNT, Warszawa 2000.

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