

SPECTRUM OF LIGHT ABSORPTION AS THE INDICATOR OF LUBRICATE OIL DISPERSED IN THE NATURAL WATER

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Abstract

Oil pollutants in the natural water masses – especially in the seawater column – can be found in two forms, namely as dissolved oil or as dispersed one. With a broad set of methods, for studying the complex structure of petroleum products, due to the ability of petroleum products to absorb UV-light, absorbance spectra could be a relevant indicator to oil identification in aquatic environment and could support methods provided by the fluorescence technique. The intention of the study described in this article is to characterise the absorption properties of lubricate oil possible to found in the marine environment. Two types of oil as the representative of lubricate oils using in the ship engines are considered. One form of oil possible to found in the marine environment – oil-in-water emulsion was taken into account for analysis. Dispersed in water lubricate oil samples were prepared for several oil concentration for each type of oil. Spectrofluorometer Aqualog Horiba was used to register the absorbance spectra of oils. Based on the Lambert-Beer law the absorbance spectra were derived and specific parameter – absorption coefficient – for each wavelength of excitation, in the range 240-600 nm, was determined. Obtained results indicate decreasing of the oil absorbance value when excitation wavelength increases. Moreover, basing on the absorbance spectra it could be concluded that the main maximum for this kind of oils is located below 240 nm. However, in the considered range of excitation wavelength small flat peak, centred about 265 nm for both types of oils, was detected. Therefore one could conclude that absorbance of oils could be used as the indicator to detect of oil pollution in the natural environment omitting the labour intensive chemical methodology.

Keywords: lubricate oil, absorption, absorption spectra of dispersed oil, oil-in-water emulsion

1. Introduction

An oil spill in the marine environment in the initial phase occurs as oil patches on the sea surface. Later becomes an object of impact of wind and waves – therefore partially evaporates, and partially, but in limited scale, dissolves to the water column. Some part of oil becomes dispersed to small droplets and as so-called oil-in-water, emulsion penetrates the bulk of water.

Method of testing of oil substances depends on the scale of oil spill. Changes made by oil on the surface of the water, whether they are visible photographically, in ultraviolet or in infrared, whether manifest themselves in a manner of reflecting electromagnetic microwaves, can be detected by satellite sensors [10] or airborne surveillance [12]. Successful detection depends on the extension of the spill as well on weather conditions. After the spill is confirmed, accurate measurements can be ordered both *in situ* and in laboratory condition using various techniques [1-4, 6, 8, 14, 15]. However, it is necessary to highlight that, the challenge is to detect of oil pollution for low oil concentration, which corresponds to small, chronic, inevitable discharges resulting from regular maritime fleet exploitation. Among a broad spectrum of methods possible to use during study the complex structure of petroleum products, like UV-Visible, Infrared or Raman spectroscopy as well as chromatography methods [5, 7, 13, 16, 17], fluorescence phenomenon, seems to be interesting and promising. However, it is necessary to point out that the highly complex mixture of hydrocarbon compounds of petroleum and its derivatives contain components

indicating the ability to absorbing the light in the UV range (which can disturb fluorescence spectra of oils). That well-known phenomenon observed for petroleum products and its derivatives could be used to study petroleum products regarding to the oil pollution detect directly in the natural marine environment in the vicinity of maritime transporting routs or offshore fields of oil/gas extraction.

In the article characterization of lubricate oil dispersed in water (one of the typical form of oil which can be found in natural condition in seawater) is discussed in relation to the protection of the natural marine environment. Two lubricate oils used in marine transport based on absorbance measurements are analysed through the absorbance spectra measurements for different oil concentration. Moreover, based on the determined absorbance spectra of lubricate oils the parameters so-called absorption coefficients were determined for each excitation wavelength in the range of 240-600 nm. In the article, absorbance measurements of dispersed oil in water are considered as a tool to oil detection and identification in the case occurrence of oil spill, which could support the measurements based on the excitation-emission spectroscopy.

2. Method

2.1. Oil samples

For this study, two representative lubricant oils used in marine transport were selected: *Marinol 1240* - used to lubricate the cylinder of vessel engines and *Cyliten N-460* - used for the lubrication of single- and multi-cylinder reciprocating compressors of synthesis gas, commonly applied in ship engine systems. *Marinol* visually indicates a brighter shade of brown and is relatively clear and more transparent than *Cyliten*. Moreover, *Cyliten* emits greater than *Marinol* amount of visual light when induced by UV-light.

2.1.1. Samples of oil dispersed in water

A high-speed stirrer was first used to disperse oil in the water sample for each kind of lubricate oil. The obtained oil-in-water emulsion for each kind of lubricate oil was seasoned for one week in order to stabilize the oil-water system. The concentration of lubricate oil was then determined by measuring the fluorescence intensity (excitation 210 nm, emission 295 nm) in relation to standard solutions of defined oil. For each type of lubricate oil, a stock solution of oil emulsion samples was prepared and further diluted in de-mineralised water. Based on the dilution method, four individual concentrations of oil-in-water emulsion samples for each type of lubricate oil were prepared. The individual oil concentrations for oil-in-water emulsion samples are presented in Tab. 1.

Tab. 1. Concentration [ppm by weight] of oil dispersed in water (oil-in-water emulsion) for the studied lubricate oils

<i>Marinol</i> (Mem) [ppm]		<i>Cyliten</i> N-460 (Cem) [ppm]	
M1em	43	C1em	12
M2em	86	C2em	24
M3em	215	C3em	60
M4em	430	C4em	120

2.2 Measurement

An *Aqualog Horiba* spectrofluorometer was applied to measure the absorbance spectra of lubricate oil samples for both types of oil. The absorbance spectra of oil samples were registered simultaneously to the EEM spectra [1, 2, 9]. The spectra absorbance for all solutions of lubricate oils dispersed in water in a 1×1 cm quartz cuvette were measured.

For absorbance spectra 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 1s integral time. Moreover, due to the technical features of the spectrofluorometer, the absorbance spectra were measured from the longest to the lowest excitation wavelength.

The absorbance spectra of oil samples were determined at a stabilised temperature of 20° C.

3. Results and discussion

Absorbance spectra $A(\lambda)$ for two kinds of lubricate oils were registered using an *Aqualog Horiba* spectrofluorometer [1, 11] based on the Lambert-Beer law described by formula (1):

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

where:

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

$I(\lambda)$ – describes the intensity of the light that has passed through the dispersed oil sample.

Figure 1 presents the absorbance spectra registered for *Marinol* and *Cyliten* lubricant oils for various oil concentrations in de-mineralised water (Tab. 1). The absorbance of oil dispersed in water achieved higher values for *Cyliten* lubricant oil. That fact can be caused by the composition of oils, which has an impact to colour, and transparency of oils (*Cyliten* visually indicates darker shade of brown than *Marinol*) what is clearly visible in VIS – light. Moreover, the absorbance spectra changes strongly in the wavelength range from 240 nm to 350 nm, while for the longer wavelengths, the values of absorbance decrease minimally and remain constant in relation to the individual concentration. In Fig. 1, it is clearly visible that, the values of absorbance and half-width of absorption spectra depend on the oil concentration. The difference in the concentrations for the considered two forms of lubricate oils do not bother to compare them because of the proportion 1:10 to the lowest and highest concentrations in both considered forms of lubricating oils. Taking into account above mentioned when *Marinol* dispersed lubricate oil is considered – the absorbance value for oil concentration 430 ppm increases about ten times in comparison to the lowest oil concentration 43 ppm while when take into the consideration *Cyliten* dispersed oil in demineralized water – the absorbance value increases about thirty times when oil concentration increases ten times. This fact regarding to the significant difference of achieved values of absorbance for two considered lubricate oils can be explained by the difference between the colour of oils (*Cyliten* visually indicates darker shade of brown than *Marinol*) and their turbidity.

Additionally, to monitor natural seawater constituents, especially when an oil spill has been detected in natural seawater, measurements of absorption spectra of oils allow determining the parameter of absorption so-called absorption coefficient $a(\lambda)$ which is closely associated with a particular excitation wavelength.

Based on the measured absorbance $A(\lambda)$ for two types lubricate oils, the absorption coefficients $a(\lambda)$ for each individual concentrations of lubricate oils sample (for both oils dispersed in de-mineralized water) were determined as follows:

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

where:

$A(\lambda)$ – describes the above-mentioned absorbance,

c – describes the 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),

d – describes the cuvette length.

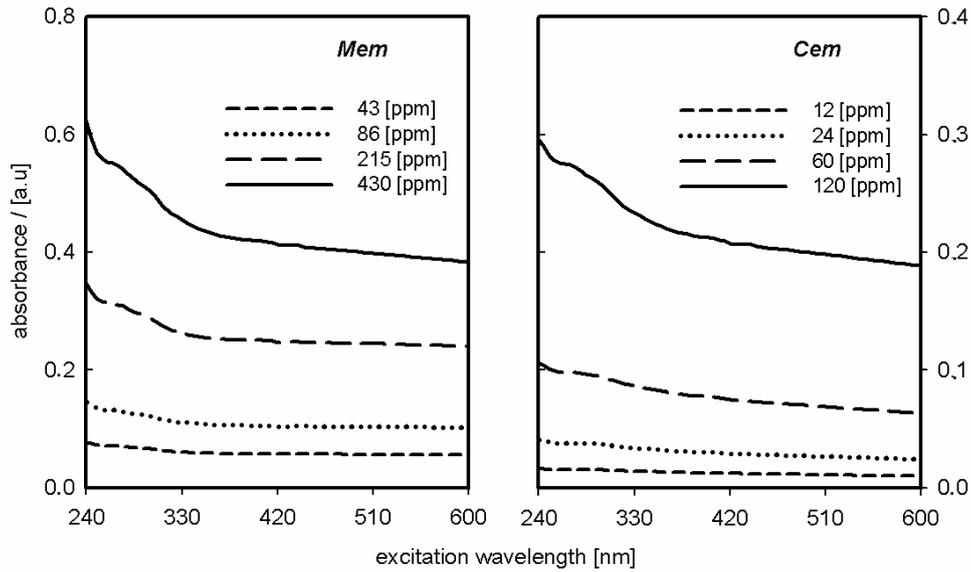


Fig. 1. Absorption spectra for Marinol (Mem) and Cyliten (Cem) in de-mineralized water for various oil concentrations

The calculated absorption coefficients for oil dispersed in de-mineralized water are presented in Fig. 2. The absorption coefficients for *Marinol* and *Cyliten* indicate changes in the wavelength range from 240 nm to 330 nm and the absorption small and flat peak is observed at 265 nm. Moreover, when we consider the results in comparison with the calculated absorption coefficients of crude oils, the absorption coefficient peak at 260 nm is broader and changes in the wavelength range from 240 nm to 420 nm [1]. Additionally, the absorption coefficient decreases, although it is never as close to zero and when calculated according to formula (2) $a(\lambda)$, oil dispersed in the water does not have the same waveforms. It was found that the attenuation of light in oil-in-water emulsion is, to a larger degree, caused by light scattering than by absorption of the light. The shape of the curves for $a(\lambda)$ probably depends on the size distribution of oil droplets dispersed in the water. The introduction of this method to operational oceanography requires a separate in-depth analysis of the problem of light attenuation spectra in water contaminated with oil.

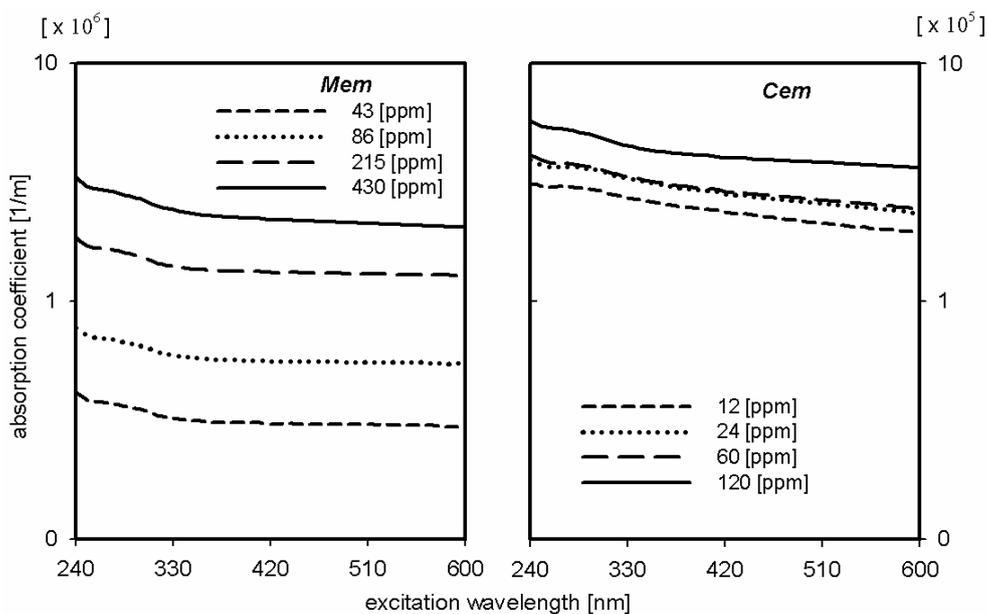


Fig. 2. Absorption coefficient of oil-in-water emulsion in de-mineralized water for Marinol (Mem), Cyliten (Cem) for various lubricate oil concentrations (derived using relation (2) based on data depicted in Fig. 1)

4. Conclusions

Obtained results for lubricate oils, used in marine transport and found in natural marine environment, based on absorption spectra indicate that absorption values of lubricate oils dispersed in water decrease when the excitation wavelength increases and indicate the presence of the small and flat peak at excitation wavelength 265 nm. Additionally, results of absorption spectra indicate the changes in over the whole range of excitation wavelength. It allows to conclude that lubricate oils absorb light in a wide excitation wavelength range. Moreover, in the shape of absorption spectra is clearly visible the difference between two considered types of lubricates oil, when we take into account the value of absorbance, which allow being a sensitive indicator to oil identification.

Summing up absorption measurements of dispersed oil in water could be considered as a tool to oil detection and identification in the case occurrence of oil spill and could support the measurements based on the excitation-emission spectroscopy of fluorescence spectra for single excitation wavelength or total spectra (excitation-emission spectra) in comparison with optical features of the natural constituents of seawater and various petroleum derivatives. To identify oil based on absorption spectra obtained results allow indicate the range of measurement of the absorbance of oils dispersed in water, respectively from 240 nm to 350 nm, where the flat peak is observed. However, in natural ecosystem it should be taken into account the absorption natural seawater components, which partially overlaps with the absorption of oil pollutants.

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