ISSN: 1231-4005
e-ISSN: 2354-0133
DOI: 10.5604/12314005.1213896

LIGHT ABSORPTION SPECTRA FOR LUBRICATE OIL QUALITY TRACKING IN THE COMBUSTION ENGINE

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Abstract

The important role in the proper functioning of combustion engines plays the quality of lubricates oil. However, the quality of oil changes with the time of exploitation. Therefore, several parameters for examination of oil quality were determined; however, the indicator for quick and efficient tracking of evolution of oil with exploitation time is still searched. Taking into account the complex composition of oils, the ability of oils components to absorb light in various wavelengths is considered. In the article absorption properties of oils is discussed in relation to the time of circulation of oil in the engine lubricate system. For this study, two lubricate oils designated to lubricate the cylinder of vessel engines with different brightness and transparency were used. Oil samples were dissolved in organic solvent – n-hexane and several oil concentration were prepared based on dilution method. Absorbance spectra for each samples of oil were registered in the range of wavelength 240-600 nm. Obtained results indicate the changes of value of absorbance in relation to the kind of oil; however, the shape of absorbance spectra is independent from the kind of oil. For studied kinds of oil, characteristic peak independent from the kind of oil located at 260 nm was determined. Based on Lambert-Beer law absorption coefficient was identified as a potential indicator to oil quality evaluation with the time of exploitation in the engine system. Preliminary test for two fresh lubricate oils allow to conclude that absorption coefficient for selected wavelength located at 260 nm could be a sensitive parameter for quick estimating the degree of deterioration of the oil in engine system.

Keywords: *lubricate oil, dissolved oil, absorption spectroscopy, absorption coefficient, engine system*

1. Introduction

Lubricate oils are commonly used in marine transport to lubricate the cylinder of vessel engines as well as for the lubrication of single- and multi-cylinder reciprocating compressors of synthesis gas. Moreover, lubricate oils generally have been used as lubricants to minimize the friction, heat, and wear between mechanical parts in contact with each other in the mechanical part of ship work system.

Lubricate oil belongs to the refinery products and are defined as highly complex mixture of hydrocarbon compounds [13]. It should be noted that same of oil components indicate the ability to absorb light and fluorescence of light in UV-range. The presence in their complex structure of mono and polycyclic compounds causes fluorescence of oil [16]. Due to the fact fluorescence, spectroscopy is commonly used to characterise the physical and chemical properties of oils. Moreover, fluorescence spectroscopy is commonly used to protect the natural marine environment by the identification or detection of oil pollution [1-4, 20].

During the development of petroleum industry, a lot of indicators to characterise the properties of petroleum products have been introduced. To the basic parameters have been using for lubricate oils description belong temperature dependence of viscosity-coefficient, water content, total acid number, total base number, rheometric and tribometric characteristics [14, 15, 18, 21]. Moreover, fluorescence of oil compounds is considered to show the evolution of oil quality used in engine system [5, 6]. In several articles the preliminary tests for description the fluorescence properties typical for one exemplary oil used in ship engine system were performed. In these studies fluorescence properties of oil were considered in different approach, taking into account time explanation of oil in ship engine system for different fluorescence methods such as excitation-emission spectroscopy, fluorescence spectroscopy for single excitation wavelength or synchronous fluorescence spectroscopy [5-9] or fluorescence using optical fibre [10, 11]. In these studies, fluorescence of oils was discussed regarding to monitor the quality of oil with time of exploitation of oil in ship engine based on changes in typical peaks determined in the shape of oil fluorescence spectra as new indicators to monitor the quality of oil.

Taking into account above mentioned, oils light absorption phenomenon could be used to expand the knowledge about the oil characterisation in relation to study the transformation of oil quality with the time of exploitation in the engine system.

In the article, preliminary tests based on absorbance measurements are analysed regarding to the work-time of lubricate oil in engine system. For analysis two fresh lubricate oils, which have been applying in the vessel engine systems, dissolved in organic solvent (n-hexane) were tested. Based on absorption spectra of oils the specific spectroscopic features of lubricate oil are analysed. Moreover, absorption coefficient as the potential tool to evaluate the quality of lubricate oil, for each kind of oil and each oil concentration in the range of excitation wavelength from 240 nm to 600 nm was determined.

2. Method

2.1. Oil samples

Two fresh lubricant oils used in marine transport were selected for this study: *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* is clearly brighter in UV-light.

2.1.1. Samples of oil dissolved in n-hexane

N-hexane (for analysis, 96.0% purity) was applied as a solvent and a stock solution of oil in n-hexane for both types of oil were then prepared. Based on this dilution method, five individual concentrations for both types of oil were prepared. The concentrations of individual oil samples were prepared in relation to the weight of the solution (n-hexane) and the weight of oil samples. The individual oil concentrations in n-hexane are presented in Tab. 1.

Tab. 1. Concentration [ppm by weight] of oil in n-hexane for the studied oils

***Marinol* (Msol)** [ppm]		***Cyliten* N-460 (Csol)** [ppm]	
M1sol	20	**C1sol**	20
M2sol	50	**C2sol**	50
M3sol	230	**C3sol**	230
M4sol	280	**C4sol**	280

2. 2 Measurement

An *Aqualog Horiba* spectrofluorometer was applied to measure the absorbance spectra of oil samples for both types of oil. The absorbance spectra of oil samples were registered simultaneously the EEM spectra [1, 12, 17]. Absorbance spectra for all solutions 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 20ºC.

3. Results

Based on the Lambert-Beer law describes by formula 1, absorbance spectra $A(\lambda)$ of considered lubricate oil samples for each oil concentration were registered using an *Aqualog Horiba* spectrofluorometer [19]:

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

where:

$I_h(\lambda)$ –describes the intensity of the light that has passed through the reference sample (n-hexane),

$I(\lambda)$ –describes the intensity of the light that has passed through the dissolved oil sample in n-hexane.

Figure 1 presents the absorbance spectra registered in the range 240-600 nm for *Marinol* and *Cyliten* oil dissolved in n-hexane for various oil concentrations (see Tab. 1).

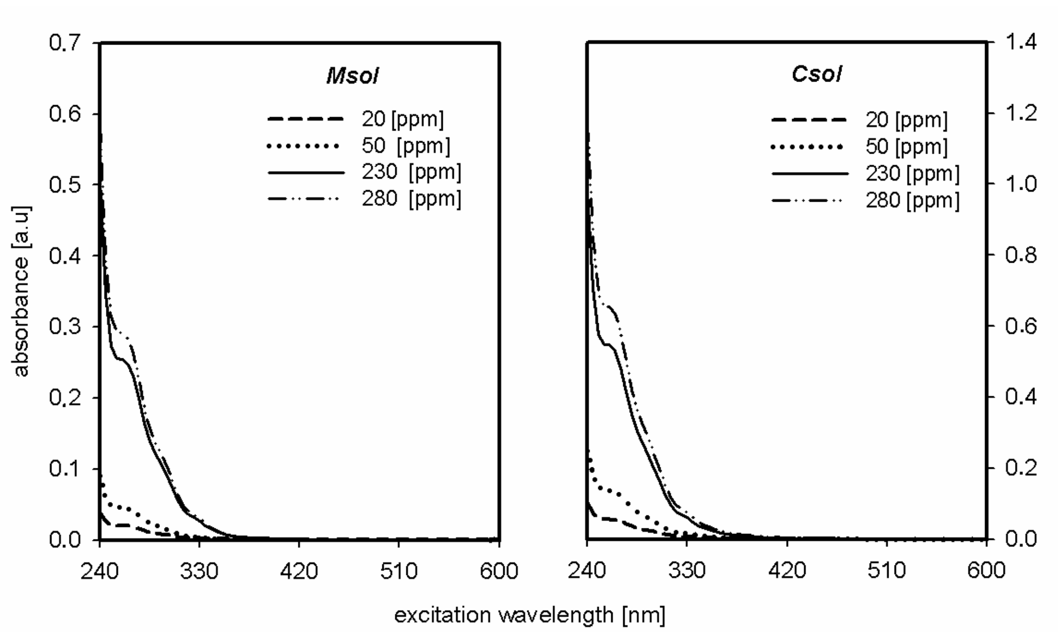

Fig. 1. Absorption spectra of oil in n-hexane for Marinol (Msol) and Cyliten (Csol) for various oil concentrations

In Fig. 1 is clearly visible that the absorbance achieved higher values for *Cyliten* oil (the absorbance values for *Cyliten* are twice as high as for *Marinol*). Moreover, the absorbance spectra changed significantly in the wavelength range from 240 nm to 350 nm, while for the longer wavelengths the absorbance values were close to zero (oils are relatively transparent in the visual range of the light spectrum). However, the absorbance and width of absorption spectra depend on the oil concentration.

4. Discussion

Measured absorbance spectra of oils based on Lambert-Beer law allow determining the specific indicator of absorption – absorption coefficient a (λ).

Therefore, based on the measured absorbance $A(\lambda)$, the absorption coefficients $a(\lambda)$ for two types of lubricate oil. All oil concentrations were determined as follows:

$$a(\lambda) = \frac{2.303\,A(\lambda)}{c\,d}, \tag{2}$$

where:

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

c – describes the concentration index of the oil solution expressed in kilograms of oil per one kilogram of n-hexane solution (ppm by weight),

d – describes the cuvette length.

The calculated absorption coefficients for lubricate oils *Marinol* and *Cyliten* dissolved in n-hexane are presented in Fig. 2.

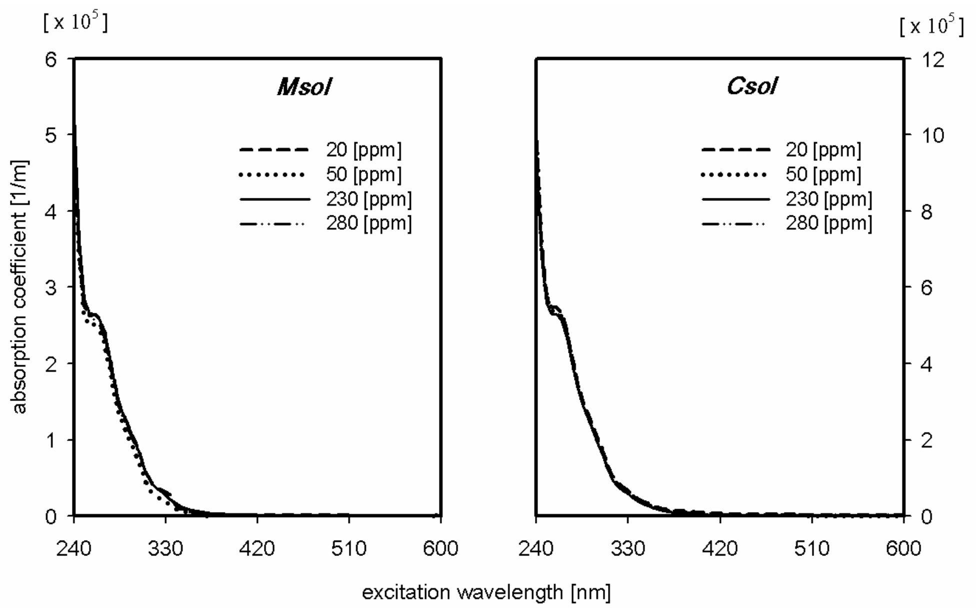

Fig. 2. Absorption coefficient of oil in n-hexane for Marinol (Msol), Cyliten (Csol) for various oil concentrations (derived using formula (2) based on the data depicted in Fig. 1)

The absorption coefficients for *Marinol* and *Cyliten* oils presented in Figure 2 indicate the changes in the excitation wavelength range from 240 nm to 360 nm and the absorption peak (sharp) is observed at 260 nm.

Moreover, when we consider the results in comparison with the calculated absorption coefficients of crude oils, the absorption coefficient peak for lubricate oils located at 260 nm is narrower and changes in the wavelength range from 240 nm to 370 nm, while for crude oils changes in range from 240 nm to 420 nm [12]. Additionally, the absorption coefficients decrease when excitation wavelength increases and are close to zero for excitation wavelength above 370 nm. Moreover, absorption coefficients do not depend on the oil concentration. However, depend on the kind of oil (absorption coefficient for *Cyliten* are twice as high as for *Marinol*). It is caused by the difference in brightness and transparency of considered lubricates oils. It allows concluding that absorption coefficient could be a good tool (indicator) to oil identification independent from oil concentration.

4. Conclusions

Obtained results for lubricate oil dissolved in n-hexane based on absorbance spectra indicate that values of absorbance decrease in the range from 240 nm to 370 nm and for values of excitation wavelength higher than 370 nm absorbance is closed to zero. In the considered range of excitation wavelength lubricate dissolved oils indicate the presence of sharp peak located at 260 nm and the position of the peak does not depend on the oil concentration. Moreover, the half-width of determined peak depends on oil concentration, and, when oil concentration decreases then the value of absorbance changes for excitation wavelength, which is lower than 330 nm. Additionally, absorbance values for *Cyliten* oil are twice as high as for *Marinol* oil; it is ceased due to the brightness and transparency of oils. Additionally, absorption coefficients determined for individual excitation wavelength in the range 240-600 nm for each kind of oil depend on the type of oil and achieved higher values for *Cyliten* oil. On the other hand, absorption coefficients indicate the independence from oil concentration.

Summarizing, the absorbance measurements for lubricate oils dissolved in organic solvent could be useful tool to evaluation of oil explanation in engine system, however for the future studies oils for different time of explanation in engine system should be analysed. Taking into account fact that oils with time explanation in engine system become darker allow to conclude that the effect of oil exploration will be reflected in decreasing of absorbance values. Therefore, to study the evolution of oil quality could be used the selected absorbance value for selected excitation wavelength (obtained results allow to point at the excitation wavelength located at 260 nm as sensitive due to maximum for absorbance peak of oils). It seems that a good indicator to track of oil quality could be used also absorption coefficient for selected excitation wavelength (also at 260 nm) due to the independence from oil concentration. Those properties of absorption coefficient parameter could allow tracking the oil quality by the change of absorption coefficient value taking small amount of oil directly from the engine system without determining oil concentration. However, in the future work oils with different explanation time in engine system should be analysed.

Acknowledgements

This article was supported by the Gdynia Maritime University grants No. DS/411/2016.

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. 13069-1-1369-5, 2013.

[2] Baszanowska, E., Otremba, Z., Toczek H., Rohde, P., *Fluorescence spectra of oil after it contacts with aquatic environment*, Journal of KONES Powertrain and Transport, Vol. 20, No. 3, pp. 29-34, Warsaw, Poland 2013.

[3] Baszanowska, E., Otremba, Z., *Oil identification based on total synchronous spectra*, Journal of KONES Powertrain and Transport, Vol. 21, No. 2, pp. 15-20, Warsaw, Poland 2014.

[4] Baszanowska, E., Otremba, Z., *Modification of optical properties of seawater exposed to oil contaminants based on excitation-emission spectra*, J. Europ. Opt. Soc. Rap. Public., Vol. 10, pp. 10047-1-15047-8, 2015.

[5] Baszanowska, E., Otremba, Z., *Spectrofluorometric characteristics of used lubricating oil*, Diagnostyka, Vol. 15, No. 4, pp. 65-71, 2014.

[6] Baszanowska, E., Otremba, Z., *Application of fluorescence to diagnose the exploitive quality of engine lube oil*, Logistyka, No. 6, pp. 1769-1778, 2014.

[7] Baszanowska, E., Otremba, Z., *Study of lubricate oil properties with engine runtime based on fluorescence spectroscopy*, Logistyka, No. 4, pp. 2426-2432, 2015.

[8] Baszanowska, E., Otremba, Z., *Synchronous fluorescence spectroscopy as a tool for used lube-engine oil description*, Zeszyty Naukowe Akademi Morskiej w Gdyni, No. 91, pp. 175-179, 2015.

[9] Baszanowska, E., Otremba, Z., *Lubricate engine oil characterization based on single excitation fluorescence*, Zeszyty Naukowe Akademi Morskiej w Gdyni, No. 91, pp. 181-185, 2015.

[10] Baszanowska, E., Otremba, Z., *Ultraviolet-induced fluorescence of lubricate oil*, Combustion Engines, Vol. 163, No. 4, pp. 21-25, 2015.

[11] Baszanowska, E., Otremba, Z., *Application of optical fibre sensor to study the engine lubricate oil fluorescence*, Logistyka, No.4, pp. 2419-2425, 2015.

[12] 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, pp. 14029.1-14029.7, 2014.

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

[14] http://www.mantech-inc.com/analytical/whatare_TAN_TBN.asp [Online] 22-04-2016.

[15] http://www.kittiwake.com/base_number [Online] 22-04-2016.

[16] Mathew, M., *A comparison study of gravimetric and ultraviolet fluorescence methods for the analysis of total petroleum hydrocarbons in surface water*, Civil Engineering Master's Theses, Article 1, 2009, http://hdl.handle.net/2047/d10019236 [Online] 22-04-2016.

[17] Meier, D., Voß, D., Zielinski, O., and 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.

[18] Młynarczak, A., *Investigation of the influence of aftermarket additive on lubricating properties of Titan Truck Plus 15W40 oil used in marine diesel engines*, Zeszyty Naukowe Akademii Morskiej w Gdyni, No. 76, pp. 62-68, 2012.

[19] Operation manual, Aqualog Horiba, rev. A (Horiba Scientific, 2011).

[20] Otremba, Z., Targowski, W., Toczek, H., *Fluorescence as a scanning method for oil type identification in the sea environment*, KONBiN'03 The 3-rd Safety and Reliability International Conference, 2003.

[21] Wierzcholski, K., Miszczak, A., *Algorithm for variable pseudoviscosity coefficients under experimental basis*, Tribologia, Vol. 44, No. 4, pp. 125-136, 2013.