



SECTROFLUOROMETRIC CHARACTERISATION OF THE LUBRICATE OIL

Emilia Baszanowska, Zbigniew Otremba

*Gdynia Maritime University, Faculty of Marine Engineering
Department of Physics
Morska Street 81-87, 81-225 Gdynia, Poland
tel. +48 58 6901504, fax: +48 58 6206701
e-mail: eba@am.gdynia.pl, zotremba@am.gdynia.pl*

Abstract

Exploitive features of lubricate oils are externalised by various physical and chemical parameters (for example temperature dependencies of density and viscosity, ignition point or water content). On the other hand it is well-known that fluorescence spectra of various types of crude oils and their derivatives are strongly differ from each other. It is reasonable thesis, that exploitive features of oil may be related to transformations of light inside the oil. Therefore, despite of that fact light transformations strongly depend on chemical composition of oil (especially from the content of cyclic and polycyclic molecules). No one can exclude, that physical conditions are for fluorescence processes closely related to changes of physical and chemical properties of oil (and consequently to exploitive features) as well as to newly arising compounds and intrusions (for example metals, caused by contact with various engine elements).

The paper presents spectra of fluorescence of exemplary lubricate oil (Marinol) in various configurations, namely: emission spectrum for individual excitation wavelength, excitation spectrum for single emission wavelength, excitation-emission spectrum, synchronous fluorescence spectroscopy and total synchronous fluorescence spectroscopy. Dynamic structures of those spectra gives reason to conclude that shapes of fluorescence spectra may be controlled by exploitive features of oils.

Keywords: *fluorescence spectroscopy, total synchronous spectra, lubricate oil*

1. Introduction

Lubricate oils are the hydrocarbon substances originating mainly from petrochemical industry. Only a small amount of this substance is formed using vegetable oils. Marine lubricate oils are produced on the basis of refined mineral oils (crude oils) and special additives to improve exploitive features (for example anti-wear, anti-corrosion and washing properties). Every type of oil can be characterised by a set of physical, chemical and physicochemical or specialised exploitive indicators of lubricate oils [4, 9] which is important from two points of view, namely: knowledge about suitability for use in a specified engine and as an indicator of actual quality of operation of the engine (signalling an increased risk of malfunction or possible damage in a short time). On the other side, petroleum substances, similarly like crude oils, have the ability to fluorescence [15]. Therefore it is natural, to crude oil derivatives emit light when are lightened and that emitted light has spectral structure depended on the excitation light spectrum and on a type of oil as well as on its degree of wear [8, 16].

Taking into account above mentioned, there is a need to study the relationships between values

of indicators of petroleum substance and their impact on the emitted fluorescence light. Furthermore, the oil fluorescence ability is utilised to protect the natural marine ecosystem from the oil contamination basing on changes of the fluorescence spectra of natural seawater caused by the presence of the petroleum substances such as crude oils, lubricate oil, etc. [5, 6, 11, 13, 14].

In this paper we characterise an exemplary type of lubricate oil, namely the *Marinol 1240* using for lubrication of high pressure ship engines, supercharged, working in conditions of high heat loads. The oil diluted in n-hexane is described based on fluorescence spectroscopy, namely: emission spectrum for single wavelength excitation (SWEx), excitation spectrum for single wavelength emission (SWEm), excitation-emission spectrum (EEMs), synchronous fluorescence spectroscopy (SFS) and total synchronous fluorescence spectroscopy (TSFS).

2. Materials and methods

Lubricate engine oil *Marinol 1240* was applied to prepare oil sample in n-hexane for analysis with 96.0 % purity. Based on dilution method from the stock solution of *Marinol* oil in n-hexane, individual concentration of *Marinol* oil, respectively, 130 mg/kg was prepared.

Using *Aqualog Horiba* spectrofluorometer the excitation-emission spectrum (EEMs) of *Marinol* oil in n-hexane was measured [1, 10]. The quartz cuvette with dimensions 1×1 cm was applied to measure EEM spectrum of *Marinol* oil.

Measurement specifications for measure EEM spectrum were applied: excitation wavelength (λ_{ex}) were changed in the range from 240 nm to 600 nm with a 5 nm sampling interval and emission wavelength (λ_{em}) were changed in the range from 212.75 nm to 622.97 nm with a 1.623 nm sampling interval. Specification for excitation slit, emission slit and integral time were applied, respectively, 5 nm, 5 nm and 1 s.

EEM spectrum for lubricate oil *Marinol* diluted in n-hexane was measured at a stabilised temperature of 20° C. Raman and Rayleigh scattering automatically were removed based on the software package of the *Aqualog Horiba* spectrofluorometer [10].

3. Results and discussion

Measured EEM spectrum for *Marinol* oil in n-hexane with concentration 130 mg/kg was presented in figure 1. Particular axis of EEM spectrum describe, respectively: axis *X* – excitation wavelengths, axis *Y* – emission wavelengths and axis *Z* – intensity of fluorescence. This spectrum has fixed oil spectral information in excitation and emission wavelengths [2, 12].

Basing on measured EEMs spectrum of *Marinol* oil in n-hexane, different possibilities of consideration of data presentation are presented. Other possibility to oil identification based on synchronous fluorescence method could be the possibility of measured data presentation as synchronous fluorescence spectra for different wavelength-interval $\Delta\lambda$ [3].

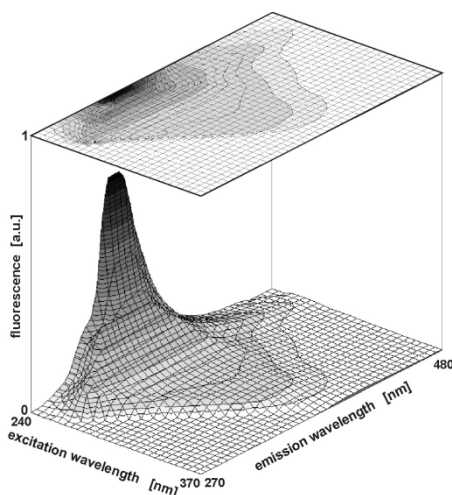


Fig. 1. Excitation-emission spectrum (EEMs) of the lubricate oil *Marinol* as 3D and contour-map visualisations

Figure 2 presents emission spectra for different individual excitation wavelengths changing in the range from 240 nm to 340 nm. There is observed the change of the shape of emission spectrum while the excitation wavelength changes. The intensity of fluorescence strongly decreases when the excitation wavelength increases. For the shortest excitation wavelength 240 nm in the shape of emission spectrum two individual maxima show up, while for higher excitation wavelengths the peaks decrease and the shape of emission spectrum is planar.

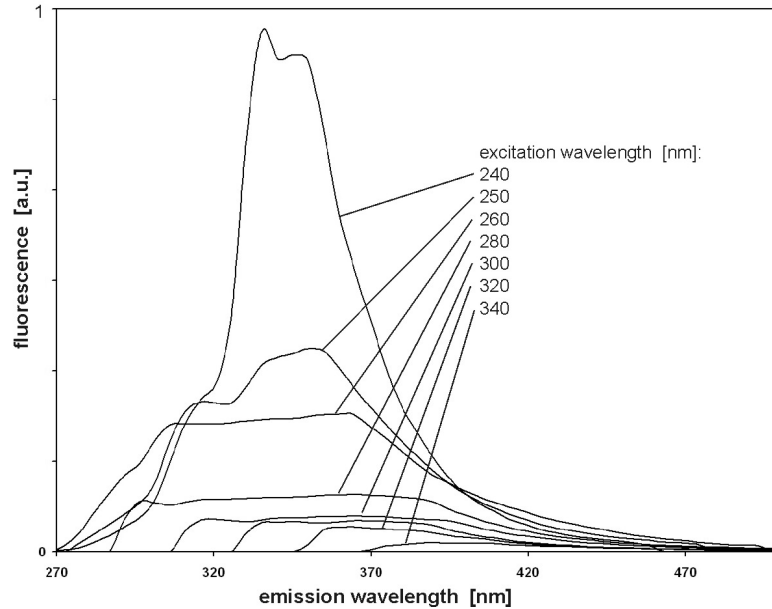


Fig. 2. Fluorescence emission spectra (SWEx) of lubricate oil Marinol for various excitation wavelengths

Based on measured excitation-emission spectrum it is possible to obtain also excitation spectra. Figure 3 presents excitation spectra for different emission wavelength changes in the range from 340 nm to 480 nm. In Figure 3 there is observed the change of the shape of the excitation spectra when the emission wavelength is changing. When the emission wavelength increases the intensity of fluorescence decreases and achieves low value for longer excitation wavelength in range from 440 nm to 480 nm.

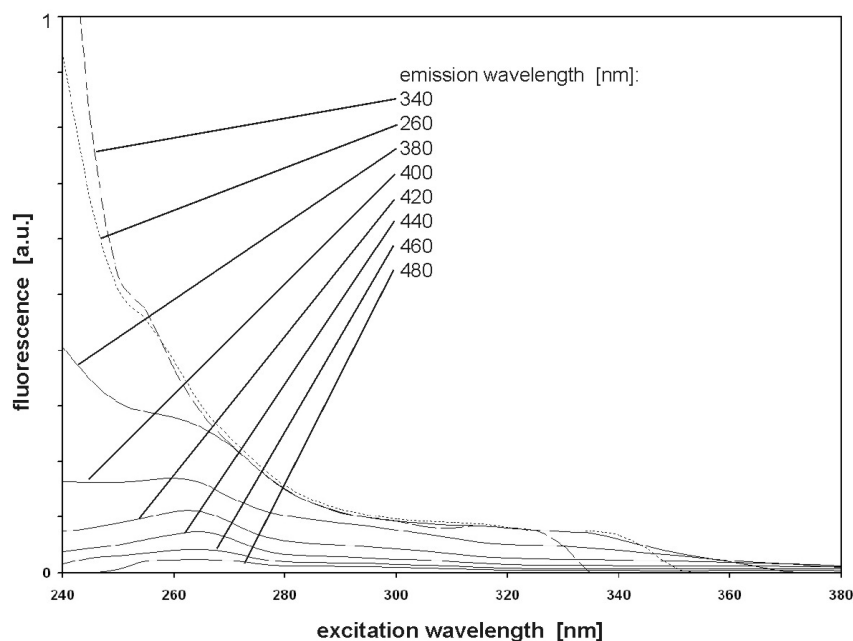


Fig. 3. Fluorescence excitation spectra (SWEm) of lubricate oil Marinol for various emission wavelengths

Other possibility to data presentation can be explained as synchronous fluorescence spectrum (SFS) and total synchronous fluorescence spectrum. These spectra were determined based on the wavelength interval ($\Delta\lambda$) – parameter described by the dependence (1) [7, 12]:

$$\Delta\lambda = \lambda_{em} - \lambda_{ex}, \quad (1)$$

where:

- $\Delta\lambda$ – the wavelength interval,
- λ_{ex} – the excitation wavelength ,
- λ_{em} – the emission wavelength.

Figure 4 presents synchronous fluorescence spectra (2D spectra) for lubricate *Marinol* oil in n-hexane for various wavelength intervals - $\Delta\lambda$ for 130 mg/kg concentration, respectively: Figure 4(a) non-normalised spectrum and Figure 4(b) normalised spectrum. The values of wavelength-interval $\Delta\lambda$ were respectively: 20 nm, 40 nm, 60 nm, 80 nm, 120, nm, 160 nm. Both in figure 4(a) and 4(b) is observed strongly change of the maximum fluorescence pick position in the synchronous fluorescence spectra. Figure 4(a-b) indicate that the maximum fluorescence intensity will be reached for excitation wavelength below 240 nm.

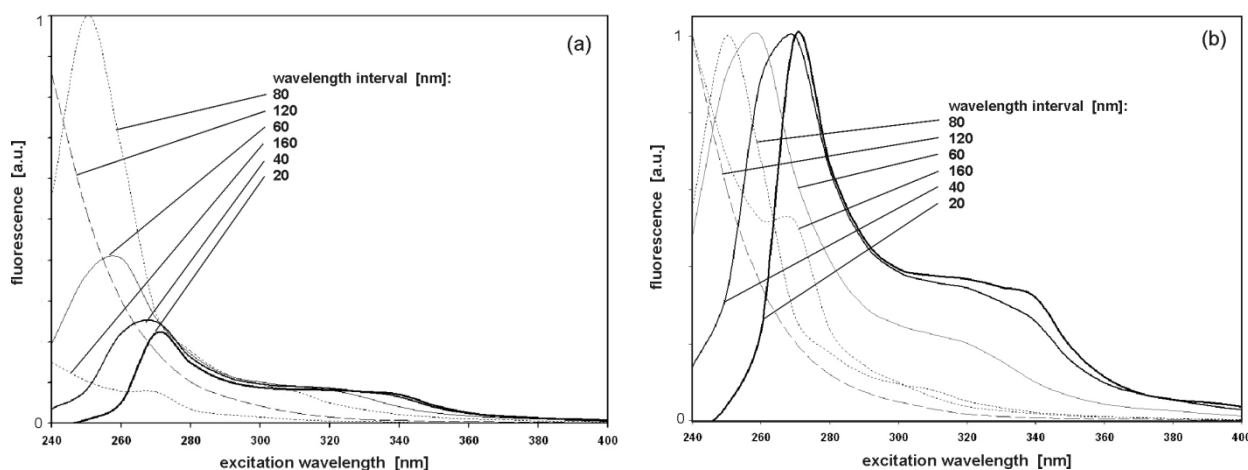


Fig. 4. Synchronous fluorescence spectra (SFS) of the lubricate oil *Marinol* for non-normalised (a) and normalised (b) for various wavelength intervals

Taking into account both excitation wavelength, wavelength interval $\Delta\lambda$ and fluorescence intensity the data could be presented as total synchronous fluorescence spectra (3D spectra). Axis of total synchronous spectra are described by: excitation wavelengths – axis X , wavelength interval $\Delta\lambda$ – axis Y , intensity of fluorescence – axis Z .

Figure 5 present total synchronous spectra for *Marinol* oil in n-hexane for concentration 130 mg/kg for various wavelength intervals $\Delta\lambda$ changing from 20 nm to 200 nm for six considered concentration of oil. At the top of figure 5 there is visible contour-surface visualisation as a 2D contour map of 3D synchronous fluorescence spectra. There is detectable pick typical for this kind of oil characterised by excitation wavelength and wavelength interval $\Delta\lambda$. The pick is described by excitation wavelength maximum about 240 nm and wavelength interval $\Delta\lambda$ in the range from 80 nm to 100 nm.

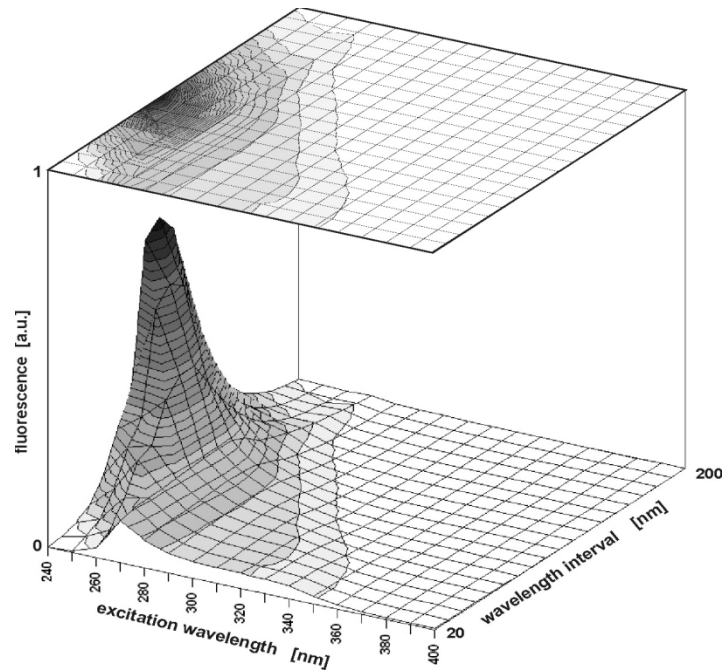


Fig. 5. Total synchronous fluorescence spectrum (TSFS) of the lubricate oil Marinol as 3D and contour-map visualisations

Taking into account presented results we indicate, that in the fluorescence area there is broad spectrum of techniques to characterise petroleum substances. Particular methods allow to characterise fluorescent substances (in our case oil substances) basing on different parameters. Thinking into account considered *Marinol* oil, the most important spectral information about *Marinol* oil are fixed in the excitation-emission spectra described by excitation wavelength and emission wavelength and total synchronous spectra described by the wavelength-interval $\Delta\lambda$. In the future, it would be interesting to monitor the changes of oil fluorescence spectra with changes of particular oil indicators.

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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., Toczek, H., Rohde, P., *Fluorescence spectra of oil after it contacts with aquatic environment*, Journal of KONES Powertrain and Transport, Warsaw, Poland, Vol. 20, No. 3, 29-34, 2013.
- [3] Baszanowska, E., Otremba, Z., *Oil identification based on total synchronous spectra*, Journal of KONES Powertrain and Transport, Warsaw, Poland, Vol. 21, No. 2, 2014. (in press)

- [4] Cipris, D., Millburn; Thirumalai G. Palanisamy, Morristown; Walsh, A. T., Plains, M., all of NJ, US patent: *Lubricant oil monitoring system and method of monitoring lubricant oil quality*, US 4792791
 A <https://docs.google.com/viewer?url=patentimages.storage.googleapis.com/pdfs/US4792791.pdf>, 4,792,791 Dec. 20, 1988.
- [5] Paula G. Coble, *Marine Optical Biogeochemistry: The Chemistry of Ocean Color*, Chem. Rev., Vol. 107, Iss. 2, 402-418, 2007.
- [6] Paula G. Coble, *Colored dissolved organic matter in seawater*, Chapter 5 in *Subsea Optics and Imaging*, J. Watson and O. Zielinski, 1st Edition, Woodhead Publishing, 2013.
- [7] Lloyd, J.B.F., *Synchronyzed excitation of fluorescence emission spectra*, Nature (London) Phys. Sci., 231, 64-65, 1971.
- [8] Markova, L. V., Myshkin, N.K., Ossia, C.V., Kong, H., *Fluorescence Sensor for Characterization of Hydraulic Oil Degradation*, Tribology in industry, Vol. 29, No. 1&2, 2007.
- [9] Mignani, A.G. , Ciaccheri, L. , Díaz-Herrera, N., Mencaglia, A.A., Ottevaere, H. , Thienpont, H., Francalanci, S., Paccagnini, A., Pavone, F., *Optical fiber spectroscopy for measuring quality indicators of lubricant oils*, 19th International Conference on Optical Fibre Sensors, edited by David Sampson, Stephen Collins, Kyunghwan Oh, Ryoza Yamauchi, Proc. of SPIE Vol. 7004, 70045R, 2008.
- [10] *Operation manual*, Aqualog Horiba, rev. A, 2011.
- [11] Otremba, Z., Baszanowska, E., Toczek, H., Rohde, P., *Spectrofluorometry in application to oil-in-water emulsion characterization*, Journal of KONES Powertrain and Transport, Warsaw, Poland, Vol. 18, No. 3, 317-321, 2011.
- [12] Patra, D., Mishra, A.K., *Total synchronous fluorescence scan spectra of petroleum products*, Anal. Bioanal. Chem., Vol. 373, Iss. 4-5, 304–309, 2002.
- [13] Patsayeva, S., *Fluorescent remote diagnostic of oil pollutions: oil in films and oil dispersed in the water body*, Advances in remote sensing, Vol. 3, No. 3 - VII, 1995.
- [14] Poryvkina, L., Babichenko, S., Davydova, O., *SFS characterisation of oil pollution in natural water*, Proc. 5th Intern. Conf. on Remote Sensing for Marine and Coastal Environments, 5-7 October, San Diego, California, Vol. 2, 520-524, 1998.
- [15] Steffens, J., Landulfo, E., Coronato, L., Guardani Courrol & Roberto, *Application of Fluorescence to the Study of Crude Petroleum*, Journal of Fluorescence, DOI 10.1007/s10895-009-0586-4, 2010.
- [16] Stelmaszewski, A., *Fluorescence method for determination of oil identity*, Optica Appl., XXXIV No. 3, 2004.