

## Ultraviolet-induced fluorescence of lubricate oils

*The paper describes the study on relationship between the engine lubricate oil quality and fluorescence phenomenon. In order to determination the Excitation-Emission spectra (EEMs) of oil samples, spectrofluorometer combined with the optical fiber system were applied. Two methods of fluorescence measurement, respectively: when oil diluted in non-fluorescent solvent (n-hexane) is placed in the quartz-cuvette inside the spectrofluorometer, and when oil sample is placed outside the spectrofluorometer (then EEMs is measured through the optical fiber sensor) were applied to analysis the shape of EEMs of lubricate oil. Moreover in the second case of measurement, the optical fiber sensor was placed for the angle of 45 degrees to the oil surface, respectively, above the oil surface and beneath the oil surface, directly in oil. Preliminary scientific results presented in this paper – on the one hand – indicate diversity in the shape of EEMs depending on the method of fluorescence measurement, on the other hand – indicate possibility to measure fluorescence of oil directly in engine lubricate oil circuit.*

Key words: *lubricate oil, fluorescence, optical fiber*

### Fluorescencja oleju smarnego indukowana światłem ultrafioletowym

*W artykule przedstawione są wyniki badań dotyczące związku pomiędzy jakością oleju smarnego a zjawiskiem fluorescencji. W celu wyznaczenia widm zupełnych fluorescencji próbek oleju wykorzystano spektrofluorometr połączony ze światłowodowym systemem pomiarowym. Analizowany jest kształt widm odnoszących się do oleju smarnego w dwóch przypadkach, odpowiednio, gdy: olej jest rozpuszczony w niefluoryzującym medium (n-hexan) i umieszczony jest w przyrządzie w kwarcowej kuwecie oraz w przypadku kiedy próbka oleju znajduje się na zewnątrz przyrządu, sygnał jest przenoszony światłowodem. Ponadto w przypadku pomiarów z zastosowaniem światłowodu ustawiona pod kątem 45o głowica pomiarowa zestawu światłowodowego znajduje się, odpowiednio: w powietrzu nad powierzchnią oleju albo pod powierzchnią oleju. Przedstawione w niniejszym artykule wstępne wyniki badań, z jednej strony wskazują na zróżnicowanie kształtów widm zupełnych fluorescencji względem metody pomiarowej, z drugiej strony – wskazują na możliwość wyznaczenia fluorescencji bez wstępnej obróbki laboratoryjnej, bezpośrednio w silnikowym obiegu oleju smarnego.*

Słowa kluczowe: olej smarny, fluorescencja, sensor optyczny

### 1. Introduction

In the history of the development of internal combustion engines lubricating oils play an important role. In the past various physical and chemical indicators of lubricate oil usefulness have been introduced. In general, temperature dependence of viscosity is in use as the essential parameter for oil characterisation. To other significant parameters belongs water content, total acid number, total base number, rheometric or tribometric characteristics [6,9]. Every alteration of measurable in oil values contain information about the changes of exploitive quality of the lubricate oil.

Polycyclic hydrocarbons found in refinery products have ability to absorb ultraviolet (UV) radiation, in order to further emit light which interact with numerous components of petroleum and finally may come out of the sample to hit the photodetector of spectrofluorometer. Due to this reason

changes in composition of petroleum products affect composition of light emitted from UV excited oil. Moreover, spectral composition of emitted light depends also on a spectrum of illuminating (exciting) light. Spectrofluorometry in relation to the crude oil refinery products have been applied yet, for example Markova et al. [4] tested fluorescence sensor for characterization hydraulic oil deterioration, Omrani et al. [7] analyzed oxidative stability of lubricant oil measuring fluorescence excitation-emission spectra. Moreover, Stelmaszewski [8] evidenced that individual types of refinery products are characterized by different fluorescence spectra. Furthermore, optical fiber spectroscopy with applying chosen wavelengths for measuring quality indicators of lubricant oils were carried out by Mignani et al. [5]. Our experience in this subject concerns the study of oil-in-water emulsions [3], and recently we started to study fluorescence of used lubricating oil [1,2] – differences for fresh and used oil have

been shown. Taking into account above mentioned it is worth checking out the relationship between variations in the fluorescence of oil and the quality of oil working in engine system.

In this paper we present results of introductory tests basing on so-called excitation-emission spectra (EEMs) of lubricate oil in various geometry of measurement, namely:

/1/ directly in oil, where oil sample is placed outside the spectrofluorometer (then EEMs is observed through optical fiber sensor),

/2/ oil diluted in non-fluorescent solvent is placed in a quartz cuvette (classical measurement based on spectrofluorometer is performed).

Discussion on lubricate oil fluorescence spectra for both methods of measurement is further continued.

## 2. Material and method

### 2.1. Material

Lubricate oil Titan Truck Plus 15W40 (TTP 15W40) were sampled from engine lubricate circuit after 178 hours of exploitation in the ship engine 3AL 25/30 Cegielski-Sulzer with the power 396 kW [1]. A part of oil sample was diluted in n-hexane with 96 % purity and oil samples in n-hexane with oil concentration 100 mg/kg were prepared. Oil used in engine circuit visually differs from fresh one (is darker) which is shown in Fig. 1. Moreover, in Fig. 1 the ability to fluorescence of those two forms of oils is illustrated – oil which was sampled from engine lubricate circuit fluoresces less than fresh one. In this study to detailed spectral measurement were destined partly used oil obtained from the engine.

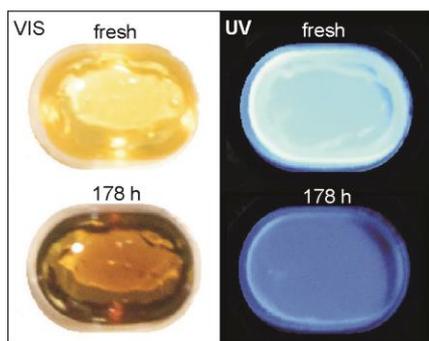


Fig. 1. Lubricate oil *Titan Truck Plus 15W40* fresh (upper) and used (lower) illuminated by filament lamp (left) and by ultraviolet lamp (right).

### 2.2. Method

To measure excitation-emission spectra (EEMs) of oil samples two different methods of samples excitation and registration of emission of light were applied, namely:

- by classical method, i.e. directly in spectrofluorometer (oil hexane-dilution in quartz cuvette)

- outside the spectrofluorometer using optical fiber system (Fig. 2).

EEMs for the n-hexane solvent and pure oil samples were measured in 1×1 cm quartz cuvette. The following measurement parameters were applied: excitation wavelength from 200 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 [1,2].

Next excitation-emission spectra of four oil samples for TTP 15W40 were measured using optical fiber set (Fig. 1) manufactured by Lumex Ltd. St. Petersburg. This device consists of 2×30 fiberglasses of diameter 0.1 mm everyone (30 fiberglasses transmit light exciting fluorescence, other 30 ones transmit light emitted by oil). Oil samples were excited above the surface of oil and beneath the surface of oil for the distance of oil surface 2 mm. The measurement were performed under 45° to oil surface (Fig. 3).

EEM spectra for n-hexane solvent at a stabilised temperature 20° C for two types of EEMs measurement, were performed. Next, EEM spectra of four oils samples were measured, also at a stabilised temperature 20° C.

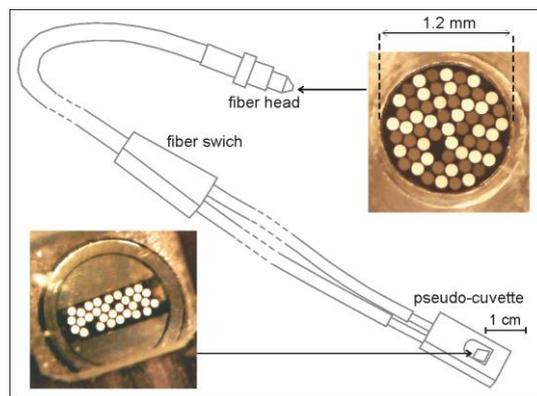


Fig. 2. Optical fiber system.

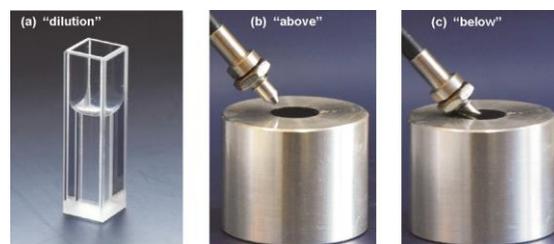


Fig. 3. Three ways to determine the EEM spectra: hexane solution of oil (a), directly in oil - above the surface (b), directly in oil - beneath the surface (c)

The EEMs is registered in numeric form as a table consisting of 3111 numbers (51 excitation wavelengths, 61 emission one). Results when emission wavelength are equal or less than excitation are blind (due to energy of emitted photon are less than

energy of excitation photon – which is an essence of fluorescence phenomenon).

### 3. Results and discussion

As was above mentioned measurements of EEM spectra were carried out in three methods (visualized in Fig. 3). Results – fluorescence as the function of two variables (excitation wavelength and emission wavelength) are visualized as normalized 3D graphs in the Fig. 4 and as map visualization in the Fig. 5. The shapes of those three spectra differ from each other significantly. Oil diluted in non-fluorescent solvent (n-hexane) indicates fluorescence spectrum in short wave region (200-300 nm), whereas fluorescence induced directly in oil is placed in longer wavelengths. Immersion of the

fiber-head in the oil changes radically the shape of EEMs (extremes are shifted toward long wavelengths). The process of the light beam forming which going through the monochromator into photomultiplier (detector) of spectrophotometer in every case is different. The photons emitted by fluorescent centers have low chance to reach detector without repeated absorption and secondary absorption is in many cases connected with reemission. Such process can be repeated many times, especially in condensed form of analyzed substance (no-diluted oil). In this way forms the final spectrum of light which reaching the detector and is registered as two-dimensional numeric table.

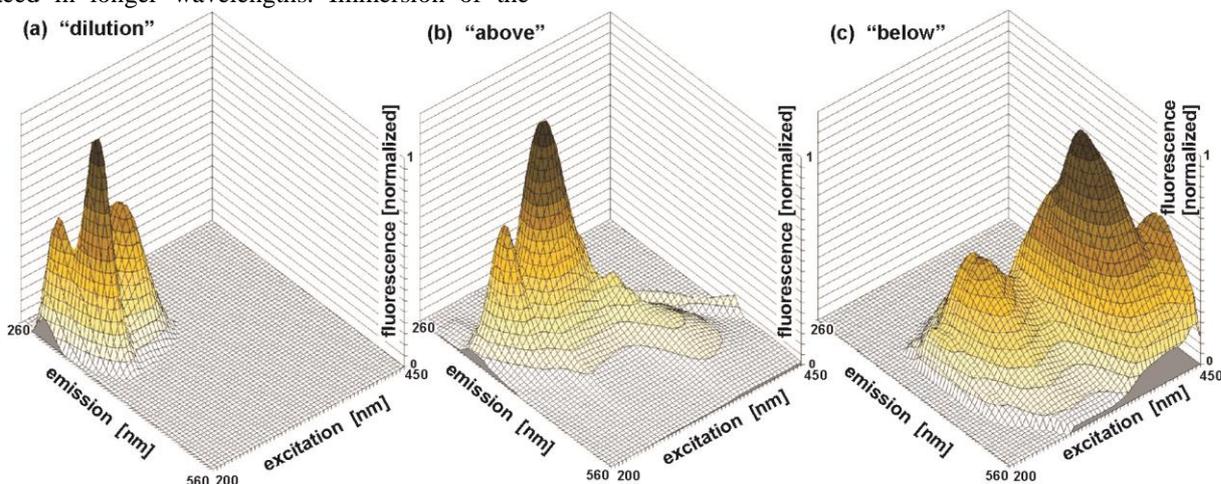


Fig. 4. Excitation-Emission spectra (EEMs) of used lubricate oil (178 h in engine circuit) measured in three methods (explained in Fig. 3)

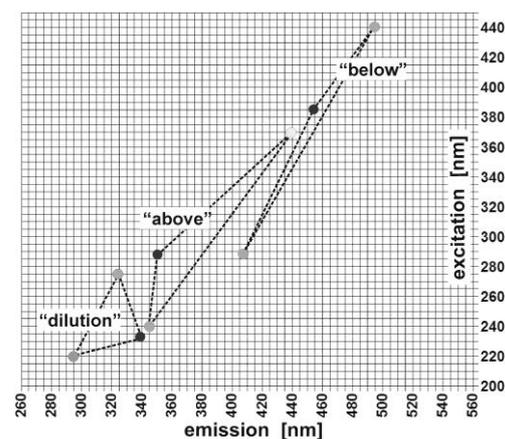
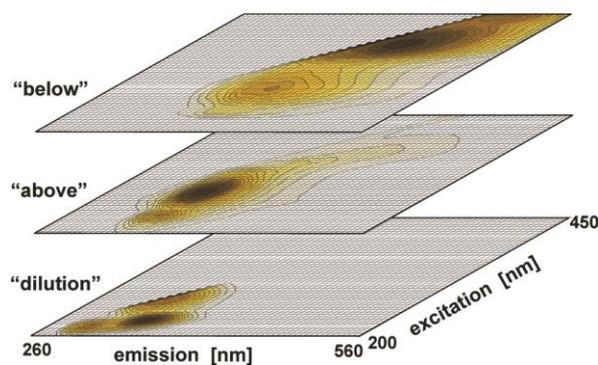


Fig. 5. Regions of oil fluorescence as the dependence on the measuring method (left) and positions of main peaks in relation to studied methods (right)

It can be assumed that in relation to the practice not necessarily measurement of the whole EEMs (like in this study) must be performed. Presumably the detector of fluorescence may be simplified to possibility of measurement in a limited number of wavelengths of both an excitation and an emission

light. To this end, further research would be needed.

At the current stage of research the categorical declaration which above method should be preferred is impossible. Presented results show indeed well developed fluorescence spectra of lubricate oil

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independently on implemented and above described method, but there is not known in which method process of deterioration of oil during its working in

#### 4. Conclusions

Fluorescence centers that are part of chemical compounds of lubricate oil deliver a possibility to implement fluorescence techniques for spectral characterization of those refinery products directly in those studied medium using optical fiber system connecting spectrofluorometer with the point where the oil is placed. The head of optical fiber sensor can be positioned above the oil surface or can be immersed into oil. It turned out that the shape of fluorescence spectrum depends on measure circumstances. Relatively well developed spectrum is observed when the head of optical fiber sensor is immersed. Obtained results allow to suggest that fluorescence may be linked to the degree of oil deterioration during its work in the engine. This is

engine lubricating circuit will be preferably exhibited.

promising part of study to verify in future measurements.

#### 5. Acknowledgements

This paper was partially supported by the Gdynia Maritime University grants No. 06/BMN/M/2015 and 360/DS/2015. Authors would like to special thanks for Andrzej Młynarczak from Gdynia Maritime University to make available samples of both fresh and used oil Titan Truck Plus 15W40.

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