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SYNCHRONOUS FLUORESCENCE SPECTROSCOPY AS A TOOL FOR USED LUBE-ENGINE OIL DESCRIPTION

To proper work of ship engine it is necessary to monitor the quality of oil exploited in ship engine. Therefore it is necessary to expand the knowledge about the futures of oils based on various possible methods which allow track the quality of oil and thereby the engine protect.
In the work total synchronous fluorescence spectroscopy as a tool to description of oil properties was applied. To tests the exemplary engine lubricate oil Titan Truck Plus 15W40 was applied. Two forms of oil, respectively, fresh oil and lubricate oil exploited in ship engine about two months were used. Based on the total synchronous fluorescence spectra the peaks typical for both forms of oil were determined. Moreover to distinguish two forms of oil based on total synchronous spectra the distinguishability parameter was defined and wavelength-interval parameter for this kind of oil was determined. Obtained results allow to conclude that synchronous fluorescence spectroscopy seems to be an efficient tool for track the quality of oil exploited in ship engine based on specific parameters.

Keywords: *fluorescence, total synchronous fluorescence spectrum, synchronous fluorescence spectrum, lubricate oil, ship engine.*

INTRODUCTION

The contemporary means of transport are still driven mainly by internal combustion engines. The proper functioning of such engine in any transporting unit depends not only on the quality of fuel but also on the kind of lubricate oil as well as on the degree of deterioration of qualitative parameters as a result of their long-term exploitation in the engine lubricating system. Therefore to ensure the best level of reliability of engine it is necessary to monitor the oil parameters changes which allows to efficiently assess the current oil exploitive quality. The changes of oil properties after exploitation of oil in engine are specified based mainly on water content, total acid number and total base number or viscosity vs. temperature [1], anti-wear performance as well as the identify additives and their concentrations, reaction products, and contamination based on the infrared analysis [5, 11], magnetically separation large ferromagnetic particles to assess the size, the shape, the composition, and concentration of the abnormal wear particles [10]. Atomic emission spectroscopy as well as rheometric and tribometric characteristics are also used to settle the lubricate oil exploitive properties [8, 12, 13].

Lubricate oils belong to refinery products consisting of highly complex mixtures of hydrocarbons and contain numerous fluorophoric components [6]. That structure of oils represented by fluorescence properties allows to study their properties based on optical spectroscopy.

In this paper, to study the oil quality total synchronous fluorescence spectroscopy (TSFS) is considered. TSFS was firstly described by Lloyd [7]. These spectra include the spectral information in a fixed form described by wavelength-interval (Δλ, also so-called offset), which describes the dependence of emission wavelength with synchronous changes of excitation wavelength [9]. Total synchronous fluorescence spectra for chosen lubricate oil used in ship engine in two forms original-fresh and oil exploited in ship engine are discussed as a tool to oil quality monitor. Numerical fluorescence signatures based on synchronous fluorescence spectra are considered for both different forms of oil. Moreover most beneficial parameter for synchronous fluorescence spectra – wavelength-interval – allowing to distinguish two different forms of oil is determined.

1. MATERIAL AND METHOD

Lubricate oil *Titan Truck Plus 15W40* (TTP 15W40) [3] in two forms, respectively, fresh oil (T) and used oil (UT) exploited 1344 hours in engine 3AL 25/30 Cegielski-Sulzer with the power 396 kW, was applied (Table 1). Both forms of oil, fresh and used were individually diluted in n-hexane with 96% purity and the stock solution were prepared. Next, based on dilution method the individual concentration of oil 100 mg/kg were prepared for both forms of oil. A detailed description of the sample preparation procedure has been previously described by the authors [4].

Table 1. The forms of lubricate oil *Titan Truck Plus 15W40* used in ship engine: fresh oil signed as (T) and used oil – exploited in ship engine signed as (UT), diluted in n-hexane for oil concentration c = 100 mg/kg [4]

Titan Track Plus 15W40 c = 100 [mg/kg]	
t [h]	
T	0
UT	1344

The fluorescence measurement were performed based on the excitation-emission spectra (EEMs). EEMs of oil samples TTP 15W40 for both forms of oil were carried out using spectrofluorometer *Hitachi F-7000 FL*. EEMs for the n-hexane solvent and each oil samples TTP 15W40 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.

First, EEM spectra for n-hexane solvent, were performed. Next, EEM spectra of lubricate oil TTP 15W40 diluted in n-hexane for particular oil samples for fresh and used oil working in ship engine 1344 hours were measured. Measurement of each of oil in n-hexane samples at a stabilised temperature 20ºC were performed. To obtain the real EEMs of lubricate oil each date of measured oil samples diluted in n-hexane were corrected by subtraction the spectra of pure n-hexane.

2. RESULTS AND DISCUSSION

Total synchronous fluorescence spectra for lubricate oil *Titan Truck Plus 15W40* were determined using the wavelength-interval Δλ described by formula (1) – characteristic parameter for synchronous fluorescence spectra [2]:

$$\Delta\lambda = \lambda_{em} - \lambda_{ex}, \tag{1}$$

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

Total synchronous fluorescence spectra in three dimensional plane (3D) for constant wavelength-interval step 5 nm for TTP 15W40 oil diluted in n-hexane are presented in Figure 1 – for fresh oil (left) and for used one (right). Total synchronous fluorescence spectra in 3D plane presented in Figure 1 are described by the particular axis, respectively: axis X – describes excitation wavelengths, axis Y – describes wavelength-interval $\Delta\lambda$ and axis Z – describes fluorescence intensity. Figure 1 shows three peaks in total synchronous fluorescence spectra typical for this kind of oil. That method based on total synchronous fluorescence spectra allows to describe the maxima of oil fluorescence by the wavelength-interval fluorescence maximum ($Ex_{max}/\Delta\lambda$) – containing information about excitation wavelength (Ex_{max}) and wavelength-interval ($\Delta\lambda$) describing the characteristic fluorescence peak position for each considered oil sample.

The wavelength-interval fluorescence maxima ($Ex_{max}/\Delta\lambda$) for TTP 15W40 are presented in Table 2. In this Figure is visible that the maximum of fluorescence is achieved for the wavelength-interval about 105–110 nm. Moreover, in Figure 1 the changes of the shape of total synchronous fluorescence spectra for two considered form of oil fresh and used oil working in ship engine an adequate time is showed. There is visible that the intensity of fluorescence for particular detected peaks changes after oil working time in ship engine – for same peaks intensity of fluorescence decreases while for same increases. These results allow to conclude that total fluorescence intensity has been preserved during working time of oil in ship engine.

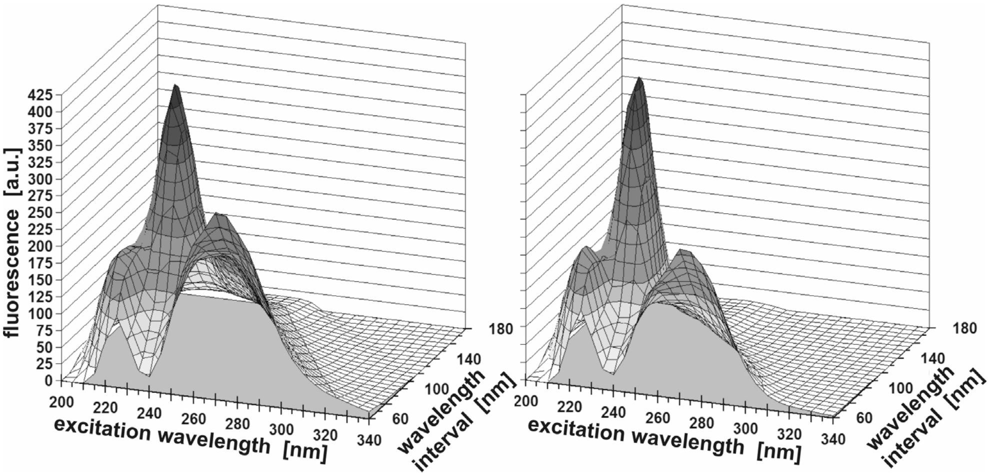

Fig. 1. Synchronous fluorescence spectra of oil *Titan Truck Plus 15W40* diluted in n-hexane in 3D plane for oil concentration *c* = 100 [mg/kg] for fresh oil (left) and used oil (right) working 1344 h in ship engine

Table 2. The range of values for wavelength-interval fluorescence maximum of oil *Titan Truck Plus 15W40* for oil concentration *c* = 100 [mg/kg] for fresh oil (T) and used oil (UT) working 1344 hours in ship engine

Ex_{max} ± 5 [nm] / $\Delta\lambda$ ± 1 [nm]			
T	220/82	235/105	275/55
UT	220/80	235/107	280/55

Moreover, important information are fixed in the shape of TSF spectra independent of the fluorescence intensity. Therefore, Figure 2 and 3 present the results of oils TSFs for fresh oil and used oil working adequate period of time hours in ship engine in two-dimensional plane as surface-contour visualisation map (2D map) – main figure. This kind of results presentation allows to clearly describe the characteristic peaks (maxima of fluorescence).

Moreover to obtain more information based on total synchronous fluorescence spectra the characteristic wavelength-interval from the whole spectrum were chosen. It allows to obtain the synchronous fluorescence spectrum for single wavelength-interval. Synchronous fluorescence spectra for different wavelength intervals $\Delta\lambda$ equal 60 nm, 80 nm and 100 nm are presented in the right corner of Figure 2 and 3. There is visible the changes of synchronous fluorescence spectra when the wavelength-interval is changing.

In the case when the wavelength-interval increases from 60 nm to 100 nm (a-c) there is observed shift of fluorescence intensity maximum from 275 nm for excitation wavelength to lower excitation wavelengths (about 240 nm). Moreover there is visible the difference in the fluorescence intensity for used and fresh oil. The fluorescence intensity decreases after working time of oil in ship engine.

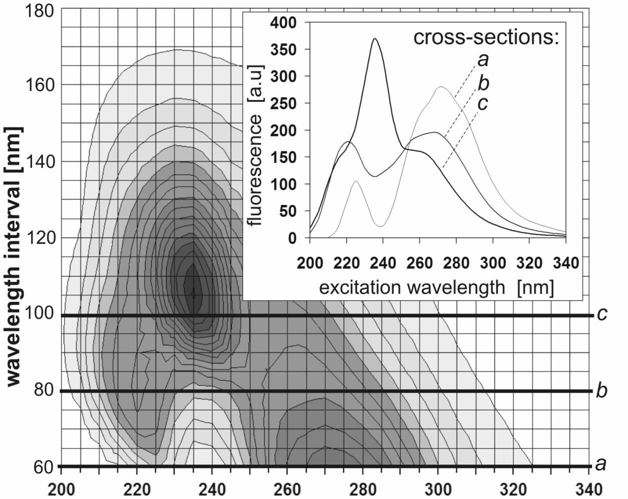

Fig. 2. Synchronous fluorescence spectra as 2D map of oil in n-hexane for *Titan Truck Plus 15W40* for oil concentration *c* = 100 [mg/kg] for fresh oil (T)

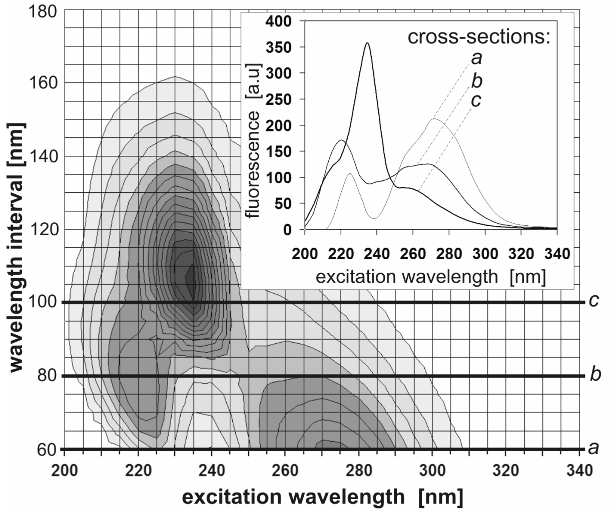

Fig. 3. Synchronous fluorescence spectra as 2D map of oil in n-hexane for *Titan Truck Plus 15W40* for oil concentration *c* = 100 [mg/kg] for used oil (UT) working 1344 h in ship engine

For wavelength-interval $\Delta\lambda$ = 80 nm is observed the difference in the shape of synchronous fluorescence spectra for fresh and used oil. In that case fresh oil is described by two similar fluorescence maxima at an excitation wavelength 220 nm and 278 nm, while for used oil maximum of fluorescence at an excitation wavelength 220 nm significantly decreases in relation to the second maximum of fluorescence for 278 nm for excitation wavelength. Presented cross-section from total synchronous fluorescence spectra for chosen wavelength-interval can be applied to check the quality of oil after an adequate time in ship engine. Taking into account presented results for this kind of oil the best way seems to be the wavelength-interval equal 80 nm due to the significant differences in the shape of synchronous fluorescence spectra for fresh and used oil seen in Figure 2 and 3.

In the description of fluorescence properties of oil working in ship engine during defined time-period the challenge is to found the parameter which allows to distinguish the difference between two various forms of oil. The parameter (d_{ab}), defined by formula 2, allows to assess the similarity between two forms of oil.

In this formula, the index i refers to adequate values of intensity of fluorescence in excitation spectra of fresh oil spectra – "a" and used oil – "b".

$$d_{ab} = \frac{\sum_i abs(w_i^a - w_i^b)}{\sum_i w_i^a + \sum_i w_i^b} 100\,\% \cdot \tag{2}$$

Results of both forms distinguishability parameter for fresh and used oil, respectively in the function of wavelength-interval are presented in Figure 4. There is visible that the distinguishability parameter depend on the wavelength-interval. The distinguishability parameter for this kind of oil achieved maximum value for wavelength-interval $\Delta\lambda$ in the vicinity of 110 nm.

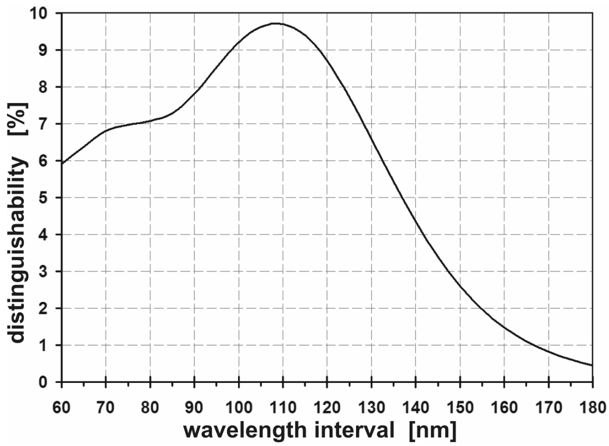

Fig. 4. Distinguishability of oil *Titan Truck Plus 15W40* for fresh (T) and used oil (UT) working 1344 h in ship engine for oil concentration *c* = 100 [mg/kg] based on wavelength-interval synchronous fluorescence spectra

CONCLUSIONS

Obtained results of tests carried out, based on total synchronous fluorescence spectra, regarding to lubricate oil (*Titan Truck Plus 15W40*) in two forms: fresh oil – original and oil working continually in the ship engine about two months, indicate spectral difference between those forms of oil. Namely, in the total synchronous spectra are noticeable differences in the intensity of fluorescence between detected three peaks in the spectrum (some of peaks increases while some decreases). Moreover, more information about changes of exploitive properties of oil working in a ship engine allow synchronous fluorescence spectra. For considered lubricate oil the wavelength-interval 110 nm was find as optimal.

ACKNOWLEDGEMENTS

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FLUORESCENCJA SYNCHRONICZNA JAKO NARZĘDZIE DO OPISU SILNIKOWEGO OLEJU SMARNEGO

Streszczenie

Dla prawidłowej pracy silnika okrętowego istnieje konieczność śledzenia jakości oleju silnikowego, dlatego też należy poszerzać wiedzę dotyczącą charakterystycznych cech olejów, wykorzystując dostępne metody, które pozwolą zarówno monitorować jakość oleju, jak i jednocześnie chronić silnik przed uszkodzeniem.

W pracy rozważane są fluorescencyjne właściwości silnikowego oleju smarnego Titan Truck Plus 15W40 na podstawie całkowitych synchronicznych widm fluorescencji jako narzędzi do śledzenia jakości oleju. Do badań użyto oleju smarnego w formie oryginalnej oraz przepracowanej w silniku okrętowym około dwóch miesięcy. Opierając się na totalnych synchronicznych widmach fluorescencji, wyznaczono charakterystyczne dla tego rodzaju oleju maksima. Ponadto w celu rozróżnienia dwóch postaci oleju i oceny jego jakości wyznaczono parametr interwału długości fali oraz zdefiniowano parametr rozróżnialności obu form oleju. Uzyskane rezultaty pozwalają twierdzić, że fluorescencja synchroniczna wydaje się być dobrym narzędziem do śledzenia zmian jakości oleju eksploatowanego w silniku okrętowym z wykorzystaniem specyficznych parametrów.

Słowa kluczowe: *fluorescencja, całkowite synchroniczne widma fluorescencji, synchroniczne widma fluorescencji, olej smarny, silnik okrętowy.*