# SPECTROFLUORIMETRIC CHARACTERISTICS OF USED LUBRICATING OIL

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Summary

Deterioration of lubricate oil in combustion engines enforces measurements of parameters essential for proper operation of define driving system or to certain engine malfunctions indicate. Since the fluorescence phenomenon is known for oil excited by ultraviolet light – the question arises whether fluorescence spectra evolving with the time of exploitation of oil in the engine.

In this paper the introductory studies of excitation-emission spectra (EEMs) for chosen lubricate oil are described. Both fresh and used oil (after 593 h of work in a ship engine), was used to measure EEMs. As a result of comparison of EEMs for both fresh and used lubricate oils more significant transformations in fluorescence spectra of oil caused by their exploitation are indicated. Obtained results allow to predict that spectrofluorimetry method could supplement present methods of used lubricating oil testing.

Keywords: fluorescence, excitation-emission spectra of oil, lubricate oil, ship engine

SPEKTROFLUORYMETRYCZNA CHARAKTERYSTYKA ZUŻYTEGO OLEJU SMARNEGO

Streszczenie

Pogarszanie się właściwości oleju smarnego w silniku spalinowym skutkuje koniecznością monitorowania jego eksploatacyjnych parametrów. Z racji wykazywania przez oleje fluorescencji w świetle ultrafioletowym – powstaje pytanie, czy widma fluorescencji ewoluują wraz z czasem przebywania oleju w obiegu smarnym silnika.

W artykule opisane są wstępne analizy zmian zupełnych widm fluorescencji (EEMs) dla różnych stężeń wybranego oleju smarnego. Do pomiaru EEMs oleju użyto dwóch form oleju – świeżego i przepracowanego w silniku okrętowym w czasie 593 h. W następstwie porównania widm uzyskanych dla świeżego i przepracowanego oleju wskazano na zachodzące najbardziej znaczące zmiany we fluorescencji oleju smarnego. Uzyskane wyniki pozwalają sądzić, że spektrofluorymetria mogłaby uzupełnić obecne metody testowania przepracowanego oleju.

Słowa kluczowe: fluorescencja, zupełne widmo fluorescencji, olej smarny, silnik okrętowy

## 1. INTRODUCTION

Used lubricating oil is characterized by several parameters that indicate its ability to perform, as required by the machine's application. Traditionally the basic objective signatures for used oil are:
- identifying the size, shape, composition, and concentration of the abnormal wear particles [1],
- matal analysis in accordance with atomic emission spectroscopy [2],
- granulometry of separated from the lubricant sample by magnets and gravity [3],
- water content,
- total acid number [4],
- total base number (measurement of its ability to neutralize the acid using basic buffers) [5],
- infrared analysis (for identifying additives and their concentrations, reaction products, and contamination) [6, 7],
- permeability changes [8],
- viscosity vs. temperature [9],
- anti-wear performance (e.g. by traditional tribometer with four-ball head).



Fig. 1. Lubricating oil *Titan Truck Plus 15W40* - fresh and used (593 h) - in visible light (left) and in ultraviolet (right)

Other attempts of using physical phenomena to detect deterioration of lubricating oil are introduced in several papers or patents, e.g.: magnetic

phenomena [10], electrical features [11, 12], resistivity [13], colorimetry [14]. More sophisticated method can be measurement of rheometric parameters (e.g. by rheometer *Haake Mars* [15]). Persons having extensive practical experience in combustion engines servicing in difficult marine conditions are able to roughly access quality of used lubricating oil by the way of observing the colour or movement of the oil droplet on an inclined plane. On the other hand in laboratory conditions every new method of used oil can improve durability and reliability of combustion engines.

It should be pointed that petroleum products are highly complex mixtures of mainly hydrocarbon compounds [16]. The presence of mono and polycyclic compounds in the complex structure of hydrocarbon compounds causes fluorescence of oil [17].

The aim of the study is searching for spectrofluorometric method to access the degree of changes in quality of lubricating oil exploiting in the ship engine room. The idea arisen as a result of insights that every lubricating oil exhibits fluorescence in ultraviolet range of light spectrum, as it was shown for considered oil *Titan Truck Plus 15W40* (*TTP 15W40*) in Figure 1 [18, 19, 20, 21]. We have taken, therefore, spectrofluorimetric study of the exemplary lubricating oil commonly used for the lubrication of bearings and cylinder liners ship engines namely *Titan Truck Plus 15W40* [22].

## 2. MATERIAL AND METHOD

### 2.1. Oil samples

Lubricate oil *Titan Truck Plus 15W40* (*TTP 15W40*) was used to prepare oil samples for fresh oil and used oil (596 h of work in engine 3AL 25/30 Cegielski-Sulzer with the power 396 kW). As a solvent n-hexane with 96 % purity was used. Oil samples in n-hexane solution were prepared based on dilution method. Three oil samples for individual oil concentrations were prepared based on the stock solution of both fresh and used oil. The concentrations of oil are presented in the table 1.

Table 1. Concentration of oil in n-hexane for *Titan Truck Plus 15W40* in two various forms: fresh oil signed as (T) and used oil after 593 h of work signed as (UT)

| Titan Track Plus 15W40 | | |
|---|---|---|
| | | c [mg/kg] |
| T1 | UT1 | 25 |
| T2 | UT2 | 50 |
| T3 | UT3 | 100 |

### 2.2. Measurement and apparatus

Spectrofluorometer *Hitachi F-7000 FL* was applied to measure three-dimensional excitation-emission spectra (EEMs) of oil samples [23]. EEM spectra for particular oil concentrations of two forms of oil and pure solvent n-hexane were measured in 1×1 cm quartz cuvette.

The following measurement parameters were applied to measure EEM spectra of oil: 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.

## 3. RESULTS

EEMs for pure solvent – n-hexane and three concentrations of fresh oil samples and used oil samples after 593 h of work in ship engine diluted in n-hexane were measured at a stabilised temperature 20º C. At the first, each measurement of oil samples diluted in n-hexane solvent were corrected by subtraction the spectra of pure n-hexane.

Figure 2 presents EEM spectra in three-dimensional plane for every concentration of fresh oil (T) and used oil after 593 h of work in ship engine (UT). The EEM spectra show the presence of three peaks, typical for this type of oil. There is observed variations of these peaks when the concentration of oil is changing. In Figure 2 is clearly visible that the fluorescence intensity of these fluorescence peaks increases when the concentration of oil increases, both for fresh oil and used oil. Moreover, there we observe the decrease of oil fluorescence intensity for used oil in comparison to the fresh oil fluorescence intensity.

Next, the three-dimensional spectra of fresh oil and used oil after 593 h of work in ship engine, for three oil concentrations, were normalised to the area under the curve of EEMs of oil. This procedure was performed to obtain information about the shape of EEMs of oils independent on the fluorescence intensity of oil. The normalised EEMs of fresh oil and used oil after 593 h of work in ship engine as 2D maps for three oil concentrations are presented in Figure 3. In Figure 3 is clearly visible the peaks position of oil presented in Figure 2. The peaks positions could be described by excitation wavelength and emission wavelength so-called wavelength-independent fluorescence maximum ($Ex_{max}/Em_{max}$) allow to characterise two forms of oil [24]. The wavelength-independent fluorescence maximums for three peaks for this type of oil were presented in Table 2.
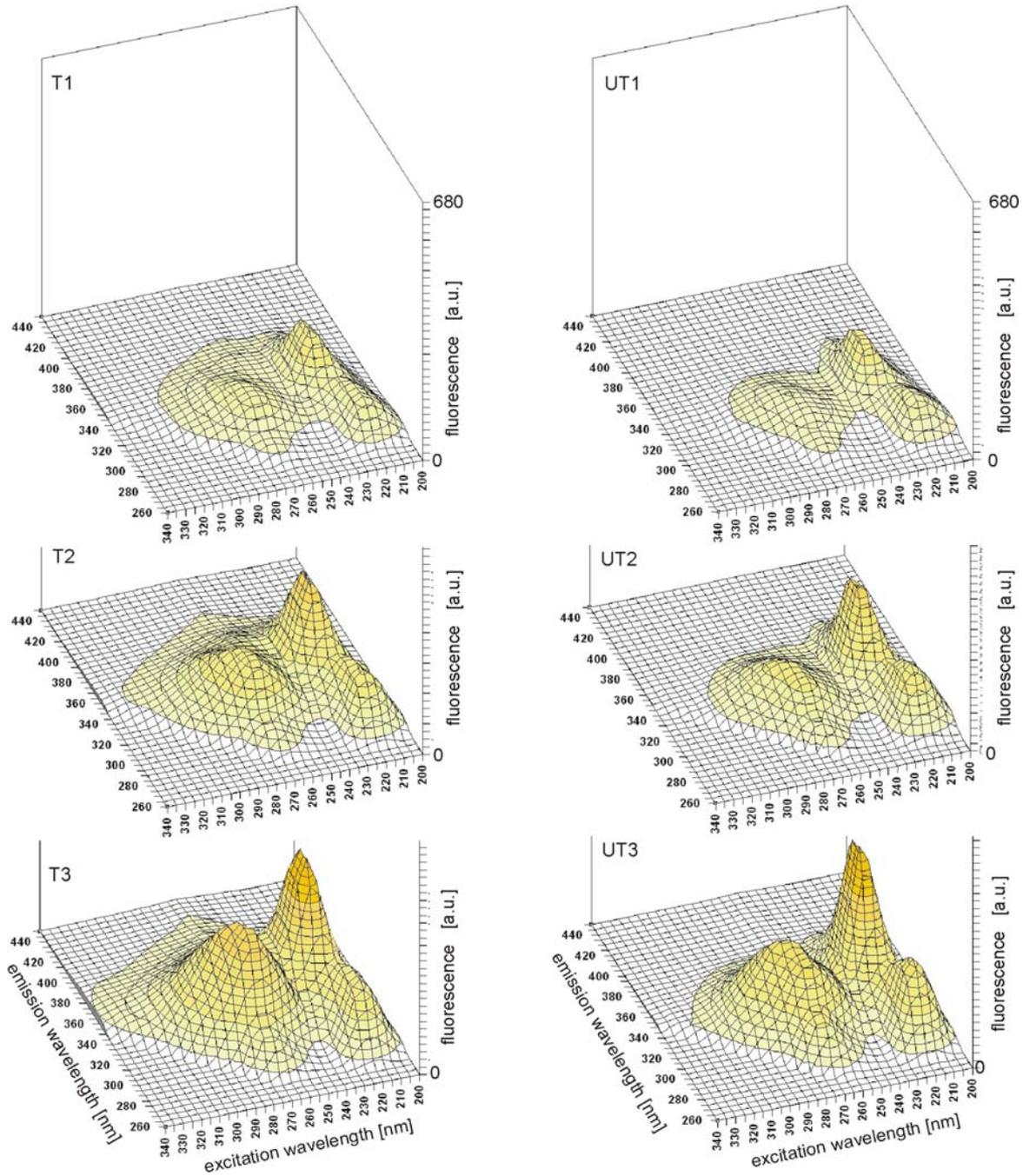
Fig. 2. Excitation-emission fluorescence spectra (EEMs) of oil in n-hexane dilutions in 3D plane for *Titan Truck Plus 15W40* in three oil concentrations *T1, UT1:* 25 mg/kg, *T2, UT2:* 50 mg/kg, *T3, UT3:* 100 mg/kg

## 4. DISCUSSION

The results presented in Figure 2 and Figure 3 show that in general, higher predisposition to fluorescence displays fresh lubricate oil *TTP 15W40* than the same oil but after 595 h of work in ship engine. This is confirmed in Figure 1 also, where is visible that the sample of fresh oil is brighter than the sample of used oil if highlighted by UV radiation. However the scale of changes of fluorescence intensity depends on the area of EEMs matrix. For example, if peak for excitation wavelength equal to 220 nm is considered, intensity of fluorescence is higher for used oil than for fresh one.

To obtain information about the spectral changes of fluorescence between fresh and used oil on the EEM spectra for both kinds of oil for three oil concentrations were normalised to the two-dimensional integral of the EEMs – $V$ – within all wavelengths (due to the expression 1). Next, the matrix $d_{ij}$ – expressing the difference between normalised EEMs for both oils were calculated respecting expression 2.
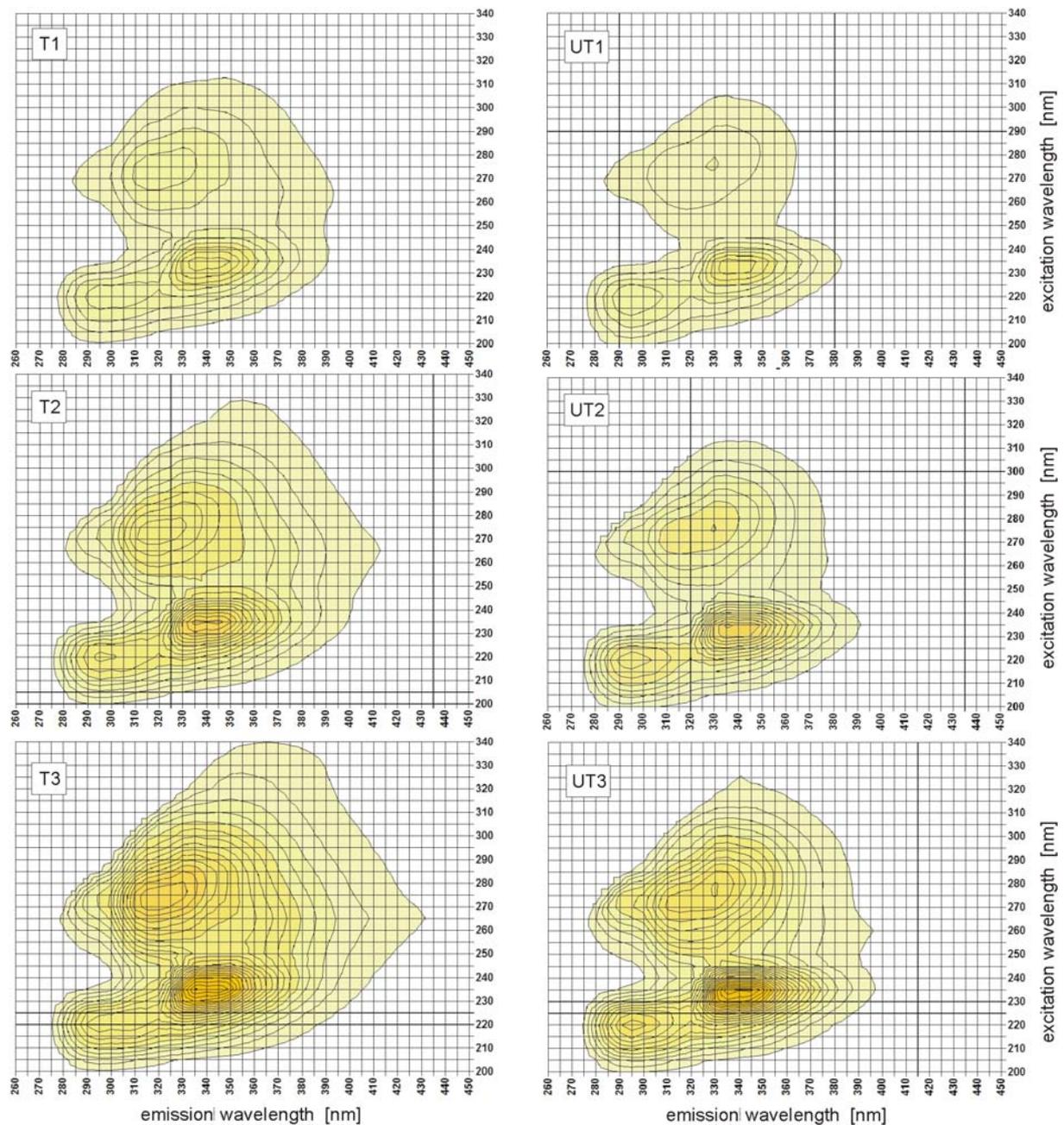
Fig. 3. Normalised excitation-emission fluorescence spectra as 2D map of oil in n-hexane dilutions
for *Titan Truck Plus 15W40* in tree oil concentrations *T1, UT1:*
25 mg/kg, *T2, UT2:* 50 mg/kg, *T3, UT3:* 100 mg/kg

Table 2. The range of values for wavelength-independent fluorescence properties of oil fluorescence peak ($Ex_{max}$ / $Em_{max}$): excitation maximum ($Ex_{max}$), emission maximum ($Em_{max}$) for fresh oil and used oil after 593h of work in engine

| | $Ex_{max} \pm 5$ [nm] / $Em_{max} \pm 5$ [nm] | | |
|---|---|---|---|
| **fresh oil** (*TTP 15W40*) | 220/295 | 235/340 | 275/320 |
| **used oil** (*TTP 15W40*) | 220/295 | 235/335 | 275/330 |

$$V = \sum_{i}^{n} \sum_{j}^{k} f_{ij} \qquad (1)$$

where:
$f_{ij}$ - registered value of fluorescence for define excitation and emission wavelengths,
$i$ - the number of successive excitation wavelength,
$n$ - total number of excitation wavelength,
$j$ - the number of successive emission wavelength,
$k$ - total number of emission wavelength

$$d_{ij} = \frac{f^{UT}_{ij}}{V^{UT}} - \frac{f^{T}_{ij}}{V^{T}} \qquad (2)$$

where:

$d_{ij}$ - matrix element of differences between EEMs for both used and fresh oils,

$f^{UT}_{ij}, f^{T}_{ij}$ - relatively fluorescence for used and fresh oil,

$V^{UT}$, $V^{T}$ - relatively the two-dimensional integral of EEMs for used oil and for fresh oil – fluorescence for fresh oil.

The results of this procedure are presented in Figure 4. On the left side of Figure 4 there is presented the differences between fresh oil and oil
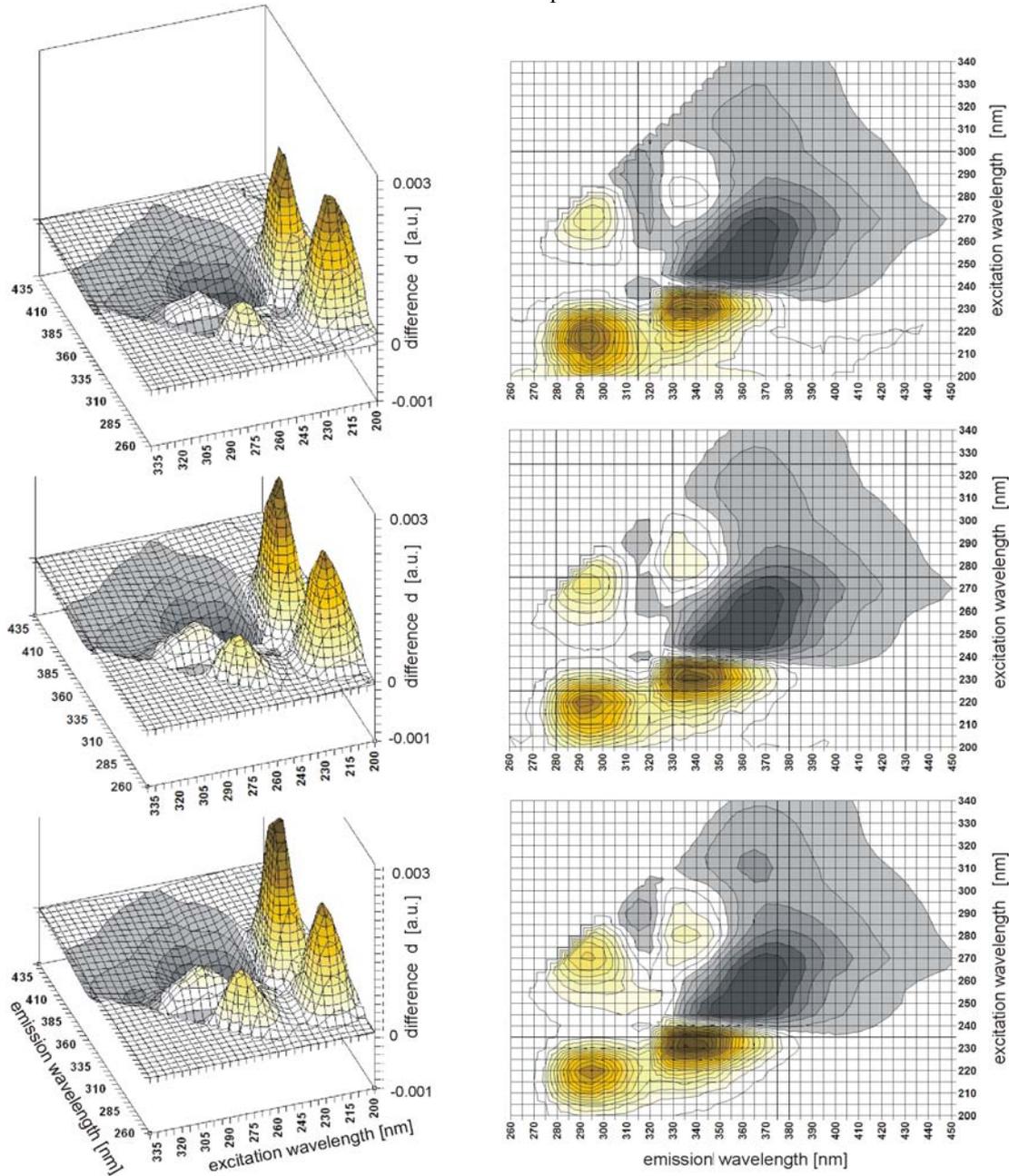


Fig. 4. Difference between normalised excitation-emission fluorescence spectra as 3D chart and 2D map of oil in n-hexane dilutions for *Titan Truck Plus 15W40* in three oil concentrations *T1, UT1:* 25 mg/kg, *T2, UT2:* 50 mg/kg, *T3, UT3:* 100 mg/kg

after 594 h of work in ship engine in three-dimensional plane (3D) while on the right side of Figure 4 the difference was presented in two-dimensional planes as contour maps (2D). The gray areas on Figure 3 present the losses of the oil fluorescence intensity, while the yellow areas on the Figure 3 present positive values of oil

fluorescence intensity for the difference between two forms of oil.

On the present phase of research it is difficult to decidedly say what atomic or molecular quantum processes are responsible for fluorescence peak intensity changes or for peak shifts on the plane of EEMs matrix. It seems that while the engine is running define chemical compounds are destructed

or transformed, whereas other can be synthesised or can be transferred from engine elements. In any way some lubricate oil changes manifests themselves in EEM spectra.

## 4. CONCLUSIONS

Taking into account presented results with considered oil concentration for *Titan Truck Plus 15W40* (TTP *15W40*) we can conclude that the fluorescence seems to be promising method to classify fresh and used oil based on change of fluorescence intensity and description of the peak position.

Going forward, it is necessary to consider the changes of EEMs between fresh oil and used one for higher oil concentration and for other periods of exploitation of lubricating oil in engine system. Moreover, in the future it is desirable to compare results of fluorescence measurement with properties of oil changes based on viscometric and rheometric measurements for used oil [15, 22]. One can provide that such comparison will create new possibilities of used lubricate oil testing.

## 4. ACKNOWLEDGEMENTS

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