

OIL IDENTIFICATION BASED ON TOTAL SYNCHRONOUS SPECTRA

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Abstract

Contribution of marine carriage in the global transport is in permanent developing. It leads to increase the unintentional oil spills, which may induce serious disturbances in functioning of the natural marine ecosystem, especially when it interferes with other technical activities in the marine space. That fact contributes to increase the interest in searching of new research techniques to protect the natural ecosystem. Therefore, the main task of marine international organisations concentrates on the effective and rapid detection of oil spill and on the possibility of identifying oil pollutants as well as on origin of pollution.

The purpose of the study is to characterise the oil belonging to the vessel engine lubricate oils. We analyse the stage results of investigations based on one of types of fluorescence spectroscopy, namely: synchronous spectra. To characterise the oil, the Aqualog Horiba spectrofluorometer was applied, which allows performing precise measurement in a short time. Based on the measured excitation-emission spectra, total synchronous fluorescence spectra for oil were obtained using various wavelength intervals. Total synchronous fluorescence spectra of petroleum substances allow finding wavelength interval typical for particular type of oil. This approach could allow obtaining of complex mixtures, such as oils, more efficient description. We discuss the total synchronous fluorescence spectra for engine oil (Marinol type) dissolved in n-hexane in various concentrations of oil as a possible tool proposed to oil type identification. We present changes and variation of the total synchronous fluorescence spectra for oil with various oil concentrations.

Keywords: fluorescence spectroscopy, total synchronous spectra, lubricate oil, vessel engine room, marine environment

1. Introduction

Marine transport really most increased in recent years, which allows concluding that shipping in these days is one of the most popular way of transport over the world [8, 11]. This fact leads to increase the potential accident in the sea or ocean area, with an oil spill and in consequence leads to the contamination of the natural marine environment. To protect the natural marine environment it is necessary to detect the potential oil spills as well as to indicate their source in really short time.

Oil pollutants are highly complex mixtures of hydrocarbon compounds and contain numerous fluorophoric components [10]. In order to study multifluorophoric systems such as oil substances the efficient tool is still desirable. Although in literature there were described a lot of method for oil spills detection. Methods using in oil detection were divided in three areas such as [20, 24]: satellite and airborne detection [18] allow rapidly remote sensing oil spill detection, laboratory measurements [1-3, 7] allows for oil pollution detection and identification and *in situ* measurements allows for identification of oil substances [5]. Measurements apply in these areas are based on different methods such as chromatography, Raman-, infrared- ore visible spectroscopy [14, 6, 9, 22, 23]. Investigations of multifluorophoric systems (here oil substances) requires to apply really sensitive method.

In laboratory and *in situ* fluorescence measurements there is really broad spectrum of methods

basing on fluorescence, starting from stationary methods such as fluorescence spectroscopy for single excitation wavelength, excitation-emission spectroscopy and synchronous fluorescence spectroscopy [15, 17]. Synchronous fluorescence spectroscopy was introduced and described by Lloyd [12]. Synchronous fluorescence spectroscopy was used to study petroleum products [16] also in marine environment [21]. Moreover, the intensive development of science allows studying hydrocarbon compounds basing on time-resolved fluorescence spectroscopy [4, 19, 25].

Synchronous fluorescence spectroscopy based on simultaneously measurement of the emission spectrum for particular excitation wavelength and measurement of excitation spectrum for particular emission wavelength. These spectra include the spectral information in a fixed form described by wavelength interval ($\Delta\lambda$) also so-called offset, which describes the function of emission wavelength with synchronous changes of excitation wavelength [15].

In this paper, we present total synchronous fluorescence spectroscopy as a tool to oil pollution identification in seawater. We study engine lubricate oil *Marinol* using for lubrication of high-pressure ship engines, supercharged, working in conditions of high heat loads. We consider the total synchronous fluorescence spectra of *Marinol* oil for six oil concentrations, which contain spectral information relating to this type of oil.

2. Materials and methods

Procedure of oil samples' preparation

Marinol oil belongs to engine oils was used to prepare oil samples. N-hexane for analysis with 96.0% purity as a solvent was applied. Next, the stock solution of *Marinol* oil in n-hexane was prepared. In the next step, six individual concentrations of *Marinol* oil samples in n-hexane were prepared basing on the dilution method. The concentration of *Marinol* oil samples were presented respectively, in Tab. 1.

Tab. 1. Concentrations of *Marinol* oil samples in n-hexane

Marinol (M)	
c [mg/kg]	
M1	18
M2	40
M3	82
M4	180
M5	345
M6	680

Measurement

Aqualog Horiba spectrofluorometer was applied for measure three-dimensional excitation-emission spectra (EEMs) of oil in n-hexane samples [1, 13]. EEM spectra of oil samples for all concentration of oil in a 1×1 cm quartz cuvette were measured.

The measured spectral area of EEM spectra for excitation wavelength (λ_{ex}) were changed in the range from 240 nm to 600 nm with a 5 nm sampling interval and for emission wavelength (λ_{em}) were changed in the range from 212.75 nm to 622.97 nm with a 1.623 nm sampling interval. Other specifications such as 5 nm excitation slit, 5 nm emission slit and 1 s integral time were applied.

3. Results

EEM spectra for *Marinol* oil samples diluted in n-hexane for six considered oil concentrations presented in Tab. 1, were determined at a stabilised temperature of 20° C. Raman and Rayleigh scattering automatically were removed based on the software package of the *Aqualog* Horiba spectrofluorometer [13].

Total synchronous fluorescence spectra for *Marinol* oil were determined based on measured excitation-emission spectra using the wavelength interval ($\Delta\lambda$) – parameter described by formula (1) [12, 15]:

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

where:

$\Delta\lambda$ – the wavelength interval,

λ_{ex} – the excitation wavelength,

λ_{em} – the emission wavelength.

Figure 1 presents total synchronous fluorescence spectra in three-dimensional (3D) plane for *Marinol* oil in n-hexane for various wavelength intervals (from $\Delta\lambda = 10$ nm until 200 nm) for six considered concentration of oil. Particular axis of total synchronous fluorescence spectra in 3D plane on Fig. 1 describe, respectively: axis X – excitation wavelengths, axis Y – wavelength interval $\Delta\lambda$ and axis Z – intensity of fluorescence.

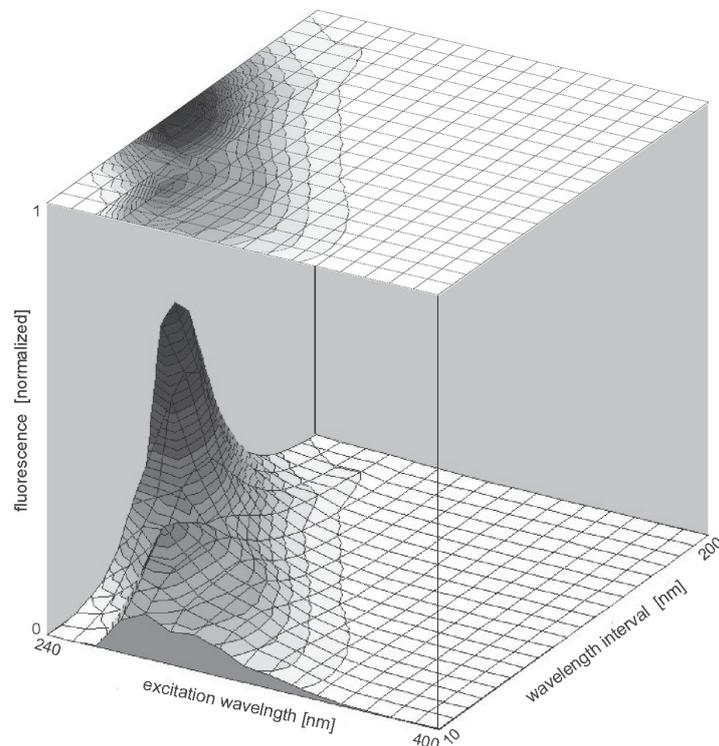


Fig. 1. Example of the total synchronous fluorescence spectra of oil (main picture) and 2D map (on the top)

On the Fig. 2 there is observed change of the shape of the total fluorescence spectra when the concentration of oil is changing. When the oil concentration increases the intensity of fluorescence increases and achieves the critical value for concentration near 340 mg/kg. For higher concentrations, the intensity of fluorescence decreases. It can be explained as the dilution effect. There is observed that fluorescence intensity covers progressively area for higher values of the excitation wavelength when the concentration of oil increases.

The highest fluorescence intensity is observed when $\Delta\lambda$ is equal to about 80-90 nm, whereas, if only a shape of spectrum is considered (normalized to the maximum value), the waveforms depend on $\Delta\lambda$. Moreover, excitation wavelength achieved for maximal value of fluorescence intensity also depends on $\Delta\lambda$. Fig. 3 presents synchronous fluorescence spectra normalized to maximum of fluorescence intensity for *Marinol* oil for different wavelength intervals $\Delta\lambda$. There is clearly visible that the fluorescence intensity maximum is below 240 nm (lowest border of the spectrofluorometer possibility) for $\Delta\lambda$ values above 120 nm, while for $\Delta\lambda$ equals to 80 nm the maximum of fluorescence falls on 250 nm and for $\Delta\lambda$ equals to 40 nm the maximum is situated near 270 nm. For every $\Delta\lambda$ the waveforms seems bimodal, however when $\Delta\lambda$ is 80 nm bimodal shape is rather

poorly signed. One can say that there is very difficult to point up which $\Delta\lambda$ should be chosen to capture the signal about the oil substance existence in the investigated sample. Therefore, the total synchronous fluorescence is proposed to detect oil substances in samples taken mainly from marine area and even from technological water reservoir or the drinking water network.

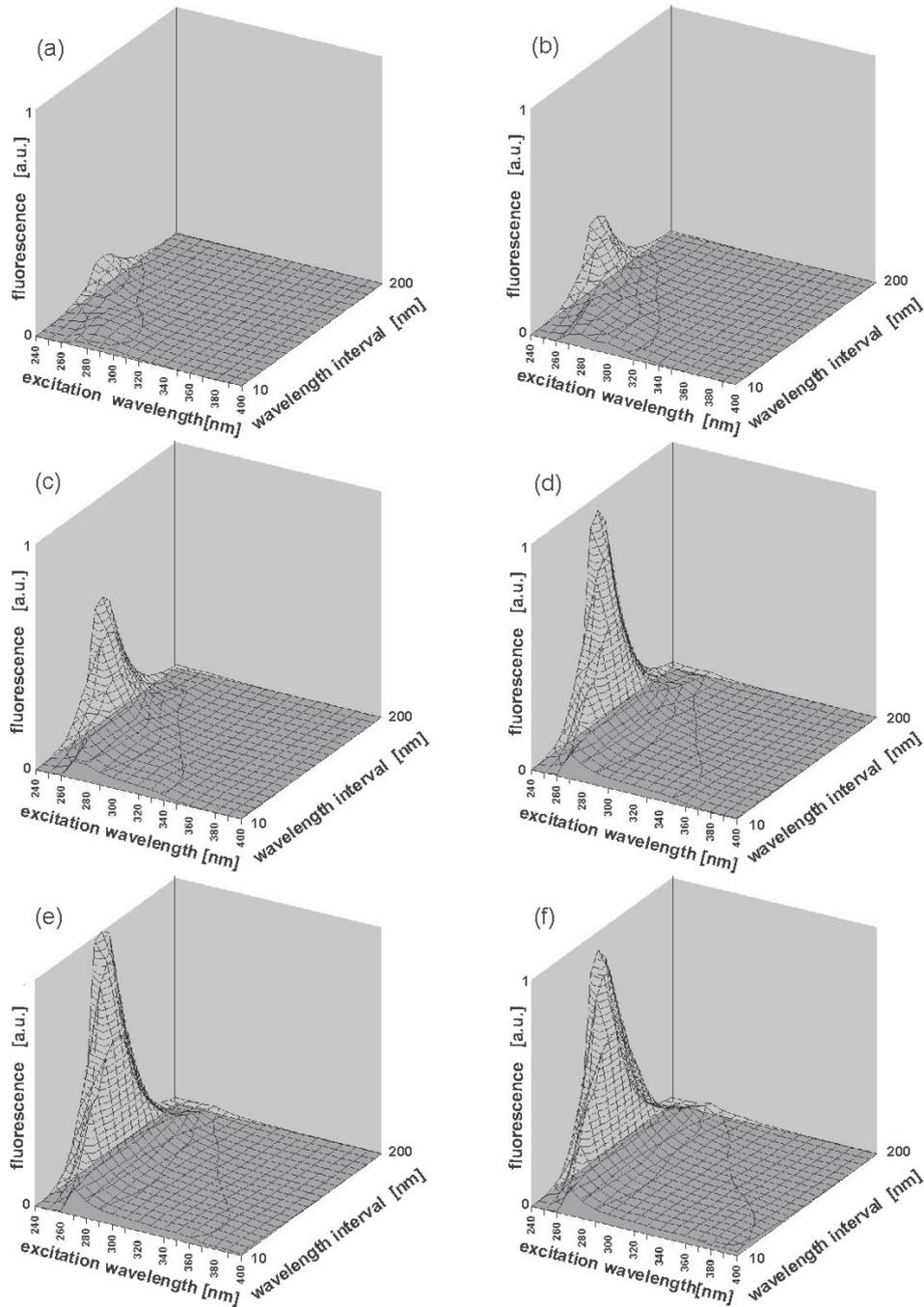


Fig. 2. Total synchronous fluorescence spectra for constant wavelength interval – $\Delta\lambda$ for Marinol oil in *n*-hexane for various concentration, respectively: (a) 18 mg/kg, (b) 40 mg/kg, (c) 82 mg/kg, (d) 180 mg/kg, (e) 345 mg/kg, (f) 680 mg/kg

4. Conclusions

Presented spectra plays a role of the stage results on the way to obtain the final method for finding the spectral signatures of defined kind of oil extracted from the oil polluted water. Based on *Marinol* oil synchronous-fluorescence-spectra we conclude that synchronous fluorescence method seems to be suitable for detection of oil, because of their peaks (below 270 nm) are

situated far from fluorescence peaks of the main constituents in the natural waters (for example chlorophyll shows maximum of fluorescence near 580 nm).

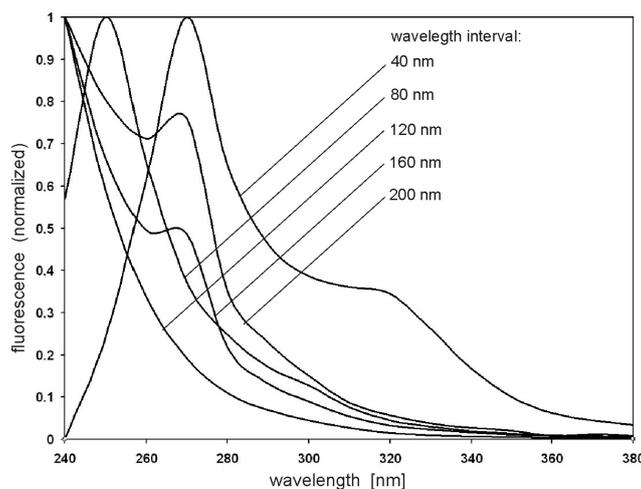


Fig. 3. Synchronous fluorescence spectra for Marinol oil in *n*-hexane for oil concentration 82 mg/kg normalized to the maximum value for various wavelength intervals

Taking into account presented results for exemplary oil (lubricate oil *Marinol*) based on total synchronous fluorescence spectroscopy we indicate, that the most important information about this kind of oil is fixed in synchronous spectrum for defined wavelength-interval. Summarising up we can conclude that, synchronous fluorescence spectroscopy, characterised by the wavelength-interval – probably typical for each type of oil, could give the possibility to separate the responsible for oil parts of fluorescence spectra.

Further studies will also focused on synchronous spectra for various types of oils (crude, lubricate, transform, hydraulic, bio). We provide that the substantially differences of various types of oils could be observed in the shape of the synchronous spectra of various types of oils. The information will play an important role to identify the kind of oil.

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