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DESCRIPTION OF DIESEL FUEL BASED ON SYNCHRONOUS FLUORESCENCE SPECTROSCOPY

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

The purpose of the study is spectrally characterise fuel Diesel used in diesel ship engine. For description of Diesel fuel the techniques of total synchronous fluorescence spectroscopy was applied. To characterise the oil, the spectrofluorometer 'Aqualog Horiba', which allows performing precise measurement in a short time, was applied to measure the excitation-emission spectra. Total synchronous fluorescence spectra of oil were obtained using various wavelength intervals basing on the measured excitation-emission spectra of Diesel fuel. Total synchronous spectra of Diesel oil are considered for several oil concentration. Synchronous fluorescence spectra were used to describe the detected maxima of Diesel fuel fluorescence by the wavelength-interval fluorescence maximum, containing information about the excitation wavelength and the wavelength-interval describing the characteristic fluorescence peak position for each considered fuel sample. That approach is discussed in relation to find a universal indicator – the wavelength-interval – as a possible tool proposed to Diesel fuel description independent from the fuel concentration. Therefore, we discuss the changes of the total synchronous fluorescence spectra for different oil concentration. Obtained results indicate that the best indicator for this kind of oil characterisation seems to be the wavelength-interval for 60 nm due to the independence of the synchronous spectra from the oil concentration.

Keywords: *synchronous fluorescence spectroscopy, total synchronous spectra, Diesel fuel, wavelength-interval, offset*

1. Introduction

The protection of the marine environment requires continuous research of petrochemical products using in maritime transport in terms of their operational quality and their impact on the marine environment. Therefore, various methods of describing the composition and properties are analysed. Thy study oil pollutants such as fuel, lubricate or crude oils, which are highly complex mixtures of hydrocarbon compounds. They contain numerous fluorophoric components [3], efficient method, should be used. Taking into account the possibility of fluoresce of fuels due to its composition (mono-aromatic and polycyclic aromatic hydrocarbons – PAHs) methods based on fluorescence seems to be the best way due to the efficiency. The spectrum of methods basing on fluorescence is relatively wide – fluorescence spectroscopy for single excitation wavelength, fluorescence spectroscopy for single emission wavelength (excitation spectra), excitation-emission spectroscopy and synchronous fluorescence spectroscopy [6, 8]. Synchronous fluorescence spectroscopy was already used to study petroleum products [7]. Moreover, obtained results using this method to study lubricate oils used in ship engine system seems to be promising [2]. Therefore, we decided to apply that approach based on synchronous fluorescence spectroscopy for fuel description.

The synchronous spectra include the spectral information in a fixed form described by wavelength-interval ($\Delta\lambda$) (offset), which describes the function of emission wavelength with synchronous changes of excitation wavelength [6].

In this auricle, we present results of measurements of the total synchronous fluorescence spectra as a tool to *Diesel* fuel characterisation. We consider the total synchronous fluorescence spectra of *Diesel* fuel for several oil concentrations. Moreover, synchronous fluorescence spectroscopy was applied to find universal indicator independent from the oil concentration – wavelength-interval, which contain spectral information relating to this type of oil.

2. Materials and methods

2.1. Fuel samples characterisation

The representative, fresh fuel oil used in marine transport was selected for this study: *Diesel F-75* – applied in ship diesel engines. Tested fuel is transparent bright liquid, coefficient of kinematic viscosity: 2.6 mm^2/s, density: 835 kg/m^3, flash point: 78ºC.

2.1.1. Procedure of fuel oil samples preparation

Diesel fuel applied in diesel engine system was used to prepare oil samples. N-hexane for analysis with 96.0 % purity as a solvent was applied. Next, the stock solution of *Diesel* fuel in n-hexane was prepared. In the next step, four individual concentrations of *Diesel* fuel samples in n-hexane were prepared basing on the dilution method. The concentrations of individual oil samples were prepared in relation to the weight of the solution (n-hexane) and the weight of oil samples. The concentration of *Diesel* fuel samples were presented respectively, in Tab. 1.

Tab. 1. Concentration [ppm by weight] of Diesel fuel dissolved in n-hexane

	Diesel
	c [ppm]
D1	200
D2	400
D3	450
D4	900

2.2 Measurement

The *Aqualog Horiba* spectrofluorometer was applied for determination three-dimensional excitation-emission spectra (EEMs) of oil in n-hexane samples [1, 5]. 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.

Raman and Rayleigh scattering to yield a digital matrix of excitation-emission spectra was automatically removed using the software package of the spectrofluorometer. The EEM spectra of oil samples were determined at a stabilised temperature of 20ºC.

3. Determination of synchronous fluorescence spectra

Based on measured excitation-emission spectra (EEMs) of *Diesel* fuel, total synchronous fluorescence spectra were determined. To determine the synchronous fluorescence spectra the procedure, using the wavelength interval (offset) ($\Delta\lambda$) – parameter described by formula (1) [4, 6] was applied:

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

where:
$\Delta\lambda$ – the wavelength interval (offset),
λ_{ex} – the excitation wavelength,
λ_{em} – the emission wavelength.

4. Results and discussion

Figure 1 presents excitation-emission spectra of *Diesel* fuel in n-hexane for chosen concentration of oil. Moreover, in Fig. 1 the chosen offsets ($\Delta\lambda$) – 20 nm, 40 nm, 60 nm, 80 nm, 100 nm and 120 nm, respectively, have been marked.

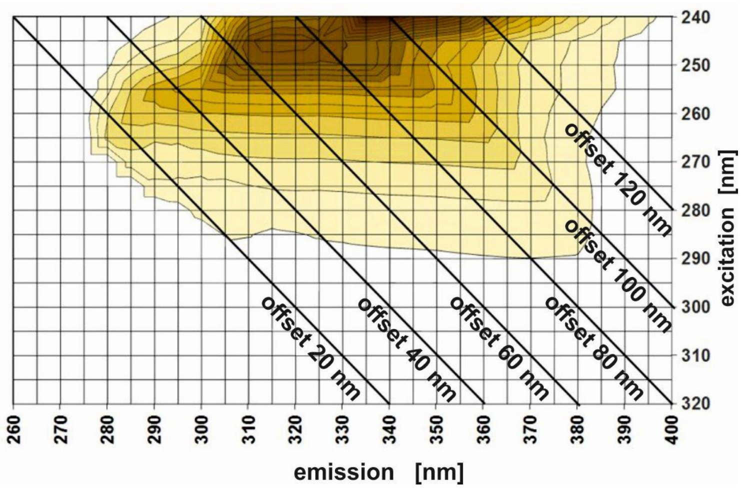

Fig. 1. Contour map of fluoresce Excitation-Emission Matrix of exemplary fuel oil with marked transects for synchronous spectra formation for chosen offsets (oil concentration in n-hexane: 200 ppm)

Figure 2 presents total synchronous fluorescence (TSF) spectra in three-dimensional (3D) plane for *Diesel* fuel in n-hexane for various wavelength intervals (from $\Delta\lambda$ = 10 nm until 120 nm) for exemplary concentration of oil. Particular axis of total synchronous fluorescence spectra in 3D plane in Fig. 2 describe, respectively: axis *X* – excitation wavelengths, axis *Y* – wavelength interval (offset) $\Delta\lambda$ and axis *Z* – intensity of fluorescence.

Synchronous fluorescence spectra allow 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.

To characterise *Diesel* fuel based on synchronous fluorescence spectroscopy it is necessary to present the changes of total synchronous fluorescence spectra when the concentration of oil is changing. However, the most important information is fixed in the shape of TSF spectra independent from the fluorescence intensity. Therefore, Fig. 3 presents the results of oils TSF spectra for *Diesel* fuel in two-dimensional plane as surface-contour visualisation map (2D map). This kind of results presentation allows to clearly describing the characteristic peaks (maxima of fluorescence).

The changes of TSF spectra in 2D plane for various oil concentration 200 ppm, 400 ppm, 450 ppm and 900 ppm were presented in Fig. 3. Fig. 3 indicates the presence of two peaks in 2D synchronous fluorescence spectra typical for this kind of oil. In this figure is visible that the maximum of fluorescence is achieved for the wavelength-interval about 95-105 nm (described by the Peak 1) and the second maximum is achieved for the wavelength-interval about 70-80 nm (described by the Peak 1). However, it is clearly visible that, the maximum of Peak 2 is shifted to the longer wavelength-interval when oil concentration increases. Additionally, the second peak does not formed for the highest fuel concentration 900 ppm. The changes of the wavelength-interval fluorescence maxima ($Ex_{max}/\Delta\lambda$) for *Diesel* fuel for various fuel concentration are presented in Tab. 2.

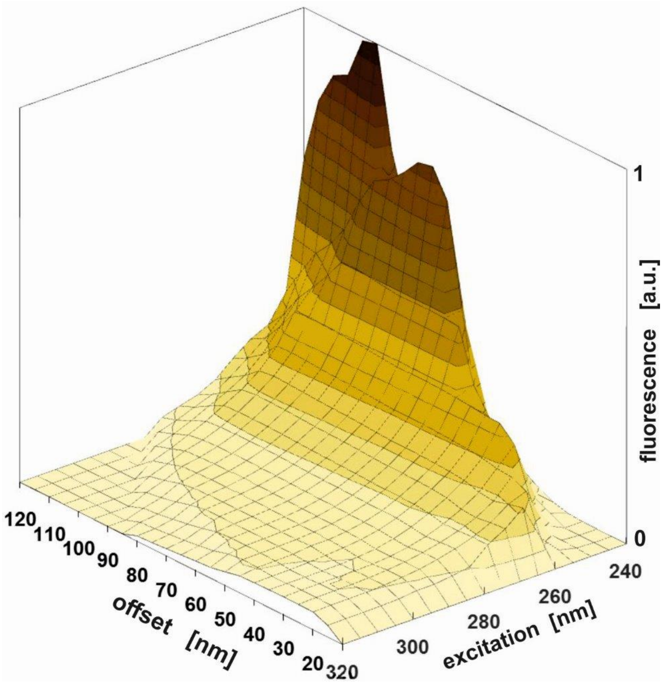

Fig. 2. Exemplary 3D synchronous spectrum of fuel oil dissolved in n-hexane (concentration the same as at Fig. 1)

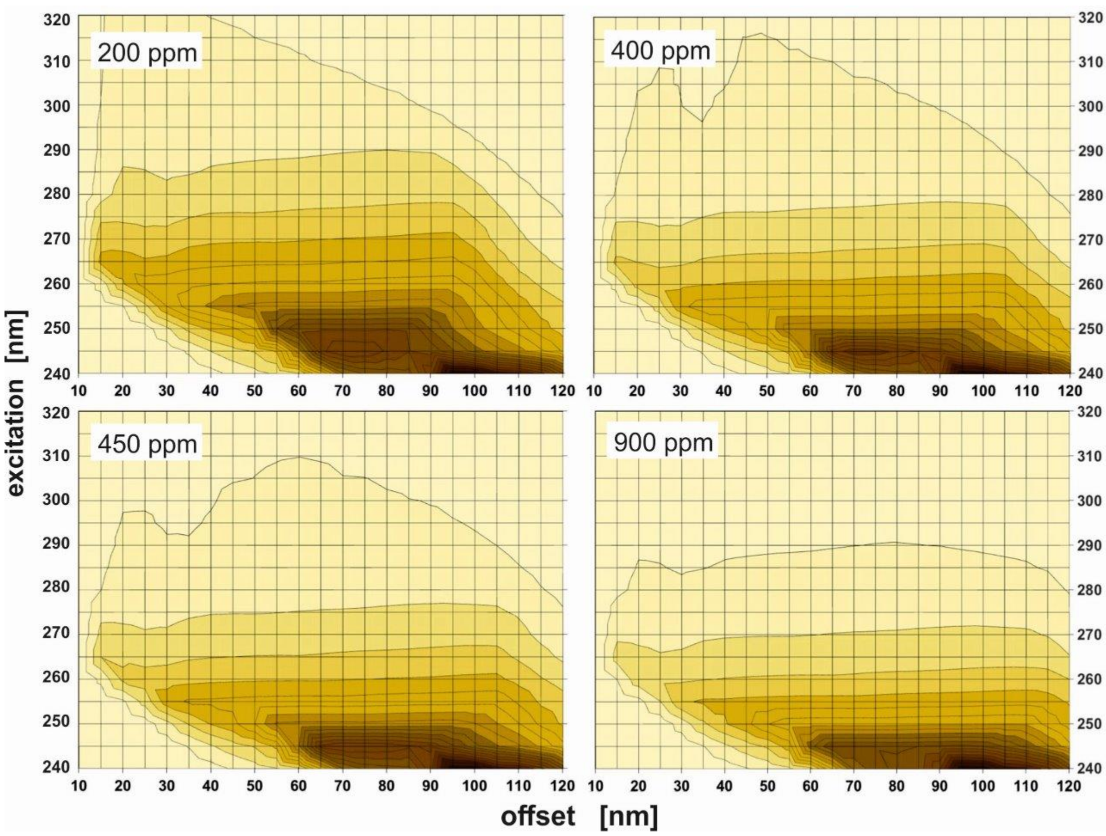

Fig. 3. Contour map of the total synchronous spectra of Diesel fuel for various concentration of fuel 200 ppm, 400 ppm, 450 ppm and 900 ppm, respectively

Tab. 2. The range of values for wavelength-interval fluorescence maximum of Diesel fuel for various fuel concentration

	Diesel	
	$Ex_{max} \pm 5$ [nm] / $\Delta\lambda \pm 1$ [nm]	
	Peak 1	Peak 2
D1	240 / 100	245 / 75
D2	240 / 100	245 / 75
D3	240 / 100	245 / 75
D4	240 / 100	unformed

Moreover, to obtain more information based on TSF spectra the characteristic wavelength-interval (Δλ) from the whole spectrum was chosen. It allows obtaining the synchronous fluorescence spectrum for single wavelength-interval (Δλ). Synchronous fluorescence spectra for *Diesel* fuel for fuel concentration 200 ppm for different wavelength intervals Δλ equal 20 nm, 40 nm, 60 nm, 80 nm, 100 nm and 120 nm are presented in Fig. 4. There is visible the changes of synchronous fluorescence spectra when the wavelength-interval increasing. In the case when the wavelength-interval increases from 20 nm to 120 nm there is observed the shift of fluorescence intensity maximum from about 265 nm for excitation wavelength to lower excitation wavelengths (about 240 nm).

Presented synchronous spectra extracted from TSF spectra for chosen single wavelength-interval can be applied to check the properties and probably the composition of *Diesel* fuel. However, the aim is to find an indicator to fuel characterisation independent from the oil concentration. Therefore, thinking into account obtained results it is necessary to find the universal wavelength-interval (Δλ) for different oil concentration. Therefore, synchronous spectra for single wavelength-interval (Δλ) for different oil concentration were chosen. Synchronous spectra for single wavelength-interval Δλ = 60 nm, 80 nm and 100 nm for different oil concentration were presented in Fig. 5-7, respectively. Considering, the synchronous spectra for these wavelength-intervals there is clearly visible that both for Δλ = 80 nm and Δλ = 100 nm the variations of the shape of synchronous spectra with oil concentration is observed, whereas for Δλ = 60 nm in the shape of synchronous spectra only small variations with oil concentration is observed. Moreover, the independence from the fuel concentration is observed for lower oil concentration (200 ppm and 450 ppm).

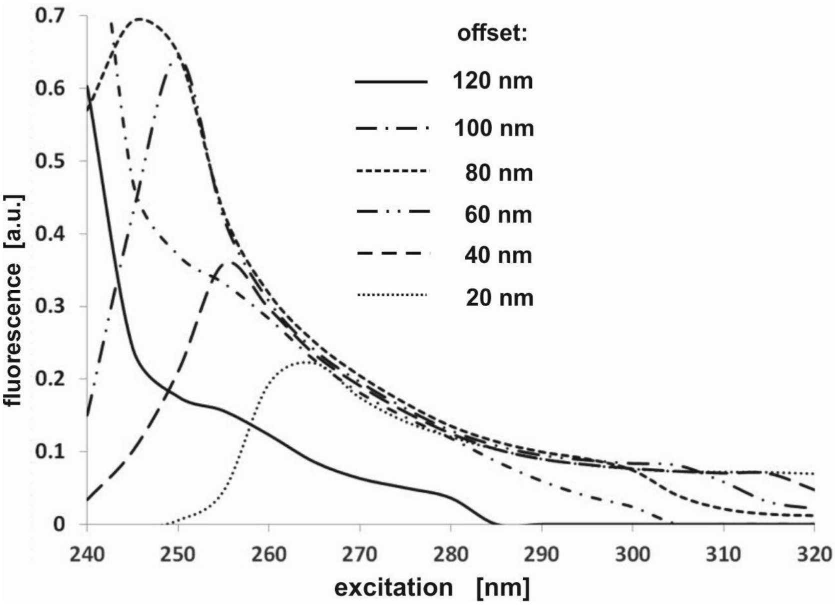

Fig. 4. Synchronous spectra for chosen wavelength-intervals (offsets) for Diesel fuel dissolved in n-hexane for 200 ppm of fuel concentration

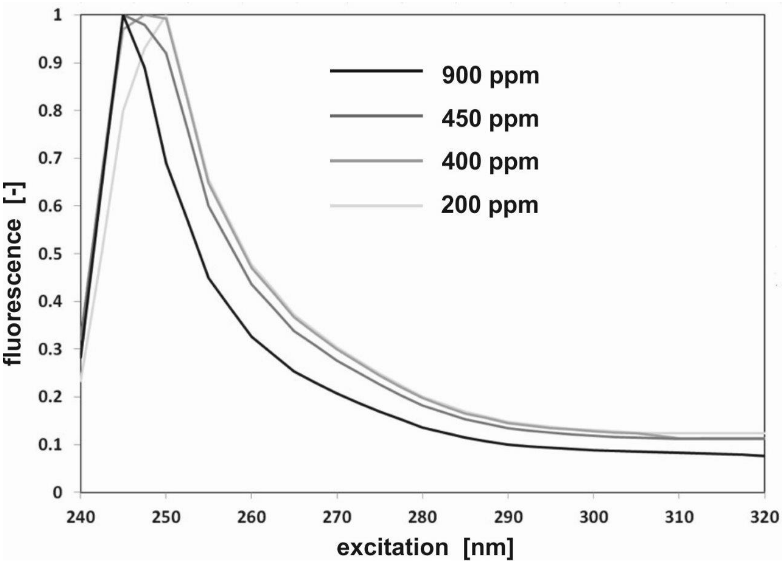

Fig. 5. Normalized synchronous spectra for offset 60 nm for various fuel concentrations

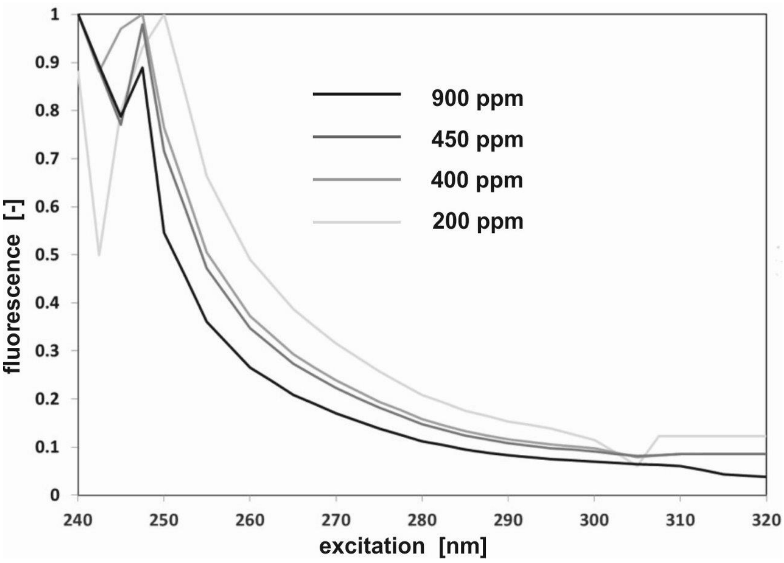

Fig. 6. Normalized synchronous spectra for offset 80 nm for various fuel concentrations

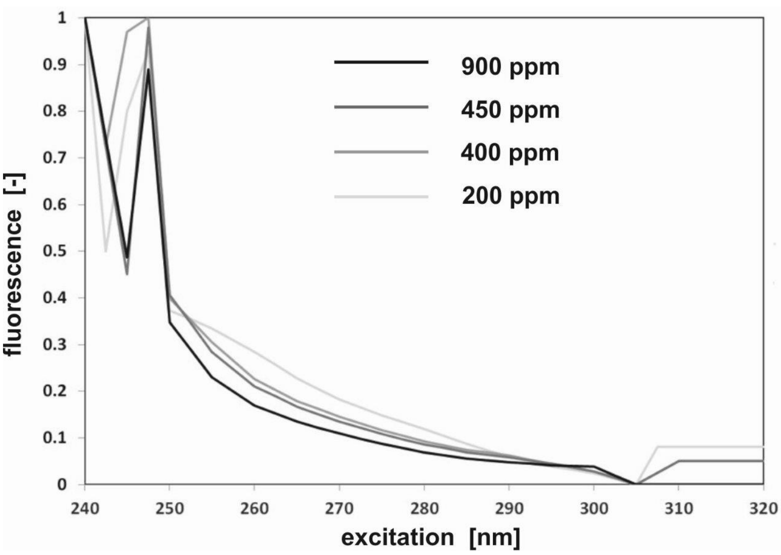

Fig. 7. Normalized synchronous spectra for offset 100 nm for various fuel concentrations

5. Conclusions

To characterise *Diesel* fuel, synchronous fluorescence spectra were considered. Based on synchronous spectra the indicator – wavelength-interval (offset) of fuel characterisation for different oil concentration, were determined. Thinking into account obtained results based on synchronous fluorescence spectra, we can conclude that wavelength-interval $\Delta\lambda = 60$ nm does not caused the changes in the shape of synchronous spectra, when the oil concentration is changing however does not excide 900 ppm. Therefore, the best way to *Diesel* fuel characterisation seems to be the wavelength-interval equal 60 nm due to independence of shape of synchronous spectra from the fuel concentration.

Acknowledgements

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