

ENGINE FUEL CHARACTERISATION BASED ON EXCITATION-EMISSION SPECTRA

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Abstract

Considering that correctly functioning of diesel ship engine depends on the composition of applied fuel, it is necessary to easily characterise fuels in terms of quality. Therefore taking into account above mentioned, appropriate analyses have been undertaken and the intention of this article is to inform that characterisation of fuel used in marine transport can be described by the specific parameter based on fluorescence excitation-emission spectroscopy. Therefore, for this study fuel typically used in ship engine – Diesel fuel – is considered. For analysis, Diesel fuel dissolved in *n*-hexane was used and several oil samples for various oil concentration were prepared. Spectrofluorometer Aqualog Horiba was used to record the excitation-emission spectra (EEMs). EEM spectra determined for each of oil concentration were described by two specific peaks for this kind of oil. Based on registered EEMs, the specific indicator - the wavelength-independent fluorescence maximum – coded in two specific wavelengths – excitation and emission, respectively, described as Ex_{max}/Em_{max} was determined for considered oil concentration. Obtained results indicate the independence from oil concentration only for one detected peak described by $Ex_{max}/Em_{max} = 240/332$. Taking into account obtained results, we can conclude that the wavelength-independent fluorescence maximum detected for excitation wavelength at 240 nm corresponds to the emission wavelength at 332 nm due to the independence from the oil concentration, could be a good indicator to characterise this kind of oil – Diesel fuel. We can conclude that the changes in the composition of fuel could be detected in EEM spectra by the change of detected peaks position.

Keywords: fuel, diesel, engine, excitation-emission spectra, fluorescence

1. Introduction

Various factors can influence on the fuel, resulting in a change of its parameters. Apart from the possibility of mistakes during delivery from the producer, the reasons for the loss of parameters can be seen in long time of residence in tanks or frequent pumping in the ballasting process – which favours the possibility of contact with water or other types of petroleum products. In addition, some components of the fuel may escape to the atmosphere [1].

Petroleum and its derivatives such as fuels or lubricate oil are highly complex mixtures of chemical components consist of aliphatics, asphaltenes as well as mono- or polycyclic aromatic compounds. Therefore, for substances containing organic compounds – particularly aromatic hydrocarbons, which are responsible for the occurrence of fluorescence, fluorescence spectroscopy can be applied. Moreover, due to the complex structure of fuels the fluorescence spectroscopy as relatively sensitive method seems to be a good tool to fuels characterization [4, 6].

In this article diesel, fuel is analysed based on excitation-emission spectroscopy (EEMs) [2, 3, 5] through the spectra measurements for various oil concentration. The goal of this study is to characterize fuel establishing the indicator independent from the oil concentration. Therefore, peaks determined in the registered EEM spectra were described by the indicator – wavelength-independent fluorescence maximum described as Ex_{max}/Em_{max} for each considered oil concentration. Taking into account obtained results, we can conclude that the wavelength-

-independent fluorescence maximum detected for excitation wavelength at 240 nm corresponds to the emission wavelength at 332 nm due to the independence from the oil concentration could be a good indicator to characterise this kind of oil – Diesel fuel.

2. Method

2.1. Fuel samples

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 mm²/s, density: 835 kg/m³, flash point: 78°C.

2.1.1. Samples of fuel oil dissolved in n-hexane

N-hexane (for analysis, 96.0 % purity) was applied as a solvent and a stock solution of oil in n-hexane for *Diesel* fuel was then prepared. Based on this dilution method, for individual concentrations of fuel were prepared. 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 individual oil concentrations in n-hexane are presented in Tab. 1.

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

Diesel	
	c [mg/kg]
D1	200
D2	400
D3	450
D4	900

2.2. Measurement

An *Aqualog Horiba* spectrofluorometer was applied to measure the excitation-emission spectra (EEMs) of fuel oil samples for Diesel oil [2, 3, 5]. The EEM spectra for all solutions of fuel oil dissolved in n-hexane in a 1×1 cm quartz cuvette were measured.

For EEM measurements, the following measurement parameters were applied: excitation wavelength from 240 nm to 600 nm with a 2.5 nm sampling interval, emission wavelength from 212.75 nm to 622.97 nm with a 1.623 nm sampling interval, 2.5 nm excitation slit, 5 nm emission slit. 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 20°C.

3. Results and discussion

The results obtained directly from the instrument are arranged in the form of a rectangular array of numbers that show the intensity of fluorescence in the individual wavelengths of light emitted from the sample for the individual wavelengths of light incident on the sample.

Figure 1 presents excitation-emission spectra (EEMs) in three-dimensional plane (so-called 3D spectra) for two extreme concentrations of *Diesel* fuel diluted in n-hexane, 200 ppm and 900 ppm, respectively. Fig. 1 allows to be notice the significant changes in the shape and the intensity of the

main peak of EEMs, located at 240 nm for excitation wavelength corresponds to the emission wavelength at 330 nm, caused by oil concentration. Moreover, in Fig. 1 the presence of the second peak was detected.

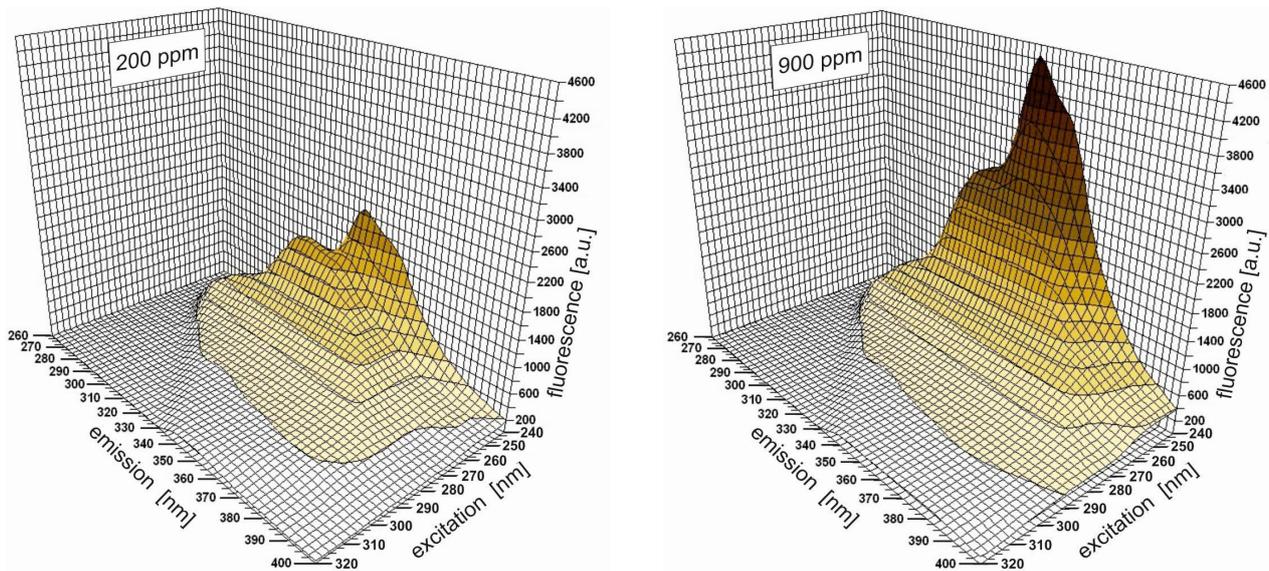


Fig. 1. 3D Excitation-emission fluorescence spectra (EEMs) of oil in *n*-hexane dilutions for Diesel fuel, in two oil concentrations (200 ppm and 900 ppm respectively) on the same scale of intensity of fluorescence

However, the most important information is fixed in the shape of EEMs independent from the fluorescence intensity. Therefore, measured EEMs of each Diesel fuel oil samples were normalized to the maximum value. Normalized excitation-emission matrices to the maximum values in two-dimensional plane (2D) are shown in Fig. 2, where the tendencies to transformation spectra caused by changes in oil concentration are clearly visible. EEMs spectra for Diesel fuel change in the excitation wavelength from 240 nm to 320 nm and emission wavelength from 270 nm to 400 nm. Moreover, Fig. 2 allows describing the second peak shown in Fig. 1, respectively, by excitation wavelength in range from 240 nm to 260 nm and emission wavelength from 300 nm to 330 nm in EEMs spectra. However, the peak is visible the most for the lowest concentration of oil and when oil concentration increases then the intensity of fluorescence of this peak decreases and the maximum of this peak shifts to longer emission wavelengths. Additional, in Fig. 2 the intensity of fluorescence maximum increases when the concentration of oil increases, although excitation and emission wavelengths related to fluorescence maximum remain constant.

The shape of fluorescence spectra demonstrates the presence of peaks, typical for these kinds of fuel Diesel. Based on EEMs, the peaks typical for this kind of oils can be described by the specific wavelengths: excitation and emission – described as the peak position of wavelength-independent fluorescence maximum, written as Ex_{max}/Em_{max} . The specific peaks described as wavelength-independent fluorescence maximum were determined for Diesel fuel for various considered oil concentrations. The values of wavelength-independent fluorescence maximum are presented in Tab. 2. The permanent value of this parameter was observed for different concentrations of oil for the Peak 1 described by $Ex_{max}/Em_{max} = 240/332$ nm. However, in contrast, the position of the Peak 2 is changing when oil concentration is changing and the maximum as well as the wavelength-independent fluorescence maximum of Peak 2 is shifted to longer wavelengths with an increase in oil concentration. Moreover, for the highest oil concentration 900 ppm in both Fig. 1 and 2 the total disappearance of Peak 2 is observed. Taking into account the variations of the wavelength-independent fluorescence maximum, the range of changes of these parameters for this kind of oil were determined. Tab. 3 presents the range of wavelength – independent fluorescence maximums for the studied oils.

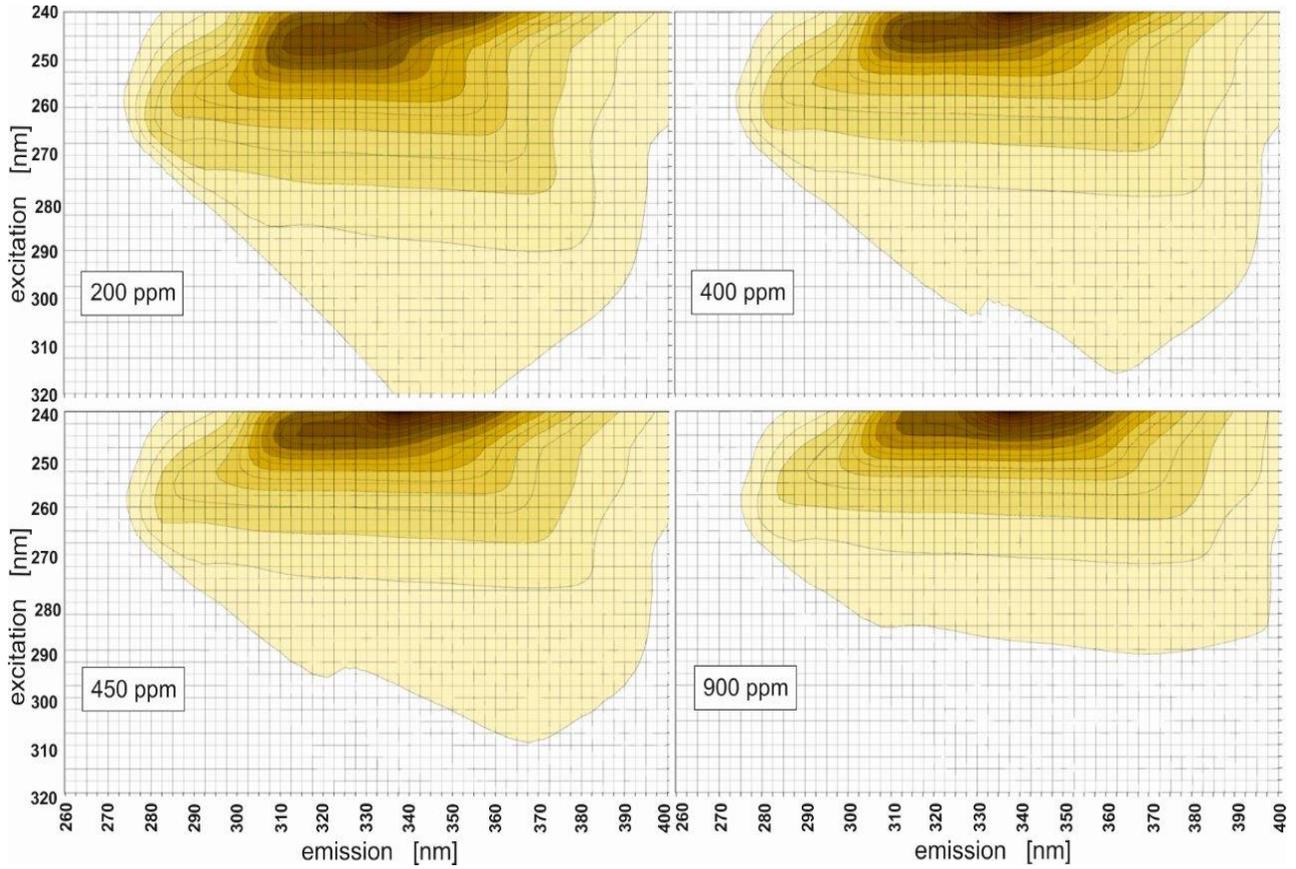


Fig. 2. Excitation-emission normalized spectra of fuel oil diesel dissolved in n-hexane for oil concentration: 200 ppm, 400 ppm, 450 ppm and 900 ppm, respectively

Tab. 2. The values for wavelength-independent fluorescence maximum of fuel Diesel dissolved in n-hexane described by the fluorescence peak: excitation maximum (Ex_{max}), emission maximum (Em_{max})

Diesel		
	Ex_{max} [nm] / Em_{max} [nm]	
	Peak 1	Peak 2
D1	240/332	246/318
D2	240/332	243/318
D3	240/332	242.5/320
D4	240/332	unformed

Tab. 3. The range of values for wavelength-independent fluorescence properties of oil fluorescence peak: excitation maximum (Ex_{max}), emission maximum (Em_{max})

Diesel		
	Ex_{max} [nm] / Em_{max} [nm]	
	Peak 1	Peak 2
	240/332	242.5-246/318-320

Taking into account above-mentioned consideration, to characterise Diesel fuel based on EEM spectra, there is a need for independence of oil concentration of the detected EEMs peaks for considered kind of oil. Therefore, the dependence on maximum fluorescence position of oil concentration for Peak 2 in EEM spectrum could not be the best way to characterise this kind of oil. Moreover, when we take into account the fluorescence spectrum for single excitation wavelength

considered for Peak 1 described by $Ex_{max}/Em_{max} = 240/332$ nm, there is clearly visible the independence of this peak from the oil concentration. Fluorescence spectra for single excitation wavelength at 240 nm for Diesel fuel are presented in Fig. 3.

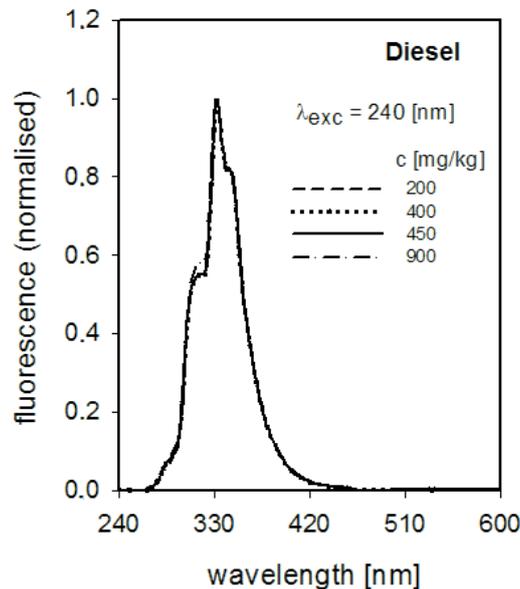


Fig. 3. Fluorescence spectra of fuel diesel dissolved in n-hexane for oil concentration 200 ppm, 400 ppm, 450 ppm and 900 ppm, respectively

Therefore, we can conclude that wavelength-independent fluorescence maximum detected for Peak 1 for this kind of oil could be a good indicator to oil characterization due to the independence from the oil concentration.

4. Conclusions

For this study Diesel fuel, typically used in marine transport and applied in ship diesel engine was used to consider the fluorescence excitation-emission spectra as a technique to characterise this kind of oil. The key of this consideration was to find an indicator, which allows describing considered oil in an easy way, independent from the oil concentration. EEM spectra allow to consider oil by specific parameter the wavelength-independent fluorescence maximum – characterise the EEM peak by specific maximum excitation and maximum emission wavelengths. This parameter allows encoding the information in characteristic indicator written as Ex_{max}/Em_{max} .

Obtained results for Diesel fuel, based on EEM spectra indicate the presence of two EEM peaks detected at 240 nm for excitation wavelength corresponds to the emission wavelength at 330 nm and the second peak located for excitation wavelength in range from 240 nm to 260 nm and emission wavelength in the range from 300 nm to 330 nm. Peak 1 described by $Ex_{max}/Em_{max} = 240/332$ indicate the independence from the oil concentration, while the position of Peak 2 is changing when oil concentration is changing and in a consequence the wavelength-independent fluorescence maximum of Peak 2 is shifted. Therefore, we can conclude that for characterisation of this kind of oil only Peak 1 described by $Ex_{max}/Em_{max} = 240/332$ could be used as an indicator. Moreover, based on obtained results we can suggest that considered wide range of oil concentration could be useful for further studies.

Acknowledgements

This article was supported by the Gdynia Maritime University grants No. 427/DS/2017.

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