ADOPTION OF THE TIME RESOLVED FLUORESCENCE TO OIL TYPE IDENTIFICATION

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Abstract

The present development of a basic science, including physics of stimulated emission of light, opens up new diagnostic possibilities in relation to the quality of oils, including marine fuels and lubricants. In complicated chemical composition of oils both light absorbing compounds and compounds that emit light (fluorescent) are included. This causes the formation of complex structures in the spectral plots of fluorescence intensity as a function of wavelength of light exciting fluorescence and as a function of the wavelength of light emitted. Since the fluorescence excitation occurs in a short time of its disappearance. The shape of the fluorescence decay function depends on the chemical composition of oil, therefore, includes a mention of its kind, quality, level of degradation, and the like. In this paper exemplary charts of the intensity decay curves in different parts of the fluorescence spectra are shown (for light fuel). Presented charts are obtained using the experimental device constructed in Bremerhaven University of Applied Sciences (Germany) and are the attempt to use ability of oil substance to manifest its composition in the form of the fluorescence decay curve. An analysis of the chart shows that decay of fluorescence in this case is described by biexponential curve, therefore a kind of oil can be represented by two numerical values – two decay time constants. Operational use of this method will be possible only after a comparative study of different types and quality of oil in relation to the shape of the fluorescence decay curves.

Keywords: oil, fuels, lubricants, aquatic environment protection, time resolved fluorescence, diagnostics

1. Introduction

Time-resolved fluorescence (TRF) is applied to study dynamical changes of various chemical compounds and processes in the materials. Usually dynamical processes are studied after illumination of a sample. TRF consists in monitor the intensity of emitted light after the flash of light which initiate fluorescence. The shape of a curve of decay of fluorescence intensity depends on a type of fluorophores and their chemical surroundings in investigated matter. The decay curve due to his exponential shape is represented by the so called lifetime, i.e. time in which intensity of fluorescence decreases e-fold (where e is the base of natural logarithms). Commonly, it is said that fluorescence lifetime refers to the average time of a molecule staying in the excited state before emitting a photon. In fact, the lifetime is a likelihood of leaving the state of excitation in a given unit of time. It is expected that the fluorescence decay curve of complex structures (e.g. oils) will have a more complicated shape than first-exponential decay.

In the case of derivatives of crude oil the main fluorophores are connected with cyclic and polycyclic molecules. The first attempts to apply the TRF to identify the type of oil have already

been conducted in the seventies of the twentieth century [1, 2]. It was concluded that the fluorescence decay curves are differ and depend on the type of oil. So far, despite several attempts [3-5], this method has been not used fully operationally. Now, thanks to the development of techniques arises feasibility of operational application of the time-resolved fluorescence. Currently various underwater devices are built using this technique for detection and identification of oil pollution in open marine waters. TRF has been used in the subLIF-system. This underwater device will be applied to detection of oil pollution in marine environment. For this case, a research was made in cooperation with Gdynia Maritime University (Poland) and Bremerhaven University of Applied Sciences (Germany). The samples were prepared in Poland and the measurements were performed in the laboratory in Germany.

2. Materials and apparatus

In this paper we report our study on fluorescence lifetimes of one type of fuel-oil, which previously has been contacted with the natural seawater (salinity 8 PSU) collected from the Gulf of Gdańsk (Southern Baltic Sea). A sample of oil (1 ml) were mechanically dispersed in 1 litter of water, and after one week taken from the bottom of the bottle to extract it with the hexane. Obtained in this way the sample of hexane-solution of oil were analyzed in device constructed in the Bremerhaven University of Applied Sciences for marine environment uses (Fig. 1).
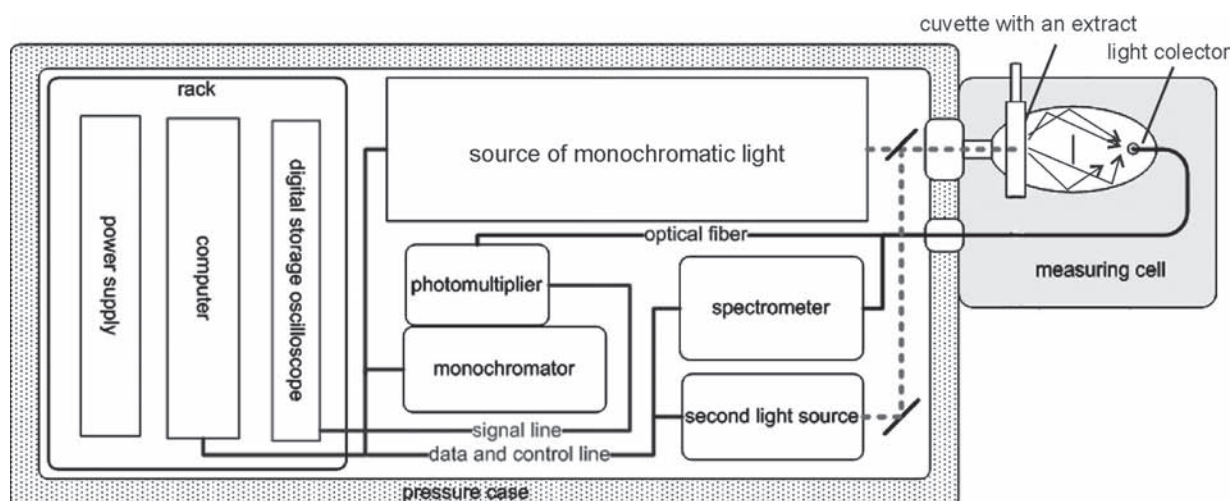

Fig. 1. Scheme of the measure apparatus "subLIF"[6]

At the present this device is improved to use directly in marine environment for investigation and monitoring of marine biological processes, but is well-suited for laboratory testing, including testing of petroleum in sea water [7]. It is expected that eventually will be able to set the fluorescence spectra and fluorescence lifetimes not only in the hexane-extract, but directly in the water column of the sea in addition in a continuous mode.

3. Results and discussion

The TRF method has been used to determine the fluorescence lifetime of fuel-oil sample. The curves of fluorescence decay were measured for four excitation wavelengths (360, 375, 435 and 490 nm). Digital results of measurements, that is intensity of fluorescence emission as the function of a time were processed for lifetime detect. After applying the results on the logarithmic plot there were proved that the fluorescence decay runs in biexponential way. It is evidenced by straight (dotted) lines in Fig. 2. Slopes of those lines are inversed lifetimes of two dominant fluorophores in investigated oil. Therefore two values of lifetime were assigned for each excitation wavelength. For example for excitation of 360 nm life times are respectively 5.72 ns and 38.3 ns.
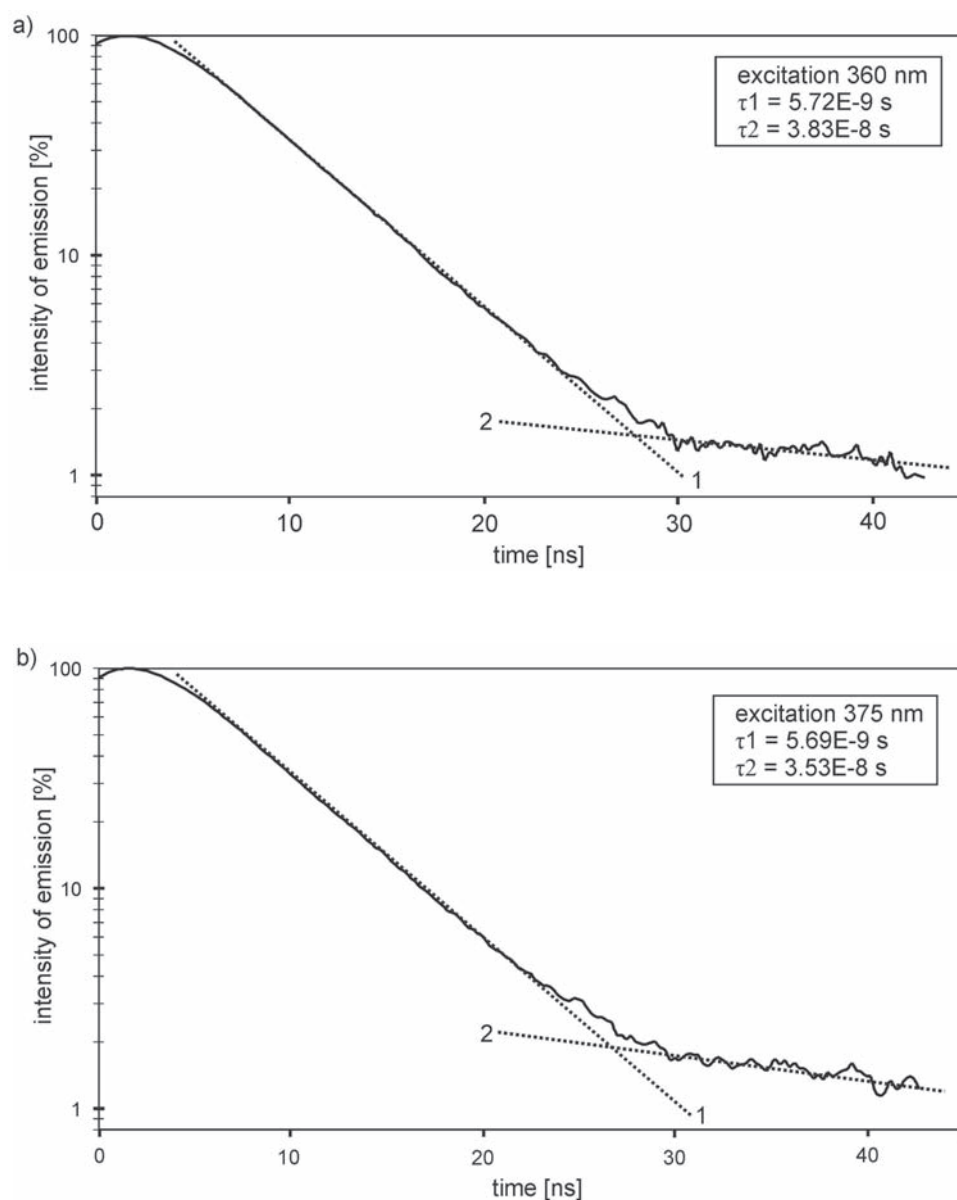
Fig. 2ab. Fluorescence decay curves of exemplary oil dissolved in hexane for excitation by light of 360 nm (a) and 375 nm (b)

In general, lifetimes increase with decreasing excitation wavelength (Fig. 3), with one exception at excitation of 435 nm. The nature of various lifetimes at various excitation wavelengths for hydrocarbons is difficult to determine at this stage of research. In any case, a set of fluorescence decay times for different excitation wavelength is a kind of sign for the type of oil. Much more about the ability to differentiate between the types of oil you will be able to say after addition of measurements of other types of oils. In any case, at this point one can clearly confirm the presence of fluorescence. In conjunction with the possibility to assign the fluorescence lifetime to the type of oil offers the prospect of developing a number of studies. We will continue this trend of investigations in our future work.

It is estimated, that if the exploitation of the vessel engine rooms is considered, studies on relationship between the fluorescence life time of oils and their physicochemical parameters as well as the degree of lubricating oil's wear should be performed. Considering the protection of marine environment it will be necessary to study relationships between the fluorescence lifetime and the type of oil and the degree of oil degradation.
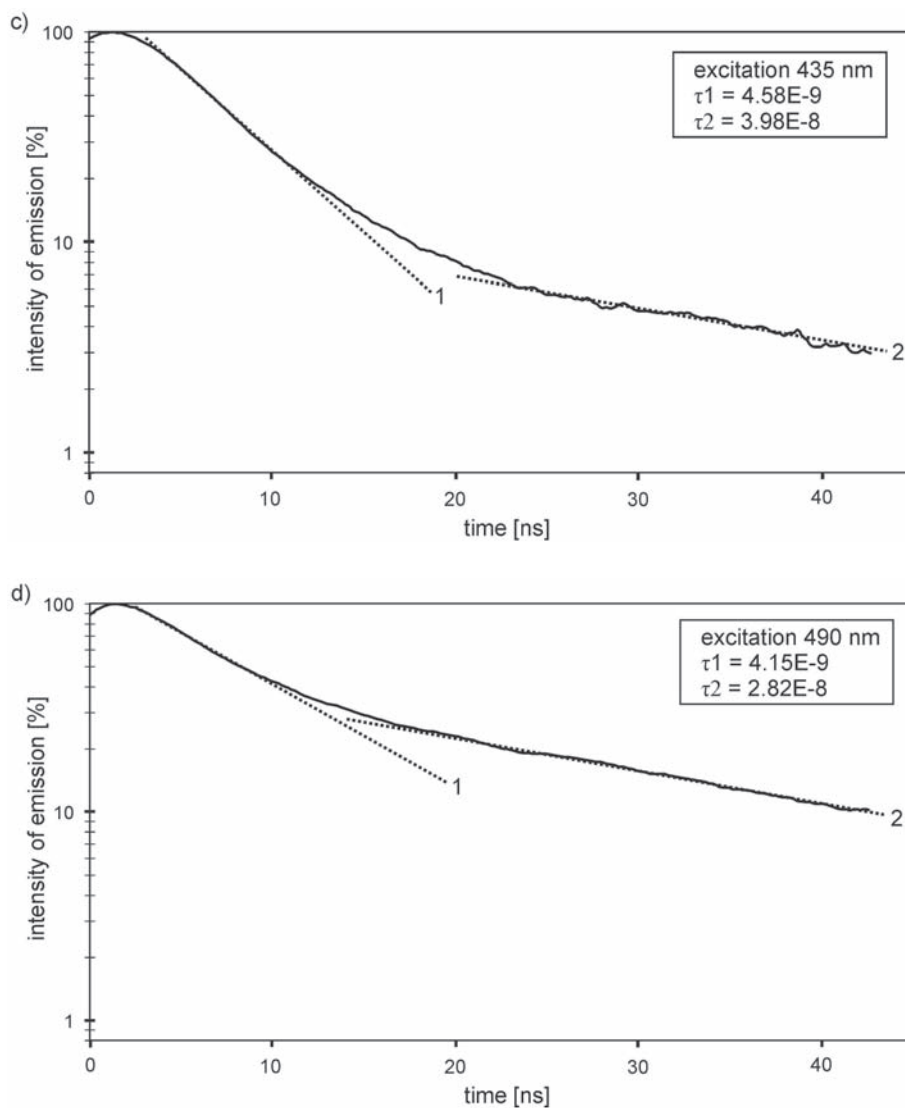
Fig. 2cd. Fluorescence decay curves of exemplary oil (the same like in Fig. 1ab) dissolved in hexane for excitation by light of 439 nm (c) and 490 nm (d)
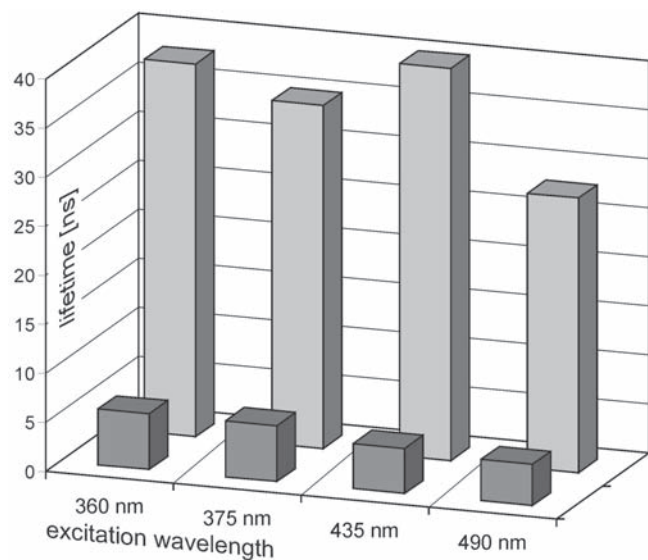

Fig. 3. Fluorescence lifetimes for various excitation wavelengths

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