Influence of oil-in-water emulsions on fluorescence properties as observed by excitation-emission spectra

E. Baszanowska
eba@am.gdynia.pl
Department of Physics, Gdynia Maritime University, Morska 81-87, 81-225, Gdynia, Poland

O. Zielinski
University of Oldenburg, Institute for Chemistry and Biology of the Marine Environment, Oldenburg, 26-111, Germany

Z. Otremba
Department of Physics, Gdynia Maritime University, Morska 81-87, 81-225, Gdynia, Poland

H. Toczek
Department of Physics, Gdynia Maritime University, Morska 81-87, 81-225, Gdynia, Poland

Oil poses a major threat to marine ecosystems. This work describes a set of studies focused on introducing an efficient method for the identification of oil in the form of oil emulsions through fluorescence spectra analyses. Hence the concept of classification of oil pollution in seawater based on fluorescence spectroscopy using a high sensitive fluorimeter [1] suitable for laboratory and *in situ* measurements is introduced. We consider that this approach, in the future, will make it possible to collect specific fluorescence information allowing us to build a base of the oil standards.

Here we examined excitation-emission fluorescence spectra (EEMs) of water containing oil-in-water emulsion prepared artificially under laboratory conditions. Water polluted with oil-in-water emulsion was studied with the objective to estimate differences in three-dimensional fluorescence spectra. Studies included various types of oils and oil concentrations. Essential differences in fluorescence spectra for various oils are indicated.
[DOI: http://dx.doi.org/10.2971/jeos.2013.13069]

1 INTRODUCTION

Main prerequisites for the protection of marine ecosystems are to track changes and occurrence of potential hazards as well as the prevention of contamination by detecting contaminants occurring in various forms [2]. Given the increase of maritime transport over the last decades there is a significant chance and historic evidence for oil leakages [3]. These oil pollutions may occur in various forms such as oil spills on the surface or in an emulsified form eventually floating below the water surface. The latter one constitutes a dangerous situation for natural marine environment since it is difficult to detect and identify. Despite the fact that the chemical composition of petroleum substances it is well known, a sensitive method for the *in situ* measurement oil emulsions content is still needed. The key in this case will be to find an adequate and field applicable method of measurement, allowing for quick detection of oil pollution in this special form of oil-in-water emulsion. Fluorescence spectroscopy allows for ample opportunity to determine the origin of oil [4]. Crude-oils and most of their derivatives such as fuels or lubricating oils possess complex structures consisting of a composite mixture of hydrocarbons of various molecular weights and other liquid organic compounds. Moreover, crude oils as well as products of petroleum refining contain specific chemical compounds showing the ability to fluoresce, which exhibits itself in the shape of their fluorescence spectra. On the other hand some petroleum compounds show the ability to absorb light. In addition to that, natural surface waters show characteristic absorption and fluorescence signatures in relation to various dissolved substances and to the composition of phytoplankton. Contamination by oil substances may disturb or superimpose these natural fluorescence spectra and hamper discrimination of the individual components. This phenomenon is valid for both oceanological and limnological investigations.

A possible method of oil pollution detection and characterisation in the aquatic environment is analysing the shapes of fluorescence spectra. One of the first cases of using spectral fluorimetry for the characterisation of hydrocarbon substances in seawater was reported by Frank in 1978 [4] and further for example by Patsayeva [5] or Poryvkina et al. [6]. Recently, a similar approach utilising total fluorescence was considered by Baszanowska and Otremba [7].

In a wider range the problem of detection and identification of oil pollution based on fluorescence spectroscopic method was considered in the paper by Dolenko et al. [8]. Their results, determined for small concentration of oil in the order of a few micrograms per kilogram in seawater, show that fluorescence intensity is nearly undetectable in natural conditions. They highlight that one particularly important task is to solve the problem of separating the small amount of oil fluorescence from the humic substance (coloured dissolved organic matter denoted as CDOM) background in the spectrum.

Oil spills detection in seawater was also performed based on laser fluorescence (LIDAR fluorosensor) [9]–[11]. The fluorescence LIDAR technique is a remote sensing technique that enables to analyse a remote object without direct contact with the object itself. This technique is non-destructive and essentially consists in analysing from a distance the light emitted (fluorescence) by the object when the latter is illuminated with a light pulse of a proper colour. Attention is required to considerable technical problems concerning *in situ* measurements, such as the distance of the laser to the water as well as the optical influence of water or the fluorescence of CDOM or other organic substances. Karpicz et al. discuss using the new method of oil detection which eliminated above mentioned problems for oil detection.

Taking into account approaches presented in literature, based on various fluorescence method of oil pollutant detection, it should be pointed that is particularly important to find an effective tool of oil-in-water detection aiming at the protection of the natural marine environment. Fluorescence methods as presented in this paper can be highly relevant, since fluorimeter are applicable both for *in situ* and laboratory measurements. First results presented in this paper indicate the possibility of using these devices as a tool for the identification of oil pollution in the form of oil emulsions. Furthermore, it should be highlight that oil spills in emulsion form, especially for low concentrations of oil, will probably be impossible to detect, utilising airborne and satellite detection approaches [12]–[14].

2 MATERIAL AND METHOD

Three types of oil (crude oil, lubricate oil and fuel oil) were used to prepare oil emulsions in demineralized water. To prepare oil-in-water emulsion samples five various oils belonging to *Petrobaltic*, *Romaskino*, lubricate oils *Cyliten* and *Marinol* and fuel oil *Diesel*, were applied. A high-speed stirrer was used for oil emulsification in the water. Obtained oil-water system was one week seasoned in order to obtain stability of emulsion. For each kind of oil the obtained base oil emulsion samples were further diluted in demineralized water. Using the base for each type of oil, diluting oil emulsion samples in various proportions of oil were prepared. Based on dilution method four individual concentrations for each type of oil were prepared. The relative concentrations of oil emulsion samples in demineralized water were respectively: 1, 0.5, 0.2, 0.1 for each types of oil, whereas the base concentrations for each type of oil was different. The concentration of oil for *Petrobaltic*, *Romaskino*, *Diesel*, *Marinol*, *Cyliten* were respectively: 56 ppm, 63 ppm, 318 ppm, 432 ppm and 119 ppm.

Spectrofluorimeter Aqalog Horiba was used to register three-dimensional excitation-emission spectra (EEMs) of fluorescence of oil-in-water emulsion samples with various oil concentration in demineralized water for various excitation wavelengths. Simultaneously to the excitation-emission spectra absorbance and transmittance of oil emulsion samples was registered.

Absorbance spectral information can be used to immedi-

ately correct the fluorescence spectrum involving both the excitation light absorption and fluorescence reabsorption in the sample cuvette. Absorbance data provide additional- and often vital-concentration-dependent information on non-fluorescent compounds in the water sample [15].

By means of spectrofluorimeter, *Aqualog Horiba*, the fluorescence and absorbance of solutions in a quartz cuvette 1×1 cm have been measured. The following measurement parameters were applied: excitation wavelength from 240 nm to 600 nm with sampling interval 5 nm, emission wavelength from 212,75 nm to 622,97 nm with sampling interval 1,623 nm, excitation slit 5 nm, emission slit 5 nm, integral time 1 s. The fluorimeter consist of a polychromator and a CCD camera. This technical solution allows to perform fluorescence measurements in a relatively short time (about from 2 to 5 minutes for a full EEMs). Measurement time depends on the specific settings, suitable for examined samples and the measurement time significantly increases for fluorescence measuring of the temperature dependence. For absorbance spectra measurement specific parameters were applied: excitation wavelength from 240 nm to 600 nm with sampling interval 5 nm, excitation slit 5 nm and integral time 1 ns. A continuous source of light shines onto an excitation monochromator which selects a band of wavelengths. Absorbance measurements were performed from the longest to the lowest excitation wavelength firstly for reference sample (demineralised water) and next for oil-in-water sample. To measure absorbance, light is shone into the sample, and detector measured signal diminishing into the sample.

One additional advantages of this spectrofluorimeter is the possibility to scan the excitation and absorbance wavelengths from low to high energy. It allows to reduce the exposure of the sample to UV and hence photochemical transformations [15]. The AquaLog software package can remove Raman and Rayleigh scattering. Subtraction of the blank EEMs from the sample EEMs effectively removes the Raman scatter line. Applying a Rayleigh-masking algorithm based on the excitation and emission spectral bandwidth nullifies the signal intensities for both the first- and second-order Rayleigh lines [15]. Taking into account above mentioned the corrections for Raman and Rayleigh scattering for the EEMs measurements were performed.

3 RESULTS AND DISCUSSION

To obtain information about the fluorescence properties of oil-in-water emulsion samples containing various concentrations were measured by assessment of their EEMs spectra at a temperature of 20°C. The specific fluorescence properties manifest themself in the shape of total fluorescence spectra.

Figure 1 presents determined fluorescence spectra for various oils and oil concentrations respectively for considered crude oil- *Petrobaltic* (extracted from the Baltic Sea bottom), *Romaskino* (extracted at Romashkino field in Tatarstan, Russia), lubricate oils *Cyliten* and *Marinol* and fuel oil *Diesel*. For each kind of oil type we observe an "evolution" of the shape of spectrum when the concentration of oil is increased.
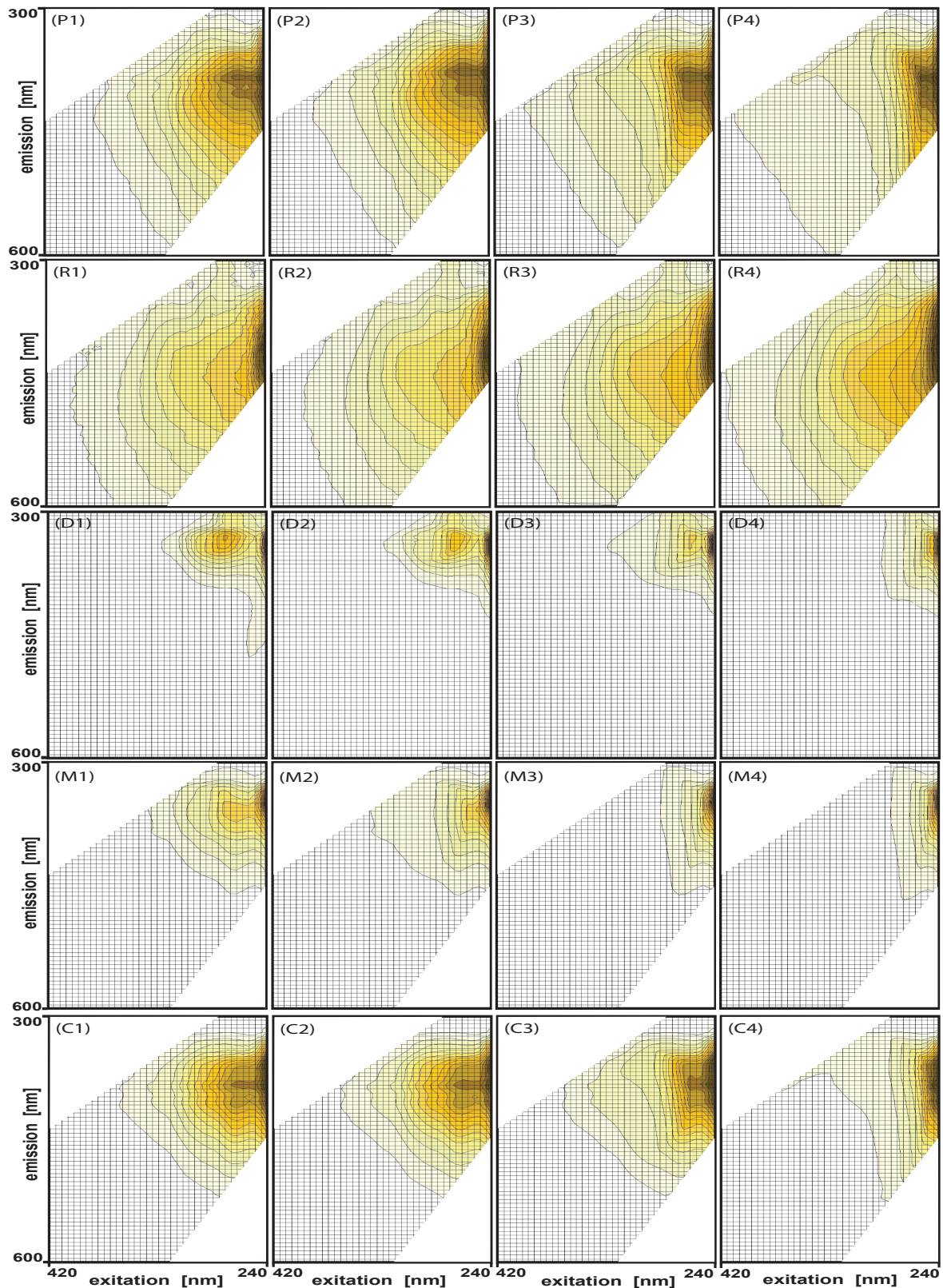
FIG. 1 Total fluorescence spectra of oil-in-water emulsion for *Petrobaltic* (P), *Romaszkino* (R), *Diesel* (D), *Marinol* (M.), *Cyliten* (C) for various oil relative concentrations: 0.1 (1), 0.2 (2), 0.5 (3), 1 (4).

The problem of dependence of the shape of 3D (EEMs) spectra on the concentration of oil was studied by utilizing the similarity ratio s_{ab} between the spectra as given by formula (1). In this formula indexes "ij" refer to relative columns and rows in tables representing spectra "a" and "b", the quantities w_{ij}^a, w_{ij}^b refer respectively to normalised elements of EEM matrix of reference emulsion "a" and compared emulsion "b". Those comparisons were performed after spectra normalization related to the maximum of fluorescence.

$$s_{ab} = 1 - \frac{\sum\limits_{ij} \mathrm{abs}(w_{ij}^a - w_{ij}^b)}{\sum\limits_{ij} w_{ij}^a}, \qquad (1)$$

The similarity ratio of the spectrum for lowest concentrations of oils in relation to other concentrations is shown in Figure 2: it decreases when the oil concentration increases. However, the similarity within the different concentrations, but for the same oil, is always greater than the similarity between the spectra of different oil emulsions. This phenomenon is advantageous if the recognition of the type of oil dispersed in the water is considered.
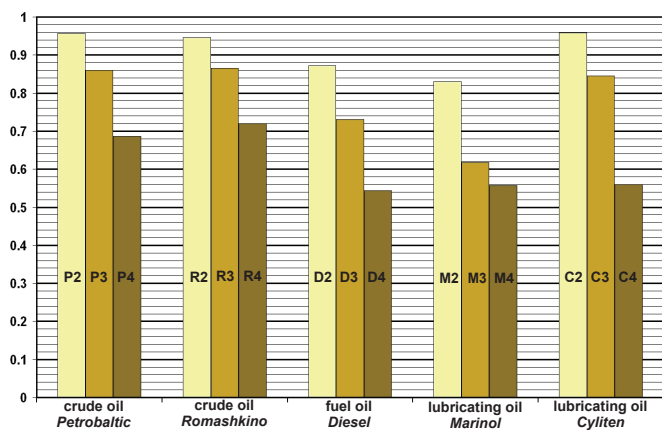
In order to obtain the data for the light absorption influence for the examined oil-in-water emulsion samples, the curves of absorption spectra were registered simultaneously to the excitation-emission spectra using the same spectrofluorimeter. Taking into account the Lambert-Beer law the absorbance values *Abs* at a given wavelength λ are calculated as follows [15]:

$$Abs = -log(T), \qquad (2)$$

where the transmission *T* is given as a formula (3):

$$T = \frac{I}{I_0}, \qquad (3)$$

and the *I* and I_o describe respectively the intensity of fluorescence for blank sample (demineralised water) and oil-in-water emulsion sample.

Figure 3 presents registered absorption spectra for various kinds of oils and oil concentrations respectively for considered crude oil extracted from the Baltic bottom - *Petrobaltic*, *Romaskino*, lubricate oils *Cyliten* and *Marinol* and fuel oil *Diesel*.

FIG. 2 Decrease of similarity degree of spectra for various oil concentrations (analogously like in Figure 1) related to the lowest concentration.
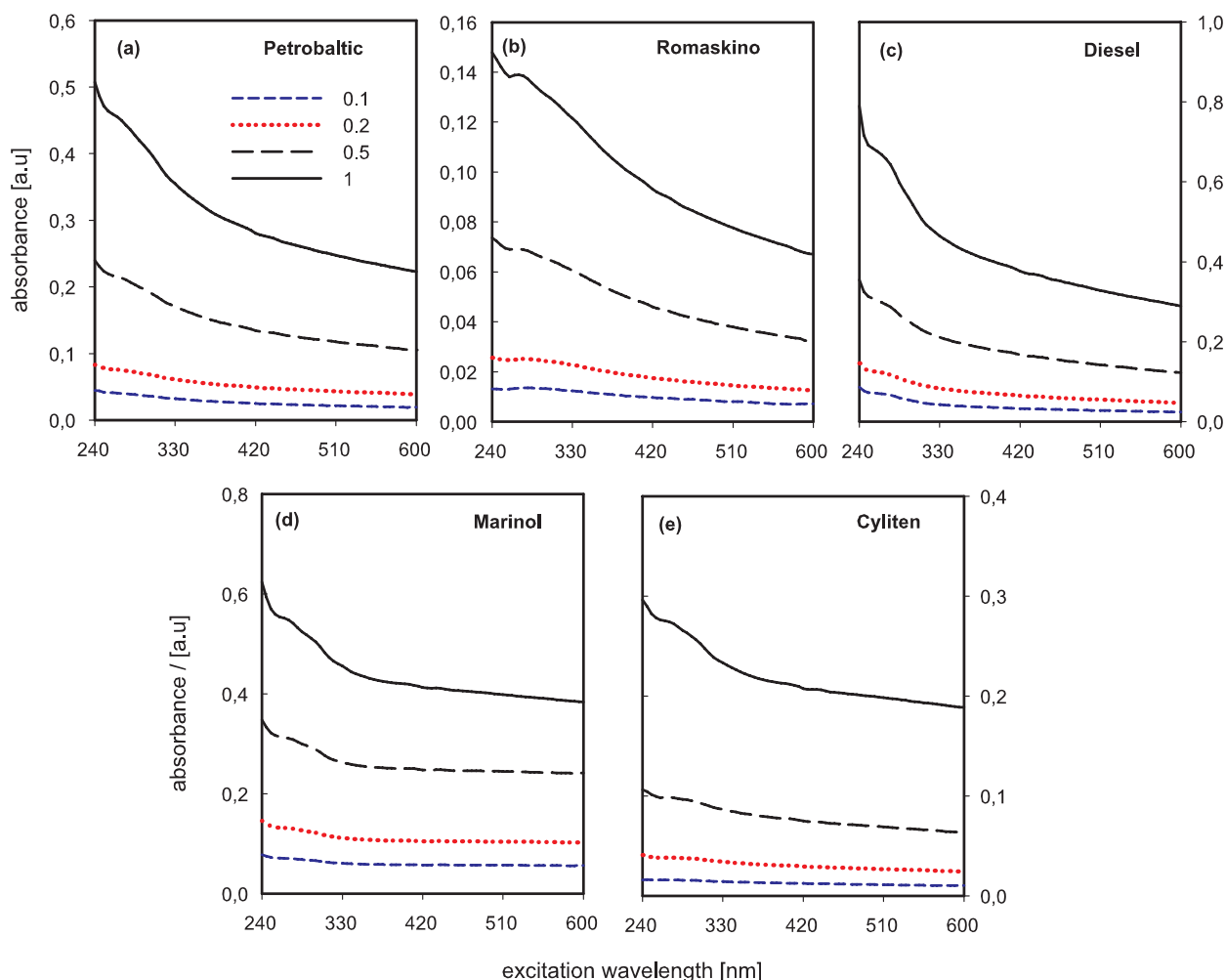
FIG. 3 Absorption spectra of oil-in-water emulsion for *Petrobaltic* (a), *Romaskino* (b), *Diesel* (c), *Marinol* (d), *Cyliten* (e) for various oil relative concentrations marked respectively: black solid line for 1, black dashed line for 0.5, read dotted line for 0.2 and blue dashed line for 0.1.

J. Europ. Opt. Soc. Rap. Public. **8**, 13069 (2013)

E. Baszanowska, *et al.*

Presented results show that absorbance depends on the kind of oil. Thinking into account the concentration of oil in the oil-in-water emulsion for considered kinds of oil the highest value were detected for the crude oil *Petrobaltic*. However, unfortunately in the absorbance spectra for various concentrations of oil there are no observed regular similarities (determined analogously like for EEMs).

4 CONCLUSIONS AND OUTLOOK

The work presented shows that water polluted with oil emulsion (for example as discharges from vessels, bottom seepages, river inflow) fluoresces in a wide range of wavelengths where the shape of EEMs spectra depends on the type of oil. As these studies were performed under laboratory conditions with demineralised water, it is clear that the oil recognition in natural waters polluted with oil emulsions by comparing the fluorescence spectra requires further analyses to choose an optimal EEM area. Taking into account the presented results, it can be concluded that the fluorescence results on the presence of oil pollution in the specify form of an oil emulsion in natural seawater will depend on, the detection and discrimination of other optically active components as they might interfere with the spectral features observed.

In the future activities are envisaged that cover laboratory measurements of fluorescence spectra of oil emulsions and their temperature dependence and in the next step we consider comparing EEMs of natural seawaters free of oil with artificially contaminated ones. This will lead to improved classification of oil polluted water bodies i.e. harbour waters or near the outlet of storm waters collectors. An important aim of these studies is to establish a method of differentiation of fluorescence signatures observed from natural seawater constituents against anthropogenic substances as, i.e., dispersed oil. This will help to attempt both detection and identification of oil substances in the marine environment as well as potential disturbances introduced by pollutions in the context of water masses studies through spectrofluorimetric methods.

5 ACKNOWLEDGEMENTS

References

[1] O. Zielinski, "Rediscovering 'Sky-Blue Fluorescence'," Das Forschungsmagazin der Universität Oldenburg **55**, 26–31 (2012).

[2] O. Zielinski, J. A. Busch, A. D. Cembella, K. L. Daly, J. Engelbrektsson, A. K. Hannides, and H. Schmidt, "Detecting marine hazardous substances and organisms: sensors for pollutants, toxins and pathogens," Ocean Sci. **5**, 329–349 (2009).

[3] M. Fingas, *The Basics of Oil Spill Cleanup* (CRC Press Taylor & Francis Group, Boca Raton, 2013).

[4] U. Frank, "A review of fluorescence spectroscopic method for oil spill source identification," Toxicol. Environ. Chem. Rev. **2**, 163–185 (1978).

[5] S. Patsayeva, "Fluorescent remote diagnostic of oil pollutions: oil in films and oil dispersed in the water body," EARSeL Adv. Remote Sens. **3**, 170–178 (1995).

[6] L. Poryvkina, S. Babichenko, and O. Davydova, "SFS characterisation of oil pollution in natural water," in *Proceedings to 5th International Conference on Remote Sensing for Marine and Coastal Environments*, 520–524 (Michigan Tech Research Institute, San Diego, 1998).

[7] E. Baszanowska, and Z. Otremba, "Spectroscopic methods in application to oil pollution detection in the sea," J. Kones **19**, 15–20 (2012).

[8] T. A. Dolenko, V. V. Fadeev, I. V. Gerdova, S. A. Dolenko, and R. Reuter, "Fluorescence diagnostics of oil pollution in coastal marine waters by use of artificial neural networks," Appl. Optics **41**, 5155–5166 (2002).

[9] R. Karpicz, A. Dementjev, Z. Kuprionis, S. Pakalnis, R. Westphal, R. Reuter and V. Gulbinas, "Oil spill fluorosensing lidar for inclined onshore or shipboard operation," Appl. Optics **45**, 6620–6625 (2006).

[10] J. Vasilescu, L. Marmureanu, E. Carstea, and C. P. Cristescu, "Oil spills detection from fluorescence lidar measurements," U. P. B. Sci. Bull., Series A **72**, 149–154 (2010).

[11] A. G. Abroskin, S. E. Nol'de, V. V. Fadeev, and V. V. Chubarov, "Laser fluorimetry determination of emulsified-dissolved oil in water," Sov. Phys. Dokl. **33**, 215–217 (1988).

[12] H. Visser, "Teledetection of the thickness of oil films on polluted water based on the oil fluorescence properties," Appl. Optics **18**, 1746–1749 (1979).

[13] O. Zielinski, "Airborne pollution surveillance using multi-sensor systems," Sea Technol. **44**, No. 10, 28–32 (2003).

[14] O. Zielinski, T. Hengstermann, and N. Robbe, "Detection of oil spills by airborne sensors," in *Marine Surface Films*, M. Gade, H. Hühnerfuss, and G. M. Korenowski, eds., 255–271 (Springer-Verlag, Berlin, 2006).

[15] *Operation manual, Aqualog Horiba*, rev. A (Horiba Scientific, 2011).