

## FLUORESCENCE SPECTRA OF OIL AFTER IT CONTACTS WITH AQUATIC ENVIRONMENT

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### **Abstract**

*The main task for natural marine environment protection is to prevent the inflow of various contaminants including oil substances and the real challenge is the ability to rapidly detect these pollutants. Moreover important is to find the source or the maker of the oil spill. In this paper, we consider fundamental physical aspects in the area of possibility of monitoring the natural marine ecosystem based on fluorescence spectroscopy. We utilize the fluorescence ability of numerous oil components – mainly polycyclic hydrocarbons. The paper concerns the spectrofluorimetric characterization of oils have been in use during exploitation of the marine fleet, i.e. lubricate oil, fuels, transformer and hydraulic oils as well as crude oils or their residues. Every kind of oil has a chance to enter the marine environment, especially in a case of ship emergency or after collision with other vessel or shoreline structure as well as when ship enters the stranding. After discharge of oil, some of oil components are dissolved in the water, bacteria or photochemical reactions, which results in transformation of composition of oil, degrade some.*

*Fluorescence spectrometer Perkin Elmer LS55 was applied to obtain the fluorescence spectra using different excitation wavelength in the range from 240 nm to 500 nm. We discuss the changes of the shapes of excitation-emission spectra (EEMs) of various types of oil and the EEMs spectra after contact of oil with seawater as an oil-in-water emulsion, which is the most frequent form of oil in the water column. Significant changes in the shape of spectra and displacement of the peaks are observed.*

**Keywords:** *oil pollution, fluorescence spectroscopy, excitation-emission spectra, seawater, environment protection*

### **1. Introduction**

Appearances of oil substances in the sea environment are connected with well-developed marine transport – greatest of spillages are registered along transportation routes [5]. Within the broad problem how to reduce the negative environmental impact of oil development of the research methods plays important role – fluorescence phenomena among others.

Fluorescence can be explained basing on the quantum theory. However, in practice can be understood as a phenomenon of emission of photons from defines substance in a specific spectral range, whereas energy of this emission origin from energy of photons previously absorbed. The fluorescence is characterised by the basic parameters such as excitation and emission spectra, fluorescence quantum yield, lifetime and emission anisotropy [6, 7].

Fluorescence is a phenomenon characteristic for substances containing organic compounds,

particularly aromatic hydrocarbons. Oils are highly complex mixtures of chemical components consisted of aliphatic hydrocarbons, as well as mono- or polycyclic aromatic compounds, which are responsible for the occurrence of fluorescence phenomenon. For this reason, fluorescence spectroscopy is really sensitive method, which allows detection and identification of oil [4, 12].

A lot of organic natural constituents of the seawater exhibit absorption as well as emission properties, which are useful for investigation complex processes in the marine environment. They manifest itself in the shape of the fluorescence spectra. It should be noticed that analyses of the fluorescence spectra of various natural components of seawater, both *in situ* and in laboratory, enables the quantity of various organic components of seawater determination. It allows monitoring variations of natural organic components of seawater as well as human made organic components entering marine environment [1, 2, 10].

The main objective for the prevention of the natural marine ecosystems bases on quantitative determination of natural seawater components. For example, thanks to fluorescence, amount of efficiently fluorescing chlorophyll “a” can be applied as the indicator of phytoplankton in the seawater [11]. So-called Colored Dissolved Organic Matter (CDOM), which comes from decomposition of plants and animals products due to bacterial activity, is also determined by fluorescence spectrum analysis [8].

The impact of oil on the fluorescence spectra of the seawater is currently studied by oceanographic institutes [3]. It should be highlight that the presence of oil in the seawater leads to fluorescence intensity decreasing of natural components of seawater [3, 9]. In this paper, we consider the excitation-emission spectra (also known as Excitation-Emission Matrices, EEMs) of oil and oil-in-water emulsion. The main interest is focused to changes of the shape of fluorescence spectra after contact of oil with the water environment.

## 2. Materials and methods

Three types of oils were used, namely: crude oil *Petrobaltic* – extracted from the Baltic Sea in the Polish Exclusive Economic Zone and two crude oil derivatives – *hydraulic oil* and *transformer oil*. In the first step, solutions of those oils in the *n*-hexane were prepared. Afterwards samples of extracts from the oil-in-water emulsion for each type of oils were prepared. Oil-in-water emulsion were made by mechanic dispersion (by high-speed stirrer) of oil in the free of biological substances water in appropriate proportion: 1 cm<sup>3</sup> of oil per 1 dm<sup>3</sup> of seawater. Next, the oils emulsion samples were stored in the 1-litter bottles in darkness for a week and finally sucked from the bottom of the bottle for extraction into *n*-hexane.

The spectrofluorimeter *Perkin Elmer LS55* was applied for determine the excitation-emission spectra for oils solutions in *n*-hexane as well as *n*-hexane extracts from those oil-in-water emulsions. The apparatus were programmed to excitation wavelengths from 240 nm to 500 nm, emission wavelengths from 300 nm to 790 nm and sampling interval for excitation – 5 nm and for emission – 1 nm.

## 3. Results and discussion

The EEMs for both solution of oil and extract from oil-in-water emulsion were normalized to the maximum. The example of such transformed EEMs for *Petrobaltic* crude oil in 3D plane presents Fig. 1. Axis of 3D plane describe respectively: axis *X* – excitation wavelengths, axis *Y* – emission wavelengths and axis *Z* – intensity of fluorescence. In the top of Fig. 1 there is so-called the surface contour visualisation of 3D plane, which is the second possibility of data presentation in 2D plane. In this case of date presentation axis of plane describe excitation and emission wavelengths for contours combining all points for the same fluorescence intensity.

Excitation-emission spectra for crude oil (*Petrobaltic*) and exemplary oils use in marine transport (*Hydraulic oil* and *Transformer oil*) and for extracts from oil-in-water samples in water

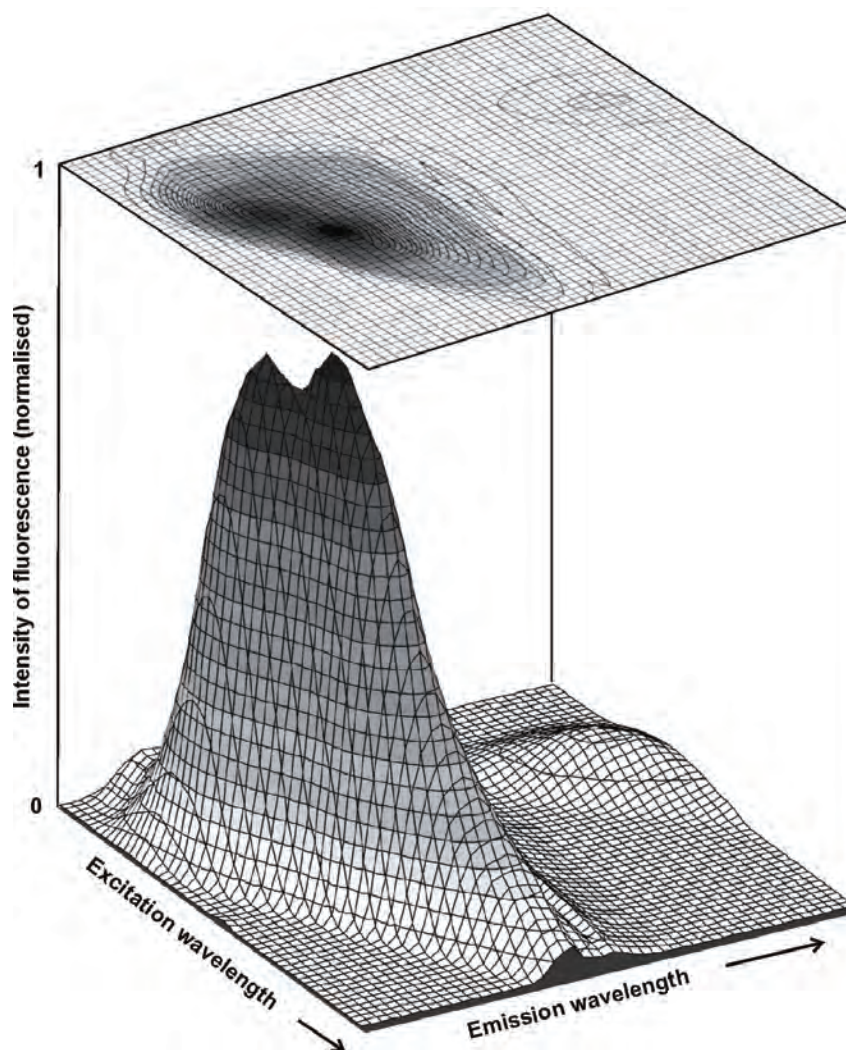


Fig. 1. Excitation-emission spectrum of oil (main picture) and the surface-contour-visualization (on the top)

(for all types of oil) were presented in the Fig. 2. In the shape of total fluorescence spectra there information about the specific fluorescence properties is conveyed. For each kind of oil, an “evolution” of the shape of fluorescence spectrum after contact of oil with water is observed. It was presented in Fig. 2(b), 2(d) and 2(f) for each considered oils. Fig. 2 shows the total fluorescence spectra with characteristic emission maxima for specific excitation wavelengths typical for each type of oil. The examples of emission spectra for different excitation wavelength correspond to the maximum of emissions of considered oils and their extracts (shown in Fig. 3). These fluorescence spectra characterise the presence of emission maximum typical for each types of oil.

It should be noticed that the recorded fluorescence of organic molecules in the water is characterized by a broad spectrum of excitation and emission. This is a consequence of the strong interaction with the surrounding water molecules [6]. Furthermore, oil after contact with water is deprived from hydrophilic components, therefore composition of oil is transformed in define scale which also causes modifications of fluorescence spectra.

Taking into account above findings, it should be emphasise that in the case of contact of oil with natural seawater probably will lead to the changes in the shape of fluorescence spectra in relation to measure for pure oil or oil-in-water emulsion after contact with demineralised water. It will be the consequence of interaction between natural compounds of seawater such as the dissolved organic matter, the presence of dispersants or salinity [3]. Therefore, results presented in this paper should be threaten as signal only and indicating the line of development of investigations in the future.



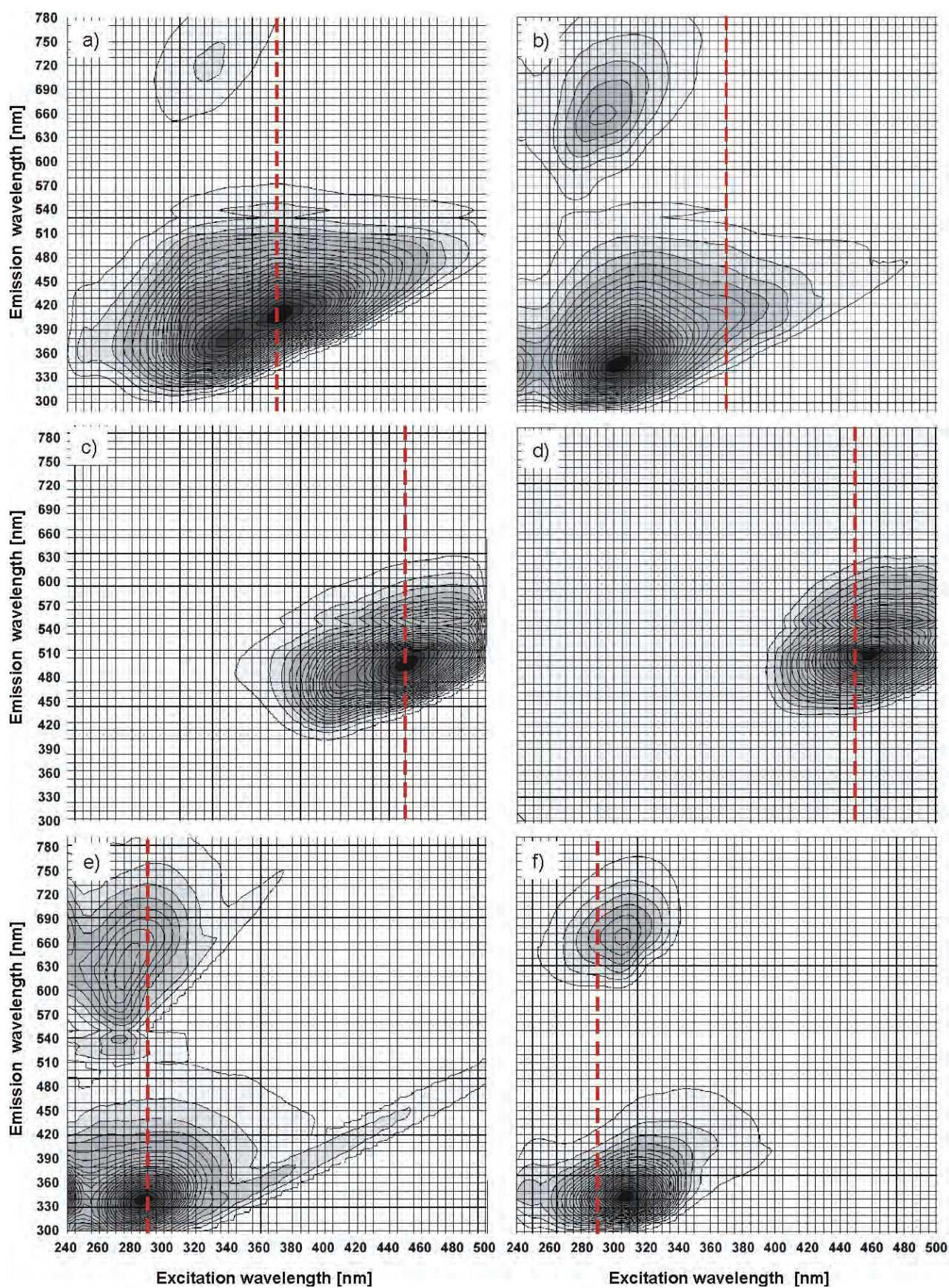


Fig. 2. Excitation-emission spectra for oils: a) Petrobaltic, c) Hydraulic, e) Transformer and their oil-in-water emulsion extracts: b) Petrobaltic extract, d) Hydraulic extract, f) Transformer extract. Vertical broken lines indicate cross-sections used for preparation of emission spectra presented in Fig. 3



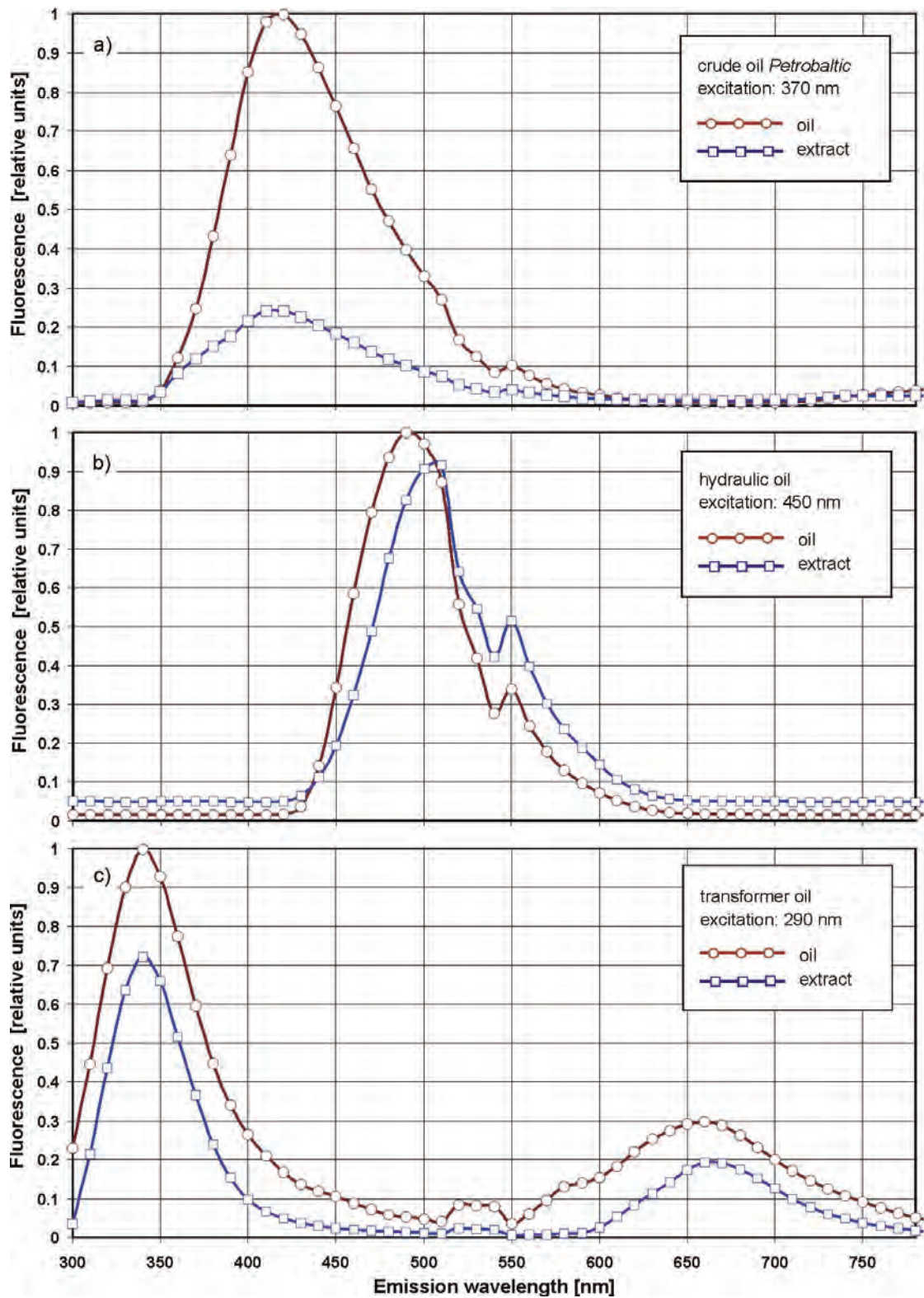


Fig. 3. Emission spectra for various excitation wavelengths for three kinds of oils and their extracts of oil-in-water emulsion

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## References

- [1] Belin, C., Croue, J. P., Lamotte, M., Deguin, A., Legube, B., *Characterization of Natural Organic Matter Using Fluorescence Spectroscopy*, Proceedings, Natural Organic Matter Workshop, Poitiers, France 1997.
- [2] Belin, C., Quéllec, C., Lamotte, M., Ewald, M., *Characterization by Fluorescence of the Dissolved Organic Matter in Natural Water*, Application to Fractions, 1993.
- [3] Drozdowska, V., *Study on Variability of Fluorescence of Surface Marine Waters by the Lidar Techniques* [in Polish], PhD Thesis, Instytut Oceanologii, PAN, Sopot 2005.
- [4] Frank, U., *A Review of Fluorescence Spectroscopic Method for Oil Spill Source Identification*, Toxicological and Env. Chem. Reviews, Vol. 2, pp. 163-185, 1978.
- [5] HELCOM, *Manual on Co-operation in Response to Marine Pollution within the Framework of the Helsinki Convention*, Baltic Marine Environment Protection Commission, Helsinki 2001 (updated 2012).
- [6] Kawski, A., *Fotoluminescencja roztworów*, PWN, 421, 1992.
- [7] Lakowicz, J. R., *Principles of Fluorescence Spectroscopy*, Springer, 1999.
- [8] Otremba, Z., Baszanowska, E., Toczek, H., Rohde, P., *Spectrofluorymetry in Application to Oil-in-Water Emulsion Characterization*, Journal of KONES Powertrain and Transport, Vol. 18, No. 3, pp. 317-321, 2011.
- [9] Reuter, R., Diebel, D., Hengstermann, T., *Oceanographic Laser Remote Sensing: Measurements of Hydrographic Fronts in German Bight and in the Northern Adriatic Sea*, Int. Rem. Sens., Vol. 14, No. 5, pp. 823–848, 1993.
- [10] Schubert, H., Sciewer, U., Tschirner, E., *Fluorescence Characteristics of Cyanobacteria (Bluegreen Algae)*, J. Plankt. Res., Vol. 11, pp. 353-359, 1989.
- [11] Woźniak, B., *Energetyka morskiej fotosyntezy*, habilitation thesis, 1-3, Instytut Oceanologii, PAN, Sopot 1990.
- [12] Zielinski, O., Busch, J. A., Cembella, A. D., Daly, K. L., Engelbrektsson, J., Hannides, A. K., Schmidt, H., *Detecting Marine Hazardous Substances and Organisms: Sensors for Pollutants, Toxins and Pathogens*, Ocean Science, Vol. 5, pp. 329-349, 2009.