SPECTROSCOPIC METHODS IN APPLICATION TO OIL POLLUTION DETECTION IN THE SEA

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Abstract

The escalating maritime transport as well as offshore crude oil exploitation and pipeline transportation leads to the increase of feasibility of the discharge of petroleum substances to the sea environment events. Therefore, it is necessary to rapidly detect of oil pollution to minimize the extent of contamination in the seawater. The aim of this study is to discuss the assumptions of the optical methods using for detection of oil pollution in the seawater. We consider the different approaches of oil-in-water detection using spectral active and passive techniques with emphasis on fluorescence techniques. The intensive development of scientific apparatus and methods in light spectroscopy leads to build various airborne or underwater specialized devices (UV-, IR-scanners, fluorosensors), which allows to detect oil pollution in relatively large areas of the sea. The possibility of measurements of oil pollution in the seawater is particularly important for monitoring, especially in very difficult weather conditions and highly waved sea surface. Such possibilities should be given by devices for in-situ measurements based on time-resolved fluorescence. Such measurements allow obtaining the significant information about presence of oil in really short time. As we show in this study, the wide-range development of fluorescence techniques opens the diagnostic opportunity not only for detection of the oil-in-water content but also for identification the type of oil directly in seawater or even determination of the source of oil pollution.

Keywords: marine transport, oil pollution, spectroscopic methods, fluorescence, time-resolved fluorescence

1. Introduction

There are a lot of biological, chemical and physical phenomena that deliver specific signatures for oil detection in the sea environment. If biological ones are considered a good example is the number of oiled birds found in the seashore which indicates the scale of contamination of define area by oil substances [1, 2]. Chemical methods use combined both gas chromatography and mass spectrometry (GS-MS) to identify the kind of oil or even source of oil polluting define sea area by comparing the spectrum of collected and secured samples with spectra of oil from special set of oil from the whole of the world [3, 4]. Physical methods rely on analysis of light reflected from the surface directly in the environment (using variety of technical equipment) as well as on spectrophotometry and spectrofluorymetry of samples collected in the sea [5]. Physical techniques include radar methods also [6]. In this study we analyze the efficiency of spectroscopic methods in application to detection of oil in the sea environment and identification of a type of oil in laboratory and directly in the sea conditions.

Spectroscopic methods in relation to application for oil detection and identification directly in the sea can be active or passive. Passive methods based on the natural (solar) light leaving the seasurface whereas active methods require artificial source of light.

Among various spectroscopic devices applied to analysis of oil substances in laboratory the most popular are UV-spectrophotometers (ultraviolet range), VIS-spectrofluorymeters (visual range), IR-spectrophotometers (infrared range) and spectrofluorimeters. Spectrofluorymeters based on the phenomenon which is producing of light that is emitted by some of substances including

majority of oils. Spectrofluorimetric spectra in greatest cases take a form of emission spectra, that means that wavelength of excitation is fixed whereas device register spectrum of emitted fluorescence. In physical laboratories are carried out nonoperational (for the present) experiments with phenomenon called time-resolved-fluorescence (TRF). We perform the tests with using the TRF to analyze of sea water to determine participation of various seawater components (including oil substances) in process of fluorescence decay and fluorescence spectra shaping.

2. Marine operational spectral devices

2.1. Visible

Visual and camera observation bases on electromagnetic spectrum (approximately 400 to 700 nm). Oil can manifest throughout the entire visible spectrum, but it depends on variety factors like the weather conditions (the sea surface state, clouds), the elevation of sun, the angle between the plane of incidence of solar radiation and the velocity of wind direction, direction of observance as well as optical properties of sea water in inspected sea region. Generally, in all these cases there is the real probability that oil slick on the sea surface should be observed. There is the largest probability that oil spill will be observed when the observation is carried out from direction of the reflected sunlight. This is due to the fact that oil reflects light two times more than water. A lot of scientific articles present the significant rules of observations oil slick in define situation. Unfortunately there is no universal rules how organize visual observations in potentially oiled area. One thing is currently certain: the most important are the human eyes (of the experienced aerial inspector), whereas technical devices – cameras combined with Global Positioning System (GPS) – provide possibility of documentation of the circumstances of the spillage.

Fig. 1. Image after the process of signals from the satellite Terra (EOS AM-1) equipped by MODIS. There is known that the bright areas show area polluted by crude oil ("Deep Horizon" disaster). There are a lot of oceanic situations (free of oil)) in which similar images appear; source: http://commons.wikimedia.org/wiki/File: Gulf_Oil_Spill_Creeps_Towards_Mississippi_Delta_detail_2010-04-29.jpg

High hopes in the use of visible light applications create projects of using of multispectral digital cameras and scanners. Then digitized signals can be processed before display. There is even a real probability of preparation of the software for automatic interpretation of signals from devices observing the seasurface.

If satelitary monitoring is considered, only the Moderate Resolution Imaging Spectroradiometer (MODIS) can be taken into account, but is still not in operational using for oil spill detect. MODIS-system installed on several satellites merely serves as an additional source of information about the spread of oil in the case of very large spills.

2.2. Infrared

Thick layer of oil (> 150 μm) absorbs solar radiation and reemits some energy in 8 to 14 μm region of the infrared (IR) spectrum. In this manner oil slick is seen as more hot than clean part of the seasurface. Thin films (< 10 μm) are not detected. Layers thinner than 50–150 μm (depending on the type of oil) appears as colder, because of destructive interference of the thermal radiation waves emitted by the water, thereby reducing the amount of thermal radiation emitted [7]. Floating on the seasurface emulsion water-in-oil is not detected by IR devices – such emulsion does not show a temperature differences probably due to the high thermal conductivity [8].

Some devices use differential reflectance of oil and water at 2.5 and 3.1 μm [9]. Thermal cameras (3 to 5 μm) are marginally useful [10]. In general, images created by devices using IR are treated as showing thickness of oil spillage (Fig. 1a).

Aircrafts taking part in marine surveillance are equipped with IR scanners as well by ultraviolet (UV) scanners.

2.3. Ultraviolet

The base of ultraviolet (UV) scanners is given by the high reflectivity of thin oil layers. Pictures from UV scanners show the extension of oil slicks (Fig. 2b), while the Fig. 2a allows to view the same oil spillage in IR spectrum. Both IR and UV are often subjects to much interferences or false signals. There is significant probability that image given in UV shows extension of oil slick. Therefore IR and UV pictures can be numerically combined to produce image showing oiled area.
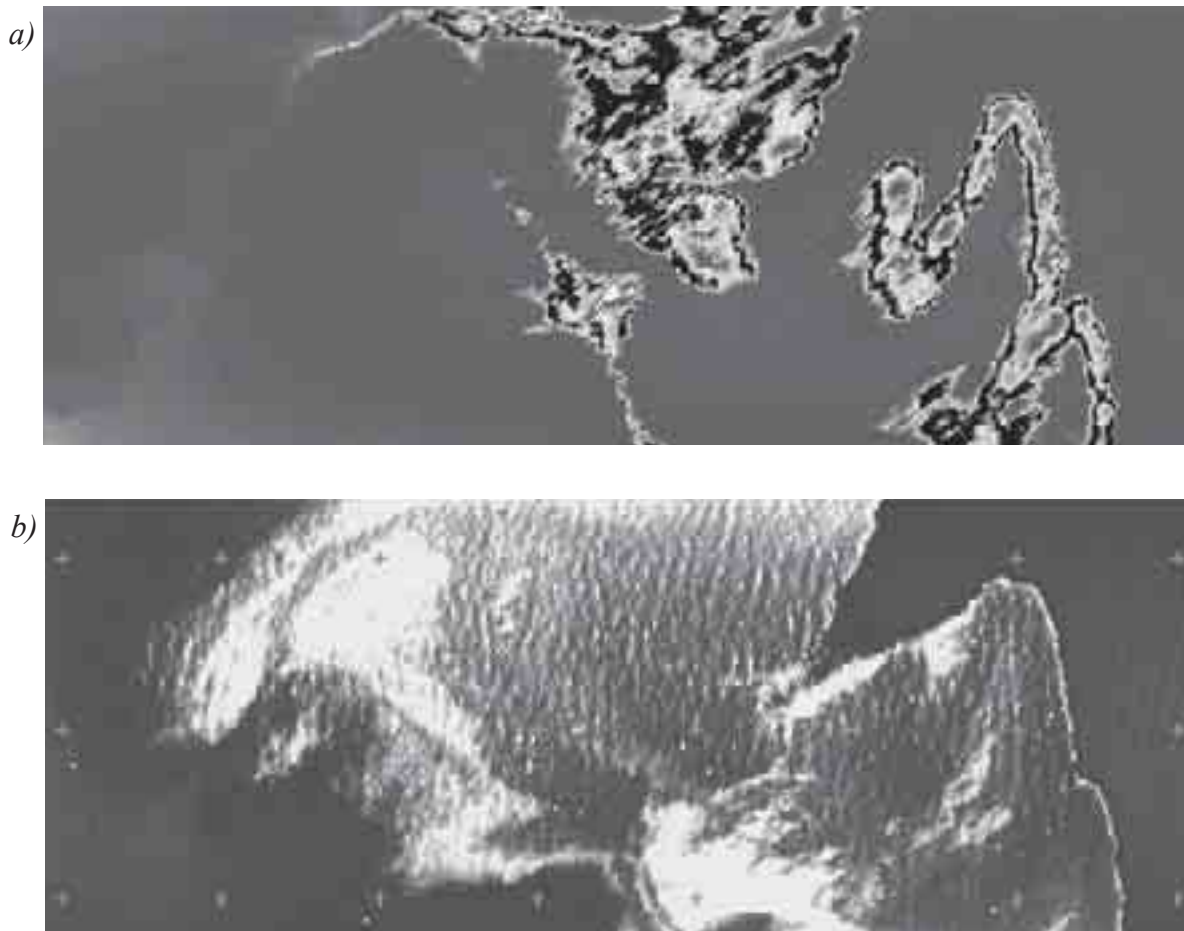
a)

b)

Fig. 2.   Images of the same oil spillage captured at the came time. IR-image shows oil layer thickness (a), UV-image shows extension of oil shin (b); source: OPTIMARE (www.optimare.de) – personal communication

3. Laboratory spectral analyses

Among spectral methods using in laboratory studies various versions of fluorescence are in use for oil detection and a source of this pollution identification. Devices based on fluorescence methods are characterized by high sensitivity and really short measurement time. Spectral analyses of fluorescence spectra allows to register information characteristic for define samples of pure oil or oil taken in marine environment in various forms of oil-water systems (oil-in-water emulsion, water-in-oil emulsion, oil film).

Bellow we shortly report our studies on the specificity of spectrophotometric measurements in relation to oil substances. We present so called "total fluorescence method" based on determination of three dimensional fluorescence spectra in which intensity of fluorescence is depicted as the function of two variables: excitation wavelength and emission wavelength (Ex-Em spectra) and so called time-resolved fluorescence (TRF).

Before fluorescence measurements, oil samples were contacted with sea water and were proper prepared in laboratory. In the first step oil samples were emulsified and then extracted into hexane (the details of sample preparation were presented in paper [11]). An example of total fluorescence spectra and emission spectra for different excitation wavelength of exemplary oil are shown in Fig. 3 and 4 [11]. These fluorescence spectra characterize the different emission spectra with maximum for various excitation wavelengths (maximum of emission spectra are shifted towards to the long-wave excitation). An analysis of these spectra for different types of oils allows not only detecting of oil pollution but moreover to classify the type of oil.
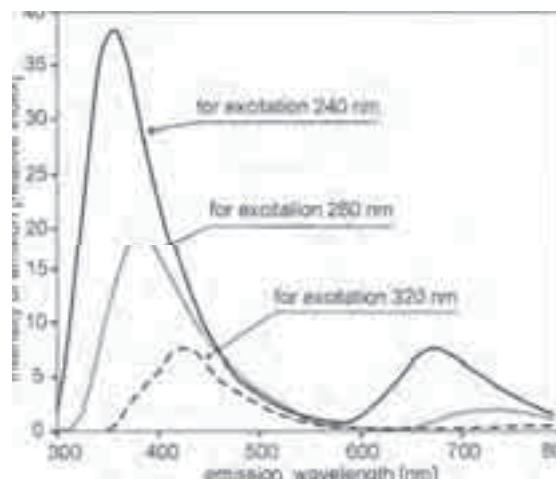

Fig. 3. Emission spectra for various excitation wavelengths for crude oil ("Petrobaltic")
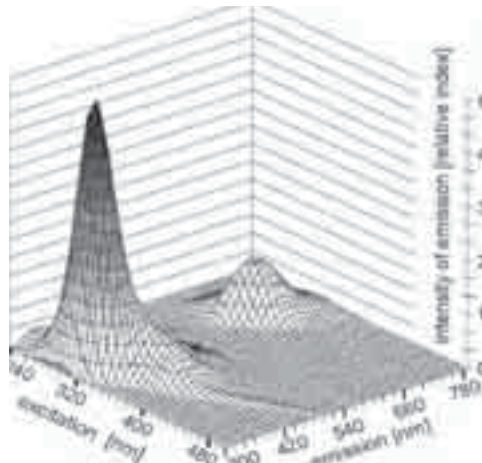

Fig. 4. Total fluorescence spectrum for fuel oil

Recently to monitor of oil pollution observed building of measurements sites or really sensitivity sensors based on time-resolved fluorescence. The principle of this method based on laser induced fluorescence. This method is very promising because allows obtaining in the same time much more information than measurements of total fluorescence spectra such as: fluorescence spectra and the curve of fluorescence decay. There are more significant information include in the curve of fluorescence decay. Various chemical compounds of oil samples influences the shape of curve of fluorescence decay, so the shape includes information about the type of oil or the level of oil degradation. Such information enables concluded of oil spill origin or to determine the time of penetration of oil into the water. Moreover, the curve of fluorescence decay allows determining the lifetime of fluorescence, which is typical for some kind of oil. Fig. 5 shows curve of fluorescence decay for chosen oil using subLIF system based on TRF. The details about this measurements site were presented in papers [12-14]. Also there are methods based on TRF allows to examine the time evolution of emission spectra. Such possibility permits to achieve a piece of information about time changes of oil compounds.
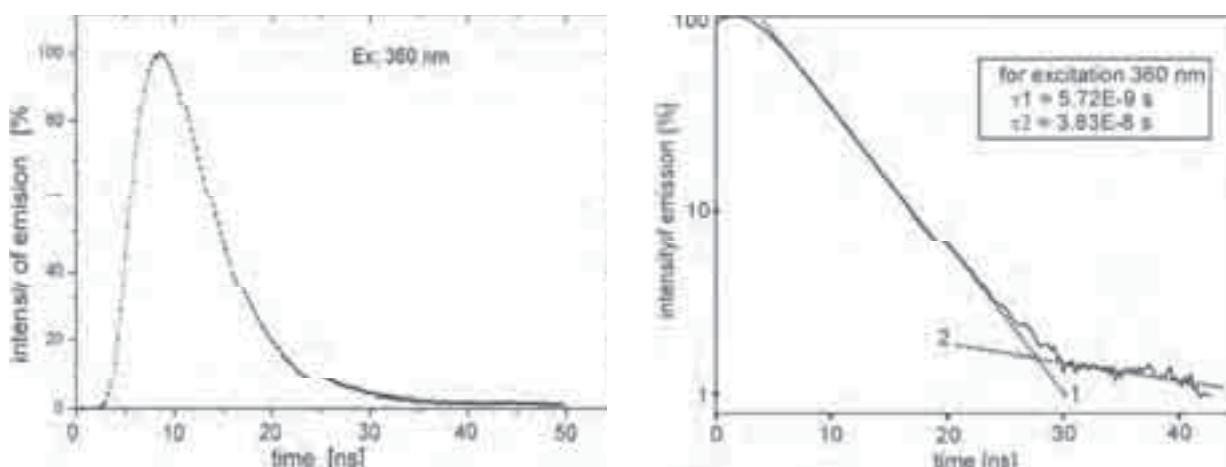

Fig. 5. The curve of fluorescence decay for exemplary oil dissolved in hexane for excitation by light of 360 nm (crude result from the fluorometer - left) and after processing for determine of biexponetial lifetimes τ_1, τ_2 (right) [14]

4. Final remarks

In this paper we have been pointed out relationships between spectral issues and marine transport through the problem of vessel exploitive materials which can impact marine natural environment. Against the background of operational methods and technical equipment using in detection of oil derivatives and oil residues in marine areas investigations on implementation of nonoperational (for this time) chosen spectral methods are described.

As presented results show - there are high hopes that the spectral techniques in marine environment monitoring and in preventing the entry of harmful substances into the sea will be more widely adopted in the future than at present. Especially particular implementations of fluorescence phenomenon - which are time resolved fluorescence and total fluorescence – are of interest. Therefore our studies are concentrated in various ways of preparing of probes (before testing in a spectral apparatus) and technical conditions of measurements, as well as in calculative methods of analyzing of results.

Above described studies are not completed yet – they are continuously curried out in Physics Department with cooperation with physical laboratories in other universities.

References

[1]   Camphuysen, C., Huebeck, M., *Marine oil pollution and beached bird surveys: the development of a sensitive monitoring instrument*, Environmental Pollution, Vol. 112, pp. 443-461, 2001.

[2]   Meissner, W., *Decline in strandings of oiled seabirds in Gdansk Bay, Poland*, Sula, Vol. 6, No. 3, pp. 102-105, 1992.

[3]   NORDTEST 1991, Nordtest Method on Oil Identification, NT CHEM 001 Edition 2, Approved 1991-02, Published by NORDTEST, SF-02101, Finland 1991.

[4]   Dahlmann, G., Timm, D., Averbeck, C., Camphuysen, C., Skov, H., Durinck, J., *Comparative Investigations on Oiled Seabirds and Oiled Beaches in the Netherlands*, Denmark and Germany (1990-93), Mar. Poll. Bull. 28, pp. 305-310, 1994.

[5]   Dolenko, T., Fadeev, V., Gerdova, I., Dolenko, S., Reuter, R., *Fluorescence diagnostics of oil pollution in coastal marine waters by use of artificial neural networks*, Applied Optics Vol. 41, No. 24, pp. 5155-5166, 2002.

[6]   Migliaccio, M., Nunziata, F., Brown, C., Holt, B., Li, X., Pichel, W., Shimada, M., *Polarimetric Synthetic Aperture Radar Utilized to Track Oil Spills*, NASA's Earth Observing System (EOS) Transactions, Vol. 93, No. 16, pp. 161–168, 2012.

[7]   Fingas, M., Brown, C., *Review of oil spill remote sensors*, Seventh International Conference on Remote Sensing for Marine and Coastal Environments, Miami, Florida 20-22 May 2002. *http://www.ecy.wa.gov/programs/spills/response/taskforce/Veridian%20Miami%20Fingas.pdf*

[8]   Wang, Z., Stout, S., Oil Spill Environmental Forensics: Fingerprinting and Source Identification, Elsevier 2007.

[9]   Skou, N., Sorensen, B., Poulson, A., *A New Airborne Dual Frequency Microwave Radiometer for Mapping and Quantifying Mineral Oil on the Sea Surface*, in: Proceedings of the Second Thematic Conference on Remote Sensing for Marine and Coastal Environments, ERIM Conferences, Ann Arbor, pp. II559-II565, Michigan 1994.

[10] Hover, G. L., *Testing of Infrared Sensors for U.S. Coast Guard Oil Spill Response Applications*, in Proceedings of the Second Thematic Conference on Remote Sensing for Marine and Coastal Environments: Needs, Solutions and Applications, ERIM Conferences, Ann Arbor, pp. I47-I58, Michigan 1994.

[11] 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, Warsaw, Poland 2011.

[12] Rohde, P., Busch, J. A., Henkel, R. H., Voss, D., Zielinski, O., *Detection and identification of hydrocarbons in marine waters using time-resolved laser-fluorescence: set-up and first results of a new submersible sensor*, Proceedings OCEANS 2009 – EUROPE, pp. 1-5, Bremen 2009.

[13] Zielinski, O., Dittmar, T., Rohde, P., Ungermann, R., Voss, D., *CDOM and PAHs in the Marine Environment - in situ Sensing with Time Resolved Fluorescence and Liquid Core Waveguides*, Ocean Optics Conference 2010, Anchorage, Alaska 2010.

[14] Baszanowska, E., Otremba, Z., Rohde, P., Zielinski, O., *Adoption of the time resolved fluorescence to oil type identification*, Journal of KONES Powertrain and Transport, Vol. 18, No. 2, pp. 25-29, Warsaw, Poland 2011.