

LASER SPECTROSCOPY OF MINERAL OILS ON THE WATER SURFACE

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ABSTRACT

The spectral properties of oil films ranging from sub-micrometer thickness up to an optically thick layer on the water surface are studied under controlled laboratory conditions. LIDAR systems operating at excitation wavelengths of 308 and 355 nm were used in these experiments. Measurements of the fluorescence lifetime were performed for different mineral oils. It was found that the decay time varies from 1 to 3.5 ns for crude oils, and from 3.5 to 8 ns for refined products. A blue shift of the maximum position of the emission spectra was observed for crude oils under of fluorescence saturation conditions at 355 nm excitation. Since the value of the blue shift depends on the oil type we suggest to use this value for the mineral oil characterisation in remote sensing. The technique of oil spill quantification using the water Raman signal suppression has been improved. The algorithm of film thickness estimation experimentally tested in this work involves the calculation of the amplitude ratio of two spectral components contributing to the water Raman spectrum. Thus, the influence of accidental factors affecting the integral Raman intensity is eliminated.

INTRODUCTION

The detection and quantification of mineral oil spills on water is one of the most important issues of environmental protection. The possibility to measure oil film thickness within micrometer accuracy is enabled by the fact that oil films on water affect aquatic and atmospheric processes such as vaporisation, gas-exchange, photochemical reactions which are altered by a spill. This also affects the distribution of light in the solar spectrum penetrating the water column. Several LIDAR systems have been developed for remote monitoring of oil spills on water surfaces (1-5). A remote diagnostics of oil spills on water surfaces includes fast mapping of oil spills, identification of the oil type, and finally estimation of the oil spill volume. Currently, LIDAR monitoring of oil spills on water surfaces is based on the detection of the pollutant fluorescence response (1,3), oil characterisation using its fluorescence signal (1,3,5,6) and on the estimation of oil spill thickness using the suppression of the water Raman signal by an oil film (1-4). The aim of this work was to study the spectral properties of oil films (ranging from parts of a micrometer up to optically thick layers) on a water surface under controlled laboratory conditions and to highlight the problems of remote diagnostics of oil spills.

EXPERIMENTAL METHODS

Three laser fluorosensors were used in this study. To obtain the fluorescence response of mineral oils spilled on a water surface in the container the laser fluorosensor built at ENEA was used. The third harmonics of a Nd:YAG laser (355 nm, pulse duration 0.3 ns) was used for the excitation. The emission signal was collected by a lens at an angle of about 30° and transmitted via a quartz fibre optics either to an optical multichannel analyser (EG&G model OMA-III) for spectrally resolved measurements, or to optical interference filters (450 or 550 nm) and a streak-camera (Hamamatsu model SC) for time-resolved measure-

ments. Another system, an excimer-laser based LIDAR was assembled at ENEA to measure water Raman spectra with high spectral resolution. A low divergence high power XeCl excimer laser operating at 308 nm was used as the excitation source. Raman spectra of water in the container were detected at high resolution in the range of 330...365 nm. Measurements were performed after adding fixed amounts (in drops) of different crude oils on the water surface in a 6 litres container with a surface area of 400 cm². The third LIDAR with excitation at 308 nm by an excimer laser was built at the Institute of Ecology in Tallinn. It was used to measure the fluorescence response of sub-micrometer films of crude oils and oil products on the water surface remotely at 10 m distance. Homogeneous oil films with a thickness of a hundredth part of a micrometer were created on water in a 50 litres container (surface area 950 cm²) using an acetone solution of mineral oil at a known concentration.

Oil samples were supplied by the research institute EniTechnologie SpA (Monterotondo, Rome, Italy) which covered representative oils often transported at sea to European coastal refineries and oil terminals. The Institute of Ecology (Tallinn, Estonia) provided samples of crude and refined oils from Russia and Estonia. The selection criteria included variability in the origin and the high risk of sea pollution. Humic acid from Aldrich was used to prepare an aqueous solution of humic compounds at a concentration of 0.1 mg/l.

FLUORESCENCE RESPONSE OF OIL ON THE WATER SURFACE

The typical response of water covered by an optically thin oil film with UV laser excitation consists of a water Raman stretching peak whose position is ruled by the excitation wavelength and a wide band of oil fluorescence. Oil emission shows a maximum in the UV range for light refined oils and in the visible range (420...490 nm) for crude oils. In general, the emission maximum depends on the type of oil, the thickness of the film, as well as the presence of oil dispersed in water (7,8).

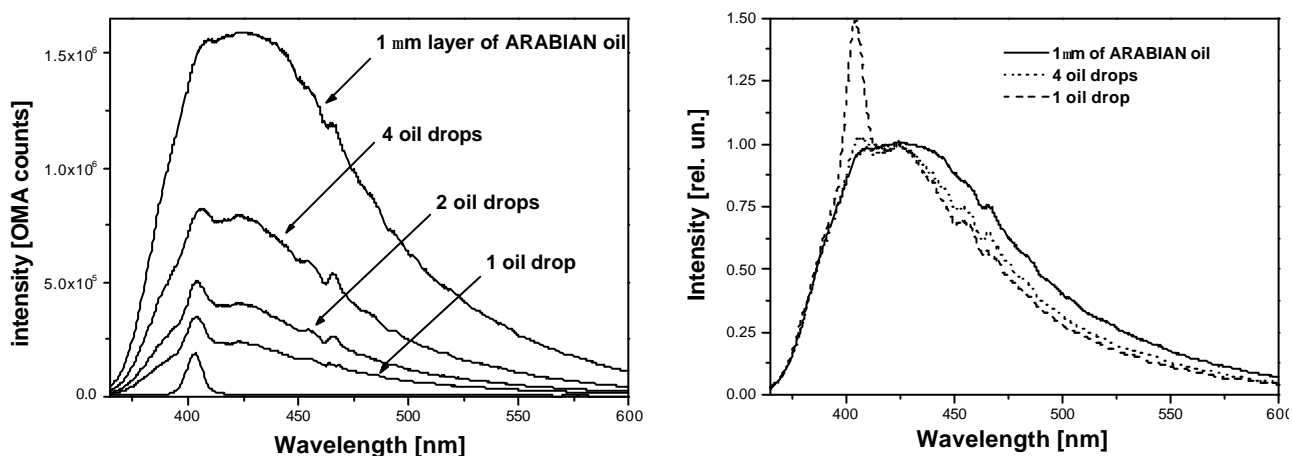


Figure 1: Fluorescence of crude oil measured with the OMA (left); spectra normalised to their maximum intensity (right).

Figure 1 presents the spectral response of Arabian Extra Light crude oil spilled on water, and the fluorescence of the same sample in a quartz cell of 1 μ m path length placed on the water surface. The peak at 405 nm corresponds to the backscattered Raman signal excited at 355 nm in water below the oil. With a greater volume of oil spilled on the water surface the fluorescence intensity rises and water Raman scattering is depressed in intensity. The fluorescence signal of oil in the 1 μ m cell placed on the water surface is almost twice as large as the fluorescence signal of an oil film produced with 4 drops on the water surface which also corresponds to 1 μ m thickness. The quantitative estimation of fluorescence intensities in the case of oil in a quartz cell needs to take into consideration the reflection of excitation light and fluorescence from the bottom plate of the cell.

To compare the emission band-shape for films of different thickness the spectra were normalised to their maximum intensity (Figure 1, right). The band shifts about 20 nm towards longer wavelengths as the thickness increases. This red-shift of the trailing edge of the emission bandshape maximum for crude oils can be explained by re-absorption of emission by the film in the linear excitation regime.

The attempt to distinguish different mineral oils using their emission spectra is hampered also by other serious difficulties. Among them are the similarity of the fluorescence response for various crude oils, the penetration of oil into water and formation of a dispersed fraction (7), and the interference of fluorescence signals for mineral oil and dissolved organic matter (DOM) (7). We conclude that emission spectra alone do not constitute a decisive fingerprinting criterion since the emission is dominated by complex excitation transfer and re-absorption, smoothing out the individual oil characteristics. This however does not completely rule out fingerprinting, provided that the acquisition of emission data is supported by other techniques.

THE FLUORESCENCE LIFETIME OF MINERAL OILS

Fluorescence decay time measurements for mineral oils were performed on bulk material and on oil layers of known thickness in a quartz cell, as well as on artificially produced oil films on the water surface. Fluorescence was excited at 355 nm and detected at 450 nm. Mono-exponential fitting was used to derive the fluorescence decay time. The accuracy of fluorescence lifetime estimation is 0.2 ns for crude oils and 0.5 ns for refined products (Figure 2).

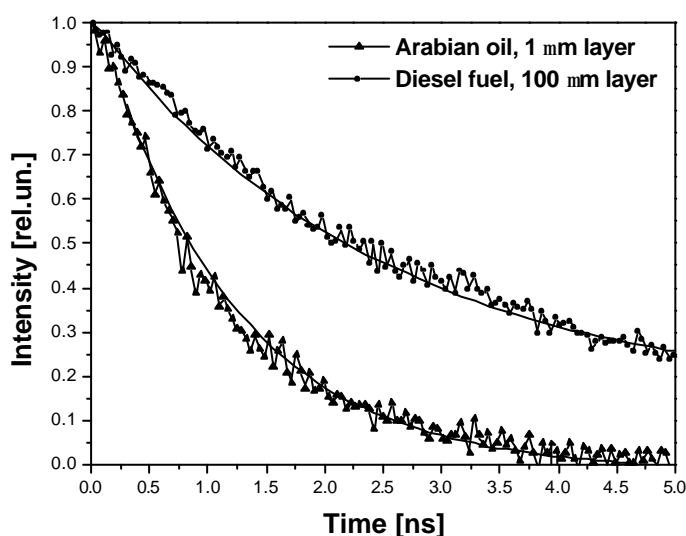


Figure 2: Fluorescence decay for 1 mm layer of Arabian oil and a 100 mm layer of diesel fuel.

The results of these kinetics measurements can be summarised as follows:

- (1) crude oils give different fluorescence life-times varying from 1 to 3.5 ns;
- (2) refined oils have a slower kinetics (3.5...8 ns) compared to crude oils;
- (3) fluorescence lifetimes for crude oils show a trend to rise with the increasing thickness of the layer from 1 μm up to optically thick layers. Repeated observations prove that this trend is well reproducible.

To study the influence of oil-water interactions on the fluorescence kinetics, oil was spilled on the water surface in a 5-litre container. Fluorescence decay was measured twice. First, just after oil spilling, and secondly, when the water was well mixed in the container. After mixing most of the oil goes into the water column. One might expect some changes in fluorescence decay due to the appearance of emulsified oil. The experiment showed, however, that both crude oils spilled smoothly on the water surface and dispersed in the water column have fluorescence decay times very similar to the bulk material. To evaluate the fluorescence lifetime of DOM in water we measured the fluorescence decay of 0.1 mg/l Aldrich humic acid in

water with 355 nm excitation. Its lifetime is quite distinguishable from that of crude oils, and is equal either to 4 ns (emission at 450 nm), or to 5 ns (emission at 550 nm). Therefore, DOM can be distinguished from crude oil in the water column with local measurements at different depths, since oils are by far more localised at the surface (floating).

Fluorescence lifetime measurements are difficult to apply for crude oil characterisation in field conditions. To distinguish different oils on water surface remotely we applied the technique of fluorescence saturation, or non-linear fluorimetry.

Table 1: Fluorescence lifetimes [ns] for mineral oil films of different thickness. Excitation at 355 nm, detection at 450 nm

Sample	Oil film thickness		
	1 μm	100 μm	optically thick layer
Kirkuk crude oil, Iraq	1.2 ± 0.2	1.3 ± 0.2	1.4 ± 0.2
Saharan Blend crude oil			3.5 ± 0.2
Arabian extra light crude oil	1.2 ± 0.2	1.3 ± 0.2	1.6 ± 0.2
Libyan crude oil	1.8 ± 0.2	2.7 ± 0.2	2.6 ± 0.2
Buzachinsk crude oil, Russia			1.0 ± 0.2
Diesel fuel, Estonia	3.6 ± 0.5	3.6 ± 0.5	4.6 ± 0.5

CHARACTERISATION BY FLUORESCENCE SATURATION SPECTROSCOPY

Fluorescence saturation spectroscopy, or non-linear fluorescence spectroscopy, considers the cases of spectra excitation by high power laser sources where the resulting fluorescence intensities are not proportional to the excitation intensity. Some features of fluorescence saturation at non-stationary conditions are considered in (9,10). This deviation from linearity, or so-called fluorescence saturation, is noticeable for conditions of 10^{24} exciting photons per second per square cm, which can be easily achieved with industrial laser sources. The effect is ruled by such spectroscopic parameters as absorption cross-section, fluorescence lifetime, singlet-triplet conversion, quenching processes, etc. Non-linearity of fluorescence response versus excitation intensity renders more difficult the quantitative monitoring of fluorescent pollutants. But the investigation of fluorescent organic material at saturating conditions provides additional information on its nature and possible sources.

The non-linear fluorescence response of several crude oils and diesel fuel with pulsed laser excitation at 355 nm was investigated. It was found that the integral emission intensity for all samples including both crude and refined oils is non-linear versus excitation intensity. For the first time the manifestation of non-homogeneous spectral broadening was observed for samples of crude oils. When the intensity of excitation rises the fluorescence emission of crude oils shows a blue shift of about 20...50 nm. The value of this shift depends on the oil type and correlates well with the optical density of the oil. For the diesel fuel we did not observe changes in the emission spectral shape due to saturation. As an illustration of the effect the spectra of some oils measured under two conditions of excitation are given in Figure 3 (excitation with non-attenuated laser pulses at $r_1 \sim 10^{25} \text{ cm}^{-2}\text{s}^{-1}$ - dashed curves and left ordinate axes; excitation at $r_2 = r_1 / 100 \sim 10^{23} \text{ cm}^{-2}\text{s}^{-1}$ - solid curves and right ordinate axes). The shift of the emission maximum under conditions of fluorescence saturation was observed for pure substances in thin quartz cells as well as for oil films on the water surface (Figure 3). We explain the shift as a manifestation of non-inhomogeneous broadening. Mineral oils represent a large group of different fluorescent species, and there is a wide dispersion of energetic levels for fluorescent centres in the media. Due to energy transfer from «blue» luminophores to «red» ones in crude oil we observe mainly the emission of «red» centres under conventional conditions of excita-

tion. But with high intensity laser excitation mainly the fluorescence of «red» centres are saturated since they have slower emission kinetics, resulting in the relative increase of «blue» fluorescence. The higher the intensity of excitation, the deeper is the blue shift of the maximum. The blue shift is more pronounced for heavy species such as crude oils, and is less or almost negligible for diesel fuel and other refined oil products. Refined oils contain very few types of individual chromophoric compounds, and their fluorescence spectra are more specific and narrower compared to crude oils.

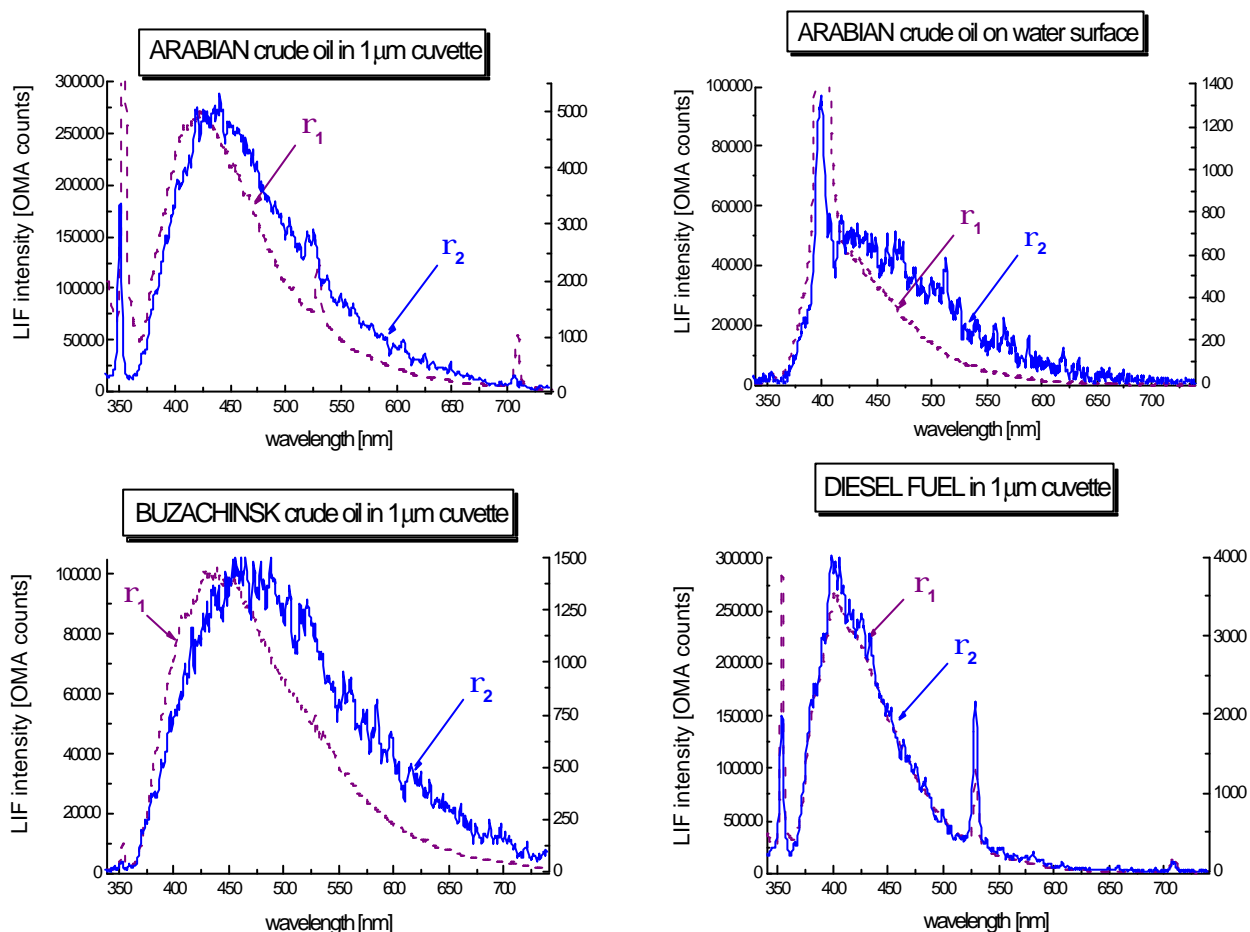


Figure 3: Fluorescence spectra of oils measured at conditions of fluorescence saturation.

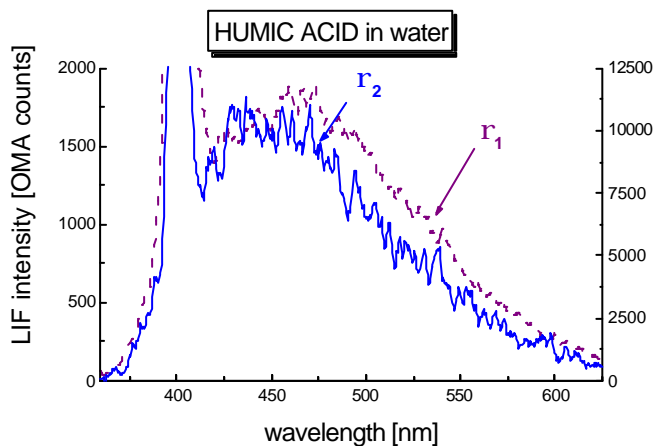


Figure 4: Fluorescence spectra of Aldrich humic acid in water (concentration 0.1 mg/l) measured at conditions of fluorescence saturation at 355 nm excitation.

We suggest for an oil characterisation using remote LIDAR techniques to use the value of the blue shift measured at fluorescence saturation conditions. DOM of natural origin can be easily distinguished from crude oils using fluorescence saturation spectroscopy since humic substances in contrast to mineral oils give rise to a red-shifted maximum position (Figure 4).

MEASUREMENT OF OIL FILM THICKNESS IN THE SUB-MICROMETER RANGE

The suppression of the integral water Raman signal by an oil film is used in remote sensing to measure the thickness of oil spills spread over water (1-4). The equation for oil film thickness d is

$$d = -1/(k_e + k_r) \ln (R^*/R),$$

where R^* and R are the water Raman intensities measured above and outside the oil slick, k_e and k_r are the attenuation coefficients at the excitation and Raman wavelength.

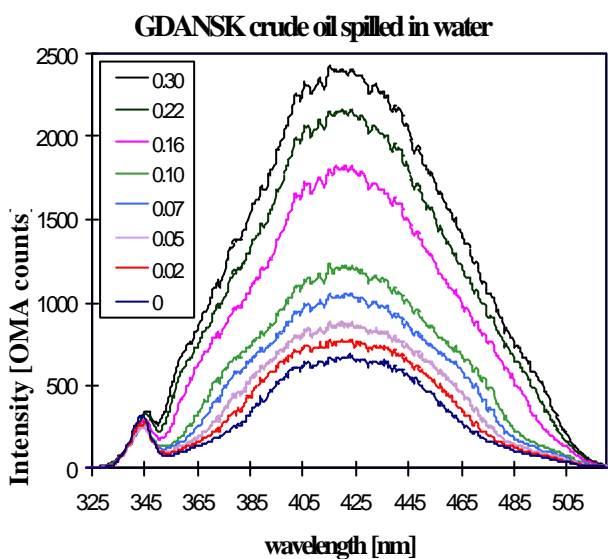


Figure 5: Spectra of sub-micrometer oil films on the water surface, film thickness is given in micrometers.

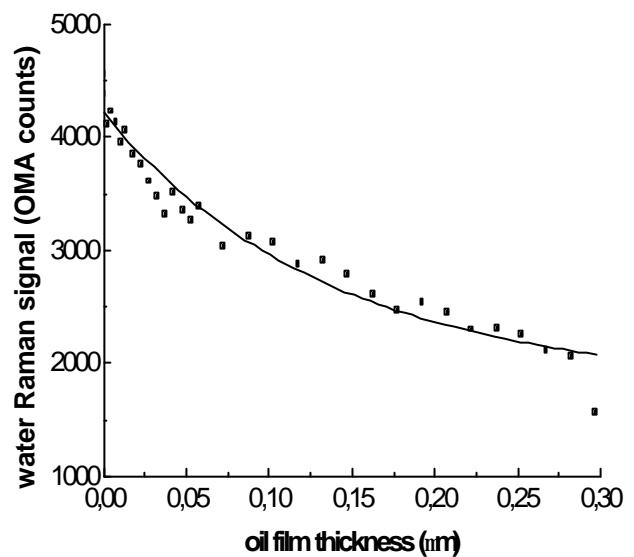


Figure 6: Exponential fit of the water Raman signal versus oil film thickness.

To test the accuracy of oil thickness measurements a special experiment was made with sub-micrometer films of known thickness on the water surface (Figure 5). To create films thinner than that produced by direct dropping of oil on water and with known thickness we used the following approach. The measured volume of mineral oil was mixed with a certain amount of acetone, and the mixture was spilled on the water surface (area 950 cm²) in a container. The emission of films created through acetone solution is similar in shape to the emission of spills directly dropped on water, but the fluorescence efficiency is higher in this case. Moreover, the effect of the maximum shift due to re-absorption is lower in sub-micrometer films. The minimum thickness of oil films prepared using acetone solutions was estimated as 0.01 µm, and typically 1 drop of crude oil gives a film of 0.2...0.3 µm thickness. To perform the experiment in conditions close to reality we used natural water with DOM whose fluorescence signal exceeded the intensity of water Raman scattering. The experiment proved that oil films can be reliably quantified even in the presence of DOM with an accuracy better than 0.05 µm.

The technique has demonstrated good results in measuring small oil discharges. However, there are some factors affecting the integral intensity of the water Raman signal, and, hence, the result of oil thickness estimation. The detected integral Raman intensity depends on such experimental conditions as laser power

variations, altitude of the sensor, turbidity of the water column. To eliminate the influence of accidental factors, which cannot be controlled, a new technique of oil film thickness estimation has been suggested (7,8,11), due to the fact that the Raman spectrum of water under a film is distorted in shape due to the wavelength-dependent absorption of oil.

MEASUREMENT OF OIL FILM THICKNESS USING HIGHLY RESOLVED WATER RAMAN SPECTRA

The algorithm of film thickness estimation involves the amplitude ratio r of two spectral components contributing to the water Raman spectrum. The intensity ratio at two wavelengths within the water Raman spectrum is a function of the oil thickness d (7):

$$r_{film} = r_0 \exp(-((k(I_1) - k(I_2))d),$$

where r_0 is the ratio of two Raman intensities measured at I_1 and I_2 from clean water outside the oil spill, and r_{film} is the ratio of Raman intensities at I_1 and I_2 from the water layer under the film. For the estimation d it holds:

$$d = (k(I_1) - k(I_2))^{-1} \ln(r_0 / r_{film}).$$

The algorithm was experimentally tested for highly resolved water Raman spectra excited at 308 nm (11). The Raman spectra were deconvoluted into spectral components using the following procedure. The fluorescence background was approximated by a polynomial function of fifth degree with variable coefficients, and the water Raman stretching band was fitted by two Gaussian curves with fixed positions and bandwidths. The amplitude ratio of the two Gaussian curves r obtained in this way was used as a measure of distortion of the water Raman spectral shape. It is necessary to note that the obtained spectral components have no meaning concerning their nature, but just manifest the relative weights of low-frequency to high-frequency Raman intensities.

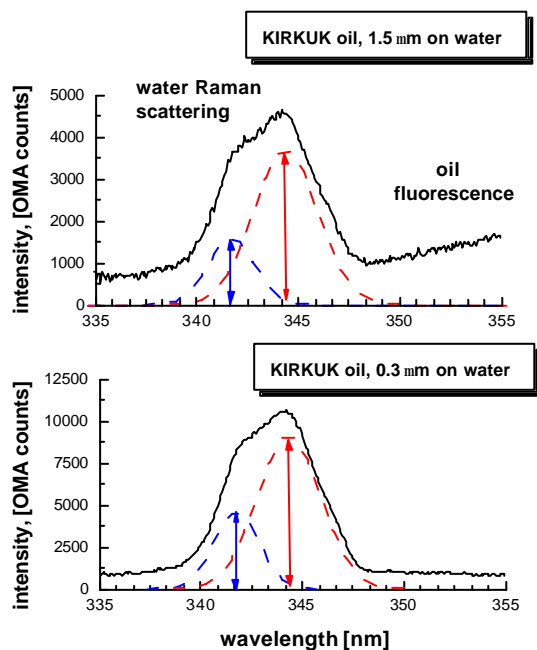


Figure 7. Raman spectra of water under an oil film of different thickness.

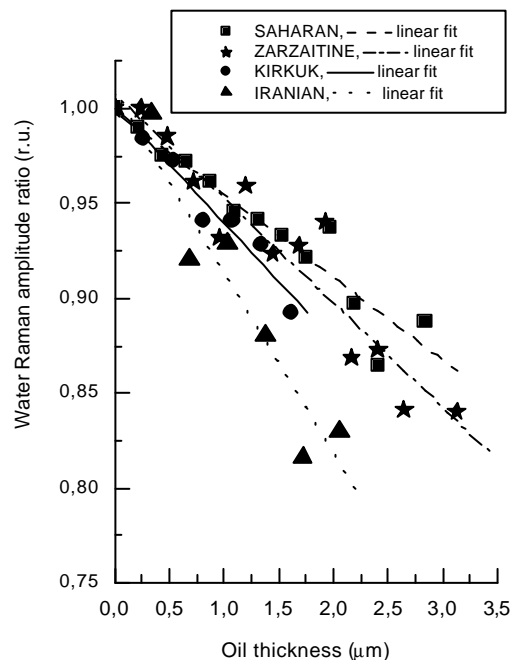


Figure 8: Amplitude ratio of water Raman components versus oil film thickness.

The relative amplitude ratio r_{film} / r_0 is shown in Figure 8 as a function of the oil film thickness on the water surface. The data demonstrate the apparent trend of the ratio to decrease with the increase of the amount of oil spilled in water. The slope of the linear fit for each crude oil represents the wavelength-dependent part of absorption coefficient for the same mineral oil. The ratio r_{film} / r_0 can be used to estimate the thickness of oil film. The new approach has some advantages compared to the traditional one. First, applying the technique of integral water Raman suppression to field monitoring is necessary to detect the signal from clean water every time before starting measurements on the spill. Based on this information, a quantitative film thickness estimation can be done with the approach described above. Since it makes use of amplitude ratios, the knowledge of absolute water Raman intensity is not necessary for its application. Secondly, the influence of accidental factors affecting the integral Raman intensity is eliminated in the new approach. However, one has to note that the new approach demands the detection of water Raman spectra with high resolution, and a very accurate estimation of the fluorescent background. Additionally the temperature effect that also leads to distortion of water Raman spectral shape must be taken into account (12).

CONCLUSIONS

The research presented here focuses on the following objectives:

- to study fluorescence and water Raman scattering of oil-covered water under controlled laboratory conditions to analyse the problems of LIDAR remote diagnostics of oil spills;
- to develop criteria for an oil type recognition based on fluorescence kinetics and fluorescence saturation measurements;
- to analyse the accuracy of oil film thickness quantification in the sub-micrometer range and to demonstrate the performance of a new approach based on contour analysis of water Raman spectra.

The thorough investigation of spectral properties of oil films ranging from sub-micrometer thickness up to optically thick layers on the water surface under controlled laboratory conditions proves that LIDAR fluorosensing is a very sensitive tool for oil detection and mapping. However, during remote spill recognition the factors affecting fluorescence signal should be taken into account. The film thickness affects the emission band-shape and maximum position for crude oils due to re-absorption. Accompanied with interference of DOM and oil fluorescence this phenomenon complicates the task of pollution identification using fluorescence imaging. It was confirmed that emission spectrum alone does not constitute a decisive fingerprinting criterion. Fluorescence lifetime varies for different crude oils, but its value also depends on oil film thickness. The fluorescence decay of humic acid (4...5 ns) is slower than the decay of crude oils (1...3.5 ns), which gives us the possibility to separate the contribution of DOM and oil emission using time-resolved spectra.

For the first time we suggest to use fluorescence saturation spectroscopy for oil characterisation. This is due to a blue shift of the emission maximum which occurs at saturating conditions and depends on the oil type. This is better demonstrated for heavy oils than for light ones, and the maximum position remains constant for diesel fuel. In contrast to mineral oils for humic substance we observed the «red shift» of emission maximum upon excitation at 355 nm. In spite of the fact that the fluorescence saturation is ruled by fluorescence lifetime, fluorescence saturation spectroscopy does not require time-resolved measurements and can be performed in a remote mode.

The detection of the water Raman integral signal enables the measurement of considerably small oil discharges producing films thinner than 0.05 μm on the water surface. However, there are certain factors affecting the integral signal of water Raman scattering. To overcome the existing problem a novel technique

of oil film thickness measurement was tested. Contour analysis of highly resolved Raman spectra from the water column under an oil film was performed. The amplitude ratio of two water Raman components is linearly varying with the oil film thickness on the water surface, and the slope of this linear regression represents the wavelength-dependent part of the attenuation coefficient.

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