Fluorescent Remote Diagnostics of Oil Pollutions: Oil in Films and Oil Dispersed in the Water Body

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ABSTRACT

The objective of this work is the experimental spectroscopic study of two types of pollution produced by an oil spill - oil in film and oil dispersed in water body. Their spectroscopic characteristics are very different, so these two oil species can be recognized by remote monitoring of water surface. We describe the new technique of oil film thickness measurement using contour analysis of water Raman spectrum. This technique operates with ratio of intensities at different wavelengths inside the Raman stretching band from water under an oil film. The possibilities and limitations of the new technique are considered.

1. INTRODUCTION

The importance of oil pollutions monitoring is certainly increasing in our days. The fluorescent spectroscopy with laser excitation due to its sensitivity has shown promising results in remote detection of oil pollutions. And recently, several investigators have developed lidar systems for the remote sensing of oil spills (Andersson, 1987; Hengstermann and Reuter, 1990,1992; Gruner, 1991; Dick, 1992, Cecchi, 1992).

However, there still remain a few problems to be solved in oil remote diagnostics using fluorescent techniques: (1) The problem of distinguishing oil in film on the water surface, and oil dispersed in the water body... Discrimination between these two forms is necessary, because fluorescence yield and other spectral characteristics change when crude oil transfers from a film to the water body (Gumneberg, 1993).

(2) Separation of oil fluorescence from that of dissolved organic matter (DOM, Gelbstoff) naturally occurred in water.

(3) Classification of oil in film as well as dispersed in the water body. Quantitative analysis of oil pollutions both in film and dispersed in water demands a priori knowledge of some spectral characteristics, for instance, the attenuation coefficient or fluorescence efficiency etc. These spectral characteristics vary for different oils.

In this work it is shown that the intensities of three major bands in fluorescence spectrum characterize the form of oil pollution and can be used for rough classification (light/medium/heavy) of the oil type. Therefore, the question is how the inaccuracy of oil recognizing affects oil content measurements.

And finally, (4) oil content measurement - estimation of thickness of the oil film on the water surface and concentration of oil in the water body under an oil film. To solve some of the above-mentioned problems a fluorescent spectroscopic study of DOM, different types of mineral oils (gasoline, kerosene, diesel fuel, machine oil, few crude oils) in 1...100 μm film and dispersed in water was carried out in this work. Excitation wavelength was changed from 222 to 532 nm and corresponded with one of the laser sources.

2. INSTRUMENTATION

The fluorescent investigation of different types of mineral oils (gasoline, kerosene, diesel fuel, some crude oils) in film micrometer thickness, as well as dispersed in water was carried out using a fluorometer “Jobin Yvon 3CS”. Fluorescence was excited by a Xenon lamp. The intensity of excitation fluorescence spectra was corrected for spectral intensity of the light source and the sensitivity of the installation. The spectral resolution of fluorescence spectra was equal 4 nm. In our investigation of fluorescence emission the excitation wavelength was changed from 222 to 532 nm corresponding with one of the laser sources.

Thin oil films were made in ring quartz cells of special shape with constant distance between parallel plates from 1 to 100 mm. We varied the thickness of the oil film choosing different quartz cells. The diameter of cells is 3 cm, the thickness of each quartz plate is about 3 mm. The fluorescence emission from oil films was measured from the same side as the exciting light. The angle between the exciting beam and the direction of spectrum detection was about 90°. The samples of oil in water were made by mixing few milligrams of mineral oil in 1 liter of distilled water previously checked for fluorescence. Then the water
samples were kept under laboratory conditions at room temperature for three months. Part of the oil produced an oil film on the water surface, so the concentration of oil dispersed in water was less than the total oil content during the mixing process. The water under the film from the center of the glass bottle was analyzed for fluorescence. In our spectroscopic studies we do not distinguish emulsified and truly dissolved oil species. We tried to approach a process of water sampling nearer to natural conditions.

The fluorescence spectra of water samples in standard 1 cm x 1 cm spectroscopic quartz cells were detected at the right angle to the exciting beam.

The absorption spectra were detected using a spectrophotometer “Spectord M40”.

3. SPECTROSCOPIC STUDY OF OIL IN FILM AND OIL DISPERSED IN WATER

The fluorescence emission spectra excited at different wavelengths are presented in Figs. 1, 2. The emission intensity is not corrected for exciting light intensity to compare the spectral shape at different excitation wavelengths. One can see the difference between spectra for oil in film and oil dispersed in water.

The fluorescence spectra of the oil film show a very conservative behaviour with excitation wavelength alteration. The emission maximum location is constant while the excitation wavelength remains below the fluorescence emission band. The maximum wavelength does not depend on film thickness for light oils with small extinction coefficient. But for some crude oils the emission maximum shifts for 10...40 nm (depending on oil type) to longer wavelengths with a film thickness increasing from 1 to 100 μm because of reabsorption. This effect does not allow us to use the maximum wavelength for oil type recognizing among crude oils.

The fluorescence spectral shape for pure oils keeps constant even when the excitation wavelength (532 nm) exceeds the emission maximum. The spectral shape independence of the excitation wavelength is apparently observed for crude oils, but can be broken for light oil cuts (diesel fuel). We explain this excitation-independent spectral behaviour for crude oils by the process of transfer of photoexcitation energy. The very high local concentration of fluorescing molecules in crude oil provides the good conditions for energy migration which shifts the emission maximum to higher wavelengths. Another situation can be observed for light oil cuts or for oil solutions in organic solvents. The distance between fluorophores rises, and the probability of energy transfer to fluorophores responsible for fluorescence in visible range decreases. In solutions and light oil cuts the same molecules absorb light and emit the fluorescence spectrum, the number of fluorescence maxima and their intensities depend on the kind of luminescence centers.

Excitation spectra for pure oils do not exhibit any structure: the intensity of excitation spectrum, after correction for spectral sensitivity and intensity of the lamp source, increases with excitation wavelength shortening. Only for gasoline we observed a maximum in the excitation spectrum at 270 nm. Very similar spectral features are obtained from absorption spectra for different pure oils: the sharp peak for gasoline and shoulder for other oils in the region of 260...270 nm, and very broad absorption contour increasing in intensity towards shorter wavelengths. The absorption spectra for oil films are shown in Fig. 3.

Excitation spectra for oils dispersed in water are in contrast to pure oils. Corrected excitation fluorescence spectra exhibit a very apparent structure with a very intensive band at 220...230 nm and the second maximum at 260...270 nm for all mineral oils in water. The spectral shape and the ratio of intensities at 220/260 nm in the excitation spectrum differ for various detection wavelengths. This ratio is decreasing in the row of emission fluorescence wavelength: 330, 360, 400 nm.

The spectral shape and maximum location for oil dispersed in water strongly correspond with the variation of excitation wavelength. In the fluorescence spectrum pure gasoline shows only one band with a maximum at 290 nm, but the emission spectrum for gasoline in water has two maxima at 290 and 330 nm (see Fig. 1, 2). The crude oil films exhibit only one maximum in fluorescence spectra located at 420...490 nm, its location depending on film thickness and oil type. On the contrary, the same oil samples but dispersed in water have three maxima located at 290 nm, 330-340 nm, and 400-450 nm.

Let us consider in detail these three basic fluorescent bands in emission spectrum for oil pollutants dispersed in water. The spectral band with maximum 340 nm appears in fluorescence spectra of all investigated aqueous samples of oils, and is absent in spectra of oil films. So we suppose that this band caused by some specific hydrophilic molecules or molecular aggregates can be used for oil diagnostics. The intensity of this fluorescence band at 340 nm provides information about presence and content of oil dispersed in water (emulsified and truly dissolved). To separate the spectral contribution of oil in film and oil dispersed in water we need wavelengths shorter than 308 nm to excite fluorescence at 340 nm.

Another emission spectral band in UV range with a maximum of 290 nm also appears for all oils in water. This band corresponds with the spectral maximum for light oil cuts (for example, gasoline, see Fig. 1). In our opinion some monocyclic aromatic compounds could produce this fluorescence band.

The fluorescence band in the visible region (400...450 nm)
Fig. 1 - Fluorescence emission spectra of oil films excited at different wavelengths.
Fig. 2 - Fluorescence emission spectra of oil pollutions dispersed in water excited at different wavelengths. RS - water Raman scattering.
can apparently be observed only for heavy oils when the excitation wavelength exceeds 337 nm. The intensity ratio of three basic bands characterize the type of mineral oil (light/medium/heavy), and could be used for rough oil classification. To detect all three basic bands in fluorescence spectrum one needs at least two excitation wavelengths: a first one in the range of 220...308 nm, and a second wavelength longer than 337 nm.

As mentioned above, oil spectra have a very special behaviour with excitation wavelength alteration. The fluorescence emission maximum for oil dispersed in water depends on the excitation wavelength contrary to the constant oil film emission maximum location.

Another situation is observed for the fluorescence of dissolved organic matter of natural origin. While the excitation wavelength is less than some wavelength limit (approximately 330 nm), the maximum of the emission spectrum is practically constant, the variation of the maximum location does not exceed 10 nm. But with an increasing excitation wavelength above 330 nm the spectral maximum shifts to longer wavelengths, in a way that the difference between excitation wavelength and emission maximum is nearly constant. This spectral behaviour of DOM fluorescence is very unusual for organic molecules, and has not been explained yet. Possibly it is caused by the heterogeneous nature of the DOM fluorescence spectrum and presence of several luminescence centers of different origin.

The described spectral rules can be used to distinguish DOM and oil fluorescence signals. The shortwave excitation in region 220...308 nm can be used to discriminate DOM and oil dispersed in water. As mentioned above oil pollutants dispersed in water produce few fluorescence bands in UV range, but dissolved organic matter (humic substance) exhibits only the fluorescence band in the visible region with a maximum about 420 nm. The additional excitation wavelength from 350...400 nm spectral range could help recognizing DOM and oil in film. The opportunity of such discrimination follows from the excitation-independent character of the emission maximum for pure crude oils, but choosing the second excitation wavelength longer than 350 nm we observe a shift of the emission spectrum for DOM comparable to the spectrum excited at the first wavelength. The possible methods of quantitative calculation of contributions of these three fluorescent species are being elaborated now.

4. DISTINGUISHING THE OIL FLUORESCENCE AND DOM FLUORESCENCE

The fluorescence of naturally occurring dissolved organic matter (DOM, Gelbstoff) in the water interferes with the oil fluorescence signal. The fluorescence spectra excited at 337 nm for dissolved organic matter of natural origin and crude oil (in film and dispersed in water) are very similar in shape, width and spectra location. In the reference (Burlamacchi, 1983) it was shown that for oil film thickness in the 0.01-mkm range the water fluorescence may be of the same order as the oil fluorescence, and discrimination between the two contributions using a fluorescence emission band becomes very difficult.

The time resolution technique (Verdebout, 1992) also means some difficulties in distinguishing the fluorescence of an oil film and of DOM in the water column, because different oils have very wide ranges of fluorescence decay time from 0.4 to 18 ns covering the lifetime of dissolved organic matter.

In this work we have tried to figure out distinctive spectral features for DOM in water and oil pollutions.
5. THE USE OF WATER RAMAN CONTOUR ANALYSIS FOR OIL FILM THICKNESS EVALUATION

The fluorescent technique with laser UV excitation was used for remote measurement of oil film thickness (Visser, 1979; Hoge, 1983). But direct fluorescent oil film detection on the water surface is problematic because of a few difficulties. There is the existence of oil pollution in two fluorescing species (oil in film and dispersed in the body under the film) with different fluorescence yields, and interference of spectra of oil and dissolved organic matter of natural origin in the water.

In another technique it was proposed for film thickness estimation to use depression of water Raman integral signal by an oil film (Hoge and Swift, 1983). In first experiments a Nitrogen laser was used to excite the 3400 cm⁻¹ OH stretch band of natural ocean water beneath the oil slick from an altitude of 150 m. Upon removal of the fluorescent background, the ratio of depressed-to-undeepred airborne water Raman signal intensities is used to calculate the oil film thickness. The equation for oil film thickness (d) estimation can be written:

\[ d = \frac{1}{(k + k_i) \ln (R'/R)} \]  

where \( R' \) and \( R \) - water Raman components consequently over and outside the oil slick, \( k, k_i \) attenuation coefficient at excitation and Raman wavelength. Because the authors have used Nitrogen laser emitting at 337 nm for spectra excitation, the detected Raman signal has a very intensive fluorescence background from the oil film which must be separated.

Hengstermann and Reuter (1990; 1992) put this technique into practice using an airborne lidar system with excimer XeCl laser operating at 308 nm. The possibilities of this technique using the same excitation wavelength 308 nm were investigated by Barbini and colleagues (1992). The Raman spectrum excited at 308 nm is not so dramatically influenced by fluorescence background from an oil film. The water Raman band can be separated from the fluorescence signal for two oils up to 2...4 μm of film thickness. This is the upper limit of oil film thickness evaluation using water Raman scattering excited at 308 nm.

However, there are some problems arising from this technique. The detected absolute Raman signal depends on experimental conditions such as accidental laser power variations, altitude of sensor system, turbidity of water column, etc.

The Raman backscattered signal from water molecules can be used in remote fluorescent techniques as an internal standard to minimize the effects of laser beam penetration into the water column (Klyshko, 1978, Bristow, 1981). The resulting intensity ratios are independent of the laser output power and other experimental conditions, which could not be controlled. Another usage of the water Raman stretching band is the measurement of temperature and salinity of seawater. This method is based on the dependence of the spectral shape of the water Raman stretching band 3100...3700 cm⁻¹ on water temperature and salinity. Though this dependence is relatively weak, using the “least squares method” or mathematical “reduction method” has allowed us to achieve good results in temperature and salinity evaluation both in laboratory experiments and remote sensing of the seawater surface (Patsayeva, 1990, 1991a).

In this article we offer a new technique for oil film thickness measurement, using contour analysis of water Raman spectra. The Raman backscattered signal from water under an oil film is depressed in intensity, and the attenuation is not the same at different wavelengths. This effect is caused by dispersion of the attenuation index. Thus the spectral shape of Raman spectrum from water under the oil film of thickness “d” is distorted comparable to the Raman spectrum from clean water. In the presence of oil on the water surface the Raman intensity at wavelength 1 is multiplied by the exponential factor \( \exp (-k(\lambda_1) d) \). The Raman intensity at wavelength 2 is multiplied by the factor \( \exp (-k(\lambda_2) d) \).

The intensity ratio at two wavelengths is a function of the oil thickness (d):

\[ r(\text{film}) = r(0) \exp (- (k_1 - k_2) d) \]  

where \( r(0) \) - the ratio of two Raman intensities from clean water without oil spill, \( r(\text{film}) \) - the ratio of Raman intensities at the same wavelengths from the water layer under the oil film of thickness d.

For oil film thickness measurement we can use the formula:

\[ d = \frac{1}{(k_2 - k_1) \ln [r(\text{film})/r(0)]} \]  

The oil film thickness calculated from the equation (6) is independent of laser power output, altitude of fluorosensor and other experimental conditions. This is a big advantage compared to the above-mentioned technique of oil film thickness measurement using integral Raman signal depression by an oil film.

Another approach of the new method is the “multichannel” technique of analysis of Raman spectral shape operating with spectra, normalized to a unit area. So the Raman intensity in each spectral channel of optical multichannel analyzer does not depend on accidental variations of the laser output power and other experimental conditions.

If temperature and salinity of seawater are known or constant, the measured Raman intensity of the normalized spectrum in each spectral channel is linear with respect to the oil film thickness \( d \) (Patsayeva, 1993):

\[ I_i(d) = A_i + B_i d \]
Coefficient B. is proportional to the dispersion of the attenuation coefficient. For d estimation from a measured water Raman contour we can use any method of Raman spectrum analysis, developed for the measurement of water temperature earlier (Patsayeva, 1990, 1991a).

The accuracy of oil film thickness estimation depends on the absorption coefficient of the oil under investigation, as well as on the excitation wavelength. The change of the water Raman spectral shape by a factor exp ((k2-k1)d) caused by the dispersion of attenuation could be detected if this value exceeds the noise level in the Raman spectrum. The maximal thickness of the oil film which can be estimated by analysis of the water Raman contour is limited by the possibility of water Raman backscatter registration. This upper limit depends on the extinction coefficient at excitation and Raman wavelength for an oil film.

Another limitation of this technique for real oil spill monitoring is caused by the fluorescence background from oil film and oil dispersed in water, as well as from dissolved organic matter of natural origin. The maximum of the emission fluorescence spectrum for oil film is located at 420...490 nm, the maximum for dissolved organic matter equals approximately 420 nm. So to avoid, or at least decrease the interference of fluorescent and Raman signals one needs to use the excitation source operating at 266 or at 308 nm.

The lower and upper limits of oil film thickness estimation using contour analysis of water Raman spectrum are presented in Table 1.

They are calculated from absorption data for pure oils for experimental conditions with a signal-to-noise ratio of 100 in the Raman spectrum.

The type of oil must be identified, and the dispersion of the attenuation coefficient must be known in advance for using this technique. Let us note, that for all other techniques proposed for oil film thickness measurement the type of oil spilled on the water surface must also be known a priori.

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**Table 1: The limits of oil film thickness estimation using contour analysis of the water Raman spectrum for heavy (first value) and light (second value) crude oil.**

<table>
<thead>
<tr>
<th>Excitation wavelength, nm</th>
<th>Water Raman wavelength, nm</th>
<th>Halfwidth of water Raman band, nm</th>
<th>Minimal limit of d, mkm</th>
<th>Maximal limit of d, mkm</th>
<th>Influence of fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>266</td>
<td>293</td>
<td>3.4</td>
<td>0.06...0.2</td>
<td>0.7...2</td>
<td>very weak</td>
</tr>
<tr>
<td>308</td>
<td>344</td>
<td>4.7</td>
<td>0.1...0.4</td>
<td>1...8</td>
<td>weak</td>
</tr>
<tr>
<td>337</td>
<td>380</td>
<td>5.8</td>
<td>0.25...0.75</td>
<td>2...13</td>
<td>strong</td>
</tr>
<tr>
<td>355</td>
<td>404</td>
<td>6.5</td>
<td>0.4...1.3</td>
<td>3...25</td>
<td>very strong</td>
</tr>
<tr>
<td>488</td>
<td>586</td>
<td>13.7</td>
<td>0.8...1.5</td>
<td>25...110</td>
<td>strong</td>
</tr>
<tr>
<td>532</td>
<td>650</td>
<td>16.9</td>
<td>1.3...5.0</td>
<td>35...140</td>
<td>strong</td>
</tr>
</tbody>
</table>
CONCLUSIONS

We can summarize the basic spectral features obtained in this work as follows:
The fluorescence spectra of the oil film show a very conservative behaviour with excitation wavelength alteration. The emission maximum location is constant while the excitation wavelength remains below the fluorescence emission band. For oil dispersed in water the emission maximum location and spectral shape strongly correspond with the excitation wavelength. Basic bands in the fluorescence emission spectrum for oil dispersed in water are located at 290, 340 and 400...450 nm.

For dissolved organic matter of natural origin the fluorescence emission maximum is practically constant while the excitation wavelength varies from 200 to 337 nm, but shifts towards the longer wavelengths when excitation exceeds 337 nm.

These distinctive features of spectra behaviour can be used to distinguish DOM and oil fluorescence.

On the basis of these experimental results we can propose the lidar system for oil diagnostics with two excitation wavelengths. The first excitation wavelength must be chosen from the spectral region 220...308 nm. Using fluorescence at 340 nm with this excitation we can determine the concentration of oil dispersed in water and detect pure light oil cuts. For accurate diagnostics of gasoline film the first excitation wavelength must be less than 266 nm. The second excitation wavelength for diagnostics of crude oils must be selected from the spectral range of 350 nm...400 nm. The second wavelength can be used for discrimination between oil and dissolved organic matter of natural origin. There is a special need in using two different excitation wavelengths in remote oil diagnostics in natural water. Oil in film, oil dispersed in water, and dissolved organic matter, become distinguishable if we use different spectral ranges for spectra excitation.

The new technique for oil film thickness measurement is also described in this work. The proposed technique operates with intensity ratios at two wavelengths inside the contour of the water Raman scattering band under an oil film. The advantages and limitations of this new method are considered.

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