

PROBLEMS OF REMOTE DIAGNOSTICS OF MINERAL OIL IN SEA WATER: OIL FILMS AND OIL DISPERSED IN THE WATER BODY

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ABSTRACT:

The global ecological problems we are facing nowadays urge us on creating the new methods of environmental monitoring. This work is aimed to make a contribution into the elaboration of sensitive and express technique for monitoring of oil spills in natural water. The work presents spectroscopic study of different crude and refined oils as well as their mixtures with water. It is shown that fluorescence spectra of pure mineral oils and dispersed in water are different, what allows us to distinguish them by means of remote technique. The fluorescence spectra of oil pollutions are compared with that of dissolved organic matter of natural origin. The new technique for oil film thickness measurement is suggested. It uses contour analysis of water Raman spectrum distorted in shape due to dispersion of attenuation index of mineral oil. Oil film thickness calculated in this way is independent of laser power output, altitude of fluorosensor and other experimental conditions which can not be controlled. This is a very important advantage of this technique comparatively with others. The possibilities and limitations of the proposed technique for oil film thickness measurement are considered.

1. INTRODUCTION

The most wide-spread organic pollutions in ocean water are represented by crude and refined mineral oils. The actual problem of environmental control demands the elaboration of express and highly sensitive techniques for oil pollutions monitoring. Recently, several lidar systems using fluorescent techniques have been developed for remote detection of oil spills (Hengstermann and Reuter, 1990; Cecchi et al., 1992, Pantani et al, 1992).

If an oil spill is spread on water surface the laser fluorosensor detects a fluorescence band caused by oil pollution, and a suppression of intensity of water Raman scattering by an oil film. The careful spectral analysis of the fluorescence spectral shape for an oil spill, and its comparison with spectra of classified oils permit to recognize the type of mineral oil spread on water surface (Hengstermann and Reuter, 1990, 1992). The thickness of oil film, and consequently the total oil volume estimate, can be calculated from airborne data using the information about water Raman suppression by an oil film (Kung, Itzkan, 1976; Hoge, Swift, 1980; Hengstermann, Reuter, 1990).

The case when oil spill is mixed with sea water is more difficult for remote analysis because of interference of two fluorescence signals - from oil film on water surface, and oil pollution dispersed in the water body. The presence of oil in dispersed form may influence the

result of oil type classification from fluorescence spectra. Fluorescent experimental studies described in scientific literature earlier have been carried out only for mineral oils as pure substances, but not for oil dispersed in water body.

During the application of fluorescent techniques for oil spill diagnostics investigators have faced also serious difficulty caused by similarity of emission fluorescence spectra for crude oils and dissolved organic matter of natural origin (Patsayeva, 1995b). This effect is more important for thin oil films of micrometer thickness.

To solve the problems mentioned above the fluorescent spectroscopic study of different types of mineral oil (gasoline, kerosene, diesel fuel, engine oil, several crude oils) as well as their mixtures with water was carried out in this work. For comparison fluorescence spectra of water samples containing dissolved organic matter of natural origin were detected.

2. FLUORESCENCE SPECTRA OF OIL POLLUTIONS

The measurement of emission and excitation fluorescence spectra of mineral oils and water samples was performed using luminescence spectrometer "Jobin Yvon 3CS". The excitation wavelength was altered from 222 to 532 nm, and corresponded with one of laser sources.

2.1 Fluorescence of Oil Films

Thin oil films were made in quartz cells of special shape with constant distance between parallel plates varied from 1 to 1000 microns.

Fluorescence of gasoline excited at 220 or 270 nm has a maximum at 290 nm. The emission maximum of diesel fuel is located at 350...400 nm under excitation wavelength up to 337 nm. Fluorescence spectra for different crude oils have broad emission bands similar

in shape, with maximum located at 420...490 nm, depending on oil type and film thickness. As thickness rises from 1 to 100 microns the spectral maximum shifts for 10...40 nm to longer wavelengths depending on oil type.

The fluorescence of oil film show very conservative behaviour with excitation wavelength alteration. The emission maximum location and spectral shape keep constant while excitation wavelength remains below the emission maximum.

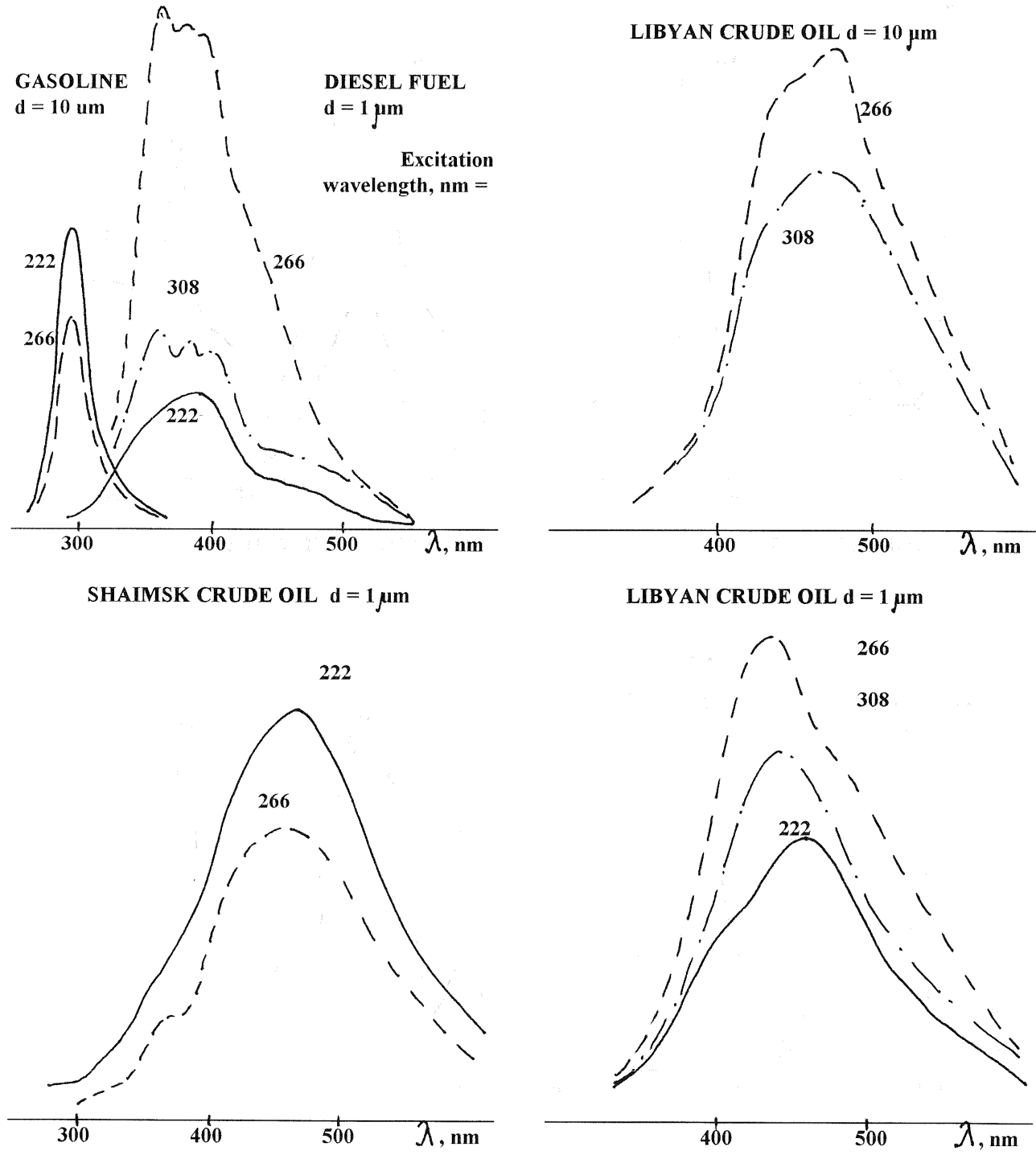


Fig. 1. Fluorescence emission spectra of mineral oils at different excitation wavelengths.

2.2 Fluorescence of Oil Dispersed in Water

The samples of oil in water were prepared by mixing few milligrams of mineral oil with 1 liter of distilled water. Part of the oil produced an oil film on water

surface, so the concentration of oil dispersed in water was lower than the total oil content during the mixing process. In our spectroscopic study we do not distinguish emulsified and truly dissolved oil species, because we tried to bring a process of sample preparation to natural conditions.

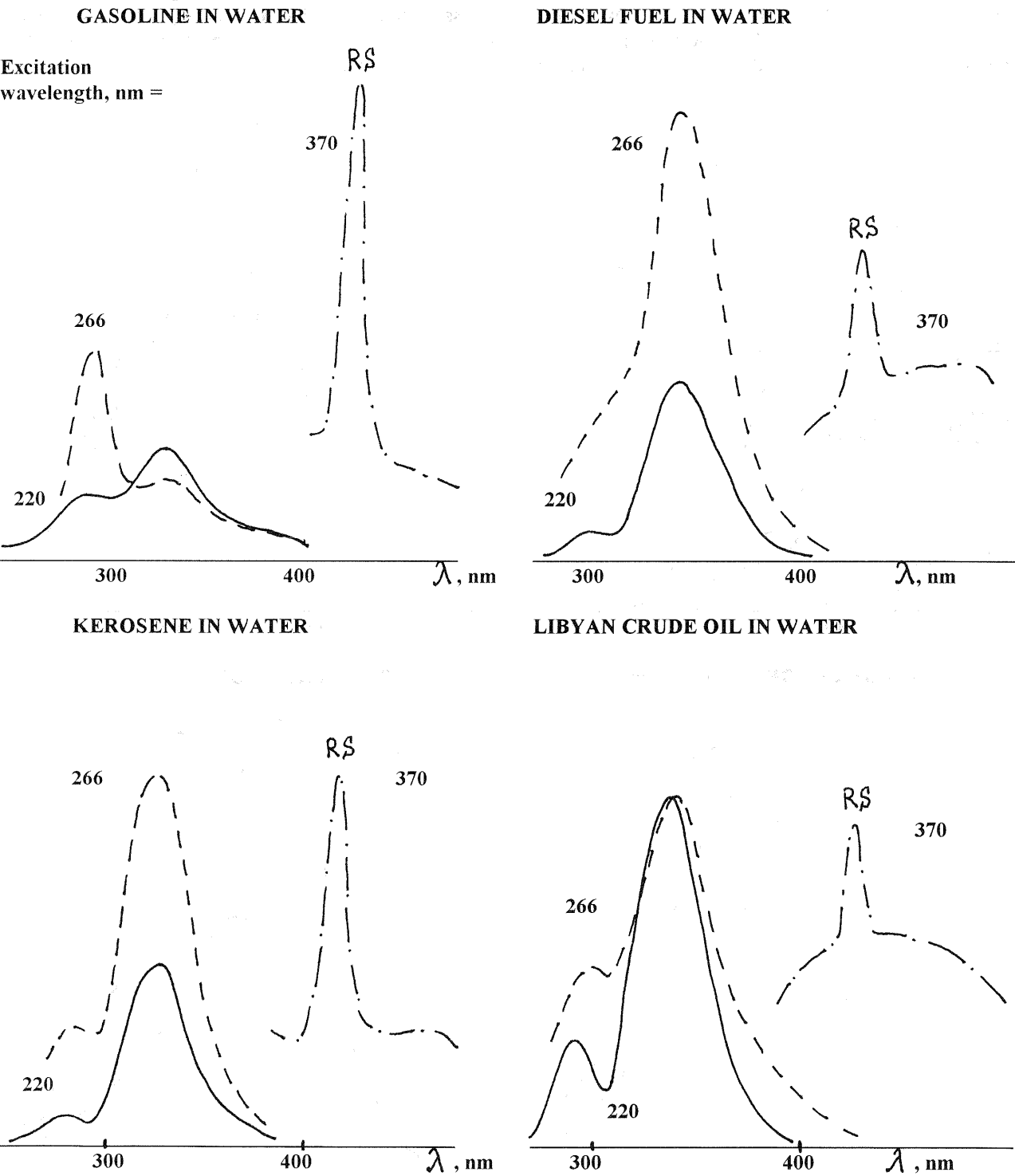


Fig. 2. Fluorescence emission spectra of oil dispersed in water excited at different wavelengths.
RS - water Raman scattering

Fluorescence emission spectra of oil dispersed in water exhibit more complex structure comparatively to spectra of pure mineral oils. Under shortwave excitation several maxima are presented in emission spectrum of water mixed with oil. For example, pure gasoline has the only one fluorescence maximum located at 290 nm, but spectrum of sample of gasoline in water presents two maxima at 290 and at 330 nm.

For oil dispersed in water emission maximum location and spectral shape strongly correspond with excitation wavelength. Basic bands in fluorescence emission spectrum for mineral oils dispersed in water are located at 290, 330...340 and 400...450 nm. The number of bands in emission spectrum, and ratio of their intensities vary for different mineral oils, and could be used for oil type classification.

3. FLUORESCENCE OF DISSOLVED ORGANIC MATTER

Naturally occurring organic compounds are found in significant concentrations in water throughout the world. Many organic chemicals found in natural waters can be regarded as products of both biosynthesis and biodegradation. Until now not more than 30% of dissolved organic matter have been chemically characterized.

For natural water samples two spectral components are observed with excitation below 270 nm. The first component with maximum at 340 nm is called in literature "protein-like fluorescence". The second one is caused by humic substances, and has blue fluorescence with maximum located at 400...460 nm depending on excitation wavelength. For the last component the emission maximum is practically constant while excitation wavelength is varying from 200 to 308 nm (with small blue shift of maximum when excitation is changed from 270 to 308 nm). With rising the excitation from 308 nm to higher wavelengths, the position of the emission maxima for all natural water samples shifts towards longer wavelengths. Models of the nature of fluorescence of dissolved organic matter have been developed to explain this phenomenon. The distinctive features of spectra behaviour with excitation alteration can be used to distinguish dissolved organic matter naturally occurring in water and oil pollution.

On the basis of experimental results we can propose the lidar system for oil spill diagnostics with two excitation wavelengths. There is a special need in using more than one wavelength for excitation. Oil in film, oil dispersed in water, and dissolved organic matter become distinguishable if we use different spectral ranges for spectra excitation.

The first excitation wavelength must be chosen from the spectral region 220...270 nm. Analyzing emission at 340 nm we can estimate the concentration of oil fraction dispersed in water, and also detect the presence of light oil products emitting at 290 nm. The second excitation wavelength for diagnostics of crude oils must be selected from the spectral range of 350...400 nm. The excitation at this wavelength can be used also for discrimination between oil pollution and dissolved organic matter of natural origin.

4. MEASUREMENT OF OIL FILM THICKNESS

For oil film thickness estimation it is possible to use a suppression by an oil film of the integral intensity of water Raman stretching band (Kung, 1976). The ratio of water Raman signals over and outside the oil slick, R^*/R , can be used to calculate the oil film thickness d , if the extinction coefficients at excitation and Raman wavelengths, k_e and k_r , are known (Hoge, Swift, 1983):

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

Hoge and Swift (1983) have applied a nitrogen laser to excite Raman signal of natural ocean water beneath the oil slick from an altitude of 150 m. In the cited reference the water Raman spectrum excited at 337 nm is strongly affected by fluorescence background from oil film. Hengsternann and Reuter (1990, 1992) have used the described technique for oil film thickness estimation from an altitude of 300 m by means of the airborne laser fluorosensor with excimer laser operating at 308 nm.

There are some problems in implementation of the technique of integral water Raman suppression for estimation of oil film thickness. Remotely detected signal depends on such experimental conditions as laser power accidental variation, laser beam penetration into the water column, turbidity of water column and others. To minimize the influence of experimental conditions on estimated thickness of oil film on water surface we offer another technique which uses contour analysis of water Raman spectrum.

The Raman backscattered signal from water molecules is used in remote fluorescent techniques as an internal standard to minimize the effect of laser beam penetration into the water column. The other usage of water Raman band is measurement of temperature and salinity of sea water. The method is based on dependence of spectral shape of OH Raman stretching band 3100...3700 cm^{-1} on water temperature and salinity. Though this dependence is considerably weak, the use of "least squares method" or mathematical "reduction method" has allowed us to achieve good results in temperature and salinity evaluation both in

laboratory experiments and in remote sensing of sea water surface (Patsayeva, 1989).

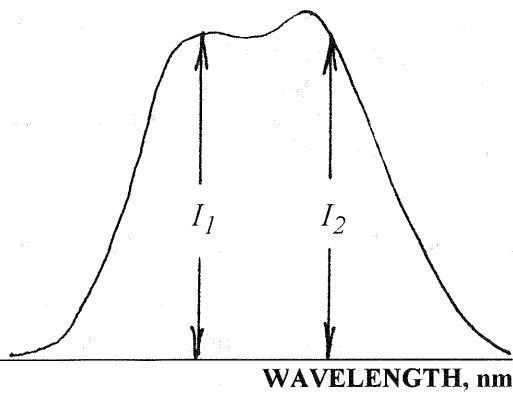


Fig. 3a - Raman spectrum from clean water.

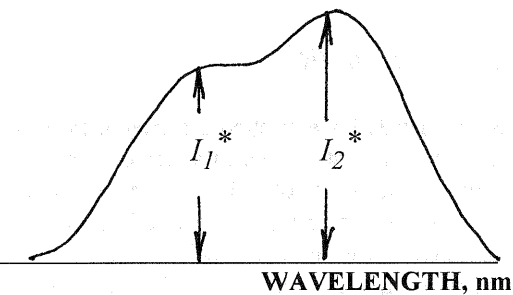


Fig. 3b - Raman spectrum from water under an oil film, suppressed in intensity.

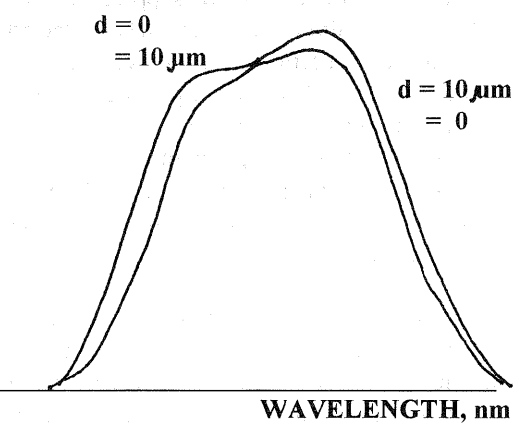


Fig. 3c - Raman spectra, normalized to a unit area, from clean water and water under the oil film of thickness $d = 10 \mu\text{m}$, $dk/d\lambda = - 0.0025 \text{ (nm } \mu\text{m)}^{-1}$.

In case of remote sounding of water under an oil film the Raman backscattered signal is suppressed in

intensity, and its spectral shape is distorted due to dispersivity of light attenuation coefficient for oil film. The Raman intensity at wavelength λ_1 in presence of oil film of thickness d on water surface is suppressed by exponential factor $\exp(-k_1d)$, where k_1 is attenuation coefficient at wavelength λ_1 . Consequently, the Raman intensity at wavelength λ_2 is suppressed by exponential factor $\exp(-k_2d)$. The intensity ratio at two wavelengths is a function of oil film thickness d :

$$I_1^*/I_2^* = I_1/I_2 \exp (k_2d - k_1d) \tag{2},$$

where I_1, I_2 - Raman intensities from clean water without oil film, I_1^*, I_2^* - Raman intensities from water layer under the oil film of thickness d .

For oil film thickness evaluation we use the formulae:

$$d = - \ln [(I_1^*/I_2^*)/(I_1/I_2)]/(k_2 - k_1) \tag{3}.$$

The oil film thickness calculated from this equation is independent of laser power output, altitude of fluorosensor, turbidity of water column and other experimental conditions which can not be controlled. This is a very important advantage of the proposed technique. For oil film thickness estimation we can use also any other method of Raman contour analysis, developed earlier for temperature and salinity measurement (Patsayeva, 1989).

The possibilities and limitations of implementation of this technique for real oil spill monitoring are derived from fluorescence background caused by oil pollution and by dissolved organic matter of natural origin. To decrease influence of fluorescence on Raman scattering signal the excitation wavelength should not exceed 308 nm.

The precision of oil film thickness estimation depends on absorption coefficient of oil under investigation, as well as on excitation wavelength. For heavy oils the accuracy of oil film estimation is better, than for light oils with smaller absorption coefficient. The shortening of excitation wavelength improves the accuracy, but decreases the possible upper limit of thickness measurement. The lower and upper limits of oil film thickness estimation presented in the Table 1 are calculated from spectroscopic characteristics for typical crude oils considering the signal-to-noise ratio in Raman spectrum as equal to 100.

It is worth mentioning, that for application of any technique proposed for oil film thickness measurement the type of oil spilled on water surface must by identified.

Table 1. Limitations of film thickness estimation using contour analysis of water Raman spectrum for typical heavy/light crude oil.

wavelength of excitation, nm	water Raman wavelength, nm	width of water Raman band, nm	accuracy of d estimation, μm	maximal d , μm	effect of fluorescence
266	293	3,4	0,06 / 0,2	0,7 / 2	very weak
308	344	4,7	0,1 / 0,4	1 / 8	weak
337	380	5,8	0,25 / 0,75	2 / 13	strong
355	404	6,5	0,4 / 1,3	3 / 25	very strong
488	586	13,7	0,8 / 1,5	25 / 110	strong
532	650	16,9	1,3 / 5,0	35 / 140	strong

5. CONCLUSIONS

In contrast to fluorescence of oil dispersed in water and dissolved organic matter of natural origin the fluorescence spectra of mineral oils as pure substances show a very conservative behaviour with excitation wavelength alteration. For dispersed oil the emission maximum location and spectral shape strongly correspond with the excitation wavelength. Basic emission bands for dispersed oil are located at 290, 340 and 400...450 nm. The distinctive features of spectra behaviour found in the work can be used to subtract oil fluorescence from that of dissolved organic matter of natural origin. These fluorescent species become distinguishable if we use multiwavelength system for spectra excitation.

Also it has been shown that contour analysis of laser induced water Raman spectra provides us with measurement of thickness of oil film on water surface. Since this technique operates with water Raman signal normalized to a unit area, the result of oil film thickness estimation does not depend on laser output power and other experimental conditions during remote sensing.

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