

Fluorometric method for determining the thickness of a crude oil film formed on the water surface

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Crude oil
Fluorescence
Oil film thickness

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Abstract

An active remote method for determining the thickness of a crude oil spill on a sea-water surface was worked out and tested in the laboratory. In this ‘fluorometric’ method, the differences in optical and fluorescence properties of various types of crude oil were employed.

For selected types of crude oil, experimental pattern curves characterising the dependence of the fluorescence intensity signal I_f on the thickness of crude oil layer d were determined for the fluorescence signal at $\lambda_f = 700$ nm, which approximately related to the sensitivity maximum. A He-Ne laser was used as the exciting source. The results of pattern curve measurements were approximated by the theoretical function $I(d)$. Values of the constant of the function $I(d)$ for particular kinds of crude oil provided the data base for further calculations of the crude oil film thicknesses on the water surface. The method of calculating the thickness of crude oil films formed on the surface of artificial seawater of various salinities on the basis of recorded values of fluorescence signals is presented. The results show that the method introduced in this paper is suitable practical application.

1. Introduction

Determining the thickness of crude oil films occurring on the water surface is one of the most important problems concerning crude oil pollution in the marine environment. The thickness is an important parameter describing the amount of spilled crude oil. Knowledge of the thickness and the thickness gradient of oil films is essential for an understanding of how oil moves on the sea surface or mixes into a water column. Moreover, the temporal and spatial distribution of the thickness is needed for evaluations of sea-air interactions. It is therefore necessary to prepare measuring methods

that provide accurate information about the crude oil spill thickness. Various methods of measurements have been investigated, and it seems that remote methods utilizing lasers provide one of the most attractive alternatives for dealing with such problems. The remote measurement of the oil film thickness using laser-induced water Raman backscatter was first theoretically proposed in 1976 by Kung and Itzkan, and the feasibility of the practical field application was described in 1980 by Hoge and Swift. Attempts at a more accurate determination of oil film thickness by using crude oil fluorescence properties were also made by other workers, *e.g.* Sato *et al.* (1978), Hoge (1983) and Mazurov *et al.* (1983), Burlamacchi *et al.* (1983). All these workers used UV lasers as the exciting source. However, such lasers can only be employed when the oil film thickness does not exceed 10 μm . The remote measurement of oil film thickness by means of laser-induced fluorescence radiation was proposed by Visser in 1979. Thickness measurements have been performed in the laboratory using an excitation wavelength of 632.8 nm (He–Ne laser). The results of that paper are the basis for the active remote method known as the fluorometric method, which will be described here in detail.

2. Theoretical considerations

The method of crude oil thickness measurement is based on oil fluorescence properties and theoretical considerations given in Visser (1979).

The following basic assumptions were made:

- the intensity of the induced fluorescence is proportional to the intensity of the exciting radiation,
- the intensity of the fluorescence increases with the layer thickness until the thickness is smaller than the penetration depth of the exciting radiation,
- in the case of crude oil the penetration depth increases with the increase in the wavelength of the exciting radiation in the UV–VIS range,
- secondary fluorescence generated in the crude oil by fluorescence radiation can be neglected in comparison with the primary fluorescence,
- light scattering in the crude oil and water can be neglected as well.

If a parallel monochromatic beam of light of intensity I_0 is directed perpendicularly onto a crude oil layer of thickness d on the sea surface, the fluorescence emitted is a derivative of the radiation from the crude oil and from the substances dissolved in the water. Therefore the intensity of fluorescence radiation includes two terms and can be written as follows:

$$I_f(\lambda_0, \lambda_f) = I_d(\lambda_0, \lambda_f) + I_w(\lambda_0, \lambda_f), \quad (1)$$

where

- $I_d(\lambda_0, \lambda_f)$ – fluorescence intensity of the crude oil layer of thickness d ,
- $I_w(\lambda_0, \lambda_f)$ – intensity of the background fluorescence (organic matter dissolved in the water),

- λ_0, λ_f – respective wavelengths of the exciting and emitted radiation.

Both terms can be written as follows:

$$I_d(\lambda_0, \lambda_f) = I_0(\lambda_0)\eta_r(\lambda_0, \lambda_f)T_0^2 \frac{k_0}{k_0 + k_f} \{1 - \exp[-(k_0 + k_f)d]\}, \quad (2)$$

$$I_w(\lambda_0, \lambda_f) = I_0(\lambda_0)\eta_w(\lambda_0, \lambda_f)T_0^2 \frac{c_0}{c_0 + c_f} \{\exp[-(k_0 + k_f)d]\}, \quad (3)$$

where

- $I_0(\lambda_0)$ – exciting radiation intensity,
- k_0, k_f – crude oil attenuation coefficients for λ_0, λ_f ,
- c_0, c_f – water attenuation coefficients for λ_0, λ_f ,
- $\eta_r(\lambda_0, \lambda_f)$ – spectral efficiency of crude oil fluorescence for λ_f ,
- $\eta_w(\lambda_0, \lambda_f)$ – spectral efficiency of background fluorescence for λ_f ,
- T_0 – transmission coefficient of the air-crude oil interface.

The detector of the measuring system records part of the emitted fluorescence at the intensity

$$I_f(d) = D \times I_f(k_0, k_f), \quad (4)$$

where

- $I_f(d)$ – fluorescence intensity registered by the detector,

- D – constant depending on the parameters of the recording device.

Combining eqs. (1), (2) and (3), the fluorescence intensity I_f in terms of layer thickness d is

$$I_f(d) = I_f(\infty) \{1 - \exp[-(k_0 + k_f)d]\} + I_f(0) \exp[-(k_0 + k_f)d] \quad (5)$$

or where the parameters in the emitting-recording system are constant

$$I = B [1 - \exp(-Ad)] + C \exp(-Ad), \quad (6)$$

where

$$I = I_f(d),$$

$$B = I_f(\infty),$$

$$C = I_f(0),$$

$$A = k_0 + k_f.$$

Taking into account eq. (6), the crude oil film thickness is given by

$$d = \frac{1}{A} \ln \left[\frac{B - C}{B - I} \right]. \quad (7)$$

If background fluorescence does not occur or is negligible, eq. (7) can be reduced to the special case considered by Visser (1979):

$$d = \frac{1}{A} \ln \left[\frac{B}{B - I} \right]. \quad (8)$$

Thus, in order to determine the crude oil film thickness, it is necessary to know A and the values of signals B , I and C . Visser found parameters A and B experimentally. For this purpose the oil was excited at two wavelengths, one in the UV (337 nm) and one in the red (633 nm). Additionally, in order to obtain more exact information about the value of B , a third intermediate excitation wavelength (490 nm) was used. The means of determining the values of constants A and B considered in the present paper is different and is described in detail by Gąsowski (1993).

3. Measuring technique

Taking into account the theoretical assumptions of the investigating method, the apparatus for laboratory examinations of the fluorescence intensity induced in a crude oil film was set up, a block diagram of which is shown in Fig. 1. A He–Ne Laser generating radiation of $\lambda = 632.8$ nm and power $P = 2.8$ mW was used as the exciting source S . After passing through diaphragm D , the laser beam was directed by the mirror Z_1 onto the free surface of the oil in the wedge K . The fluorescence radiation locally excited from this spot was focused by the lens L_3 and reflected from the mirror Z_2 and, after having passed through the optical system OU (L_1 and L_2 lenses and absorption filter F), impinged on the entrance slit of the monochromator M . The direction of both the excitation and the detected fluorescence radiation was always nearly perpendicular to the oil surface. The monochromatic light beam emerging from the monochromator M was recorded by the photomultiplier FP , the anodic signal from which was recorded by the microvoltmeter W and, after amplification, by the digital voltmeter VC . The maximum relative distribution of the sensitivity of the

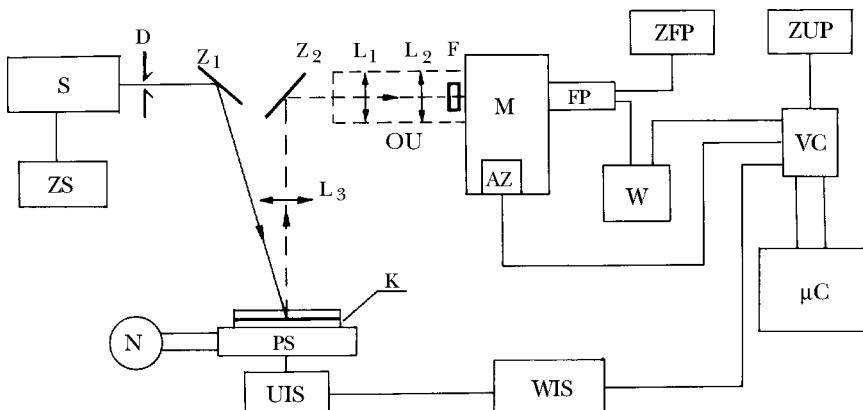


Fig. 1. Block diagram of the apparatus for excitation and measurement of fluorescence intensity *vs.* oil film thickness

detection system applied occurs at wavelength $\lambda = 696$ nm, mainly due to the use of the absorption filter F, which is a part of the optical system OU. Such a configuration of the detection path cuts off the influence of the exciting radiation and reduces the influence of scattered light on the measuring signal. The oil film thickness was changed by the horizontal pass of the wedge K. This wedge was placed on the gantry PS driven by the electric motor N. The electric motor N cooperates with the optical system UIS working in the infra-red. The UIS system emits impulses controlling the reading at the moment the exciting laser beam is incident on the oil film of thickness d . After transformation and amplification by the WIS system, the impulses were transmitted to the voltmeter VC and microcomputer μ C for reading and recording of the measurements. These were transmitted to the computer store and properly re-counted, the essential parameters of the measuring system being taken into account in the process. After software treatment, the data were stored as the fluorescence intensity I_f and presented in a graphic manner on the computer display.

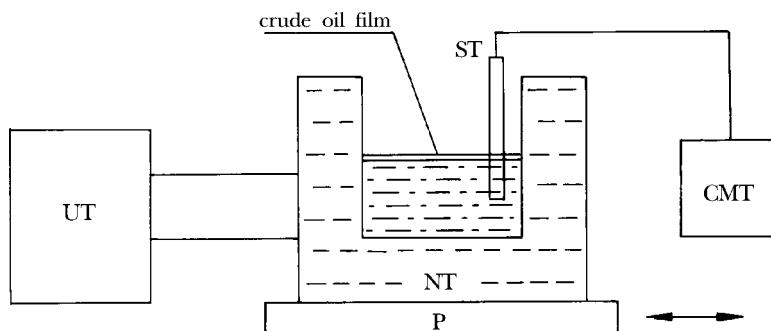


Fig. 2. Measuring vessel

The apparatus described above was also used for measuring the fluorescence intensity I_f of the oil film on the free water surface. The wedge K was replaced with two cylinders containing water, in one of which the water surface was covered with an oil film. The containers were placed on the platform P with a limited range of pass in order that the exciting laser beam could fall on the selected point of the clear or polluted water surface (Fig. 2.). The ZUP system was used for measuring the fluorescence intensity of the oil film on water surface. The system enabled the measurements to be read off and recorded at any moment. In order to eliminate the influence of the background fluorescence on the measurements, the fluorescence intensity of clear water was also measured for comparison.

4. Results

The apparatus was used to determine the spectral distribution of fluorescence intensity $I_f(\lambda)$ of selected types of crude oil of known optical properties for layers of various thickness d . These spectra served to determine the changes in fluorescence intensity as a function of d for various wavelengths λ_f . Following the introductory estimations of the variations, further measurements were carried out for the fluorescence signal at $\lambda_f = 700$ nm, which was approximately related to the maximum sensitivity of the detection system applied.

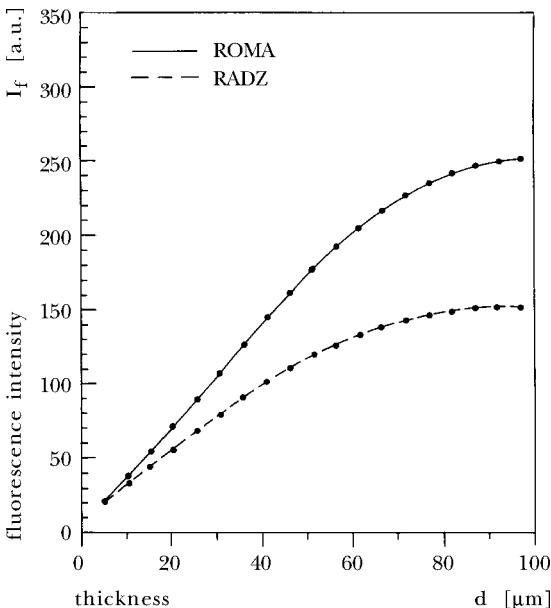


Fig. 3. Pattern curves of fluorescence signal dependence on the layer thickness at ROMA and RADZ crude oils registered at $\lambda_f = 700$ nm

For all the crude oils investigated, the authors performed the measurements of $I_f(d)$ in the range of d from 5.1 to 96.9 μm ($\Delta d = 5.1 \mu\text{m}$). The results of these measurements were used to evaluate the dependence of I_f on d . For example, Fig. 3 presents the experimental pattern curves of Romashkino crude oil (ROMA) and a mixture of Zazhaidina and pipeline oils (RADZ). The pattern curves are characteristic of various kinds of crude oil and the different slopes of the curves are caused by the differentiation of fluorescence spectra of various kinds of crude oil. For a layer of RADZ crude oil no thicker than 85 μm there is no further increase in fluorescence intensity, because the fluorescence saturation associated with the penetration depth of the exciting radiation has been attained. Eq. (6) implies that

the dependence of fluorescence on the crude oil layer thickness, in the absence of background fluorescence but with the constant parameters of the measuring system ($C = 0$), can be described by

$$I = B[1 - \exp(-Ad)]. \quad (9)$$

Since eq. (9) is a function of constant values B and A , the accuracy of estimates for the pattern curves described by this function was determined. Values of constants B and A were calculated by means of the least square method using the iterative procedure (Gąsowski, 1993). The results of calculations B and A , as well as the estimation of their errors for selected crude oils are shown in Tab. 1. Fig. 4 shows the analytically obtained curves and the results of measurements for the fluorescence intensity I_f versus the film thickness d . Good agreement was obtained between the theoretical and empirical curves. The greatest differences between the theoretical and empirical values occur for layer thicknesses close to the values approaching the limits of the measuring range applied.

Table 1. Constants B and A and the estimation of their errors

Type of oil	B	A	B error		A error	
			abs.	[%]	abs.	[%]
Arabian	220.41	2.6946×10^{-2}	3.79	1.7	1.12×10^{-3}	4.2
Kirkuck	695.32	6.7096×10^{-3}	64.97	9.3	8.03×10^{-4}	11.9
Iranian	697.69	6.7274×10^{-3}	45.19	6.5	5.58×10^{-4}	8.3
Romashkino	407.84	1.0778×10^{-2}	28.64	7.0	1.12×10^{-3}	10.4
Mixture of oils (RADZ)	189.39	1.8731×10^{-2}	5.03	2.7	9.54×10^{-4}	5.1

Values of B and A were used to determine the crude oil thickness on the water surface. The crude oil films were created by spilling a known volume of crude oil onto the surface of distilled water or artificial seawater of various salinities placed in special cylinders. During the investigations, the measuring distance as well as the opening angle remained unchanged. The fluorescence intensity I_f was recorded each time at six different points of the film surface along the selected direction of the spill and for the wavelength $\lambda_f = 700$ nm. In order to determine the crude oil thickness based on record fluorescence signals it is necessary to determine the background fluorescence *i.e.* the fluorescence of the water on which the crude oil film was formed. The spectral distributions of fluorescence from distilled water and water of salinity $S = 35$ psu were determined (Fig. 5). The results show that the record fluorescence values for both distilled water and artificial seawater vary between 0.8 and 1.1 mV. These values are comparable with the internal

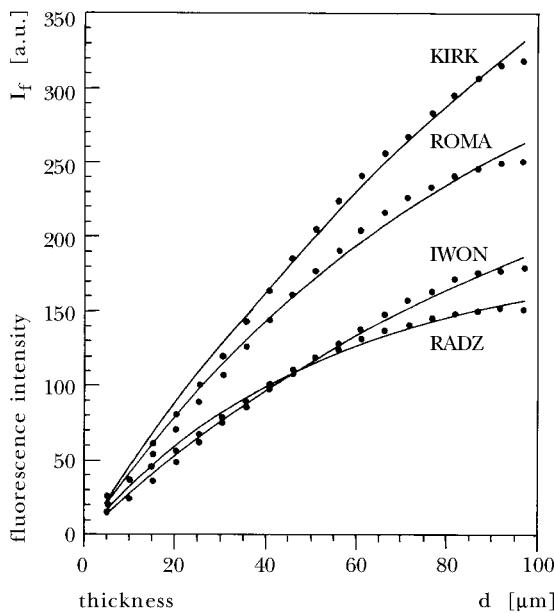


Fig. 4. Variations in the fluorescence intensity I_{ft} as a function of layer thickness d for the investigated crude oils; dots denote experimental values of I_f

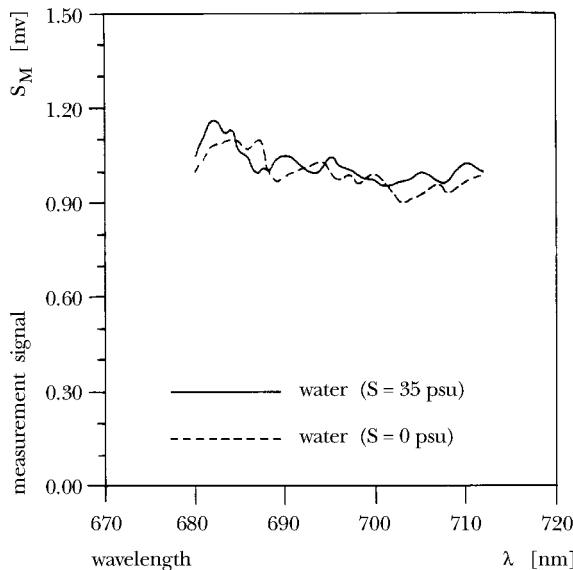


Fig. 5. Spectral distribution of signals from the distilled water and the artificial seawater ($S = 35$ psu); exciting radiation wavelength $\lambda_{ex} = 632.8$ nm

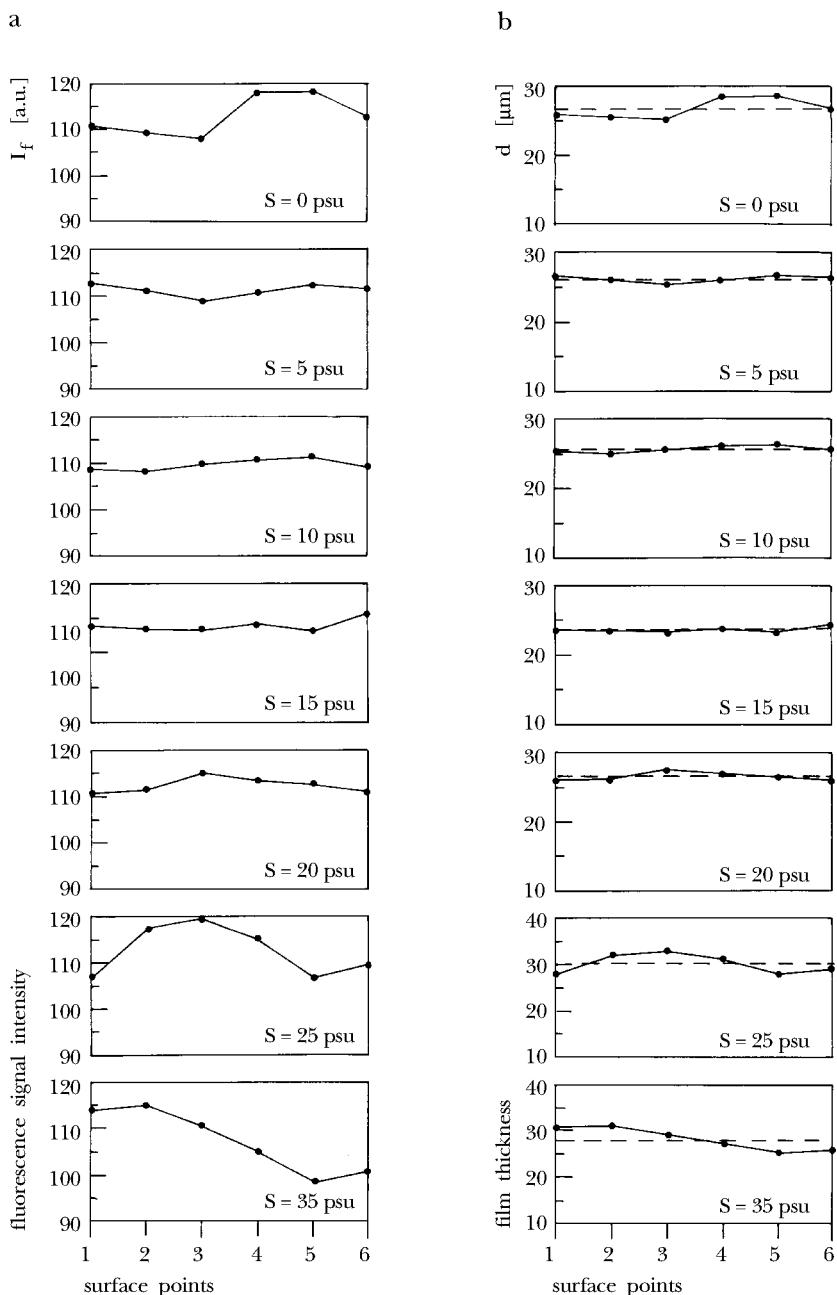


Fig. 6. Signal fluorescence values record at selected points of the ARAB crude oil film formed on the water surface of various salinities ($\lambda_f = 700$ nm) (a); variations of ARAB crude oil film thicknesses calculated from eq. (8) based on the data shown in Fig. 6a and from the constant values A and B . The broken line denotes the mean thickness of the film (b)

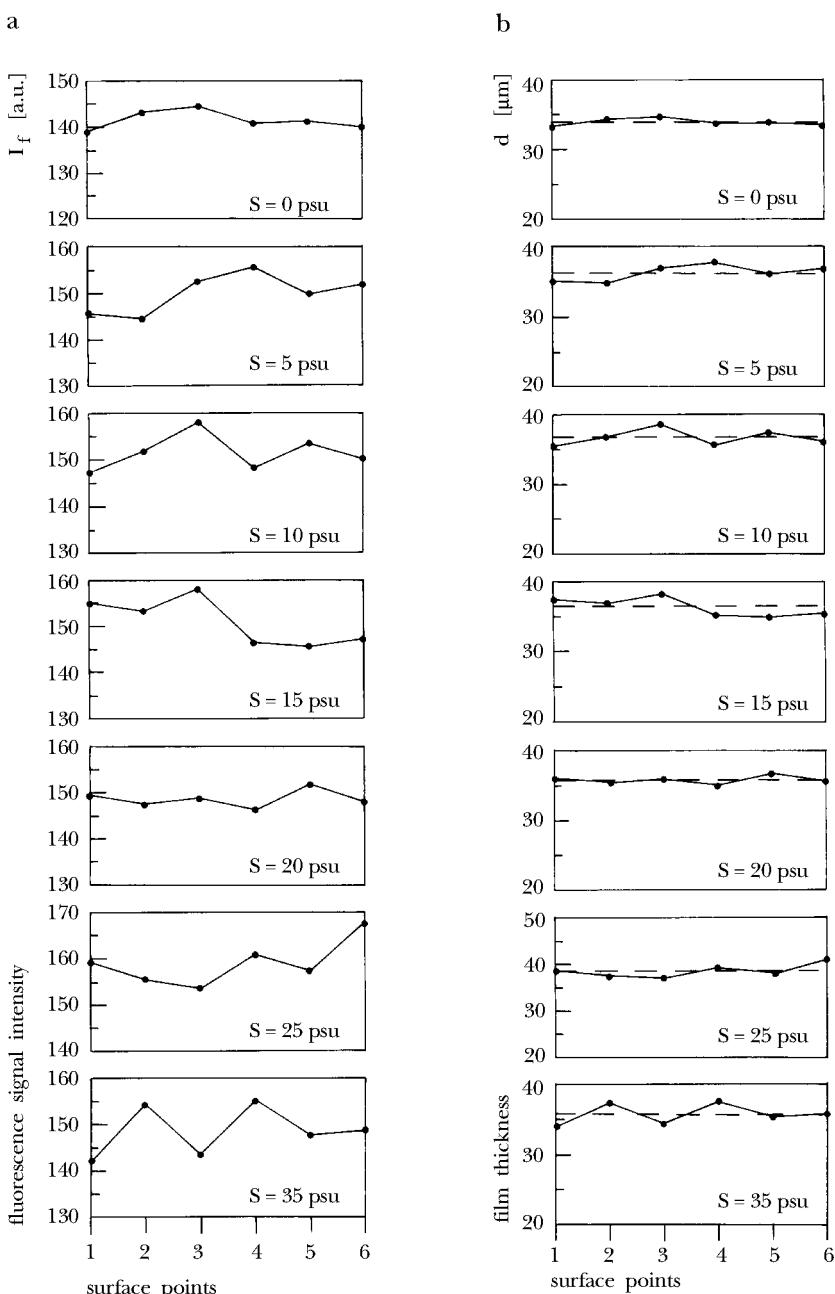


Fig. 7. Signal fluorescence values record at selected points of the KIRK crude oil film formed on the water surface of various salinities ($\lambda_f = 700 \text{ nm}$) (a); variations of KIRK crude oil film thicknesses calculated from eq. (8) based on the data shown in Fig. 7a and from the constant values A and B . The broken line denotes the mean thickness of the film (b)

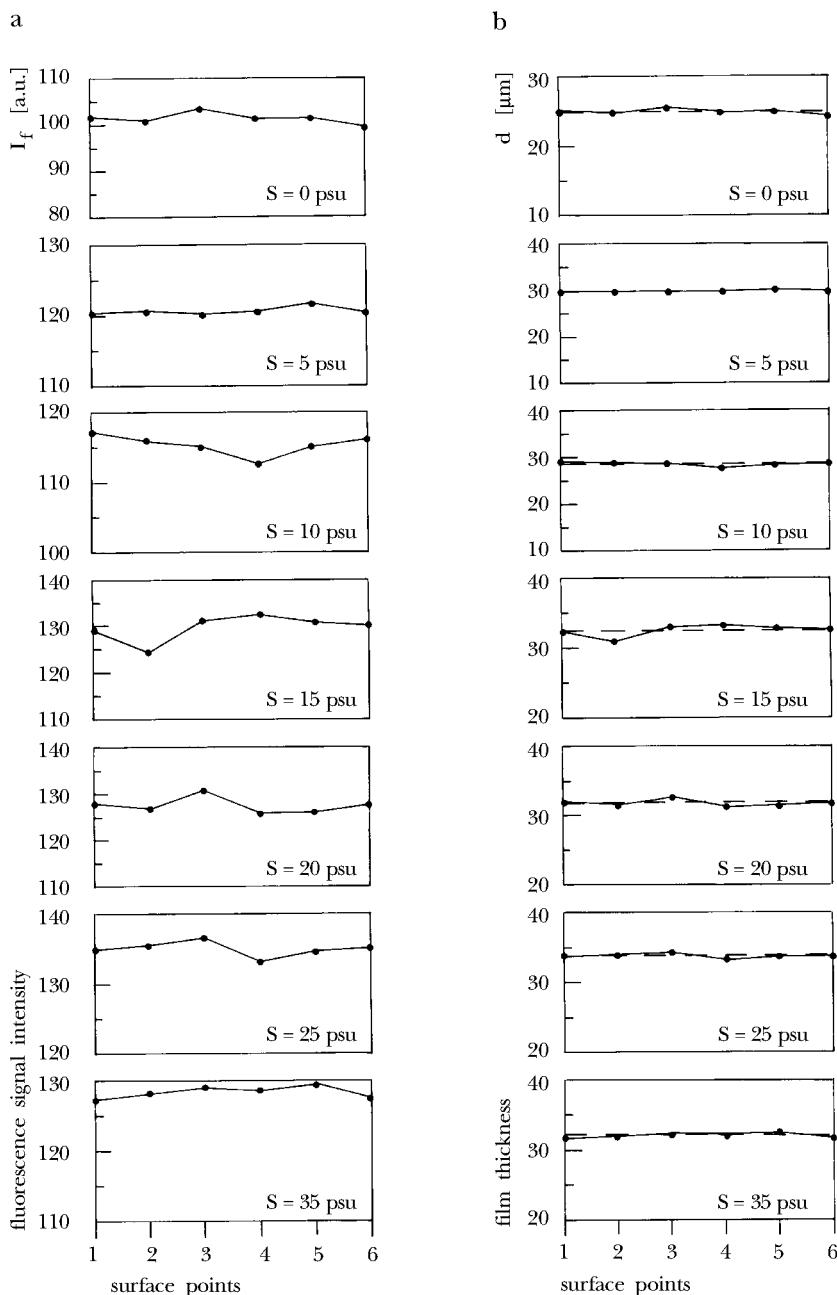


Fig. 8. Signal fluorescence values record at selected points of the IRAN crude oil film formed on the water surface of various salinities ($\lambda_f = 700 \text{ nm}$) (a); variations of IRAN crude oil film thicknesses calculated from eq. (8) based on the data shown in Fig. 8a and from the constant values A and B . The broken line denotes the mean thickness of the film (b)

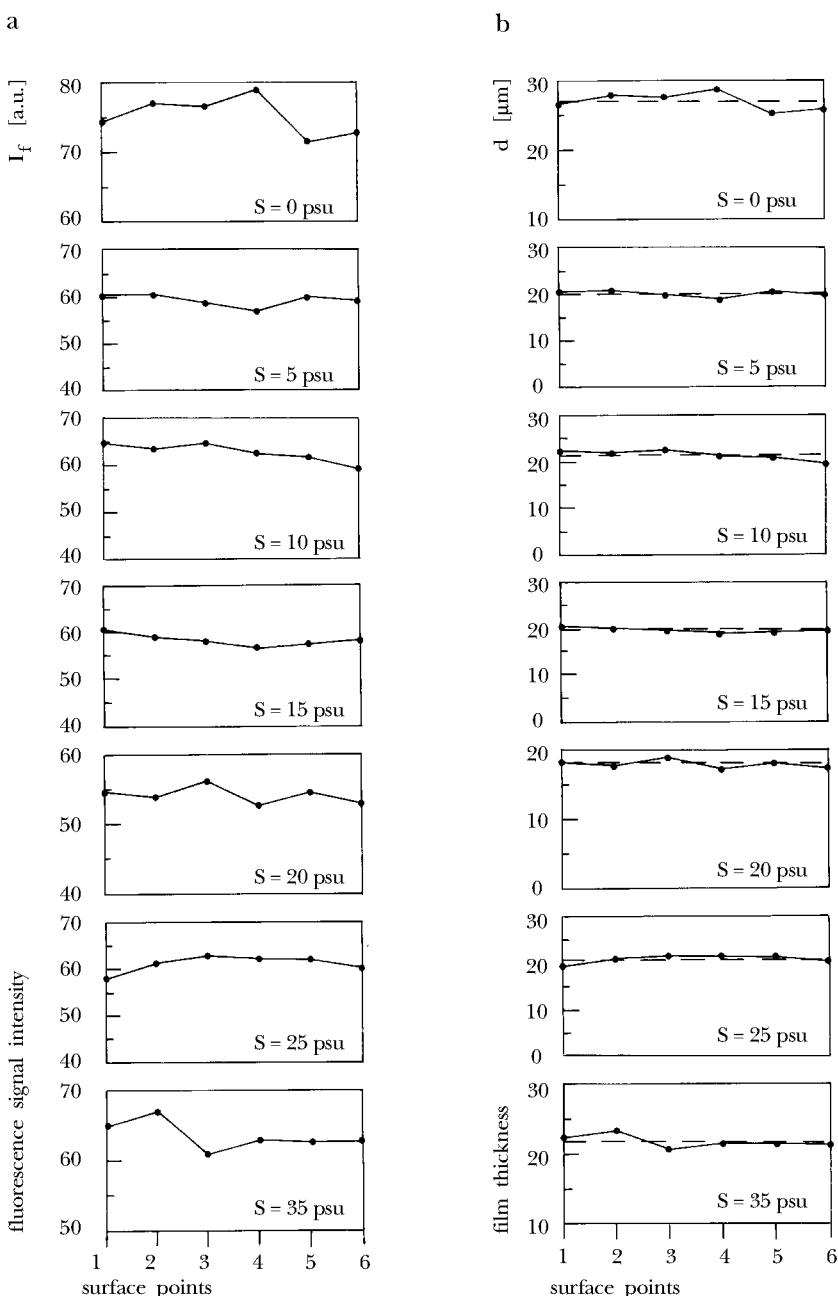


Fig. 9. Signal fluorescence values record at selected points of the RADZ crude oil film formed on the water surface of various salinities ($\lambda_f = 700 \text{ nm}$) (a); variations of RADZ crude oil film thicknesses calculated from eq. (8) based on the data shown in Fig. 9a and from the constant values A and B . The broken line denotes the mean thickness of the film (b)

noise of the measuring system (1 mV). Therefore it is correct to assume that the distilled water and artificial seawater do not show any fluorescence when excited with radiation of $\lambda = 632.8$ nm. It was further assumed that there is no background fluorescence; only the crude oil fluorescence is measured.

For each kind of crude oil seven measuring series were carried out. Figs. 6a, 7a, 8a and 9a show the results of fluorescence intensity measurements for light Arabian (ARAB), Kirkuck (KIRK), Iranian light (IRAN) crude oils and a mixture of Zazhaidina and pipeline oils (RADZ). According to Fig. 5, eq. (8) without the background fluorescence term was applied to calculations. Figs. 6b, 7b, 8b, 9b show the results of those calculations. The broken line denotes the mean value of the film thickness along the selected direction of the spill. It can be seen that the mean values of film thickness created on water of various salinities (even though the same amount of crude oil was always spilled) are different. This means that various kinds of crude oil spill differently.

5. The accuracy of the method

Clearly, the thickness measuring error depends not only on the accuracy with which the fluorescence intensity is measured, but also on that with which the pattern and experimental curves are determined, in other words, on the errors inherent in constants B and A . Therefore, a precise analysis of errors was carried out (Mrozek-Lejman *et al.*, 1990; Kopeć *et al.*, 1991; Gaśowski, 1993). This revealed that the total error for layer thickness was dependent in various ranges on the type of crude oil. Tab. 2 shows the results of calculations carried out for the total error ($\Delta d/d$) for the selected crude oils. The smallest error was made for ARAB crude oil, the greatest for KIRK crude oil. In general, the greatest errors related to thicknesses close to the boundary values of the measuring scale applied. Error evaluation allowed for the limits of measurement to be determined for various kinds of crude oil. It was decided that for some crude oils (*e.g.* RADZ) it was necessary to narrow the range to about $85\mu\text{m}$. Rejection of measurements of

Table 2. Ranges of total error for measurements of layer thickness ($|\Delta d| d^{-1} \times 100$) for selected crude oils

Type of oil	Range of value ($ \Delta d d^{-1} \times 100$)
ARAB	7.9 – 14.1
KIRK	21.2 – 25.4
IRAN	16.3 – 19.4
RADZ	10.3 – 13.4

the fluorescence intensity near saturation level, where errors are significant, leads to a reduction in errors for the constants B and A .

6. Conclusions

The differences in optical and fluorescence properties of various kinds of crude oil enable the experimental pattern curves describing the dependence of fluorescence intensity on the crude oil thickness to be determined. Indirectly, the crude oil thickness can be determined from eq. (8) on the basis of recorded fluorescence signals and the constants B and A of the approximating function for the pattern curve.

The constants B and A , determined by the least square method, constitute a data base for further calculations of the crude oil film thicknesses formed on the water surface. The useful measuring range in this method is determined by an exciting radiation wavelength. By applying a He–Ne laser ($\lambda_{\text{ex}} = 632.8 \text{ nm}$) as excitation source allows crude oil film thickness up to $100 \mu\text{m}$ to be measured. The lower limit of this range is $5 \mu\text{m}$. The method introduced in this paper allows for the determination of time and spatial distributions of the spill thickness. The practical application of this method involves the solution of a number of technical problems *e.g.* the application of excitation source a suitably powerful and increase in the effectiveness of the detection system.

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