



CHANGES OF OPTICAL PROPERTIES OF LUBRICATING OIL DURING ITS USE

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Abstract

The paper presents optical properties of mineral motor oil tested during its service in a car engine. The test was carried out in the question of oil detection and identification in water environment by means of optical methods. The light refraction and absorption coefficients were measured for the fresh oil and in particular state of its use. Light absorption as well as refractivity of oil increase during its use. The contrast, which the oil layer creates on the sea surfaces, slightly increases with oil use and this effect does not practical influence on the detection. Variations of light absorption disallow precise determination of the thickness of an oil layer. Furthermore, fluorescence spectra excited with ultraviolet radiation were measured. Both fresh and used oil has the greatest ability to photoluminescence in the range of wavelength between 300 to 400 nm. For all investigated wavelengths fluorescence increases with the time of oil use. Also shapes of spectra change. These changes disallow to determine the kind of oil by means of fluorescence methods.

Keywords: *oil, sea, identification, absorption, fluorescence, refraction*

1. Introduction

Petroleum is one of the most common pollutants of the marine environment and in some basins it is an almost constant component of seawater [4, 10]. Petroleum pollution is significant both in terms of magnitude, since the annual input of oil to global ocean is estimated at 1.3 million tons [10], and its adverse impact¹. Petroleum occurs in various forms in seawater [6]. Each of these forms exerts its own individual influence on the environment. Among other, oil modifies the optical properties of the polluted water [7, 8, 12, 13, 14, 21]. These modifications are especially significant because of remote sensing, which makes it possible to collect data providing information for monitoring marine environment. Remote sensing is optical measurements based on the real physical relationship between the parameter of interest and the measured optical variable [16, 22]. Petroleum pollutant modifies results of these measurements. On the other hand, remote sensing is an primarily tool of the oil spill detection system nowadays [10, 22]. Moreover, remote sensing is used also for determination of petroleum pollutant in more details [1, 2], however this is limited by variability of oils. The oils – many kinds of crude oil and petrochemical products – vary

¹ Impact of the petroleum on the marine environment has been reported in many papers. A number of monographs [3, 4, 9, 10, 11] present lists of the relevant papers.

in their compositions and properties [5, 17]. The variability of oils is best reflected by their fluorescence spectra [20] and therefore fluorescence is a tool for identification of oil. Comparison of the total spectra allows even similar products of one kind to be distinguished [18].

Knowledge concerning optical properties of oil, especially its coefficients of light refraction and absorption, is the key to description its influence on any optical process. Lubricating oils create a separate group among many different petrochemical products [5]. The paper presents some results of investigations of the optical properties of a lubricating oil and changes of these properties occurring service in natural conditions. These investigations were carried out in the question of detection and identification of oil spills in marine environment and the current test is an extension of earlier work [19]. The refractivity and light absorption coefficient characterizing an oil in different stages of its use as well as its fluorescence spectra are presented here.

2. Methods

The aim of investigations was to determine changes, which occur in oil during its normal, constantly controlled service in a motor. The changes may be expressed as a dependence on the degree of oil use. The assumption was made that the changes would be followed during the whole period of oil service, without machine breakdowns and in the closed system (without oil leaks).

Such conditions satisfied the car FSO 125P (SUP115CC602119663), which was equipped with an engine FSO 115 (CC7652890278). This engine uses an all season mineral oil. The volume of oil in the motor was 3.6 dm³. According to the instruction manual of the car, the oil should be changed after a year of exploitation or earlier – mileage could not exceed 5000 km. The decrease of oil amount resulted only from natural exploitation and after each sampling the same volume of fresh oil was supplemented. This procedure is similar as in ship motors, where also the same amount of oil is maintained in the lubricating system by supplementing. During the experiment the car was moderately used, in town (about 65 % of mileage) and outside town, almost entirely on hard roads. The engine most often worked at the average rotation velocity ranging from 35 s⁻¹ to 50 s⁻¹ and this speed never exceeded 70 s⁻¹. The average car speed was estimated at about 14 m/s (50 km/h). The car mileage served as a measure of oil use. The oil samples of volume 0.5 cm³ were collected directly from the car engine.

The linear absorption coefficient describes the ability of medium to absorb light. The sense of this coefficient lays in the assumption that the relative decrease of intensity $-dI/I$ of monochromatic radiation as a result of its absorption by the homogeneous medium is proportional to the penetration path dl , which can be described as follows:

$$-\frac{dI}{I} = \alpha dl. \quad (1)$$

The constant α is a linear absorption coefficient and it depends on the radiation wavelength. In order to solve this equation, a function which combines radiation intensity I with the penetration path l in the medium must be applied:

$$I(l) = I^0 \exp(-\alpha l), \quad (2)$$

where I^0 denotes the radiation intensity which reaches the medium. In this shape the function expresses the Bouguer-Lambert Law. The length of the penetration path l is proportional to a number of absorption centers. If the medium is made of a solution of an absorbing of volume concentration C in a nonabsorbing solvent, then this function can be written as follows:

$$I(l) = I^0 \exp(-\alpha Cl), \quad (3)$$

which expresses the Bouguer-Lambert-Beer Law.

The determination of the linear absorption coefficient was made using the results of light transmission for oil or hexane solution, in the range of wavelengths from 210 nm to 730 nm. The

absorption coefficient was derived as follows:

$$\alpha = \frac{1}{Cl} \ln \frac{T^o}{T}, \quad (4)$$

where T and T^o denote light transmissions for investigated solution and pure solvent.

The fluorescence spectra were measured for hexane oil solutions of constant concentration $10.0 \pm 0.3 \text{ mg/dm}^3$. For each sample, measurements of 10 emission spectra, excited with light of wavelengths from 210 to 300 nm, every 10 nm, were made. Each spectrum was measured in the range of wavelengths from 240 to 500 nm, every 5 nm. According to the Bouguer Law, light intensity I_j^{em} of j -th wavelength (λ_j), emitted through the sample, is proportional to the intensity of the exciting light I_i^{ex} of i -th wavelength (λ_i):

$$I_j^{em} = \omega_{ij} I_i^{ex} \quad (5)$$

The proportionality coefficient ω_{ij} depends on the wavelength of the exciting radiation λ_i and emitted radiation λ_j :

$$\omega_{ij} \equiv \omega(\lambda_i, \lambda_j).$$

For a given exciting light wavelength λ_i the parameter ω is a function of the emitted light wavelength, which in the reminder of the paper will be called the spectral function. The dimensionless value W , which is proportional to the intensity of light emitted through the sample and the exciting light intensity, was measured directly:

$$W = k \frac{I_j^{em}}{I_i^{ex}} = k \omega_{ij} \quad (6)$$

where k is a constant, independent of wavelength. Therefore, the spectrum measurement concerned the measurement of the spectral function ω for particular wavelengths, which were then multiplied by a certain constant.

The fluorescence and transmission spectra were measured using the spectrofluorimeter *Fluorat-02-Panorama*.² The measurements of light refraction coefficient n were made directly using the Abbe refractometer, for radiation of wavelength 590 nm and at stable temperature 20 °C. The measurement accuracy was 0.0005.

3. Results

The test comprised the whole cycle of one year of oil exploitation. The car has driven 4734 km during this cycle. The all season mineral oil *Elf* type SAE 15W/40 SRI was tested in the experiment. Density of the fresh oil was 884 kg/m^3 (at temperature 20 °C) and increased up to 892 kg/m^3 at the end of the test. During the exploitation the dynamic viscosity coefficient changed its value from 0.235 Pas to 0.146 Pas. In every time of the experiment the oil had not any contamination. Both fresh and used oil was entire dissoluble in hexane and gave a clear solution without any flock.

a. Fluorescence

For hexane solutions of the investigated oil the fluorescence is the most intense in the range of wavelengths from 300 to 400 nm. Chosen emission spectra (plots of spectral functions W) for fresh oil and used oil are presented in Figures 1 and 2. The spectra of the used oil vary significantly from spectra of fresh oil. These differences refer to both intensity of fluorescence and shape of the

² The set was made in the Research and Development Institute of Analytical Equipment *Lumex* in Sankt-Peterburg

spectra and they are noticeable after a short time of oil use. The most apparent differences in shapes are visible for spectra excited with light of wavelengths 240 and 250 nm.

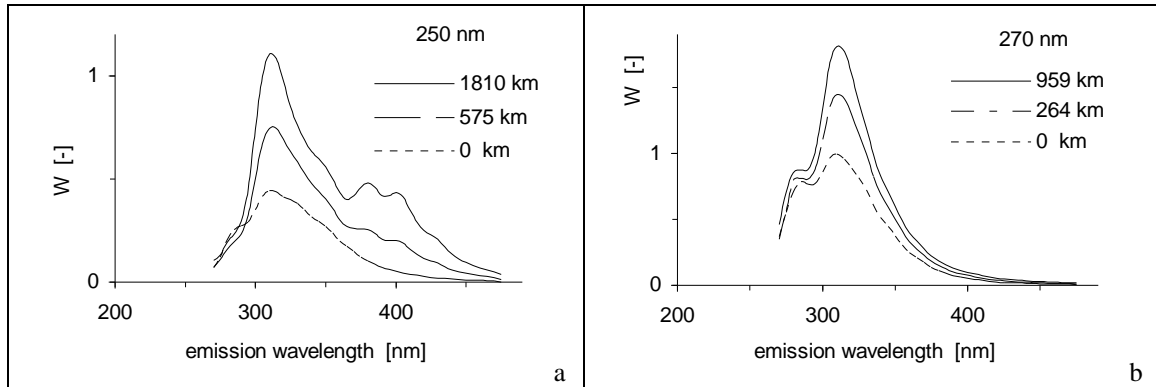


Fig. 1. Emission spectra $W = W(\lambda)$ excited with radiation of wavelengths 250 nm (a) and 270 nm (b) of hexane solutions of oil after different mileage of the car, in kilometers

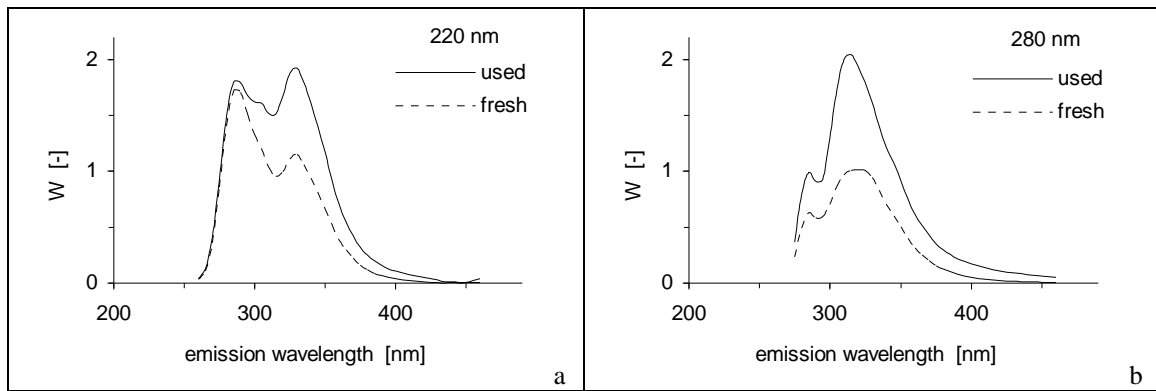


Fig. 2. Emission spectra $W = W(\lambda)$ of hexane solutions of fresh oil (dashed line) and after mileage of 3320 km (solid line) excited with light of the wavelengths 220 nm (a) and 280 nm (b).

For all wavelengths of the exciting light the increase of fluorescence of the oil solution occurs with the longer oil use. Parameter ω , which is a function of the emitted light wavelength (λ) is also a function of energy quantum of this radiation. Therefore, fluorescence in the spectral area limited by the wavelengths λ_{\min} and λ_{\max} can be characterized by the radiation energy Ω , determined as follows:

$$\Omega = \int_{\lambda_{\min}}^{\lambda_{\max}} \omega(\lambda) \frac{hc}{\lambda^2} d\lambda \quad (7)$$

where h is the Planck constant and c denotes the speed of light. Since only discrete values of function W have been determined, the total intensity of fluorescence Ω_i (for spectrum excited with light of i -th wavelength) may be evaluated as the following sum:

$$\Omega_i = \frac{2hc\Delta\lambda}{k} \sum_j \frac{W_{ij} + W_{i(j+1)}}{(\lambda_{j+1} + \lambda_j)^2}, \quad (8)$$

where $\Delta\lambda = 5$, λ_j has values 240 nm, 245 nm, ... 495 nm, and k is the constant from formula (4).

With oil use the increase of evaluated fluorescence energy of the oil hexane solution for all wavelengths of exciting light from the range 210 to 300 nm is observed. This increase is the best described by the power function of the car mileage x

$$\Omega(x) = \Omega_o(1 + ax^b), \quad (9)$$

where Ω_o is a fluorescence function for the fresh oil, while parameters a and b depend on wavelength of the exciting light. Figure 3 presents exemplary, relative fluorescence energies, related to energy of the solution of fresh oil ($\Omega^{rel} = \Omega/\Omega_o$), as a functions of car mileage.

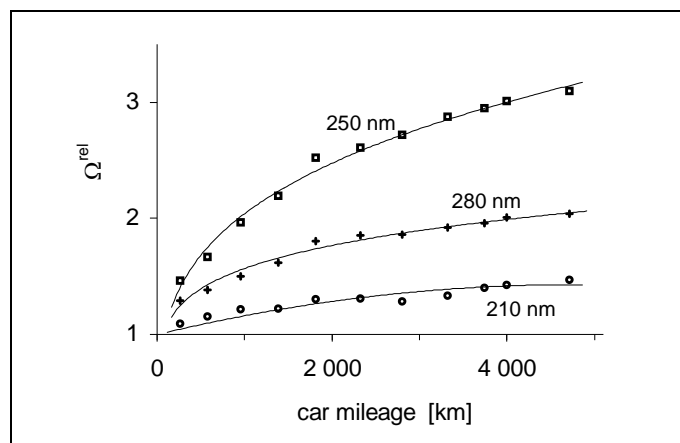


Fig. 3. Relative energy of fluorescence of oil hexane solutions Ω^{rel} (determined vs. energy of fresh oil solution) as a function of car mileage for spectra excited with light of the following wavelengths: 210, 250 and 280 nm.

b. Light absorption

Along with matter photoluminescence light is also absorbed. Absorption of the ultraviolet radiation in oil is very high and it decreases with the increase of light wavelength. The direct measurements of transmission in oil were possible for radiation of wavelengths $\lambda > 380$ nm. For shorter waves, the light intensity after passing through the cuvette, 1 mm thick, filled with oil, was negligible and thus in such cases the transmission in the hexane solutions was measured. Determination of the linear absorption coefficient from formula (4) requires that the light transmission was decreasing exponentially with an increase of the solution concentration (Beer Law). For tested oil this condition is satisfied for radiation of wavelengths longer than 400 nm (Fig. 4) and for such wavelengths the absorption coefficient was derived. For shorter wavelengths, the results of measurements of light transmission through solutions of the same concentration were used to determine the variations of the light absorption coefficient concerned with the oil use. A relative absorption coefficient A for particular samples of used oil versus the fresh oil was derived as follows:

$$A = \ln \frac{T_f - T}{T^o}, \quad (10)$$

where T_f , T and T^o denote the light transmission for a solution of the fresh oil, used oil and pure solvent, respectively.

Variations of light absorption coefficient for oil due to its use are presented in Fig. 5. The increase of light absorption by oil with its use is revealed. For radiation of wavelengths $\lambda < 500$ nm this increase is analogous to the increase of fluorescence energy (9). This dependence is not so obvious for longer wavelengths.

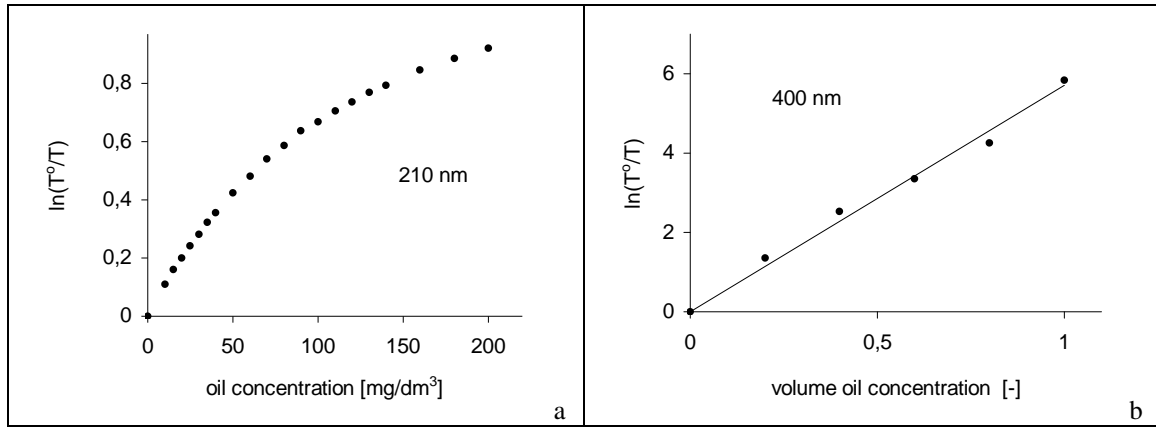


Fig. 4. Applicability of the Lambert-Beer rule: dependence $\ln(T^\circ/T)$ on fresh oil concentration in hexane solution for light of wavelengths 210 (a) and 400 nm (b); T° – transmission through hexane, T – through solution

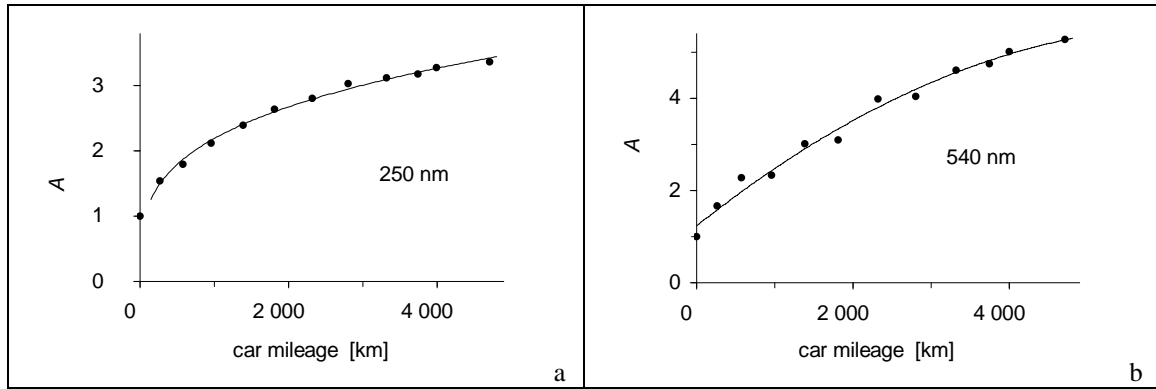


Fig. 5. Variations of relative light absorption coefficient A for Elf oil as a function of car mileage for radiation of the wavelengths 250 nm (a) and 540 nm (b)

c. Light refraction

The light refraction index n (refraction coefficient) for light of wavelength $\lambda = 590$ nm represents refractivity of a medium. Value of the index characterizing the fresh oil *Elf* is 1.4835. A small but systematic increase of this coefficient is observed along with the oil use. Value of n increased 0.001 per 1000 km of mileage during the test and the used oil have the index $n = 1,489$.

Along with increase of the light refraction coefficient the light reflection coefficient R increases. For perpendicular radiation the reflection coefficient R is combined with the refraction index n and the absorption coefficient α as follows:

$$R = \frac{4\pi(n-1)^2 + (n\lambda\alpha)^2}{4\pi(n+1)^2 + (n\lambda\alpha)^2} \quad (11)$$

For radiation of wavelength $\lambda = 590$ nm value of the absorption coefficient of the fresh oil $\alpha = 960 \text{ m}^{-1}$ and increases with the oil use to 5100 m^{-1} , thus the product $n\lambda\alpha \ll n - 1$ and the dependence (11) may be written as follows:

$$R = \left(\frac{n-1}{n+1} \right)^2 \quad (12)$$

Contrast K between the oil and water surface is concerned with reflection coefficient. It is proportional to the difference in intensities of reflected radiation from both media related to total radiation intensity (with an assumption that the light intensity incident on both media is the same). Contrast is then a relative difference between both coefficients of light reflection from both media

$$K = \frac{I_o - I_w}{I_o + I_w} = \frac{R_o - R_w}{R_o + R_w}, \quad (13)$$

where: I_o and I_w denote intensity of light reflected from oil surface and water surface, and R_o and R_w denote coefficients of light reflection from oil and water, respectively. The assumed value of the refraction coefficient characteristic for sea water was accepted as 1.335. The contrast between water and oil, described as above, increases along with oil use, which is illustrated in Figure 6a.

Contrast between oil layer and water depends on the angle of light incident. For the angle of light incident $\varphi \neq 0$ light reflection coefficient is described by the Fresnel formula:

$$R = \frac{1}{2} \left[\frac{\sin^2(\varphi - \vartheta) + \operatorname{tg}^2(\varphi - \vartheta)}{\sin^2(\varphi + \vartheta) + \operatorname{tg}^2(\varphi + \vartheta)} \right]; \quad \vartheta = \arcsin\left(\frac{\sin \varphi}{n}\right). \quad (14)$$

For large angles light reflection coefficient increase and the contrast between oil and water decreases, however, the dependence of contrast on the use of oil remains unchanged (Fig. 6b).

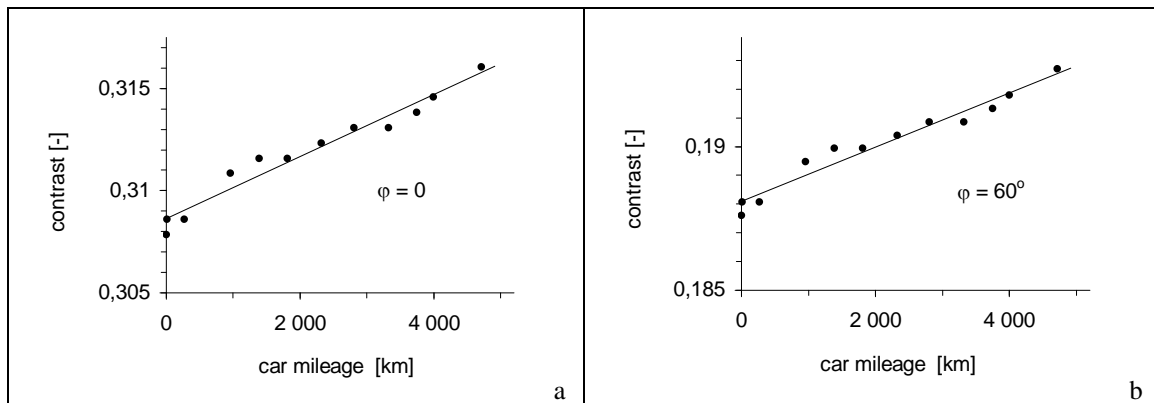


Fig. 6. Dependence of the contrast of the Elf oil layer vs. water on car mileage for radiation of wavelength 590 nm incident perpendicularly to the surface (a) and at an angle 60° (b)

4. Summary

During its use the lubricating oil changes and its optical properties change too. During use the following phenomena occur:

- linear absorption coefficient increases
- light refraction and reflection coefficients slightly increase
- the intensity of fluorescence increases and the shapes of its spectra change.

These phenomena generate concrete conclusions regarding application of optical methods to detect and identify oil spills based on the information about the properties of the oil spilled.

- Along with oil use the slightly increases the contrast, which the oil layer creates on the sea surface. This effects does not significantly influence the outcome of the detection.
- Variations of light absorption disallow precise determination of the thickness of the oil spilled by means of fluorescence method.
- Significant and increasing differences in oil spectra shapes along with oil use disallow to determine this substance, which is a derivative of the fresh oil by means of fluorescence methods.

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