Fluorescence method for the determination of oil identity

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The paper presents an objective method for distinction and identification of oils based on the comparison of total fluorescence spectra of their hexane solutions. The spectra comparison was conducted by means of the determination of the differences between the normalized functions, which describe the internal fluorescence efficiencies of the solutions of the substances under investigation. A criterion of oil identity, which involves limited accuracy of spectra measurement, has been defined. The efficiency of the method was tested on 51 lubrication oils.

Keywords: fluorescence, petroleum, oil identification.

1. Introduction

A continuously growing use of crude oil and its products by industry results in progressing pollution of the natural environment despite the development of new protective systems. Crude oils, fuels and other petroleum derivatives, further referred to as oils, and the products of their transformation have adverse impact on natural environment, which has been presented by many authors (*e.g.*, [1]–[5]). Pollution of environment with oil is violation of law. This problem is especially apparent in the marine environment, the protection of which is regulated by the *MARPOL Convention* [6]. An efficient system of pollutant detection and punishment of perpetrator of the pollution play a special role in the system of environment protection. Identification of pollutant as the settlement identity of the pollutant and oil sampled from suspected source is a fundamental element of such a system [7].

The necessary conditions of identification method are its objectiveness and effectiveness, however the speed and easiness of determination are also important. Oil is a mixture of many components, mainly hydrocarbons and their derivatives and thus the commonly used methods of their identification are based on the determination of their chemical composition, mainly by means of gas chromatography and mass spectrometry [8], [9]. Independently of the measures being taken in order to improve these methods along with the development of the instrumental analyses, simple

methods, especially objective ways of the determination of oil identity are being investigated.

The possibility of using fluorescence to detect and identify crude oil was reported in the early 1970s [10]–[13]. Studies on the distinction of oil types using the fluorescence spectra were conducted [14]–[18]. It was also confirmed that spectra of particular oil types are different.

A necessary condition for determining the identity of oils based on fluorescence spectra is their distinction. Particular oil types differ in spectral range of the fluorescence, in intensity of the phenomenon and in shapes of the spectra. These differences, which are significant in relation to substances representing different oil types, can be less distinct in the case of different products of one type. The first aim of this work was to determine the range of spectra distinction and to state whether different oils are always characterized by different spectra. Confirmation of the distinction facilitated the preparation of the methodology for distinguishing spectra of particular oils, which further led to the definition of the objective criteria for the determination of the spectra identity. The analyses of total fluorescence spectra of 63 oils, including 51 defined products, which belong to one group – lubrication oil, were made.

2. Methods

2.1. Physical backgrounds

Internal spectrum – an objective parameter describing luminescence spectrum of luminophore – is represented by spectral internal efficiency of luminescence Ψ [19]. It is a function of wavelength of emitted radiation λ^{f} (the index "f" refers througout this paper to fluorescence and the index "ex" to exciting radiation):

$$\Psi(\lambda^{t}) = Y\psi(\lambda^{t})$$
⁽¹⁾

where *Y* denotes energetic efficiency of luminescence and the function ψ is differential $\psi(\lambda) = \varphi(\lambda) d\lambda$, which fulfils the following condition:

$$\int_{0}^{\infty} \varphi(\lambda) d\lambda = 1.$$
 (2)

Internal spectrum could be presented in this manner for exciting radiation of any wavelength. If the luminescence is excited by light beam going along an axis X and having defined wavelength λ_i^{ex} and intensity I_i^{ex} , value of the spectral internal efficiency of fluorescence of the wavelength λ_j^{f} could be presented by the following expression:

$$\Psi_{ij} = \frac{\mathrm{d}\,I_i^{\mathrm{f}}}{-\mathrm{d}\,I_i^{\mathrm{ex}}}\,\psi_{ij} \tag{3}$$

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where dI_i^f denotes the intensity of the radiation emitted by an element of volume of the luminophore having longitude dx. The product of the intensity of radiation dI_i^f and the differential ψ_{ij} is the intensity of luminescence of wavelength λ_i^f

$$dI_{ij}^{f} = dI_{i}^{f} \psi_{ij}.$$
(4)

A decrease in the intensity of exciting radiation is described by the expression

$$-dI_i^{ex} = I_i^{ex} \alpha_i dx$$
⁽⁵⁾

where α denotes the light absorption coefficient, so Eq. (3) can be described as follows:

$$\Psi_{ij} = \frac{\mathrm{d}\,I_i^{\mathrm{f}}}{I_i^{\mathrm{ex}}\alpha_i\,\mathrm{dx}}.$$
(6)

The spectral internal efficiency of fluorescence is a function of two factors: wavelengths of luminescence and exciting radiation. The fluorescence could be described by function Φ . The function Φ is defined as a quotient of the intensity of radiation of defined wavelength emitted by the element of luminophore volume and the intensity of radiation exciting the luminescence

$$\omega_{ij} = \frac{\mathrm{d} I_{ij}^{\mathrm{t}}}{I_{i}^{\mathrm{ex}}} = \alpha_{i} \Psi_{ij} \mathrm{d}x.$$
(7)

The function presents the total spectrum of particular substance and covers the whole characteristics of its luminescence and absorption properties. The function Φ is differential. It is proportional to the integral *w* calculated from function Φ by the whole space, in which fluorescence occurs. The integral *w* is also a function of λ^{ex} and λ^{f} and describes intensity of luminescence emitted by the whole sample in relation to intensity of exciting radiation. The expression

$$w_{ij} = \int \frac{\mathrm{d} I_{ij}^{\mathrm{T}}}{I_i^{\mathrm{ex}}} = \int_0^l \alpha_i \, \Psi_{ij} \, \mathrm{d}x \tag{8}$$

presents value of the function w at definite point $(\lambda_i^{ex}, \lambda_j^{f})$ in the case of luminophore of longitude l along the direction of excitation.

2.2. Measurements

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The spectra measurements were carried out using the spectrofluorimeter Fluorat-02 Panorama. A narrow flux of the radiation runs through the center of a square cuvette of side dimension l = 1 cm and excites luminescence. The intensity of radiation emitted

from the entire cuvette length perpendicular to the excitation radiation is measured. The set measures directly a dimension F being the ratio of fluorescence light intensity and the intensity of the exciting radiation and thus parameter F is proportional to function w (formula (8)). In order to determine the spectral function absorption of both the excitation and emitted radiation was included. Thus the independent measurements of radiation transmission spectra in the entire spectral range were made for each sample. The values of the spectral function w at any point (λ_i^{ex} , λ_j^{f}) were determined from the following formula:

$$w_{ij} = \left(F_{ij} \frac{T_i^o \ln \frac{T_i^o}{T_i}}{T_i^o - T_i} \sqrt{\frac{T_j^o}{T_j}} - F_{ij}^o \right) \theta_{ij}.$$
 (9)

In the above dependence F is a result of the measurement of the luminescence of the solution investigated, T denotes transmission of radiation through the solution and T^o – transmission through the solvent. F^o denotes the result of background measurement for pure hexane, so the formula includes also the scattering of exciting radiation. Parameter θ is a coefficient of spectral characteristics of the measurement device and is described as follows:

$$\theta_{ij}F_{ij} = \frac{I_{ij}^{\rm f}}{I_i^{\rm ex}}.$$
(10)

During the studies different types of crude oil in the form of their hexane solutions of concentrations below 20 mg/dm³ were investigated. The measurements of luminescence spectra were made every 5 nm in the wavelength range from 260 to 500 nm for these solutions. Those spectra were excited by the radiation of wavelengths from the range of 210 to 300 nm, every 10 nm. The derived values of the spectral function create a matrix of 490 elements (10 rows and 49 columns). For computation purposes the number of elements was limited to 398, and the values of the spectral function were applied for the following wavelengths of excitation and emission radiation:

$\lambda^{\text{ex}} = 210 \text{ nm } \lambda^{\text{t}}: 270-400 \text{ nm}$	$\lambda^{\text{ex}} = 220 \text{ nm } \lambda^{\text{t}}: 270-520 \text{ nm}$
$\lambda^{\text{ex}} = 230 \text{ nm} \lambda^{\text{f}}: 270440 \text{ nm}$	$\lambda^{\text{ex}} = 240 \text{ nm } \lambda^{\text{f}}: 270460 \text{ nm}$
$\lambda^{\text{ex}} = 250 \text{ nm } \lambda^{\text{f}}: 270 - 480 \text{ nm}$	$\lambda^{\text{ex}} = 260 \text{ nm } \lambda^{\text{f}}: 270-500 \text{ nm}$
$\lambda^{\text{ex}} = 270 \text{ nm } \lambda^{\text{f}}: 270-500 \text{ nm}$	$\lambda^{\text{ex}} = 280 \text{ nm } \lambda^{\text{f}}: 280-500 \text{ nm}$
$\lambda^{\text{ex}} = 290 \text{ nm } \lambda^{\text{f}}: 290-500 \text{ nm}$	$\lambda^{\text{ex}} = 300 \text{ nm} \lambda^{\text{f}}: 300-500 \text{ nm}$

Such a range refers to the spectral area, in which the fluorescence of the solutions occurs in (Fig. 1).

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3. Assumption for the identification

In order to use these spectra to identify oil types their predicted modifications, which result from the natural changes of oil properties, should be taken into consideration. The processed oils have stable composition and properties in natural conditions, this stability may be assumed for normal conditions of their storage or transportation over a period of some time for which the identification of a pollutant is sensible. Weathering of crude oil is a natural process especially intensive in its early stage, which results in the change of petroleum composition and properties [20]. Identification of crude oil



Fig. 2. Functions *w* representing fluorescence spectra of solutions of concentration 6 mg/dm³ of fresh and weathered crude oils from: **a** – North Sea, excited with light of wavelength $\lambda^{ex} = 220$ nm, **b** – Baltic ($\lambda^{ex} = 250$ nm), and **c** – Romashkino ($\lambda^{ex} = 280$ nm).

makes sense only on assumption that naturally weathered oil is still the same substance as the fresh one.

The changes are also visible in fluorescence, due to the increase of luminescence intensity of oil solutions as a result of crude oil aeration. The value of the spectral function is a measure of the increased intensity, while the spectral shapes remain unchanged (Fig. 2). This requires the limitation of spectra analyses to investigation of spectra shapes and fluorescence areas. For solutions of small concentrations, which satisfy the Beer law, the spectral function is linearly dependent on the oil concentration in hexane and thus the spectrum which is described by such a function can be normalized [21]. The application of the natural normalization criterion for this function, *i.e.*, the value of the integral over the entire area of changes is not possible due to the fact that only a part is known. Knowledge of the entire area would involve the conduction of the impossible measurements of luminescence induced by radiation of wavelengths shorter than 210 nm. Thus an auxiliary criterion was assumed regarding the normalization of the total spectrum through matching the function values at any point $(\lambda_i^{ex}, \lambda_j^{f})$ with the maximum values in the whole area in which the measurements were made^{*}. This way the function Φ was obtained:

$$\Phi = \frac{w}{\max\{w_{ij}\}} = \frac{\omega}{\max\{\omega_{ij}\}}.$$
(11)

It describes correctly the shape of the total fluorescence spectrum of oil solution. Relative difference between such normalized spectra can be defined:

$$D = \frac{\sum_{i} \sum_{j} \left| \Phi_{ij}^{a} - \Phi_{ij}^{b} \right|}{\sum_{i} \sum_{j} \Phi_{ij}^{a}}.$$
(12)

The parameter D determines the relative difference of spectra – fluorescence regions and spectra shapes – for two oils "a" and "b" (in relation to the "a" oil spectrum). Also, this parameter describes the identity, which is greater with the smaller value of the parameter D. In the case of oil the solution of which have the same spectra the difference is D = 0.

4. Distinction of fluorescence spectra

The difference, as defined by formula (12), may be used to identify oils provided that the identity of spectral shapes and areas is identical with the substance identity. This

^{*}This seems to be the only way to normalize the spectral function since the fluorescence spectral regions of particular oils overlap but not entirely. It is impossible to find one fixed point $(\lambda_i^{ex}, \lambda_j^{f})$, for which the value of the spectral function could normalize the spectra of all oil types.

problem is reduced to two issues: distinction of spectra (do particular oils have always spectra of different shapes?) and an issue of the identity of crude oil. The problem of distinction was tested for lubricating oils. For 51 determined products measurements of spectra of their solutions were made and the spectral function w was determined and then normalized. For each of the oils the difference D was determined between the normalized total spectrum of its solution and the spectrum of solutions of every other oil.

(Oil D Oil		il	D	
Pattern	Most similar	[%]	Pattern	Most similar	[%]
Aral basic	Elf turbo	5.4	Marinol (A)	Hipol GL4 (B)	4.2
Aral multi	VAT super	4.5	Marinol (B)	Marinol (C)	10.3
BP syntetic	Statoil Lazer	30.9	Marinol (C)	Marinol (D)	9.4
Castrol coral 2	Hipol GL4	16.9	Marinol (D)	Marinol (E)	3.1
Castrol EP	Marinol (A)	7.7	Marinol (E)	Marinol (D)	3.0
Castrol GTX	Elf competition	8.2	Mobil super	Mobil super diesel	5.0
Castrol Lightec	VAT SynTech	10.8	Mobil super diesel	Mobil super	5.3
Castrol Magnetec	Mobil 1 railly form	21.3	Mobil super S	Mobil super diesel	9.0
Elf competition	Castrol GTX	8.8	Mobil-1 railly form	Castrol Magnetec	26.9
Elf SJ	Elf sporti (A)	4.5	Mobil-1 turbo dies.	Mobil 1 railly form	73.8
Elf sporti (A)	Elf turbo	3.6	Shell diesel	Elf sporti (A)	7.7
Elf sporti (B)	Elf sporti (C)	7.0	Shell plus	Shell super	5.9
Elf sporti (C)	Elf sporti (B)	6.9	Shell super	Shell plus	5.8
Elf sporti (D)	Lotos specjal	11.0	Shell ultra	Mobil 1 railly form	29.7
Elf turbo	Elf sporti (A)	3.6	Statoil classic	Lotos mineralny	6.7
Hipol 15F (A)	Hipol GL4 (A)	3.1	Statoil Lazer	VAT SynGold	19.7
Hipol 15F (B)	Hipol 15F (A)	4.8	Statoil power	Lotos diesel	6.5
Hipol 15F (C)	Marinol (A)	6.6	Statoil super	VAT SynTech	5.3
Hipol GL4 (A)	Hipol 15F (A)	3.1	Texaco diesel 1	Texaco Halvoline	4.9
Hipol GL4 (B)	Marinol (A)	4.3	Texaco Griese	Elf competition	15.5
Hipol MF	Hipol 15F (B)	7.5	Texaco Halvoline	Texaco diesel 1	5.1
Hydrol	Castrol GTX	11.9	VAT super	Aral multi	4.7
Lotos diesel	Statoil power	6.4	VAT SynGold	Lotos sintetic	12.2
Lotos mineral	Statoil classic	6.3	VAT SynTech	Statoil super	5.5
Lotos sintetic	VAT SynGold	12.1	VAT turbo	Texaco Halvoline	8.2
Lotos special	Texaco Halvoline	9.5	Average value of D		10.2

T a ble 1. Relative differences D between the normalized total spectra of lubrication oil hexane solutions^{*}.

*The original commercial names of oils have been used in the paper. Letters in parentheses denote different samples of the same product (from different sources).

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Table 1 presents the products along with their oil of origin for which the difference was the smallest. Comparison of the normalized spectra of lubrication oil types proves their good statistical distinction – an average difference between the most similar spectra was 10.2%. Such distinction is confirmed by studies of other product types: diesel oils, whose normalized spectra differ by 9.2% on average, heavy fuels (14%), and crude oils (20%).

These results do not prove yet the distinction of the oils under study, since for over 1/4 of them there are products whose spectra differ by less than 5%. The question is: what is the uncertainty with which this difference is determined? The limited accuracy of the measurements is the source of the uncertainty and appoints the accuracy of the determination of the spectral function. The uncertainty with which the normalized spectral function Φ is determined has been obtained through the investigation of the difference D in cases of independently made spectral measurements for the same oil type. Such studies have been made for 3 pairs of lubrication oils, which showed the closest similarities (Aral-multi, Elf-sporti (A), Elf-turbo, Hipol 15F (A), Hipol GL4 (A) and VAT-super) and for both fresh and weathered crude oil from the Baltic Sea and the North Sea. A number of solutions have been made for each oil, for which independent spectra measurements have been made and the normalized spectral function Φ has been determined. Using the normalized functions the average function was derived. The average function is by assumption close to the real spectrum of the given oil. Then the differences between such averaged function and the particular functions (relating to the particular measurements) were derived. These differences are presented in Tab. 2. The average error of the derivation of the spectral function, which has been determined using all results, is 1.68% with standard deviation of 0.74%. The uncertainty with which the difference D has been determined between

Oil	N	Range of D [%]	D _{av} [%]	δD [%]
Aral-multi	12	1.01-4.15	1.54	0.98
Elf-sporti (A)	14	0.92-3.71	1.93	0.73
Elf-turbo	14	0.73-3.75	1.75	0.94
Hipol 15F (A)	10	0.85-3.37	1.69	0.79
Hipol GL4 (A)	10	0.54-2.17	0.97	0.46
VAT-super	12	1.46-2.52	1.78	0.30
Fresh Baltic crude oil	22	1.49-3.57	2.23	0.48
Weathered Baltic crude oil	15	1.30-3.33	1.91	0.54
Fresh North Sea crude oil	12	0.52-1.66	0.96	0.3
Weathered North Sea crude	12	0.61-2.11	1.29	0.4

T a ble 2. Relative differences between the averaged normalized spectral function Φ and functions obtained from the measurements of spectra of particular samples (*N* – number of investigated samples of particular oil, δD – standard deviation of differences *D* from their average values).

particular spectra is higher. It may be assumed that accuracy of determination of the difference between the spectra of solutions of one oil (obtained as results of singular measurements) is two times higher than the accuracy of derivation of the function Φ . The average accuracy of the difference *D* determination, evaluated using the above results, equals 3.35% with the standard deviation of 1.48%. This means that the most probable differences between two normalized spectra of the given oil solution obtained from singular measurements will range from 1.85 to 4.85%.

The 22 normalized spectral functions Φ of the Baltic crude oil solutions were randomly divided into two groups (A and B), with 11 spectra in each. Within each of these groups the functions were averaged and the differences between the averaged function and functions related to particular samples were calculated. Eight divisions were made and in each of the cases the average differences between the averaged function and the basic functions within each of the groups $(D_{\{A\}}^{av} \text{ and } D_{\{B\}}^{av})$ were determined, as well as standard deviations of these differences ($\delta D_{\{A\}}$ and $\delta D_{\{B\}}$), and the differences between the averaged functions (D_{AB} – versus the averaged function from group A, and D_{BA} – versus the averaged function from group B). The results of these calculations, which are presented in Tab. 3, show that even in cases of relatively large measurement series the averaged spectral functions obtained for the same oil type are different. The differences $(D_{AB} \text{ and } D_{BA})$ between the averaged spectral functions of the same substance solutions are significant (even up to 2%), still they are always smaller than the average differences $(D_{\{A\}}^{av} \text{ and } D_{\{B\}}^{av})$ derived from the original functions. The numerous measurements revealed that also the shapes of spectra of solutions of weathered and fresh crude oil are very similar. The difference between the averaged, normalized spectral functions of fresh and weathered Baltic crude oil solutions was 1.4%, and this difference for fresh and weathered North Sea

T a b l e 3. Differences between the averaged spectra of the Baltic crude oil $(D_{\{A\}}^{av} \text{ and } D_{\{B\}}^{av})$ indicate the average differences between functions which relate to particular samples and the averaged functions in groups A and B, $D_{\{A\}}^{max}$ and $D_{\{B\}}^{max}$ – maximum differences in these groups, $\delta D_{\{A\}}$ and $\delta D_{\{B\}}$ – standard deviations of the differences, D_{AB} and D_{BA} – differences between the averaged functions of both groups).

Trial	$D^{\rm av}_{\{{\rm A}\}}$ [%]	$D^{\max}_{\{\mathbf{A}\}}$ [%]	$\delta D_{\{A\}}[\%]$	$D_{\rm AB}[\%]$	$D^{\rm av}_{\{ m B\}}$ [%]	$D^{\max}_{\{\mathbf{B}\}}$ [%]	$\delta D_{\{\rm B\}}[\%]$	$D_{\rm BA}[\%]$
1	2.21	3.20	0.54	0.86	2.17	3.23	0.58	0.85
2	2.22	3.31	0.71	1.49	2.00	3.54	0.74	1.47
3	2.07	2.87	0.34	0.47	2.37	3.08	0.56	0.47
4	2.19	3.02	0.42	0.38	2.25	3.60	0.58	0.38
5	2.27	3.29	0.48	0.63	2.19	2.69	0.40	0.62
6	2.12	3.44	0.67	1.13	2.22	3.10	0.59	1.14
7	2.10	3.23	0.89	1.78	2.01	3.73	0.76	1.80
8	2.15	2.77	0.49	0.73	2.23	3.30	0.56	0.74
	A	verage (A ar	nd B)		2	.17	0.58	0.96

Table 4. Differences between the averaged oil spectra $(D_{\{1\}}^{av} \text{ and } D_{\{2\}}^{av})$ indicate the average differences of functions which relate to particular samples versus the averaged functions of the 1st and 2nd oil, D_{12} and D_{21} – differences between the averaged spectra of these oils calculated versus the 1st and the 2nd sample, respectively).

Oil 1	Oil 2	$D^{\rm av}_{\{1\}}$ [%]	$D^{\rm av}_{\{2\}}$ [%]	$D_{12}[\%]$	$D_{21}[\%]$
Aral-multi	VAT-super	1.54	1.78	2.19	2.17
Elf-sporti (A)	Elf-turbo	1.93	1.75	3.71	3.83
Hipol-15F (A)	Hipol-GL4	1.69	0.97	2.10	2.07
Baltic crude - fresh	Baltic crude – weathered	2.23	1.91	1.37	1.38
North Sea crude – fresh	North Sea crude – weathered	0.96	1.29	0.81	0.81

crude oil was 0.8%. These differences are also smaller than the average differences calculated for spectra of the same substance, obtained from particular measurements. This is connected with the fact that the averaged spectrum is closer to the real spectrum, if it originates from a large number of spectra and in the case of identical substances the differences between their spectra will be smaller along with an increase of the number of measurements. A different situation was confirmed for lubrication oils. The differences derived between the averaged oil spectra for *Aral-multi* and *VAT-super* (2.2%), *Hipol-15F* and *Hipol-GL4* (2.1%) and *Elf-sporti* and *Elf-turbo* (3.7%) are greater than the average differences counted for singular spectra of particular oil. These differences are presented in Tab. 4.

5. Method of identification

The analysis of the results allows us to consider two oils as identical, if the differences between their averaged spectra, obtained from numerous measurements, are smaller than the average difference of singular total spectra of each of them. Determination of oil identity through comparison of their spectra requires a number of measurements appropriate for statistical description of the results. Confirmation of the difference between total spectra of solutions of two oils obtained from singular measurements, which exceeded some value (here 8%), rules out their identity.

The above information allows us to design a two-stage procedure for the determination of oil identity. The first, reconnaissance stage, involves the measurements of total spectra of solutions of the oils and the determination of related spectral functions. These functions are normalized to maximum values (formula (11)) and a relative difference between them is determined (12). Confirmation of the difference, which exceeds some critical value, leads to the statement that the oils under investgation are different. In another case the determination of the identity requires further studies (second stage). For each of oils it is necessary to prepare a number of solutions, measure their spectra and determine spectral functions which then must be

normalized and next derive the average function. For this average function the difference between it and the functions relating to particular measurements must be determined and then the average value of these differences should be determined. Next the difference between the averaged functions of both oils compared must be determined. If its value is smaller than the calculated average differences (between the functions obtained from particular measurements and appropriate average functions), then tested substances are identical. Otherwise the oils are different.

The studies made suggest some practical remarks (however solutions discussed in this work did not comply with following recommendations). Due to the differences in spectral areas, in which solutions of particular oil types show fluorescent properties, it seems sensible to individually match the excitation and emission radiation wavelengths to the area in which the solution of pattern oil fluoresces. This would minimize the impact of measurement errors on final results. Figure 1 shows that for majority of oils the ranges of fluorescence wavelengths, for which the measurements and calculations were made significantly deviate from the range in which the phenomenon occurs. For some types of fuels and crude oil it would be sensible to extend the spectral area investigated and to conduct measurements with the excitation radiation of wavelengths above 300 nm.

Similar concentrations of solutions of oils being compared also could minimize the impact of measurement errors. Determination of concentration is not necessary in preparing the solution. Compliance with Beer law is the only condition since this is the precondition for both correct derivation of the spectral function as the sense for comparison of spectra shapes. The recommendation for making solutions of similar concentrations results from the impact of the background confirmed during studies. This impact appears while normalizing the spectra of solutions of the same substance of very different concentrations.

6. Summary

The method of determining the identity of two oils based on determination of the difference between the total spectra of their solutions is fully objective and efficacious. It is also relatively simple and rapid. The efficiency of the method dependent on discrimination of the spectra of the oils has been confirmed by testing different lube oils making up about 70% of a group of such products available on Polish market. However, the oils tested make up only a fragment of the great number of petroleum products and it is not conceivable to find two different oils of the same spectra. This allows us to state, that the method presented is efficacious in determination of identity of oil samples.

The investigations prove that particular kinds of oil - products of individual manufacturers having defined names and the same specifications - can differ. This points to limited possibility of determination of oil type in the case of testing a sample

taken from environment and proves inexpedience of making a catalogue of the spectra. On the other hand, these differences augment the probability of finding a pollution maker, for example in case of many suspects using the same products.

Application of this method for determining the source of petroleum pollution in particular parts of natural environments needs individual studies. These must determine the influence of environmental conditions on the fluorescence properties of oils, rapidity of probable modifications of their spectra and the range of time connected with this, in which the identification can be possible. Irrespective of probable modifications, it seems that the method could be useful in determination of the identity of fresh pollutant and the oil of suspected maker.

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