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Spectroscopy**CRUDE OIL -SEAWATER SYSTEM: ELLIPSOMETRIC VIEW**

**Kh.N. Ahmedova¹, Corresponding Member of NAS of Azerbaijan N.T. Mamedov¹,
Academician of ANAS I. S. Guliyev²**

Crude oil from different oil fields in Azerbaijan and seawater from different regions of Caspian Sea were accessed by spectroscopic ellipsometry over the 200-1700nm spectral range at room temperature. Optical constants and dielectric function were obtained for massive samples of each substance, as well as for ultrathin layers of the oil spilled over the sea surface. The possibility to use dielectric function as a unique optical fingerprint for oil identification is figured out.

Keywords: *spectroscopic ellipsometry, optical constants, dielectric function, crude oil, seawater*

Introduction

Oil spills have been confirmed to have harmful influence on the marine environment. Many research groups reported results of their research on the subject [1]. Optical techniques have been widely employed in environmental monitoring because they can rapidly scan a wide region. While thick patches of oil can be easily detected and recovered there are problems to be solved with very thin (about nano size) oil layers which are beyond the capabilities of advanced skimming recovery systems and are less investigated.

It has been reported in several studies on oil spillage that day-time-contrast-based detecting of oil spots depends on the thickness of the oil film [2]. Differential heating by sunlight causes oil to rise to a higher temperature than the surrounding water because of its higher absorption of solar radiation and lower specific heat, giving rise to the commonly observed contrast of native and crude oil covered sea surfaces in day time remote sensing of oil spills. Reversal process occurs when the oil film is thin (micron size) [3]. However, there has been proposed no comprehensive physical model describing this behavior. The film thickness dependent optical properties are, therefore, of great importance for correct detection of the thin oil layer covered area, as well as estimation of the oil film thickness.

Optical methods that were applied earlier in oil studies are based on measurements of the full intensity of the light passed through or reflected

by oil sample. Although useful they are deficient because of the incomplete information retrieved.

Comprehensive information regarding the studied system is provided by ellipsometric methodology that is viewed nowadays as the global standard for studying optical properties of solids, including their thin film varieties [4]. Ellipsometry can also be very useful in oil studies. For example, the ultrathin crude oil layer's contribution into the optical parameters of the oil-seawater system can be reliably determined in a broad spectral range by using spectroscopic ellipsometry. Note that detection of the ultrathin oil layers in the oil-seawater system is beyond the capability of standard intensity-based technique [5].

One more very important aspect of the application of ellipsometric methodology to oils relates to oil identification. Dielectric function retrieved from ellipsometric studies is a fundamental material constant that accumulates all the information about electronic or vibronic transitions and represents the unique dielectric fingerprint of the oil under consideration. Oils with even small difference in the content of biomarkers and hetero-components will have different dielectric functions.

The purpose of this work is to obtain the full information on optical constants and, hence, dielectric function of crude oils from different oil fields on Absheron peninsula (Azerbaijan), and of thin layers of these oils on the surface of Caspian sea by using spectroscopic ellipsometry.

Table

Composition of the oils from ND and BL oil fields

Oil	Hydrocarbons	S
ND	99.8844 %	0.1194%
BL	99.7046 %	0.2750 %

Seawater and crude oil samples

The samples of seawater were taken from North (Nabran), South (Lankaran), and Central (Absheron) parts of Caspian sea coast of Azerbaijan. The selected parts are sufficiently distant from each other and one can observe the difference (if any) between the taken water probes.

Crude oil samples were taken from the offshore and onshore oil fields, such as Neft dashlari (ND) and Balakhani (BL), respectively.

Although oils from these oil fields were found to have the same density (0.87 g/cm^3), the elemental composition determined for the oils by XRF (X-Ray Fluorescent) examination turned out to be a little bit different. As shown in table 1, the ND and BL oils include slightly different amount of hydrocarbons and sulfur.

Details on spectroscopic ellipsometry

As before [6], we employed a Woolam 2000 spectroscopic ellipsometer to carry out spectroscopic ellipsometry studies. The ellipsometric entities ψ (amplitude parameter) and Δ (phase parameter) for seawater, crude oils, and crude oil-seawater systems were measured at incident angles of 50, 55, 60, 65, and 70° in the spectral range 200-1700nm at room temperature. Depolarization of the reflected light was not observed throughout all the accessed spectral range. Optical constants were retrieved after regression analysis of the obtained ellipsometric data. We used an optical model for isotropic media or isotropic thin film/substrate system to fit the calculated data to the experimental ψ and Δ . Several Gaussian oscillators were used to simulate the dispersion of the refractive index, n , and the absorption index (extinction coefficient), k . The mean square error

(MSE) was less than 1.5 in the worst case.

Results and discussion

Fig.1 displays the wavelength dependence of the refractive index of the seawater samples Absheron (1), Lankaran (2) and Nabran (3). The absorption index (not shown in fig. 1) was found to be negligible. As seen from fig.1, the seawater samples taken from different regions on the Caspian sea coast of Azerbaijan display little difference and this difference is bound mainly with the different NaCl concentration as our analysis using Bruggeman effective medium approximation has shown. However the situation for crude oil samples taken from different oil fields substantially differ from the above one.

The optical constants, n and k , obtained for crude oil samples within Gaussian oscillator dispersion model are shown in fig. 2. By considering the accuracy (~ 0.001 for n or k) of spectroscopic ellipsometry measurements, the difference in optical constants between ND and BL crude oil samples is obviously large. The difference between refractive indices of ND and BL oils is growing while moving from ultraviolet to near infrared spectral range. For absorption indices the situation is opposite. The difference is increasing when going from long wavelength region to shorter wavelengths. The observed differences in n and k are caused by the different sets of the optical oscillators that form complex dielectric function of ND or BL crude oil samples. Note that the complex dielectric function (ϵ) is determined through optical constants as

$$\epsilon = (n^2 - k^2) + i 2nk \quad (1)$$

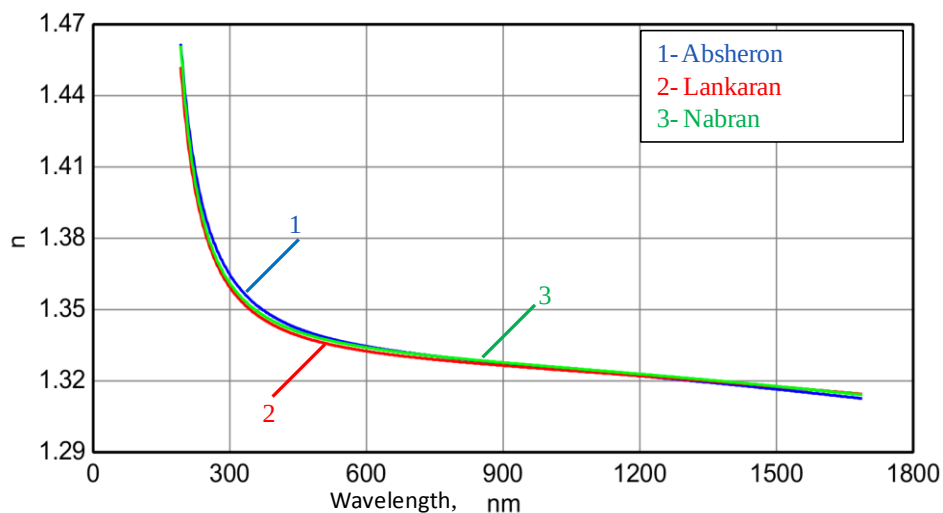


Fig.1. Refractive index (n) of seawater samples as a function of wavelength;
1-Absheron, 2-Lankaran, and 3-Nabran

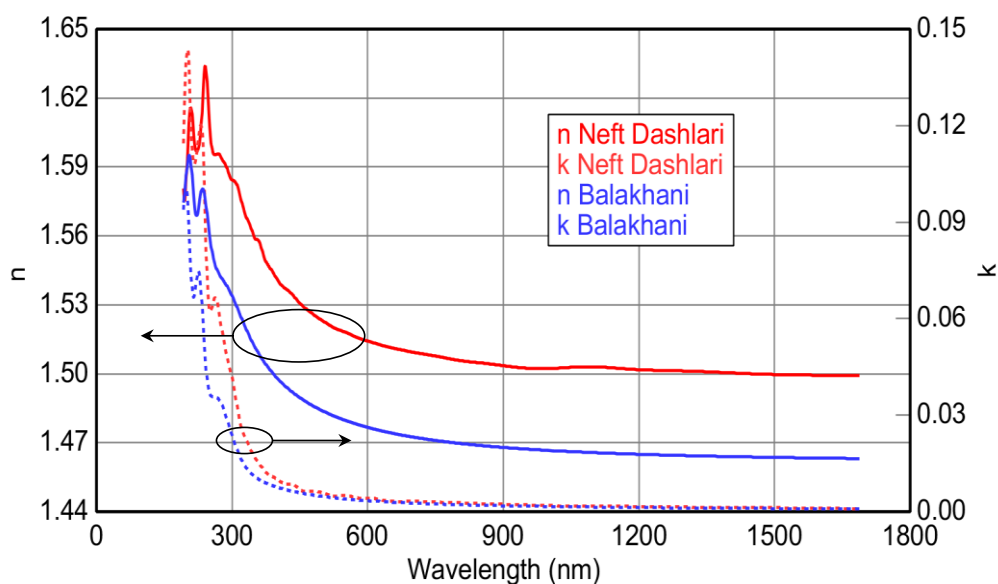


Fig.2. Optical constants (n , k) of ND and BL crude oils

And, once we know optical constants, the dielectric function is automatically determined.

As found, the parameters such as central energy, amplitude, and broadening of the different oscillators in the ND oscillator set are different from those in the BL oscillator set. This means that whatever the particular source of oil samples we can identify it by finding the

dielectric function and analyzing the oscillator content of the oil sample related to this particular source.

While such conclusion is in force for massive samples of crude oil, it is not straightforward that it will obligatory hold for oil spills. Meanwhile, just the problem of the addressed identification of the oil spilled over the sea sur-

face frequently needs solution.

Let us turn to the crude oil- sea water system and consider the results obtained for ultrathin films of ND and BL oil samples.

In fig.3 we show optical constants of ND and BL crude oil samples, together with optical constants of thin layers of these oils spilled over the surface of Nabran seawater. Careful look at the results for ND oil (Fig. 3a) and BL oil (Fig. 3b) allows us to notice that for a given oil the positions of the spectral features in the

spectrum of massive sample and that of thin film are practically the same. The exact analysis using spectral de-convolution into Gaussians shows that oscillator sets for massive samples of a given oil and its thin film specie are the same; i.e. the central energies of the oscillators are identical and the observed difference in optical constants is caused by different values of the amplitudes and broadening parameters of the same oscillators.

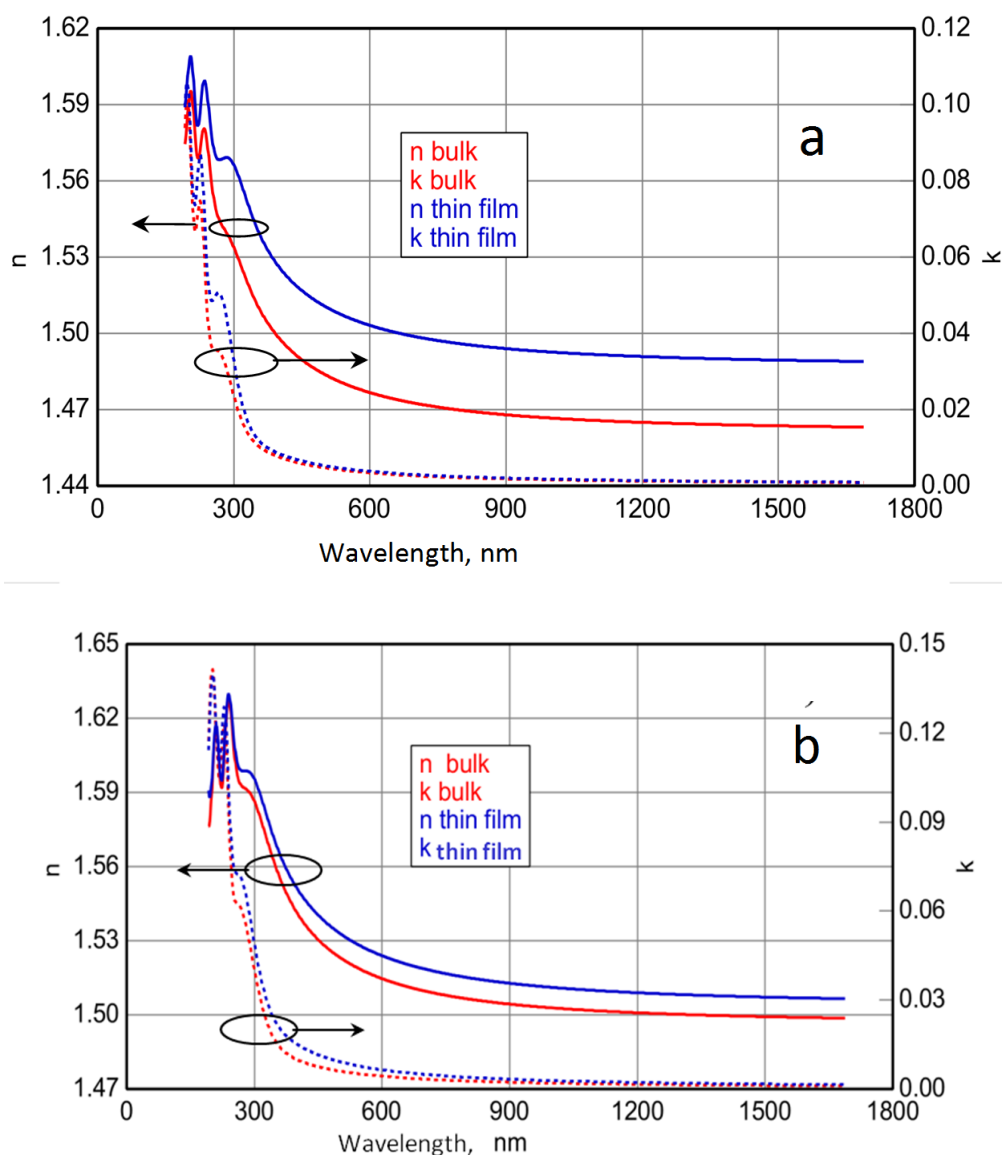


Fig. 3 Optical constants of crude oils (red curves) and their thin layers (blue curves):
a - ND oil, 60 nm thick layer; b - BL oil, 80 nm thick layer

Thus, optical parameters of the oils do depend on the thickness but this dependence is rather apparent since oscillator content is preserved. This means that by we can identify the source of the spilled oil even if the amount of this oil is negligibly small.

Over 500 hydro-carbon biomarkers with residual structural features inherent in motherly bio-organics are known and various combinations of these biomarkers are considered to responsible for the different content of the oils from the different oil fields. Determination of the fraction of each of the known biomarkers in the total volume of a given oil is a very difficult and expensive task. Therefore, it seems very attractive to replace biomarker-based classification by the one based on dielectric function which is a unique entity for any particular substance, playing role of the unrepeatable optical fingerprint.

Conclusions

We have applied spectroscopic ellipsometry to study optical constants (or dielectric function) of massive crude oil samples from the different oil fields and ultrathin film species of the different crude oils. In both cases we have managed to reliably determine the fundamental optical parameters, as well as the oscillator sets that form these parameters.

We have proposed to use dielectric function (optical fingerprint) for addressed identification of the oils. Oil genetics might also be considered if a one-to-one correspondence between the biomarker content and dielectric

function for a given oil would be established.

Further spectroscopic ellipsometry based oil studies, supported by ab-initio calculations of the electronic transitions in various hydrocarbon structures are necessary to open a gateway to wide application of the dielectric function based oils classification for addressed identification of any particular oil sample.

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¹ Institute of Physics of ANAS

² Institute of Geology & Geophysics of ANAS
khalilova@physics.ab.az

XAM NEFT-DƏNİZ SUYU SİSTEMİ: ELLİPSOMETRİK BAXIŞ

X.N. Əhmədova, N.T. Məmmədov, İ.S.Quliyev

Azərbaycanın müxtəlif neft yataqlarından götürülmüş xam neft nümunələri və Xəzər dənizinin müxtəlif yerlərindən götürülmüş dəniz suyu nümunələri spektroskopik ellipsometriya vasitəsi ilə 200-1700 nm spektral diapazonda, otaq temperaturunda tədqiq edilmişdir. Hər bir substansiya üçün massiv nümunənin həmçinin, dəniz suyu səthində alınmış ultranazik xam neft layının optik sabitləri və dielektrik funksiyası təyin edilmişdir. Neftin identifikasiyası üçün dielektrik funksiyasının unikal optik iz kimi istifadəsinin mümkünlüyü göstərilmişdir.

Açar sözlər: spektroskopik ellipsometriya, optik sabitlər, dielektrik funksiyası, xam neft, dəniz suyu

СИСТЕМА СЫРАЯ НЕФТЬ - МОРСКАЯ ВОДА: ЭЛЛИПСОМЕТРИЧЕСКИЙ ВЗГЛЯД**Х. Н. Ахмедова, Н. Т. Мамедов, И.С. Гулиев**

Сырая нефть с разных месторождений в Азербайджане и морская вода из разных мест Каспийского моря были исследованы с помощью спектроскопической эллипсометрии в спектральном диапазоне 200-1700 нм при комнатной температуре. Оптические константы и диэлектрическая функция были получены как для массивных образцов каждой субстанции, так и для сверхтонких слоёв сырой нефти на поверхности морской воды. Показана возможность использования диэлектрической функции как уникального оптического отпечатка для идентификации нефтей.

Ключевые слова: спектроскопическая эллипсометрия, оптические константы, диэлектрическая функция, сырая нефть, морская вода