

*Dedicated to the 80th anniversary
of Professor S. P. Gabuda*

MAGNETIC CIRCULAR DICHROISM ANALYSIS OF CRUDE OIL

**I. S. Edelman¹, A. E. Sokolov¹, V. N. Zabluda¹,
A. A. Shubin², and O. N. Martyanov³**

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Optical and magneto-optical properties of solutions of crude oil of different origin (i.e., taken from different fields) are studied in the visible and near-UV region of optical emission. Magnetic circular dichroism (MCD) spectra of oil are obtained in the vicinity of wavelengths of ~410 nm, 533 nm, and 576 nm. It is demonstrated that the intensity of the MCD signal depends on the origin of crude oil, and it is proportional to the oil concentration in the solution. The comparison of the magneto-optical spectroscopy data with the chemical composition of samples allows us to conclude that the observed magneto-optical activity is determined by the presence of VO²⁺ complexes in the oil samples studied. The revealed magneto-optical activity of conventional oil can form a basis of a new method for the analysis of the composition and properties of oil of different origin.

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INTRODUCTION

One of the main aspects of the research activities of S. P. Gabuda was the development of physical investigation methods and their application to complicated organic and inorganic compounds. When working at the Institute of Physics in Krasnoyarsk he devoted a series of works to the proton magnetic resonance investigation of various oil components [1-4]. These investigations have been continued in the recent years using methods based on the magneto-optical resonance in the visible region of the spectrum [5]. The interest in this problem is due to the necessity to expand the analytical base for the investigation of properties of oil and petroleum products. It is known that optical absorption spectroscopy methods are widely used to determine the features of the molecular structure of oil and its components, and first of all, of high-molecular tarry-asphaltene substances (TAS). In this case the main attention is paid to the study of infrared (IR) spectra [6] containing a large number of characteristic narrow peaks that make the interpretation of molecular structures of TAS easier [7]. For the majority of oil systems and TAS solutions the absorption spectra in the visible and ultraviolet ranges are described by rather smooth curves, therefore they are considered to be less informative [7]. However, the absence itself of characteristic features in these

¹Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, Russia; ise@iph.krasn.ru. ²Siberian Federal University, Krasnoyarsk, Russia. ³Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 57, No. 2, pp. 394-401, March-April, 2016. Original article submitted September 23, 2015.

spectra is directly related to the properties of TAS. The specific brownish color of TAS is one of their characteristic features [7, 8] and is determined by the presence of broad electron absorption bands in the visible and ultraviolet ranges. The series of works carried out by I. N. Evdokimov et al. [9, 10, 12-16] is devoted to the study of the absorption spectra of oil solutions in these ranges. The mentioned authors observed narrow bands in the vicinity of 410 nm and 570 nm against the background of a sharp growth of absorption with an increase in the light wave energy [15]. Using the procedure of “continuum removal by division” [17], they resolved two bands more centered at 533 nm and 573 nm. All the three bands were assigned to vanadyl porphyrins [15], similarly to the identification of absorption bands in the spectra of porphyrins isolated from the oil shales from Morocco [18]. At the same time in [19], the absorbance spectra of oil solutions with different asphaltene concentrations are presented by absolutely smooth curves.

When oil and its heavy fractions contain transition metal complexes, for their analysis it is possible to apply magneto-optical spectroscopy methods which are widely used in the chemistry of both organic and complex inorganic compounds and in biological studies (for example, [6, 20]). The magneto-optical spectroscopy provides additional opportunities of express- and laboratory analyses of substances. The main effect measured is the magnetic circular dichroism (MCD), which is the differential absorption of electromagnetic waves left and right circularly polarized relative to the magnetic field vector (or magnetization intensity of the substance), oriented parallel to the direction of wave propagation. As a rule, MCD spectra are characterized by narrow lines, which make it possible to obtain reliable information on optical resonances in the substance. However, until now, MCD has been rarely used to study oil and its components. There are a few works including [21, 22], where the MCD analysis was used for the analysis of nitrogen contaminants in crude oil. We presented in [5] spectral MCD dependences for a series of samples of oil and asphaltene solutions, where the MCD resonance was revealed near 576 nm.

In the present work, the resonance in the vicinity of 410 nm was detected due to the extension of the range of MCD measurements. We have also studied the possibility to observe MCD in solutions of oil from different oil fields, compared the characteristics of MCD spectra with the data on the elemental composition of the samples obtained by X-ray fluorescence analysis (XRF), and proposed a method to identify particular features of the MCD spectra observed.

SAMPLES AND EXPERIMENTAL TECHNIQUE

Samples of conventional oil from several oil fields listed in Table 1 are studied. Oil samples were dissolved in petroleum ether or toluene at different concentrations from 0.05 vol.% to 1.6 vol.%. All optical and magneto-optical measurements were carried out for both solutions and solvents using identical cells.

The elemental composition of the mentioned samples was determined by X-ray fluorescence analysis using an ARL Quant'X spectrometer located at the Center for Collective Use of the Siberian Federal University and an ARL Advant'X spectrometer at the Analytical Laboratory of the Institute of Catalysis (Siberian Branch, Russian Academy of Sciences). The spectra were recorded using a pinhole collimator.

TABLE 1. Oil Origin and MCD Lines Amplitudes

Sample #	Oil field	MCD amplitude	
		410 nm	570 nm
H1	Ashalchin (Tatar)	$5 \cdot 10^{-5} - 10^{-4}$	$2 \cdot 10^{-4} - 10^{-4}$
H2	Kazanskoe (West-Siberian)	–	$< 10^{-6}$
H3	Dzunbayan (Mongolian)	–	$< 10^{-6}$
H4	Yurubchen-Tokhom (Lena-Tunguska)	–	$< 10^{-6}$
H5	Achinsk Refinery, crude oil	–	$< 10^{-6}$
H6	Vankor (West-Siberian)	$5 \cdot 10^{-5} - 10^{-4}$	$2 \cdot 10^{-4} - 10^{-4}$
H7	Krasnooktyabr (Tatar)	$5 \cdot 10^{-5} - 10^{-4}$	$2 \cdot 10^{-4} - 10^{-4}$

Optical absorption spectra were recorded in the range of 250-2250 nm using a Shimadzu UV-3600 spectrometer.

MCD spectra were measured in the range of 350-650 nm using a spectral-polarimetric unit manufactured on the basis of a MDR-12 monochromator at the Institute of Physics. In order to achieve necessary sensitivity (10^{-5}), the light wave polarization state was modulated from the right-hand to the left-hand circular polarization. A modulator was made of a fused quartz prism to which a piezoelectric ceramic element was glued. The prism is optically isotropic when there is no acoustic excitations. The application of an alternating electric signal at a frequency ω of the eigen-frequency oscillations of the system to the piezoelectric ceramic element leads to the excitation of a standing elastic wave in the quartz prism. As a half-wave of compression propagates through the prism along its horizontal axis, the direction of the acoustic excitation propagation becomes a “slow” axis of the prism. Upon the propagation of the second half-wave (the half-wave of extension), the situation changes radically: the axis of elongation becomes a “fast” axis of the prism. Let linearly polarized light be incident on the prism so that the light polarization plane makes a 45° angle with respect to the horizontal axis of the prism, and let a standing acoustic wave be excited in the prism, then emitted light would be circularly polarized, and this circular polarization would alternate between the left-hand and right-hand with a frequency of acoustic oscillations of the prism. If the sample under study exhibits MCD, the absorption coefficients of light waves being right (k_+) and left (k_-) circularly polarized with respect to the direction of the magnetic moment of the sample will be different. As a result, the light flux transmitted through the sample and incident on the photomultiplier proves to be modulated in intensity. The direction of the magnetic moment of the sample is determined by the external magnetic field applied along the light wave direction. Upon variation of the light wavelength, the constant component of the photoelectric current of the photomultiplier was kept at the same level, and therefore, the alternating signal at the output of the photomultiplier was $2\Delta k/k$, where $\Delta k = k_+ - k_-$ и $k = k_+ + k_-$. The MCD absolute value was calibrated according to the procedure described in [23]. MCD was measured at room temperature in the magnetic field of 0.5 T or 1.2 T. The accuracy of MCD measurements was 10^{-5} ; the spectral resolution was $\sim 20 \text{ cm}^{-1}$; a 150 W HAMAMATSU Mercury Xenon Flash Lamp was used as a light source.

RESULTS AND DISCUSSION

Fig. 1 shows the absorption spectra of petroleum ether used as a solvent and of solutions of H1 oil at various concentrations in the spectral range of 200-600 nm. The strong absorption edge dramatically shifts to the long-wave region with an increase in the oil concentration in the solution. The absorption edge of oil solutions exhibits a pronounced feature near 400 nm, and a considerably weaker feature near 570 nm. These features are also observed in the absorption spectra of the H6 and H7 samples, but they are not observed in the spectra of solutions of other oil samples. The spectra of all samples

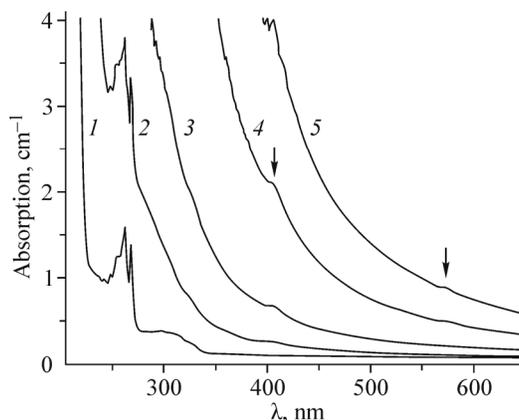


Fig. 1. Absorption spectra of petroleum ether (1) and H1 oil solutions with concentrations of 0.006 vol.%, 0.025 vol.%, 0.1 vol.%, and 0.2 vol.% (curves 2-5 respectively).

also show deviations from the smooth behavior in the vicinity of 320 nm, which is especially pronounced for the solvent, and a prominent structured peak near 250 nm. The structure and intensity of this peak are nearly the same for both solutions and solvent. Thus, it can be concluded that in the process of obtaining petroleum ether from oil, the crude oil components responsible for these features in the short-wavelength absorption spectrum are maintained. The features are observed on the short-wave absorption edge in the range of 240-300 nm for the oil samples dissolved in hexane, which were collected from the surface of the Baltic Sea as well as from Romashkino oil field (Tatarstan) [24]. The work [16] studied the absorption spectra of thin films of Tatar oil deposited on a quartz glass. Owing to this technique it was possible to observe the absorption bands at ~275 nm (4.51 eV) and ~244 nm (5.08 eV) seemingly for the first time. The authors [16] compared these observations with the data in [25], in which the absorption peaks of carbon nanotubes were observed at similar energy values. These peaks were attributed to the anisotropic properties of graphene. At the same time, the close correspondence in the results of [16] and [24] with our data allows us to assume that the absorption features in the range of 250-300 nm are associated with oil components. To our regret, we failed to measure MCD in this range.

As it is mentioned above, the features in the absorption spectra in the vicinity of 400 nm and 570 nm have been observed by many authors, and were connected with the absorption of porphyrin complexes of vanadyl. Due to the extremely low intensity in comparison with the main absorption edge, it seems expedient to use MCD spectra in order to identify them and determine their exact position.

Fig. 2 presents the MCD spectrum measured at room temperature for the H1 oil solution. In the spectrum the following two features are observed: at ~410 nm and ~576 nm, and a very weak feature in the vicinity of 535 nm.

The similar MCD spectra are measured for the H6 and H7 oils. For the other samples, the MCD value was extremely weak (at the noise level) for the sensitivity of the device used. Thus, it can be noted that: (1) in the mentioned spectral range, MCD of pronounced values are observed not in all oil samples, and (2) the similarity between the magneto-optical properties of oil samples from various oil fields located far from each other (Tatar and Vankor) is observed.

The energy of the main asymmetric S-shaped lines of MCD corresponds to the centers of gravity of the features observed in the absorption spectrum (Fig. 1). According to the microscopic theory developed in [27-29], MCD is described by the following equation:

$$\theta_{\text{MCD}} = -\frac{4\pi}{\hbar c} N_a^{(0)} \left\{ \frac{4\omega_{ja}^{(0)} \omega^3 (\omega_{ja}^{(0)2} - \omega^2) \Gamma_{ja} A}{\hbar [(\omega_{ja}^{(0)2} - \omega^2)^2 + \omega^2 \Gamma_{ja}^2]} + \frac{\omega^3 \Gamma_{ja}}{(\omega_{ja}^{(0)2} - \omega^2)^2 + \omega^2 \Gamma_{ja}^2} \left[B + \frac{C}{kT} \right] \right\} H_z, \quad (1)$$

where N is the number of optically-active centers; ω_{aj} is the frequency of the electron transition between the a and j states of the center; Γ_{aj} is the line width; k is the Boltzmann constant; T is the temperature; H_z is the magnetic field component in the

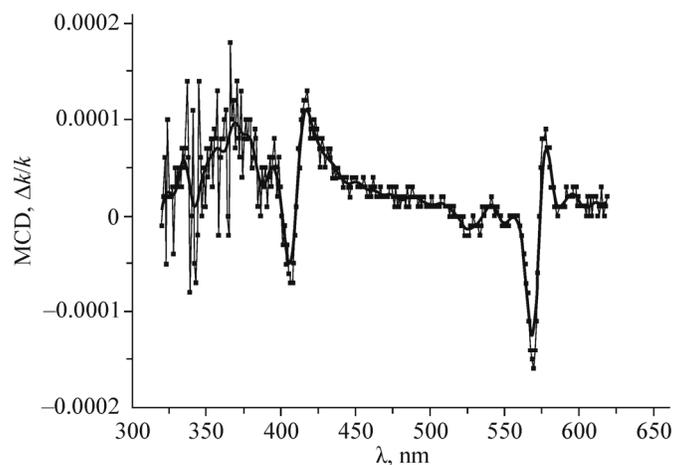


Fig. 2. MCD spectrum of the H1 oil solution (concentration of 0.2 vol.%), $H = 1.2$ T.

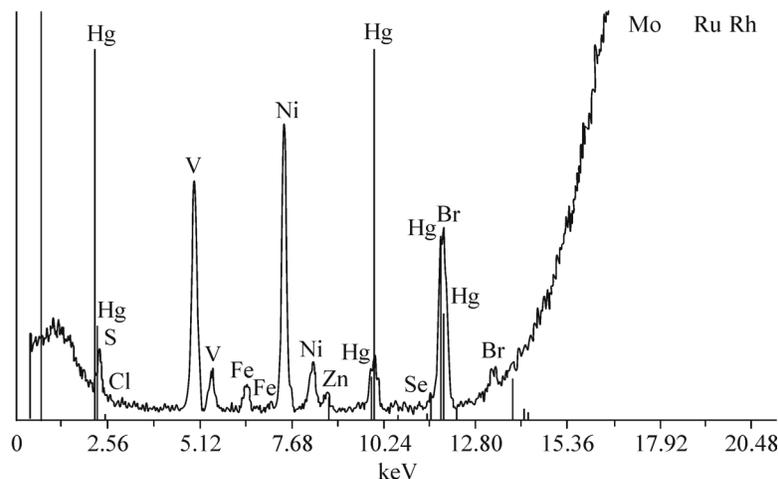


Fig. 3. XRF signal from the elements included in the H1 sample.

direction of the light wave propagation. In equation (1), the first member in the curly brackets (*A*-member) is determined by the Zeeman splitting of electronic levels in the magnetic field; the second member (*B*-member) is determined by the perturbation of wave functions of the *a* and *j* states in the magnetic field due to the admixing of wave functions of the neighboring levels, the third member (*C*-member) is related to the population differences in the sublevels of the ground states, which determines the paramagnetic contribution to MCD. The first member *A* is called diamagnetic. It is described by the symmetric *s*-shaped curve, passing through the zero axis at $\omega = \omega_{aj}$. The third member *C* is called paramagnetic. With the splitting of ground state sublevels in the magnetic field being significantly lower than the line width, it is described by a curve with the maximum at $\omega = \omega_{aj}$ of the similar absorption line, and its value depends on the temperature. The shape of the second member *B* is similar to that of the third one, but its value does not depend on the temperature. Thus, the asymmetric shape of the observed MCD lines can be explained by the sum of the diamagnetic and paramagnetic contributions. The latter can occur only at the optical excitation of the complexes containing paramagnetic ions. Analyzing the radiation wavelength (λ_0), which induced the electron transitions demonstrating MCD, by intersections of the curves with the *X* axis, we have obtained two fundamental wavelengths of 410 nm and 576 nm. Another sufficiently weaker feature of MCD is centered in the vicinity of 530 nm. At very close light wavelengths in [18], the following absorption lines were observed in the spectrum of vanadyl extracted from shale oil from Morocco: 410 nm, 533 nm, and 573 nm, which make it possible to associate the observed MCD features with this oil component.

The comparative analysis of the elemental composition demonstrated that in all the samples studied, the concentration of main elements of oil (H, C, O, N) varied from 95 wt.% to 99.8 wt.%. The remaining mass consists of impurity elements from Mg to Hg. Fig. 3 shows the X-ray fluorescence spectrum of H1 oil including only impurity elements. Table 2 summarizes the total elemental composition of the two oil samples (H1 and H3). The total content of all elements was taken as a unit. It can be seen that the transition group elements are contained in both samples, but at strongly different concentrations. Thus, the vanadium content in the H1 oil sample was 0.019 wt%, whereas in the H3 oil sample, within the sensitivity limits of the X-ray fluorescence method, this method failed to detect vanadium.

The comparison of the X-ray fluorescence and MCD data demonstrates that MCD is distinctly observed in the H1 sample with a noticeable concentration of vanadium, while the H3 sample, where vanadium was not detected, does not

TABLE 2. Relative Concentration of Elements in the H1 and H3 Samples

Oil sample	H, C, O, N	Mg	S	Cl	V	Fe	Ni
H1 (Tatar)	95.2339	0.0369	4.7037	–	0.0193	0.0011	0.0051
H3 (Mongolian)	99.7824	–	0.1969	0.0182	–	0.0006	0.0019

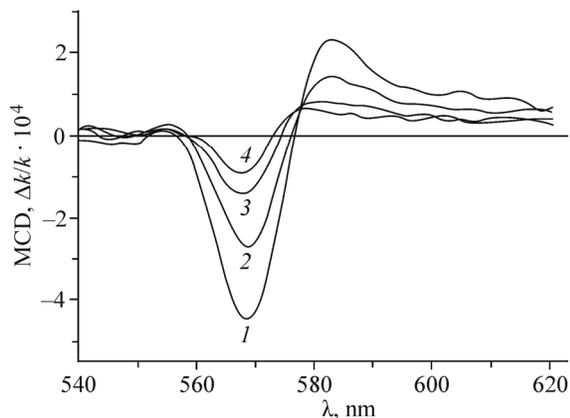


Fig. 4. MCD spectra in the range of 576 nm for the H1 solutions at the following concentrations: 1.6 vol.%, 0.8 vol.%, 0.4 vol.%, and 0.2 vol.%, curves 1-4 respectively, $H = 0.5$ T.

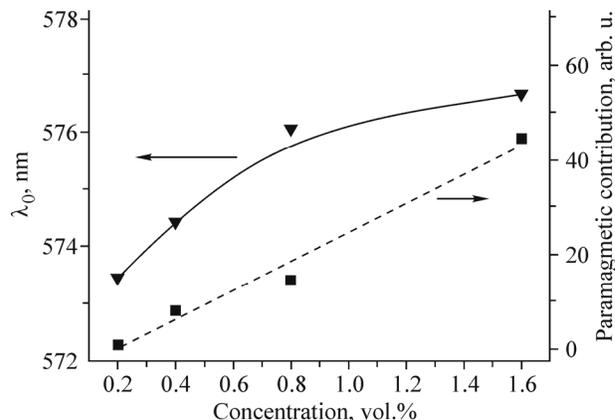


Fig. 5. Dependence of the wavelength λ_0 of the resonance line (triangles) and the paramagnetic contribution to MCD (squares) of H1 oil on its concentration in the solution.

exhibit any magneto-optical activity. This confirms the link of MCD observed in some oil samples with the presence of vanadium ions known to be contained in oil as porphyrin complexes of VO^{2+} .

Fig. 4 shows a series of MCD spectra in the range of 570 nm for various concentrations of H1 oil in petroleum ether. It can be seen that when the oil concentration decreases, the signal amplitude decreases, too. At the same time, the paramagnetic MCD component determined as an integral of the curve within the range of 550-600 nm, increases proportionally to the oil concentration in the solution (Fig. 5), which is no wonder. The dependence of λ_0 on changes in the concentration seems to be unexpected. Possibly, this is due to the aggregation of complexes responsible for the MCD appearance at higher concentrations.

The dependence of the intensity of the observed MCD lines on the vanadium content in the initial oil samples and on the oil concentrations in the solution allows us to assume that the environment of the vanadium ion strongly affects the formation of the MCD spectrum of crude oil. The features in the spectra of vanadyl, as a rule, are related to both $d-d$ -electron transitions in the V^{4+} ion and charge-transfer transition $\text{V}^+ \rightarrow \text{O}^-$. Thus, for instance, in the absorption spectrum of a diglycine calcium chloride crystal $[(\text{NH}_2\text{CH}_2\text{COOH})_2 \cdot \text{CaCl}_2 \cdot 4\text{H}_2\text{O}]$ doped with VO^{2+} , the four bands were observed at 682 nm, 646 nm, 479 nm, and 382 nm [29]. Three long-wave bands are attributed to the $d-d$ -transitions: ${}^2B_{2g} \rightarrow {}^2E_g$ ($d_{xy} \leftrightarrow d_{xz,yz}$), ${}^2B_{2g} \rightarrow {}^2B_{1g}$ ($d_{xy} \leftrightarrow d_{x^2-y^2}$), and ${}^2B_{2g} \rightarrow {}^2A_{1g}$ ($d_{xy} \leftrightarrow d_{z^2}$), respectively.

The short-wave band was assigned to the charge transfer transition between the bonding and antibonding b_z orbitals. It seems reasonable to assume that the well resolved MCD band at 576 nm and a weaker feature at 530 nm observed in the MCD spectrum are caused by the ${}^2B_{2g} \rightarrow {}^2E_g$ and ${}^2B_{2g} \rightarrow {}^2B_{1g}$ transitions. The spacing between the centers of gravity of these bands (40 nm) is roughly consistent with the similar spacing in the spectrum of the crystal mentioned above (36 nm). If we further use this analogy, then the band corresponding to the ${}^2B_{2g} \rightarrow {}^2A_{1g}$ transition should be observed in the vicinity of 430 nm, i.e. very close to the band observed at 410 nm. A certain shift of the MCD main band (576 nm) that occurs at a decrease in the oil concentration in the solution could be attributed to an increase in the axial component of the crystal field, i.e. to a slight change in the vanadyl conformation. This possibility was discussed previously in [15].

As a result of the studies carried out we have detected a series of resonance features in the MCD spectra of crude oil, which are attributed to VO^{2+} ions. Vanadyl-containing fragments are known to be widely used as natural spin probes to study oils and their heavy fractions by electron paramagnetic resonance (EPR) [30-32]. The analysis of the EPR spectra of V^{4+} ions can give information on the dimensional characteristics of asphaltenes and other vanadyl-containing fragments of oil, as well as on the molecular dynamics of the latter upon changes in the anisotropy of hyperfine interactions in the VO^{2+} complexes [30], including increased temperatures and pressures [33]. At the same time, changes in the crystal field, in which there are

paramagnetic vanadyl ions in tarry asphaltene fractions, are displayed weakly in the EPR spectra due to the prevailing anisotropy of the hyperfine interaction.

The same physical phenomenon forms the basis of the MCD and EPR spectra observed, i.e. the splitting of the energy levels of paramagnetic ions in the magnetic field and the appearance of population differences of the sublevels of the ground state. At the same time, these methods are not identical, because they record different transitions excited in different ranges of electromagnetic radiation: magnetic dipole transitions in the microwave region in the case of EPR, and, correspondingly, electric dipole transitions between the ground and excited states in the optical region in the case of MCD. The taking into account of the latter can provide us additional information on the features and structure of vanadyl complexes.

The observed resonance lines in the MCD spectra can be used to elaborate a method to study oil, which would complement the electronic magnetic resonance method. The obtained results give evidence that the MCD spectra contain information on the features of crude oil, which can considerably complement data of absorption and magnetic resonance spectroscopy. The measurement and analysis of MCD spectra of oil can underlie a new method of certification of oil and petroleum products, and they also can be useful to analyze the origin of oil spills contaminating the ocean surface, which is of great concern of ecologists (for example, [24]).

CONCLUSIONS

The optical and magneto-optical spectra of the samples of crude oil of different origin are studied in the visible and near-UV ranges of optical radiation. We have revealed MCD of oil in the wavelength ranges of ~410 nm, 533 nm, and 576 nm. The comparison of the MCD spectra with the elemental composition of oil showed that the observed magneto-optical activity is caused by the presence of vanadyl ions in the samples studied. It is demonstrated that the intensity of the MCD bands depends on the oil origin and is proportional to the oil concentration in the solution. The performed analysis of the spectra observed allowed us to assume that observed MCD was caused by $d-d$ electron transitions in tetravalent vanadium ions.

The revealed magneto-optical activity of oil can form the basis of a new method of analysis of the composition and properties of oils of different origin.

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