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MAREK IZDEBSKI, RAFAŁ LEDZION

Institute of Physics, Lodz University of Technology
ul. Wólczańska 219,90-924 Łódź, Poland, e-mail: izdebski@p.lodz.pl

MODULATION TECHNIQUE USED FOR MEASUREMENT OF VERY WEAK LINEAR BIREFRINGENCE AND DICHROISM IN LIQUIDS ON THE EXAMPLE OF CASTOR OIL BETWEEN METAL ELECTRODES

A technique for measurement of very weak linear birefringence of the order of 10^{-7} and dichroism in liquids is proposed. The method is based on the polarimetric technique. A characteristic feature is that the experimental setup enables the measurement of linear birefringence combined with electro-optic effect as well as the measurement of dichroism combined with electro-optic effect. The combination of the effect which does not show rapid changes with the effect which depends on alternating electric field allows to improve the sensitivity of the method (in comparison to the earlier static method). This was achieved by use of lock-in amplifier that measures only the selected harmonic with very high selectivity. The theoretical considerations are illustrated by the results of measurements for castor oil.

Keywords: castor oil, optical polarimetric technique, linear birefringence, dichroism, electro-optic effect.

1. INTRODUCTION

Castor oil is known for its natural optical activity, thus its internal symmetry can be described only by those Curie groups which allow for this effect, namely $\infty\infty$, $\infty 2$, and ∞. Our previous studies have shown that castor oil placed between two plane-parallel metal plates exhibits dichroism and linear birefringence of the order of 10^{-7} with the optical axis directed perpendicularly to the electrodes, which limits the possible symmetries to the $\infty 2$ and ∞ groups [1]. Moreover, our recent measurements have shown that the quadratic electro-optic and quadratic elecrogyration effect (optical activity induced by electric field) manifest themselves in castor oil, while the linear effect is not clearly observed, which indicates the $\infty 2$ symmetry [2].

The aim of this work is to propose a method for measuring very weak linear birefringence and dichroism, which should be more sensitive than the method proposed earlier in Ref. [1]. Moreover, the method should be more suitable for automation than the previous one, which required multiple search of polarizers orientations corresponding to the minimum and maximum of light transmission through the measurement system. Our main motivation to develop better measurement method involves quality control of vegetable oils of industrial importance.

Early attempts to apply optical constants for assessing the quality of vegetable oils focused mainly on refractive index and a rotation of the plane of polarization. Testing of these constants may be used as a simple method for detecting serious adulteration of castor oil with cheaper oil [3]. However, our observations show a rather poor suitability of the method due to its to low sensitivity, e.g., to study the effect of oxidation of the oil. The optical constants, which seem to be more promising, are:

- Kerr constant (describing quadratic electro-optic effect) which shows a clear relationship with aging process in castor oil [4],
- Verdet constant (describing the effect of optical activity induced by an applied magnetic field), which can be used in authentication techniques of olive oil and probably also other vegetable oils [5],
- the linear birefringence and dichroism; our preliminary observations indicate that they may be the next optical effects useful to indicate changes in the oils quality.

Liquids with very weak linear birefringence of the order of 10^{-7} are also interesting from a cognitive point of view, as a case of liquids exhibiting a slight orientational ordering of molecules, which essentially distinguishes them from the isotropic liquid as well as liquid crystals.

2. THEORETICAL ANALYSIS

2.1. Impermeability tensor

The real part of electric impermeability tensor $[B]$ at optical frequencies for non-absorbing medium of the $\infty 2$ symmetry written in the principal axes system XYZ (where the Z axis is the optical axis) with the accuracy to the terms proportional to the square of applied electric field E is as follows:

$$\mathrm{Re}[B]=\begin{bmatrix} n_{01}^{-2}+q_{13}E^2 & 0 & 0 \\ 0 & n_{01}^{-2}+q_{13}E^2 & 0 \\ 0 & 0 & n_{03}^{-2}+q_{33}E^2 \end{bmatrix}, \qquad (1)$$

where n_{01} and n_{03} are the major field-free refractive indices and q_{ij} are the components of the quadratic electro-optic tensors. Due to the observed dependence of the optical axis in castor oil on the orientation of the electrodes (see Ref. 1) we have assumed in equations (1) and (4), that the only possible form of the electric field vector written in the *XYZ* coordinates is $\mathbf{E} = (0, 0, E)$. Although the linear electro-optic effect is not forbidden by the $\infty 2$ symmetry, it may not manifest itself for this particular field direction. The forms of the tensors describing the natural linear birefringence, natural optical activity, linear and quadratic electro-optic effect, and linear and quadratic electrogyration effect can be found, e.g., in Refs. [2,6,7].

The natural and electric field induced optical activity is traditionally described by the imaginary antisymmetric part of the relative permittivity tensor $[K]$ at optical frequencies [8]:

$$\mathrm{Im}[K]=\begin{bmatrix} 0 & -G_3 & G_2 \\ G_3 & 0 & -G_1 \\ -G_2 & G_1 & 0 \end{bmatrix}, \qquad (2)$$

where G_1, G_2 and G_3 are the elements of the gyration vector $\mathbf{G}$ for a given wave propagation vector $\mathbf{s}$:

$$\mathbf{G} = [g]\mathbf{s}. \qquad (3)$$

In Eq. (3) $[g]$ is a second rank gyration axial tensor described by a real 3×3 matrix. In the case of liquids of the $\infty 2$ symmetry and the field $\mathbf{E} = (0, 0, E)$ the tensor has the form:

$$[g]=\begin{bmatrix} g_{11}^{(0)}+\beta_{13}E^2 & 0 & 0 \\ 0 & g_{11}^{(0)}+\beta_{13}E^2 & 0 \\ 0 & 0 & g_{33}^{(0)}+\beta_{33}E^2 \end{bmatrix}, \qquad (4)$$

where $g_{ii}^{(0)}$ are the components of natural optical activity tensor and β_{ij} are the components of the quadratic electrogyration tensor. When the tensors $\mathrm{Re}[B]$ and $\mathrm{Im}[K]$ are already known, the imaginary part of the $[B]$ tensor can be found using the formula [9]:

$$\mathrm{Im}[B] = -[B]\,\mathrm{Im}[K]\,[B] \approx -\,\mathrm{Re}[B]\,\mathrm{Im}[K]\,\mathrm{Re}[B]. \qquad (5)$$

The formulas (1)-(5) allow to find the total complex hermitian impermeability tensor $[B]$ for non-absorbing liquid of the $\infty 2$ symmetry. In the case of absorbing medium the symmetry $B'_{ij} = B'^{*}_{ji}$ is not exactly satisfied, however, the perturbation of the symmetry is negligible in a typical case $1/\kappa >> \lambda$, where κ [m^{-1}] is the absorption coefficient and λ [m] is the wavelength of light.

Let us consider the configuration $\mathbf{s} = [1, 0, 0]$ and $\mathbf{E} = [0, 0, E]$. The total complex impermeability tensor, found from equations (1)-(5) for this configuration and written in the XYZ coordinates with accuracy to the terms proportional to E^2, has the following form:

$$[B] = \begin{bmatrix} n_{01}^{-2} + q_{13}E^2 & 0 & 0 \\ 0 & n_{01}^{-2} + q_{13}E^2 & B_{23} \\ 0 & -B_{23} & n_{03}^{-2} + q_{33}E^2 \end{bmatrix}, \tag{6}$$

where:

$$B_{23} = \mathrm{i}\left[n_{01}^{-2} n_{03}^{-2}\left(g_{11}^{(0)} + \beta_{13}E^2\right) + g_{11}^{(0)}\left(n_{01}^{-2} q_{33} + n_{03}^{-2} q_{13}\right)E^2\right]. \tag{7}$$

The terms in Eq. (7) containing the products of $g_{11}^{(0)}$ (of the order of 10^{-7}) and q_{ij} are negligible and the term $n_{01}^{-2} n_{03}^{-2}$ is very close to n_0^{-4}, where $n_0 = (n_{01}+n_{03})/2$ is the average refractive index.

2.2. Transmission of the light beam through the measurement system

The state of a monochromatic light passing through a system of plane-parallel optical elements can be found using Jones calculus (see, e.g., [10]). In our calculations, we used one of the most general form of a Jones M-matrix derived by Ratajczyk & Ścierski [10,11], which describes the transmission of light beam through any dichroic homogeneous elliptically birefringent media. In order to express the terms occurring in the matrix directly by the components of complex hermitian impermeability tensor, an additional formulas were applied which have been recently found using the eigenvalue approach [12].

Let us consider the measurement system composed of an ideal linear polarizer of any orientation α_p, a cuvette with oil in the form of a rectangular parallelepiped, and an ideal linear analyzer of the orientation $\alpha_a = \alpha_p - 45°$ or $\alpha_a = \alpha_p + 45°$. The intensity of the light I passing though the system relative to the intensity I_p directly behind the polarizer is given by [2]:

$$\begin{aligned}\frac{I}{I_\mathrm{p}} &= \frac{T_\mathrm{f}^2+T_\mathrm{s}^2}{4}+\\ &+\frac{\sqrt{2}}{2}\sin(45^\circ\mp 2\alpha_\mathrm{p})\frac{T_\mathrm{s}^2-T_\mathrm{f}^2}{2}\frac{B'_{22}-B'_{11}}{\sqrt{(B'_{11}-B'_{22})^2+4B'_{12}B'^{*}_{12}}}+\\ &\mp\frac{1}{8}\sin(4\alpha_\mathrm{p})\frac{(B'_{11}-B'_{22})^2}{(B'_{11}-B'_{22})^2+4B'_{12}B'^{*}_{12}}\left(T_\mathrm{f}^2+T_\mathrm{s}^2-2T_\mathrm{f}T_\mathrm{s}\cos\Gamma\right)+\\ &\pm\frac{T_\mathrm{f}T_\mathrm{s}\,\mathrm{Im}[B'_{12}]}{\sqrt{(B'_{11}-B'_{22})^2+4B'_{12}B'^{*}_{12}}}\sin\Gamma,\end{aligned}\tag{8}$$

where the upper signs in the "$\mp$" and "$\pm$" symbols correspond to $\alpha_\mathrm{a} = \alpha_\mathrm{p} + 45^\circ$ and the lower signs to $\alpha_\mathrm{a} = \alpha_\mathrm{p} - 45^\circ$, and B'_{ij} are the components of impermeability tensor written in the $X'Y'Z'$ coordinate system traditionally used in Jones calculus, where the $+Z'$ axis is along the light beam **s'** = [0, 0, 1] and the $+X'$ axis defines the reference zero azimuth, T_f and T_s are the amplitude transmission coefficients for the fast and slow waves propagating in the oil sample, respectively, and Γ is the phase difference between the slow and fast waves. In order to simplify the form of equation (8) we omitted all terms containing a real part $\mathrm{Re}[B'_{12}]$, which vanishes for the symmetry under consideration both in the $X'Y'Z'$ and XYZ coordinates. Moreover, since the relation $B'_{11}+B'_{22} >> \sqrt{(B'_{11}-B'_{22})^2+4B'_{12}B'^{*}_{12}}$ is fulfilled and n_{01} and n_{03} have very similar values, we can calculate Γ as [2,7]:

$$\Gamma \approx \frac{2\sqrt{2}\,\pi L}{\lambda}\frac{\sqrt{(B'_{11}-B'_{22})^2+4B'_{12}B'^{*}_{12}}}{(B'_{11}+B'_{22})^{3/2}} \approx \frac{\pi L n_0^3}{\lambda}\sqrt{(B'_{11}-B'_{22})^2+4B'_{12}B'^{*}_{12}}\,, \tag{9}$$

where L is the light path length in the oil.

The matrix of transformation from the XYZ to $X'Y'Z'$ coordinates can be chosen in many ways, for example:

$$[\mathbf{a}] = \begin{bmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \tag{10}$$

and the selected components of the matrix $[B'] = [\mathbf{a}][B][\mathbf{a}]^\mathrm{T}$ written in the $X'Y'Z'$ coordinates are:

$$B'_{22}-B'_{11} = n_{01}^{-2}-n_{03}^{-2}+(q_{13}-q_{33})E^2\,, \tag{11}$$

$$B'_{12} = B_{23} \approx \mathrm{i}\, n_0^{-4} g_{11}^{(0)} + \mathrm{i}\, n_0^{-4} \beta_{13} E^2 \,. \tag{12}$$

Reliable and precise measurement of the intensity I relative to I_p, as in Eq. (8), is rather difficult task, but we can easily measure the changes in the intensity $I(E)$ induced by the applied field with respect to the constant component of the same intensity, I. The results of such measurements, however, do not provide sufficient data to determine the values of the coefficients T_f and T_s. Thus, in order to reduce the number of unknowns in the formula (8) we will introduce an average transmission coefficient:

$$\overline{T} = (T_f + T_s)/2 \,, \tag{13}$$

and dichroism defined as:

$$D = (T_f - T_s)/\overline{T} \,. \tag{14}$$

Now the expressions in Eq. (8), which depend on the transmission coefficients, can be written in the following form:

$$T_f T_s = \overline{T}^2 \left(1 - 0.25 D^2\right), \tag{15}$$

$$T_f^2 + T_s^2 = 2\overline{T}^2 \left(1 + 0.25 D^2\right), \tag{16}$$

$$T_f^2 - T_s^2 = 2\overline{T}^2 D^2 \,, \tag{17}$$

$$T_f^2 + T_s^2 - 2T_f T_s \cos\Gamma = 2\overline{T}^2 \left[(1 - \cos\Gamma) + 0.25 D^2 (1 + \cos\Gamma)\right]. \tag{18}$$

Substituting Eqs. (15)-(18) into (8) we can see, that all constant as well as field-dependent components are proportional to $\overline{T}^2$ and the effect of light absorption on the modulation of the emerging light can be described by only one parameter D. The dichroism described in the literature is traditionally divided into linear and circular dichroism, but the dichroism defined in this work by Eq. (14) can be used to describe any elliptical medium.

3. EXPERIMENTAL

The sample of castor oil for research purposes by SIGMA-ALDRICH company, product number 259853 (www.sigmaaldrich.com), was poured into a glass cuvette and the stainless steel plane-parallel electrodes spaced $d = 4.13$ mm were immersed in the oil. The cuvette was then placed between two polarizers and illuminated with He-Ne laser Melles Griot 05-LHP-171 at a wavelength $\lambda = 632.8$ nm, and the light beam was directed parallel to the electrodes with a length of $L = 9{,}899$ cm. The transmitted light was measured by a photodiode Thor Labs PDA100A-EC, which provides a voltage U proportional to the intensity I of emerging light. The measurements were performed at room temperature 22°C employing sinusoidally modulated electric field and the modulation index:

$$m_{2\omega} = U_{2\omega} / U_0 \tag{19}$$

was also determined, where $U_{2\omega}$ is the rms voltage measured at the second harmonic of the modulating generator by EG&G DSP Lock-in amplifier, model 7265, and U_0 is the DC component of the U voltage measured by Keithley 2700 multimeter.

The modulation voltage U_m was increased gradually from 910 to 3070 V RMS and an average values of $m_{2\omega}/U_m^2$ were fitted by least square method for each measurement series. The average values of $m_{2\omega}/U_m^2$ were found as the function of the azimuth of the polarizer α_p, which was changed from 0 to 360° with 5° steps, while the azimuth of the analyzer was $\alpha_a = \alpha_p + 45°$. Three days later analogous measurements were performed for $\alpha_a = \alpha_p - 45°$.

Then, based on the experimental dependence of $m_{2\omega}/U_m^2$ on α_p, the theoretical dependence was numerically fitted:

$$\frac{m_{2\omega}}{U_m^2} = \frac{I_{2\omega}/I_p}{I_0/I_p} U_m^{-2}, \tag{20}$$

where $I_{2\omega}/I_p$ and I_0/I_p were calculated as the coefficients in the following Fourier series:

$$\frac{I}{I_p} = \frac{I_0}{I_p} + \frac{I_\omega}{I_p}\sin(\omega t + \varphi_1) + \frac{I_{2\omega}}{I_p}\sin(2\omega t + \varphi_2) + \ldots, \tag{21}$$

for I/I_p given by Eq. (8) with substituted Eqs. (9), (11)-(18).

4. RESULTS

A large number of constants in Eqs. (8), (9) and (11)-(18) causes that we need to know in advance some of the values. We have used $n_0 = 1.48$ [2] and the Kerr constant $K = 1.5 \cdot 10^{-14}$ mV^{-2} [13], which allowed to calculate the effective coefficient of the quadratic electro-optic effect $|q_{33} - q_{13}| = 2\lambda K/n_0^3 \approx 5.8 \cdot 10^{-21}$ m^{2}V^{-2}. The value $g_{11}^{(0)} = -2.0 \cdot 10^{-7}$ was calculated on the basis of our measured optical rotation $\phi/L = -3.8°$/dm in the oil for $\lambda = 632.8$ nm and $\alpha_p = 0$ using the relationship [2]:

$$g_{11}^{(0)} = \frac{\lambda n_0}{\pi} \frac{\phi}{L}. \tag{22}$$

The measured dependence of $m_{2\omega}/U_m^2$ on α_p, obtained for the case $\alpha_a = \alpha_p - 45°$, is shown in Fig. 1, while the case $\alpha_a = \alpha_p + 45°$ is shown in Fig. 2. The combined effect of the linear birefringence with the quadratic electro-optic effect is related mainly to the component changing as $\pm\sin(4\alpha_p)$, while the combined effect of the dichroism with the quadratic electro-optic effect gives mainly the result proportional to $\sin(45° \mp 2\alpha_p)$. With these data, we can provide unambiguous numerical fit of the absolute value of the linear birefringence:

$$|n_{03} - n_{01}| = (2.2 \pm 0.2)\cdot 10^{-7} \text{ (for the both series),} \tag{23}$$

and absolute value of the dichroism:

$$|T_f - T_s|/\overline{T} = \begin{cases} (1.0 \pm 0.2)\cdot 10^{-2} \text{ for } \alpha_a = \alpha_p + 45°, \\ (0.9 \pm 0.2)\cdot 10^{-2} \text{ for } \alpha_a = \alpha_p - 45°. \end{cases} \tag{24}$$

Determining the positive or negative sign of $n_{03} - n_{01}$ and $T_f - T_s$ should be possible in future when the sign of $q_{33} - q_{13}$ will be known. Currently, we can determine only the signs of expressions involving two phenomena, namely:

$$(n_{03} - n_{01})(q_{33} - q_{13}) > 0, \tag{25}$$

$$(T_f - T_s)(q_{33} - q_{13}) < 0. \tag{26}$$

Our numerical studies have shown that for the field strengths smaller than 10^6 V/m rms, the values of the constants fitted numerically do not depend significantly on the field strength, but for larger strengths the $m_{2\omega}/U_m^2$ ratio cannot be considered as independent of U_m.

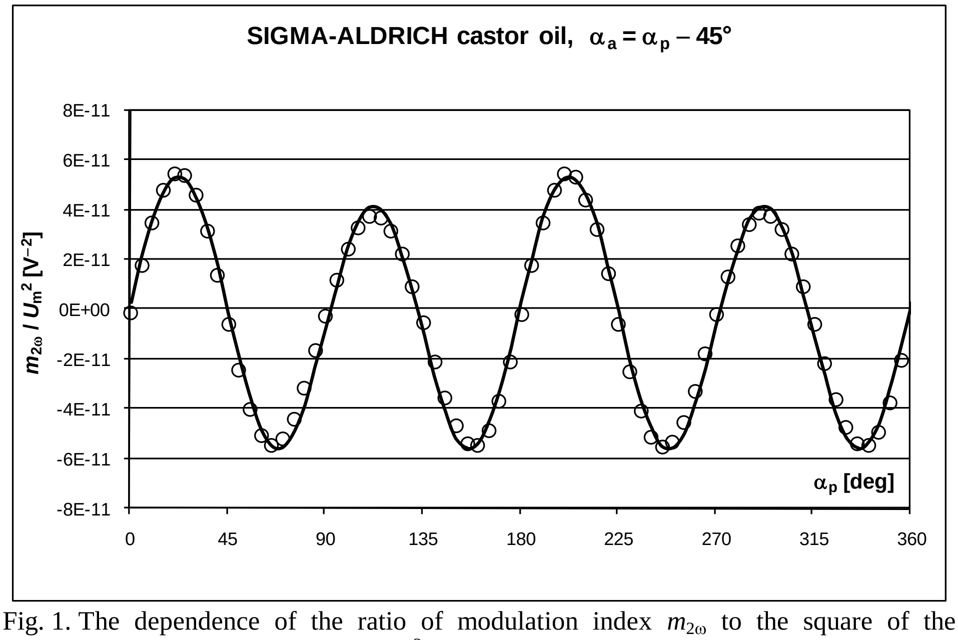

Fig. 1. The dependence of the ratio of modulation index $m_{2\omega}$ to the square of the modulation rms voltage U_m^2 on the polarizer azimuth α_p obtained for SIGMA-ALDRICH castor oil in the case $\alpha_a = \alpha_p - 45°$ and modulating field of frequency 417 Hz. Circles: the experimental data, curve: the interpolation fit

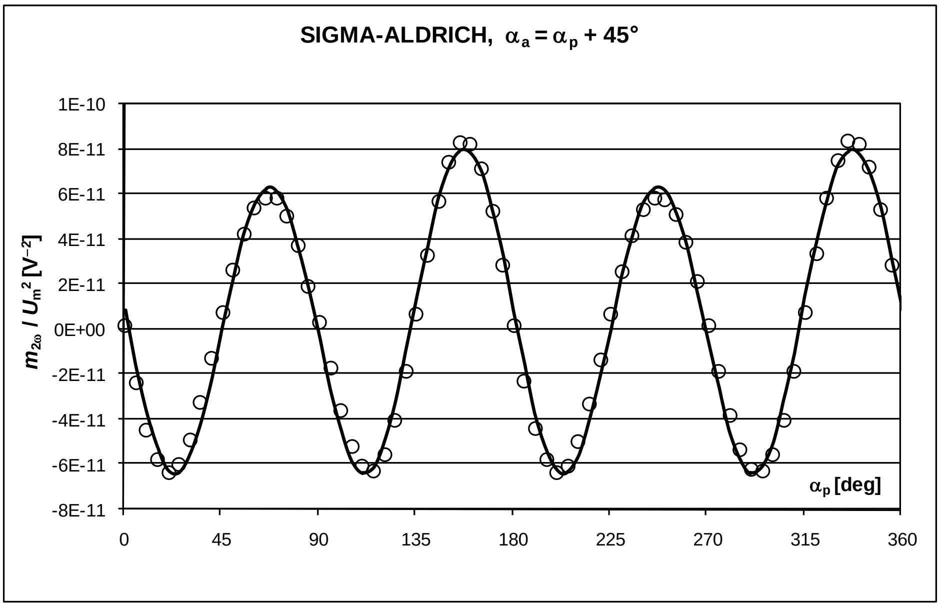

Fig. 2. The dependence of the ratio of modulation index $m_{2\omega}$ to the square of the modulation rms voltage U_m^2 on the polarizer azimuth α_p obtained for SIGMA-ALDRICH castor oil in the case $\alpha_a = \alpha_p + 45°$ and modulating field of frequency 417 Hz. Circles: the experimental data, curve: the interpolation fit

5. CONCLUSIONS

The value of the linear birefringence $|n_{03} - n_{01}| = 2.2 \cdot 10^{-7}$ obtained in this work is similar to the value $1.6 \cdot 10^{-7}$ for medicinal castor oil by PROLAB measured previously by another static method [1]. In the case of the dichroism, the discrepancy between the result $|T_f - T_s| / \overline{T} = 0.9 \ldots 1.0 \cdot 10^{-2}$ obtained in this study and the value $3.6 \cdot 10^{-2}$ from Ref. [1] is much greater. However, such a large discrepancy does not necessarily indicate an error in one of the measurement methods and a further study is needed concerning comparison of the both methods and the effect of oxidation products in the oil on the results of measurements.

The measurement method proposed in this paper requires the value of the Kerr constant, which must be measured using other method. However, this should not be a problem in a reliable quality control system, which should include several optical constants which have a strong relationship with the purity of the oil, including also the Kerr constant.

The method described in this work may be adapted for liquids belonging to other Curie groups, which allow for the linear birefringence. However, in the case of liquids described by the ∞ Curie group the method should take into account the linear electro-optic effect, which, as we expect, will dominate the quadratic one.

REFERENCES

[1] **Izdebski M., Ledzion R., Górski P.,** Sci. Bull. Lodz Univ. Tech., s. Physics, **33** (2012) 39.
[2] **Izdebski M., Ledzion R., Górski P.,** "Measurement of quadratic electrogyration effect in castor oil", in review in Optics Communications.
[3] **Babu S., Sudershan R.V., Sharma R.K., Bhat Ramesh V.,** JAOCS, 73 (1996) 397.
[4] **Stępień M., Ledzion R., Górski P., Kucharczyk W.,** Sci. Bull. Lodz Univ. Tech., s. Physics, **33** (2012) 89.
[5] **Abu-Taha M.I., Halasa M.A., Abu-Samreh M.M.,** Journal of Modern Physics **4** (2013) 230.
[6] **Sirotin Yu.I., Shaskolskaya M.P.,** Fundamentals of crystal physics, Mir Publishers, 1982.
[7] **Izdebski M., Ledzion R., Kucharczyk W.,** Sci. Bull. Lodz Univ. Tech., s. Physics, **34** (2013)
[8] **Tomkins H.G., Irene E.A.,** Handbook of Ellipsometry, William Andrew, 2005, p. 121.
[9] **Maldonaldo T.A., Gaylord T.K.,** Appl. Opt., **28** (1989) 2075.
[10] **Ratajczyk F.,** Dwójłomność i polaryzacja optyczna, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2000.
[11] **Ścierski J., Ratajczyk F.,** Optik (Stuttgart), **68** (1984) 121.
[12] **Izdebski M.,** J. Appl. Cryst., **45** (2012) 950.
[13] **Nowakowski K., Perek A., Izdebski M., Ledzion R., Górski P.,** this volume.

MODULACYJNA METODA POMIARU BARDZO SŁABEJ DWÓJŁONOŚCI LINIOWEJ I DICHROIZMU W CIECZACH NA PRZYKŁADZIE OLEJU RYCYNOWEGO POMIĘDZY METALOWYMI ELEKTRODAMI

Streszczenie

Zaproponowano metodę pomiaru bardzo słabej dwójłomności liniowej rzędu 10^{-7} i dichroizmu w cieczach opartą na technice polaryzacyjno-optycznej. Cechą charakterystyczną metody jest taki wybór konfiguracji układu, w którym możliwy jest pomiar kombinacji dwójłomności liniowej i efektu elektro-optycznego oraz kombinacji dichroizmu z efektem elektro-optycznym. Połączenie efektów niewykazujących szybkich zmian w czasie z efektem zależnym od zmiennego pola modulującego pozwoliło na poprawę czułości metody (w porównaniu do starszej metody statycznej) przez zastosowanie woltomierzy typu lock-in, które mierzą z wysoką selektywnością tylko wybraną harmoniczną. Rozważania teoretyczne zostały zilustrowane wynikami pomiarów dla oleju rycynowego.