H. V. Dorozinska

ANALYSIS OF THE METHODS FOR THE DETERMINATION OF THE MINIMUM REFLECTION CHARACTERISTIC IN THE PROCESS OF THE SURFACE PLASMON RESONANCE

The paper analyzed the most widely used methods for the determination of the reflection characteristic minimum in the process of the surface plasmon resonance and considers the impact of the refraction index change of the studied environment and its temperature on the accuracy of the measurements, performed by these methods, applying the numerical modeling. It is known that the accuracy of the minimum reflection characteristic determination greatly depends on the mathematical methods of its determination. The most widely used methods of the minimum reflection characteristic determination are the methods of the polynomial approximation, which depend on the form of the reflection characteristic, that influences the accuracy of the minimum determination. The developed alternative method of the center line provides smaller measurement error when the refraction indices change from 1.33 to 1.5 times as compared with the methods of the polynomial approximation for the area of the reflection characteristic with the angular range of 0.125 ang. deg. and almost 8.5 times for the angular range of 0.2 ang. deg, that proves the expediency of the new method application. The smallest absolute error is characteristic for the method of the center line for the area of the reflection characteristic of 0.4, that is connected directly with the number of points, comprising the area of the minimum determination. The method of the center line, used for the study of the temperature changes of the analyte also provides smaller absolute error of minimum determination as compared with the polynomial approximation and has smaller error values scattering in the range of the higher temperatures. As compared with the polynomial methods the center line method has higher accuracy of the determination of the reflection characteristic minimum, because it is less dependent on its asymmetry, which is connected with the flow of the physical processes on the surface of the surface of the plasmons excitation. The results of the numerical analysis, carried out, may be useful for the development of the algorithms of the direct measurements processing by measuring devices on the base of the surface plasmon resonance.

Key words: *numerical modeling, surface plasmon resonance, angular position of the minimum of the reflection characteristic.*

Introduction

Sensor devices, based on the phenomenon of the surface plasmon resonance (SPR) provide small dimensions of the equipment require small volumes of the studied substances and contain elements with the layers of the nanometer range. Usually such elements consist of a thin conductive layer, on the surface of which the surface plasmons are excited. Resonance excitation of the oscillations of the surface plasmons in the thin layer of the conducting material, located between two media with different refraction indices was called «surface plasmon resonance» [1]. Under condition of the p-polarized light incidence on the thin conductive layer at the angle greater than the angle of total internal reflection (TIR) on the side of optically denser medium, it became possible to observe the phenomenon of the SPR. If the opposite side of the conductive layer contacts with the investigated optically less dense medium (analyte), then the electric field of the electromagnetic wave penetrates in the analyte but only at the distance, not longer than the wavelength of the light. Change in the analyte causes the change of the reflection characteristic, which is the dependence of the radiation intensity (reflection index) on the incidence angles of this radiation or the wavelengths (Fig. 1).

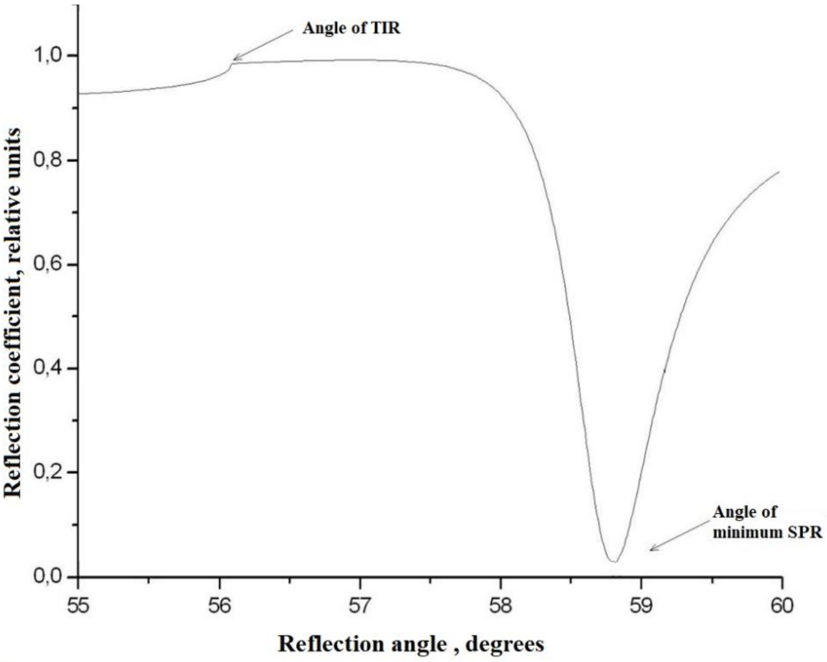

Fig. 1. Typical reflection characteristic in the process of the surface plasmon resonance

At resonance absorption of the radiant energy of incidence light photons by the surface plasmons is registered at the reflection characteristic (Fig. 1) as a minimum of the intensity at certain angle (angle of minimum of SPR). Angle of minimum of SPR depends on the refractive index of the analyte, which contacts with the surface of the conductive layer. Changes in the analyte lead to the changes of its refractive index, enabling to study the processes, occurring in the studied environment in real time, by registration the parameters of the reflection characteristic. SPR-devices are very sensitive to the changes, occurring directly at the boundary between two media. Greater part of the devices use the prism method of excitation of the surface plasmons using Kretschmann geometry, optical circuit of which consists of the radiation source, prism, sensitive element with the nanolayer of the conductive material and photo receiver [2]. Determination of the angle position of resonance minimum of the reflection characteristic occurs by means of its mathematical processing.

Accurate determination of the angle position of resonance minimum on the conditions of the observation of SPR phenomenon is rather important problem for the determination of the refraction index of the studied medium, concentration of analyte in them and the thickness of the adsorbed nanolayers. The numerous methods, used for the determination of the real angle position of resonance minimum are the following: polynomial method [3, 4], centroid method [5], interpolated centroid method [6], method of the dynamic base line [7], rapid centroid method [8]. Besides the minimum of the reflection characteristic, there exist other parameters, containing the important information: critical angle, width, asymmetry, slope, intensity.

The most widely used methods of the analysis of the SPR reflection characteristics is the method of the polynomials and centroid method (Fig. 2). Polynomial method analyses the total SPR reflection characteristic or its part, close to the area around of minimum, by means of the polynomial function of the degree n. Then the first derivative is calculated.

Centroid method finds the geometrical center of the reflection characteristic minimum. For this purpose previously determined dynamic threshold, known as the basic level, is used. For the reflection characteristic during SPR with N points the minimum value is calculated for the points with the intensity values below the base line L_B (Fig. 2, b):

$$C(t)=\frac{\sum_{k=1}^{N}(p_k(t)-L_B)k}{\sum_{k=1}^{N}(p_k(t)-L_B)} \tag{1}$$

where $\boldsymbol{p_k}$ is the value of the $\boldsymbol{k}$ point in the reflection characteristic. The base line is an important parameter, influencing the noise level of the output. As a rule, higher base line usually decreases the central noise, containing more pixels in the calculative of the reflection characteristic.

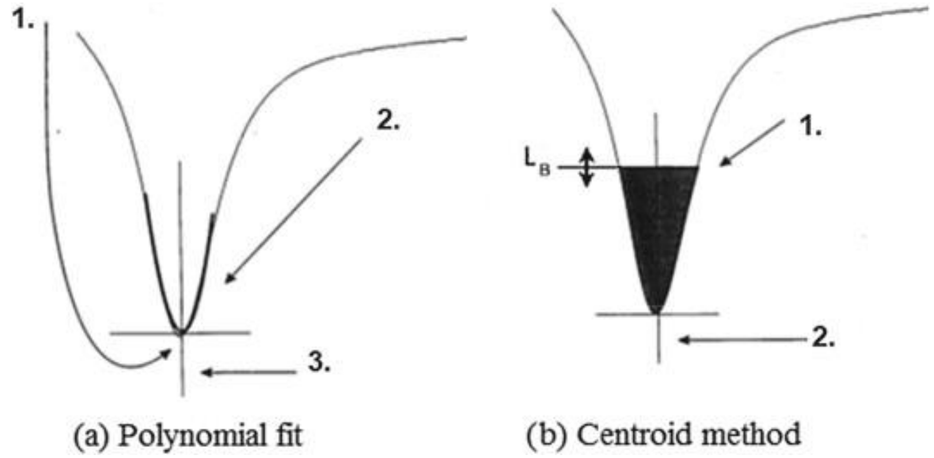

Fig. 2. Algorithms of the determination of the reflection characteristic minimum during SPR [9]
a) Polynomial method: 1 – selection of the reflection characteristic area, surrounding the minimum; 2 – selection of the polynomial for the chosen area; 3 – searching of the minimum of the polynomial. **b)** centroid method: 1 – selection of the area of the reflection characteristic below the basic threshold, which can be dynamically regulated; 2 – searching of the centroid of the selected part.

These methods have some drawbacks: they are sensitive to the correlated noise or to the drift of the light source. Any method of the data analysis requires the usage of the selected range of data points. For the centroid method the data range is selected for the data below certain base line. The result of the light source intensity change is that the range of the points increases or decreases relatively the base line in the process of the centroid calculation. As the reflection characteristic during SPR is asymmetric, any changes in the data range lead to the erroneous shift of the calculated minimum.

The alternative method of the resonance angle determination is the center line method. The essence of the method consists in determining the resonance angle as the point of intersection of the axis of the incidence angles and the line that passes across the midpoint of the sections which connect the equal reflected intensity points on the axis of the intensity of the reflected light, located on the slopes of the resonance characteristic of reflection [10]. The authors studied the change of the measurement error relatively the change of the radiation wavelength, which provided smaller value of the absolute error as compared with the polynomial methods of approximation. As the important parameters, influencing the measurement error are the change of the refraction index value of the studied medium and temperature impact, it is necessary to study the impact of these parameters on the measurement, applying the method of the center line.

Methods of study

The assessment of the impact of the mathematical methods on the value of the absolute error was carried out by means of the construction of the theoretical resonance characteristic for the multilayer system "glass-metal-analyte" and p-polarized monochromatic radiation. Theoretical characteristic of the reflection (real characteristic of the reflection during SPR) for the multilayer system “transparent plate (glass) – metal film – dielectric (analyte) – external medium” and *p*-polarized monochromatic incident radiation was calculated as the function of the angle of incidence, using Fraenkel formula and mathematical formalism of Jones dispersion matrix. As the material of the metal film gold is chosen because it is widely used in SPR-devices due to high chemical resistance and electrical conductivity. Real reflection characteristics were calculated, angle position of the minimum was determined during the change of the refractive index in the range of 1.33 to 1.50, inherent to the greater part of the investigated liquid media. Approximation of the reflection characteristic was carried out in m points x_j, y_j (j = 1, 2,…, m) by the polynomial of degree n applying the method of least squares:

$$y(x) = \sum_{i=o}^{n} a_i x^i \qquad (2)$$

Graph of reflection characteristics was built with the step of 0.01 degree, that corresponds to the step of the angular measurements, characteristic for the SPR-device «Plasmon-6», developed at the V.E. Lashkaryov Institute of Semiconductor Physics of National Academy of Sciences of Ukraine [11]. For the comparison the values of the minima of the reflection characteristics, constructed with the step of 0.00005 degree for the corresponding refraction indices were used.

Analysis of the impact of the amount of the data points of the chosen range on the value of the minimum of the reflection characteristic is rather important. These data points form certain area of the resonance characteristic of the reflection. The data points range was reduced, choosing certain angular range in the area of the minimum of the resonance characteristic on the axis of the reflection angles (axis X). The analysis of the small area of the resonance characteristic near the minimum with angular ranges of 0.4, 0.2 and 0.125 ang. degrees for three methods was carried out: method of the center line, polynomial methods of the second and third degrees. For the angular ranges of 0.2 and 0.125 real reflection characteristics of SPR were approximated by the polynomial of the second and third degrees with further minimum determination. For angular ranges of 0.4, 0.2 and 0.125 the method of the center line was used.

Results and discussion

Absolute error of the minimum of the reflection characteristic determination for the chosen refraction indices was determined by means of the methods of the center line and polynomial, depending on the area of the resonance characteristic of the reflection (data are shown in Fig. 3).

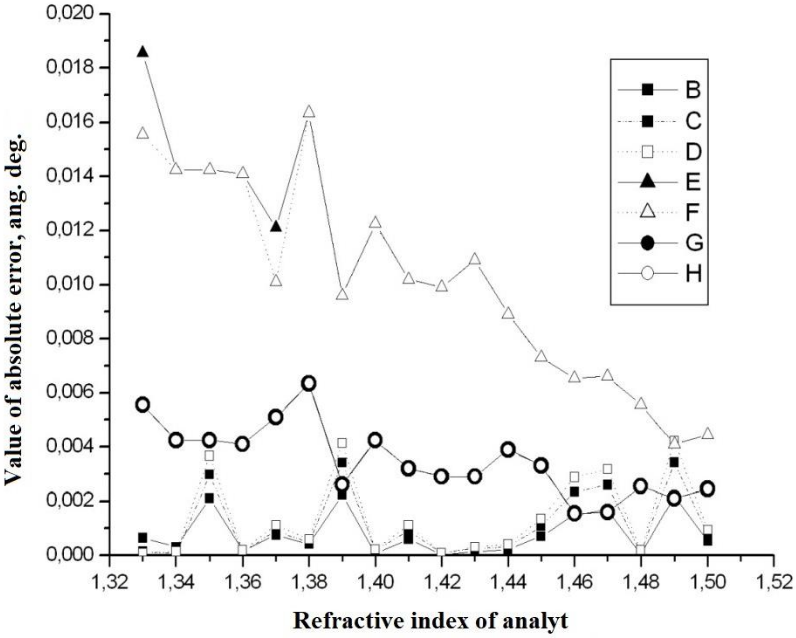

Fig. 3. Dependence of the calculated absolute error on the refraction index for three methods with different angular ranges of minimum determination: method of the center line for the ranges of 0.4 ang. deg. – B, 0.2 ang. deg. – C, 0.125 ang.deg. – D, approximation by the polynomial of the second degree for the ranges of 0.2 ang.deg. – E, 0.125 ang.deg. – G, approximation by the polynomial of the third degree for the ranges of 0.2 ang.deg. – F, 0.125 ang.deg. – H

The greater is the angular range of minimum determination the greater is the error of minimum determination for the method of the polynomial approximation (Fig. 3). Methods of the approximation by the polynomial of the second and third degrees separately for each angular range have almost similar absolute errors, which decrease with the increase of the refraction coefficient of the studied substance. The error decreases with the increase of the refraction factor for the methods of the polynomial approximation due to the change of the reflection characteristic form, which is connected with the flow of the physical processes on the excitation surface of the surface plasmons.

Maximum values of the absolute error are provided by the methods of polynomial approximation of the second and third degrees as compared with the method of the center line. The smallest absolute error is the characteristic feature for the method of the center line for the angular range of the minimum determination of 0.4 ang. deg., that is directly connected with the number of points, located in the area of the minimum determination. It follows that the larger is the area of the reflection characteristic analysis, with smaller error minimum of the reflection characteristic can be determined at SPR for the method of the center line and on the contrary, for the method of the polynomial approximation: the smaller is the area of the reflection characteristic, with greater accuracy the minimum for the methods of polynomial approximation can be determined.

Mean value of the absolute errors for the methods of polynomial approximation of the second and third degrees is almost the same but greatly depends on the angular range of the determination of the minimum of the reflection characteristic. Mean value of the error for the center line method is 2.5 times less than the method of the polynomial approximation for the angular range of the minimum of 0.125 determination and almost 8.5 times less for the angular range 0.2.

Also the study of the dependence of the analyte measurement error on the temperature change from 20 to 60°C for the center line method and polynomial approximation methods of the second and third degrees with different angular ranges of minimum determination (Fig. 7). The studies were carried out for the certain analyte (deonized water).

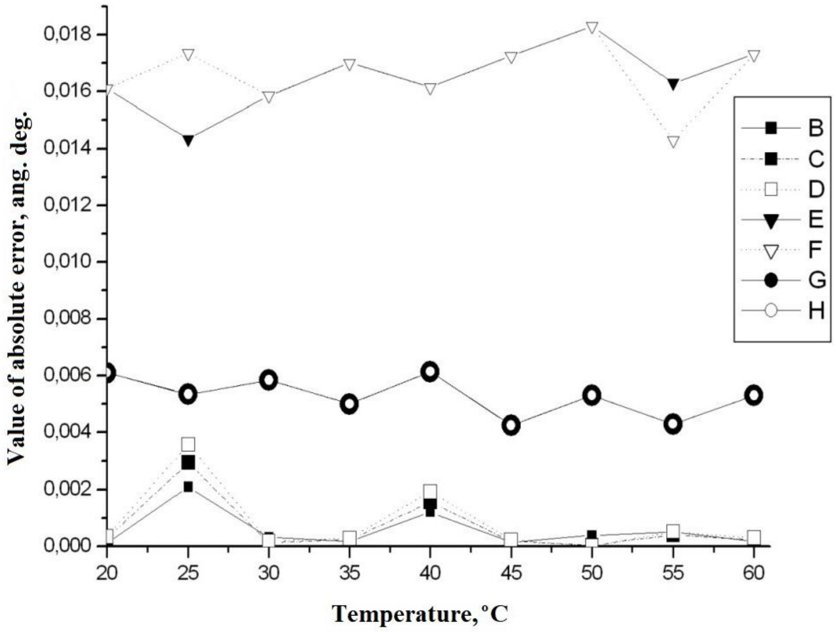

Fig. 4. Dependence of the calculated absolute error on the temperature of the analyte for three methods with different angular ranges of minimum determination: center line method for the ranges of 0.4 ang. deg. – B, 0.2 ang. deg. – C, 0.125 ang. deg. – D, polynomial approximation of the second degree for the ranges of 0.2 ang. deg. – E, 0.125 ang. deg. – G, polynomial approximation of the third degree for the ranges of 0.2 ang. deg. – F, 0.125 ang. deg. – H

The greatest absolute error of the minimum determination is characteristic for the polynomial method with the angular range of the minimum determination 0.2 ang. deg. as compared with the range 0.125 ang. deg., this is connected with the fact that the greater angular range enters the approximation area, the less valid is the approaching of the approximation curve to the reflection characteristic (Fig. 4). Method of the center line demonstrates better result, this method provides smaller absolute error of minimum determination and has smaller spread of error values in the range of higher temperatures. The value of the calculated mean absolute error for the temperature changes are the smallest for the center line method and are the greatest for the polynomial methods with the angular range of minimum determination 0.2 ang. deg.

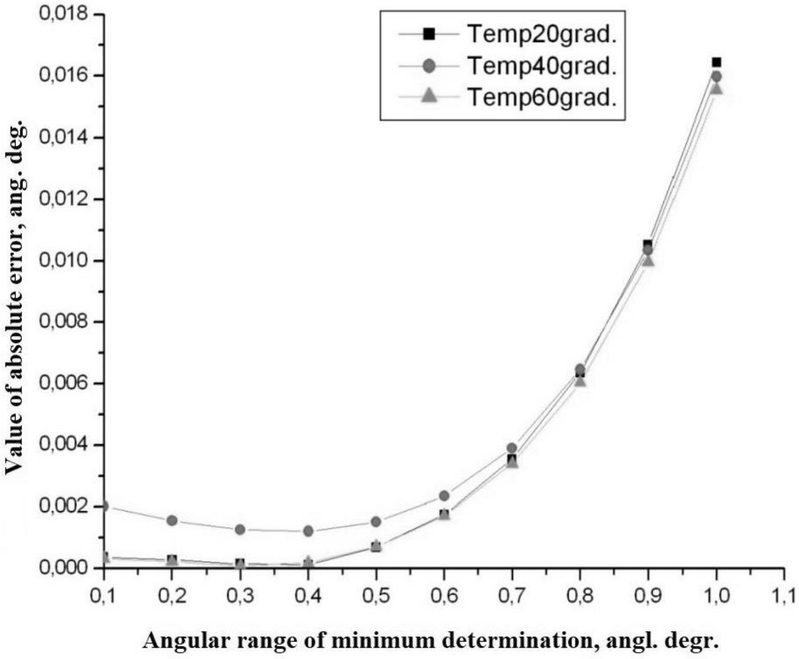

Fig. 5. Dependence of the values of the calculated absolute error on the angular range of the minimum determination for three temperatures 20°C, 40°C, 60°C for the method of the center line

Angular range of 0.4 minimum determination provides the smallest absolute error of minimum determination for various temperatures of the studied substance (Fig. 5), that can be used for further application of the center line method for the determination of the minimum of the reflection characteristic.

Conclusions

Methods for the determination of the reflection characteristic minimum in the process of SPR are analyzed. Polynomial and centroid methods which depend on the form of the reflection characteristic, that influences the accuracy of minimum determination are the most common. The accuracy of the determination of the reflection characteristic minimum greatly depends on the area of this characteristic near the minimum, which comprises certain number of points. The greater is the area of the reflection characteristic analysis, the greater is the error of the minimum determination for the polynomial methods and smaller error of the determination of SPR reflection characteristic minimum applying the center line method. Methods of approximation by the polynomial of the second and third degrees have almost the same absolute errors, which decrease with the increase of the refraction index of the studied substance due to the change of the reflection characteristic form. The greatest values of the absolute error provide the methods of approximation by the polynomial of the second and third degrees as compared with the center line method. The smallest absolute error is characteristic to the center line method for the area of the reflection characteristic of 0.4 of size, that is connected directly with the number of points, located in the area of minimum determination. Mean value of the error for the center line method is 2.5 less than the method of approximation by the polynomial for the area of the reflection characteristic with the angular range of 0.125 ang. deg. and almost 8.5 times less for the angular range of 0.2 ang. deg, that proves the expediency of the application of the new method of the center line.

Method of the center line for the study of the temperature changes of the analyte also provides smaller absolute error of the minimum determination as compared with the polynomial approximation and has smaller spread of the error values in the range of higher temperatures. Angular range of minimum determination 0.4 provides the smallest absolute error of minimum determination for various temperatures of the studied substance, that can be used for further application of the center line method for the determination of the reflection characteristic minimum.

As compared with the polynomial methods the center line method has higher accuracy of the determination of the reflection characteristic minimum as it depends less on its asymmetry, which is connected with the flowing of physical process on the excitation plane of the surface plasmons.

REFERENCES

1. Schasfoort R. B. M. Handbook of Surface Plasmon Resonance / R. B. M. Schasfoort, A. J. Tudos // Cambridge: The Royal Society of Chemistry, 2008. – p. 403.
2. Kretschmann E. Radiative decay of nonradiative surface plasmon excited by light / E. Kretschmann, H. Reather // Zeitschrift für Naturforschung A. – 1968. – Vol. 23A. – P. 2135 – 2136.
3. Chinowsky T. M. Optimal linear data analysis for surface plasmon resonance biosensors / T. M. Chinowsky, L. S. Jung, S. S. Yee // Sens. Actuator B-Chem. – 1999. – Vol. 54. – P. 89 – 97.
4. An accurate and precise polynomial model of angular interrogation surface plasmon resonance data / Z. Wang, J. Diamond, R. Hou [et al.] // Sensors and Actuators B: Chemical. – 2011. – Vol.151, № 2. – P. 309 – 319.
5. Detection of DNA hybridization using the TISPR-1 surface plasmon resonance biosensor / K. Kukanskis, J. Elkind, J. Melendez [et al.] // Anal. Biochem. – 1999. – Vol. 274. – P. 7 – 17.
6. Nenninger G. G. Data analysis for optical sensors based on spectroscopy of surface plasmons / G. G. Nenninger, M. Piliarik, J. Homola // Meas. Sci. Technol. – 2002. – Vol. 13. – P. 2038 – 2046.
7. Thirstrup C. Data analysis for surface plasmon resonance sensors using dynamic baseline algorithm / C. Thirstrup, W. Zong // Sens. Actuator B-Chem. – 2005. – Vol. 106. – P. 796 – 802.
8. Zhan S. Fast centroid algorithm for determining the surface plasmon resonance angle using the fixed-boundary method / S. Zhan, X. Wang, Y. Liu // Measurement Science and Technology. – 2011. – Vol. 22, № 2. – P. 025201.
9. Surface Plasmon Resonance Sensors / L. C. Oliveira, A. M. N. Lima, C. Thirstrup [et al.] // Springer Series in Surface Sciences, 2019. – p. 70.
10. New method for determining the angular position of the light reflection intensity minimum observed in surface plasmon resonance / V. P. Maslov, Yu. V. Ushenin, G. V. Dorozinsky [et al.] // Journal of Multidisciplinary Engineering Science Studies. – 2017. – Vol. 3, № 3. – P. 1514 – 1518.
11. Spectrometer of surface plasmon resonance “Plasmon-6” / Ye. F. Venger, S. A. Zynio, Ye. P. Matsas, A. V. Samoylov [et al.] // Abstracts of reports of the scientific-practical conference SENSOR-2007 (Odesa, Ukraine). – 2007. – P. 111.

Editorial office received the paper 24.01.2020.
The paper was reviewed 07.02.2020.

Dorozinska Hanna – Post-Graduate, Instrumentation Engineering Department.
National Technical University of Ukraine «Igor Sikorskyi Kyiv Polytechnic Institute».