Automatic Solution of the System of Equations of the Equivalent Radius of the Distribution Ellipses of Dielectric Materials for the Recognition of Gold Nanoparticles

V.M. Emelyanov
Faculty of mechanics and technology
The Southwest State University
Kursk, Russia
vmemelianov@yandex.ru

T.A. Dobrovolskaya
Faculty of mechanics and technology
The Southwest State University
Kursk, Russia
dobtatiana74@mail.ru

V.V. Emelyanov
Faculty of mechanics and technology
The Southwest State University
Kursk, Russia
wemelianov@yandex.ru

Abstract— **The presented research is aimed at developing scientific and technical bases for conducting mathematical modeling of nanostructured physical objects of small dimensions. The sensitivity of identification of biologically active nanoparticles of metallic gold to cancer cells is considered based on the results of differentiation of the equivalent radii of intersection of ellipses of the distribution of statistical values of the peaks of Raman spectra together with the XY equations. A method is proposed for the automatic solution of a multidimensional system of nonlinear differential equations for the intersection of ellipsoids of Raman spectrograms of dielectric materials with and without gold nanoparticles. When solving the problem of increasing the accuracy and speed of recognition of gold nanoparticles on the surface of the fibers, the polarization of laser radiation along and across the fibers was taken into account. When solving the system using nonlinear quadratic and XY differential equations of the equivalent radii of the ellipses of the distribution, a high accuracy of R0 and R1 is obtained up to 10^{-15}.**

Keywords—vector-matrix modeling, solution of a system of multidimensional differential correlation equations, dielectric fiber, metallic gold nanoparticles, Raman spectra, polarization characteristics of Raman spectroscopy, multidimensional correlation components of Raman spectra recognition reliability, probability of crossing the spreads of normal two-dimensional distributions, accuracy of nanoparticle identification

I. Introduction

The most important task is to increase the reliability of identification and control of gold nanoparticles on the surface of dielectric materials and in the volumes of biological subtracts. The solution of this scientific problem is aimed at developing conceptual approaches to conducting mathematical modeling of nanostructured biological objects modified by gold nanoparticles based on the polarization characteristics of raman light scattering.

Gold nanoparticles in the form of metal particles are used both directly by exposure to bacteria and viruses [1], and in the biosynthesis of nanostructures, as well as biosensers for the diagnosis of diseases [2] with high sensitivity when using Raman spectroscopy. Raman spectroscopy on nanoparticles obtains the effect of giant Raman scattering (SERS) with signal amplification up to 10^{16} [3]. This facilitates low-concentration assays both *in vivo* and *in vitro* for a number of diseases, including [4]: neurological [5, 6], diabetes [7, 8], cardiovascular [9-11], oncological [12-14] and viral [15-16].

To increase the sensitivity, nanoparticles of metallic gold with various shapes are used: spheres, cubes, disks, rings, and multidimensional materials with a combination of gold, silver, and platinum. But even this does not allow us to significantly increase the sensitivity of identification of gold nanoparticles due to the fact that nanosilver does not sufficiently change the intensity of Raman spectra compared to nanosilver. But nano silver oxidizes very quickly. Therefore, it is necessary to apply the analysis of Raman polarization spectra and the joint complex mathematical processing of all the spectra simultaneously with the polarization in X and in Y and taking into account the multidimensional correlation of statistical measurement data.

The reliability of the detection of gold nanoparticles on polyester fibers was evaluated in [17-20]. Due to the fact that nanosilver slightly changes the intensity of the Raman spectra of polyester fiber compared to nanosilver, it is necessary to develop and use a new method for composing and solving a system of multidimensional equations. Due to the great complexity of manual preparation and selection of the values of the equivalent radii of the distribution ellipses, the solution of the problem is very inconvenient and very slow in time.

The authors of the work proposed a method for statistical modeling of the random process of changing the experimental parameters of gold nanoparticles together with autocorrelation functions and interdependent parameters according to the correlation matrix and applied it at the stage of preliminary assessment of the reliability of identification of nanoparticles [1, 17]. At the same time, it was found that if the intersection of the distribution ellipses is carried out in a sufficiently large range of the number of statistically modeled data up to 10 million, then the normal multidimensional distribution law for any nonlinear transformation can be used to describe the ellipses, which greatly simplifies the use of fundamental correlation matrices. With this method of statistical data modeling, the identification accuracy is 10^{-4}-10^{-5}, which is insufficient.

In studies [1, 17-18], a method for composing and analytically solving a system of multidimensional nonlinear equations for detecting gold nanoparticles was evaluated. The obtained accuracy of the solution is $(2.689 \div 9.988) \times 10^{-4}$. However, this accuracy is not sufficient to control the gold nanoparticles application technology.

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II. METHODS AND MATERIALS

To solve these problems, it is proposed to develop a method for controlling nanoparticles on the surface of nanostructured materials. As a dielectric, a polyester fiber was used, on which gold nanoparticles were deposited.

As a result of numerical processing of the experimental values of the intensity spectra of polyester fibers, the distribution parameters and correlation matrices of the peaks of the Raman spectra were calculated, taking into account the transverse (X) and longitudinal (Y) polarization [3-12].

As shown in [1, 20], spectrograms with longitudinal and transverse polarization have significant differences in peak intensity. Raman spectra were recorded in two frequency ranges: 39.524-2558.47 cm^{-1} and 1318.81-3518.7 cm^{-1} with polarization across the X fibers and along the Y fibers. Each figure shows two graphs with these frequencies (Fig. 1-4).

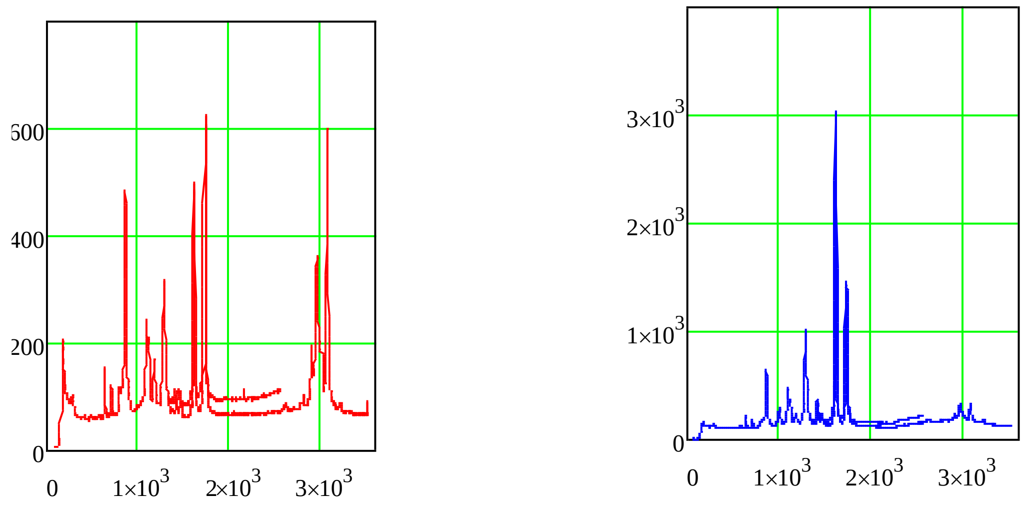

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Fig. 1. Average values of the spectrum intensities of fibers with gold nanoparticles: a- m_{xAui} polarization across X; b - m_{yAuj} polarization along Y

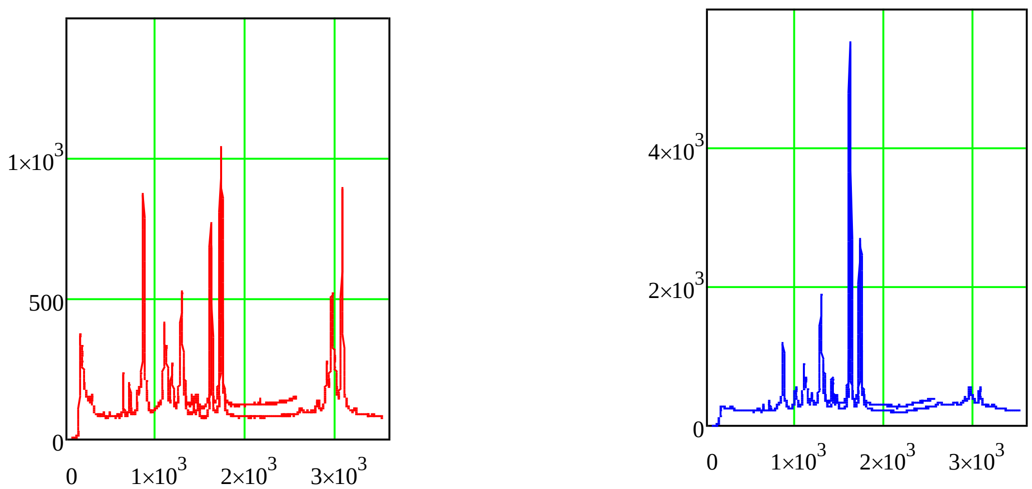

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Fig. 2. Average values of the Raman spectrum intensities of fibers without gold nanoparticles: a- m_{xi} polarization across X; b- m_{yj} polarization along Y

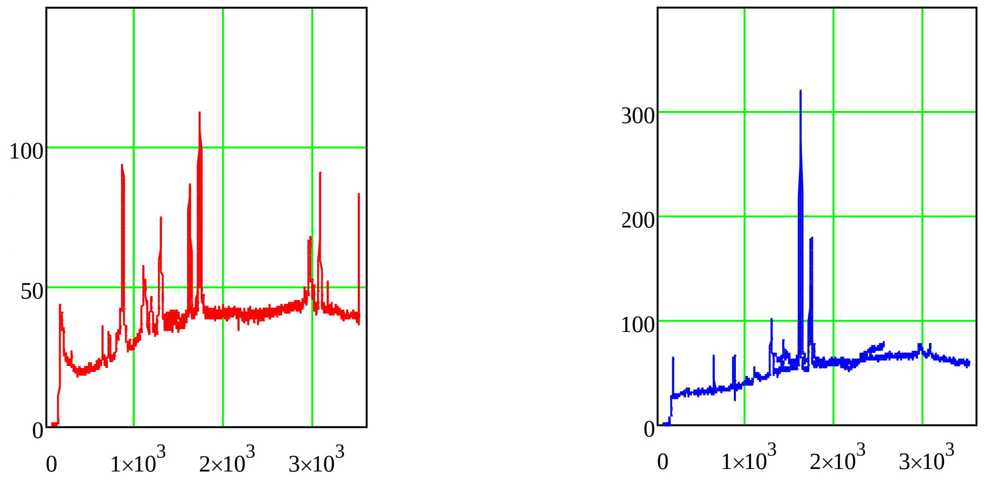

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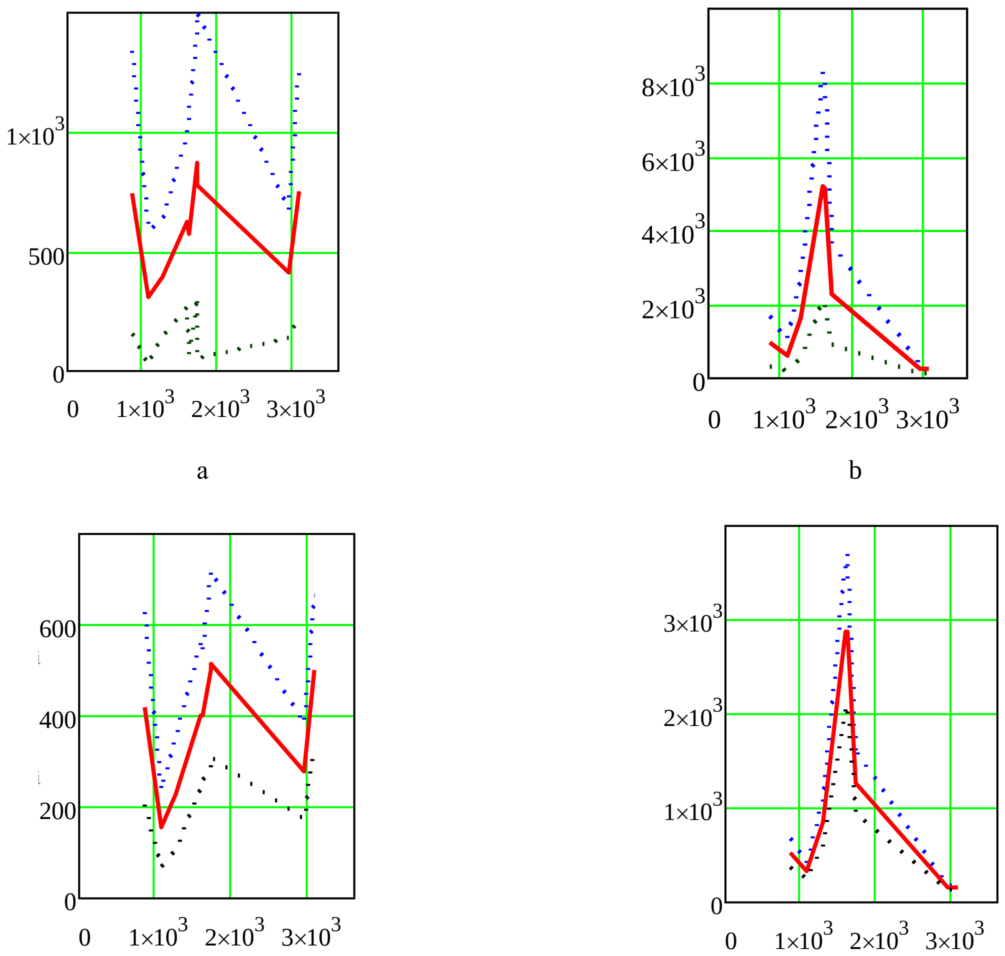
Fig. 3. The average square deviations of the intensity of the Raman spectrum of fibers with gold nanoparticles: a-the polarization of S_{xAui} across X; b - the polarization of S_{yAuj} along Y



c d

Fig. 4. Mathematical expectation with average standard deviations of the intensities of the peaks of the Raman spectrograms of Raman scattering: a - $m_{xi}\pm3\cdot S_{xi}$ polarization across fibers without nanoparticles; b - $m_{yj}\pm3\cdot S_{yj}$ polarization along fibers without nanoparticles; c - $m_{xAui}\pm3\cdot S_{xAui}$ polarization across fibers with gold nanoparticles; d - $m_{yAuj}\pm3\cdot S_{yAuj}$ polarization along fibers with gold nanoparticles

When using methods that do not automatically solve the system of differential correlation equations, uncertainty arises, since the graphical intersection of the distribution ellipses without nanoparticles and with gold nanoparticles revealed two intersection points. The accuracy of the calculated ellipse intersection radii was insufficient [13].

To automatically determine the equivalent radius R of the intersection of the distribution ellipses, it is necessary to create a system of differential correlation equations in vector-matrix analytical expressions for $R0=X0^T \cdot Kr0^{-1} \cdot X0$ and $R1=X^T \cdot KrAu^{-1} \cdot X$ [14].

The proposed method of composing the system (1) of equations allows its solution to be carried out automatically without manually selecting the values of equivalent radii. At the same time, in this method, in the analytical expression of the equation g (x,y), there is a differentiation of the equation in X and in Y. The accuracy of the solution of the system by the proposed method is quite high: f(v0, v1)=$-3.99 \cdot 10^{-15}$ and g (v0, v1)=$-1.22 \cdot 10^{-18}$. This proves a discrepancy of up to 10^{-15} in accuracy when determining R0 and R1 by this method. The same accuracy is obtained for estimating the intersection coordinates of the distribution ellipses i=4 and j=6 (i, j are the peak numbers of the Raman spectra):

$$\begin{cases} f(x,y) := (X^T \cdot Kr_{Au}{}^{-1} \cdot X) - (X0^T \cdot Kr0^{-1} \cdot X0) \\ g(x,y) := \begin{bmatrix} \frac{d}{dx}\left[\frac{-1}{2}\cdot\left(X^T \cdot Kr_{Au}{}^{-1} \cdot X\right)\right] & \frac{d}{dy}\left[\frac{-1}{2}\cdot\left(X^T \cdot Kr_{Au}{}^{-1} \cdot X\right)\right] \\ \frac{d}{dx}\left[\frac{-1}{2}\cdot\left(X0^T \cdot Kr0^{-1} \cdot X0\right)\right] & \frac{d}{dy}\left[\frac{-1}{2}\cdot\left(X0^T \cdot Kr0^{-1} \cdot X0\right)\right] \end{bmatrix} \end{cases} \quad (1)$$

The system of vector-matrix equations (1) includes the matrix correlation matrices of Raman spectra of fibers with Kr_{Au} gold nanoparticles and without Kr0 nanoparticles, as well as the vectors X and X0, including the mathematical expectations m_{xi}, m_{yj}, m_{xAui}, m_{yAuj}, and the mean square deviations S_{xi}, S_{yj}, S_{xAui}, S_{yAuj}. with transverse (x) and longitudinal polarization (y) without nanoparticles and with gold nanoparticles:

$$Kr_{Au} := \begin{pmatrix} 1 & r_{xy}Au_i \\ r_{xy}Au_i & 1 \end{pmatrix}; \quad Kr0 := \begin{pmatrix} 1 & r_{xy_i} \\ r_{xy_i} & 1 \end{pmatrix}, \quad (2)$$

$$X0 := \begin{pmatrix} \frac{x - m_{x_i}}{S_{x_i}} \\ \frac{y - m_{y_j}}{S_{y_j}} \end{pmatrix}; \quad X := \begin{pmatrix} \frac{x - m_{xAu_i}}{S_{xAu_i}} \\ \frac{y - m_{yAu_j}}{S_{yAu_j}} \end{pmatrix}, \quad (3)$$

III. Results

The solution of the system (1) was carried out using a program Mathcad:

x:= 390.0 y:= 1500.0

Given

f(x, y) = 0 g(x, y):= 0

v:= Find(x, y)

$$v = \begin{pmatrix} 412.441413 \\ 1469.257796 \end{pmatrix}$$

$$f(v_0, v_1) = -3.996802888650563 \times 10^{-15}$$

$$g(v_0, v_1) = -1.2197274440461925 \times 10^{-18}$$

If we substitute the values of v in the expressions (3) instead of the variables x and y, the vector data will have the following form:

$$X0_V := \begin{pmatrix} \frac{v_0 - m_{x_i}}{S_{x_i}} \\ \frac{v_1 - m_{y_j}}{S_{y_j}} \end{pmatrix}; \quad X_V := \begin{pmatrix} \frac{v_0 - m_{xAu_i}}{S_{xAu_i}} \\ \frac{v_1 - m_{yAu_j}}{S_{yAu_j}} \end{pmatrix}. \quad (4)$$

Then the vector-matrix expressions for determining the equivalent radii for the intersection point of the ellipses of the re-emission intensity distribution of the Raman spectra will take the following form:

$$R0_{i,j} := \sqrt{X0_V{}^T \cdot Kr0^{-1} \cdot X0_V} \quad (5)$$

$$R1_{i,j} := \sqrt{X_V{}^T \cdot Kr_{Au}{}^{-1} \cdot X_V} \quad (6)$$

R0 = 1.8395174270280354

R1 = 1.8395174270280343

A graphical estimate of the ellipse intersection for this solution is shown in figure 5.

If we solve the usual system of equations for the peaks of the Raman spectrum i=4 and j=6, then the equivalent radii will have the values: R0= 1.8395595089802907 and R1= 1.8393610998426746.

When solving a system of equations with differentiation in X, we obtain equivalent radii for the peaks of the Raman spectrum i=4 and j=6 R0= 1.8395181499853053 and R1= 1.839518149985305.

Solving a system of equations with differentiation in Y, we obtain equivalent radii for the peaks of the Raman spectrum i=4 and j=6 R0= 1.8465685489854224 and R1= 1.8465695695804494.

The graphical solution of the system of equations is shown in figure 6.

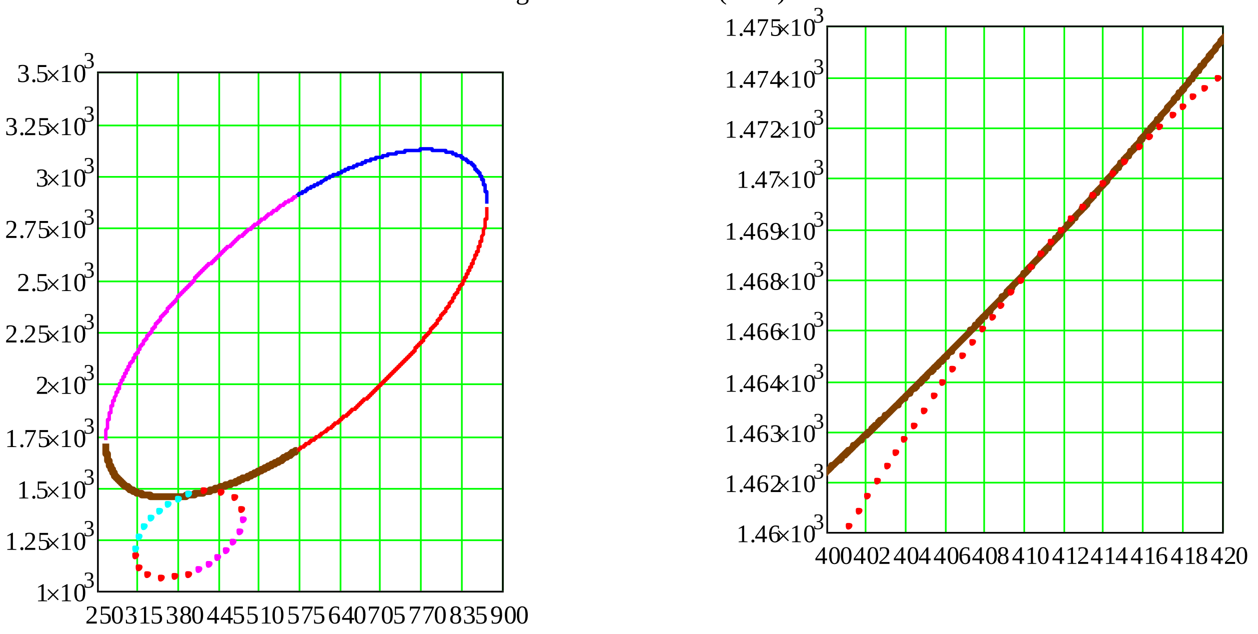


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Fig. 5. Solution of a system of equations with differentiation in XY (R0=1.8395174270280354 and R1=1.8395174270280343) in graphical form: a-general view; b-enlarged fragment of the area of intersection of the distribution ellipses

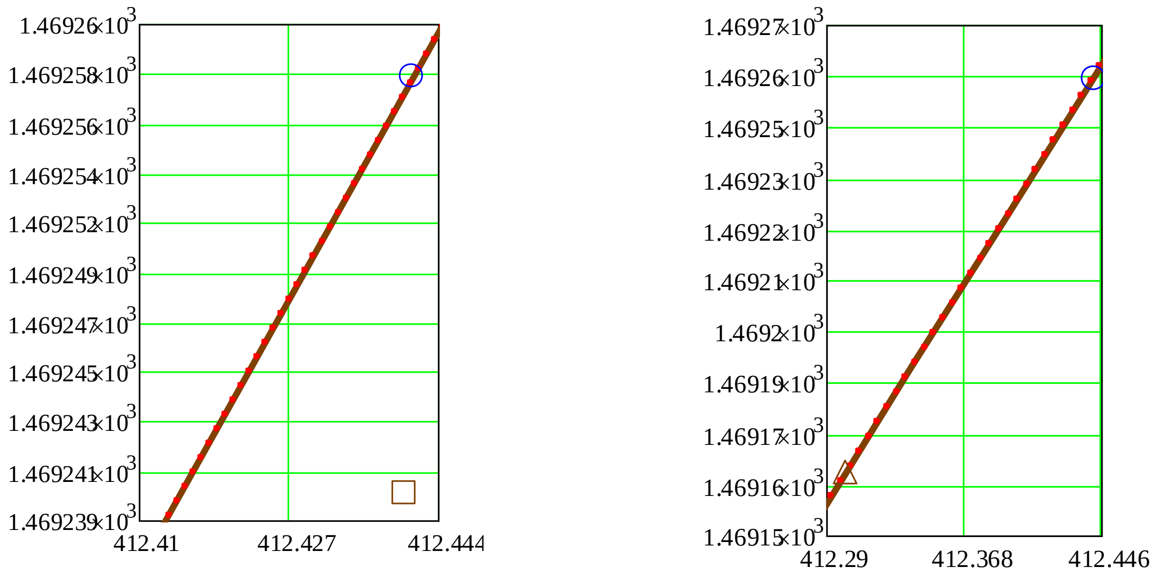

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Fig. 6. Results of solving a system of equations for the recognition of gold nanoparticles, taking into account the longitudinal and transverse polarization: a - differentiation by XY - ○ (x=412.441, y=1469.2578) and a general solution of the system of equations by XY- □ (x=412.44, y=1469.2408); b - differentiation by XY- ○ (x=412.441, y=1469.2578) and differentiation only by X - Δ (x=412.3, y=1469.165)

IV. Conclusion

The analysis of the results obtained in work allows us to conclude that the application of the method of automatic solution of differential equations (1) proposed in this study allows us to achieve high accuracy of the results in a large range of setting the initial parameters x=100 ÷ 412 and y=1470 ÷ 5500 with stable solution parameters.

The obtained values of the coordinates of the intersection of the ellipses of the distribution X=412.4414128828934, Y=1469.2577956410264 were found with sufficiently high accuracy, their estimation is not affected by the initial value of the parameters x and y in the studied range.

In this paper, the accuracy of the solution for the equation f(v0, v1) = $-2.220446049250313 \cdot 10^{-15}$ and for the equation g(v0, v1) = $2.710505431213761\cdot10^{-19}$ is revealed for the initial set parameters x = 412, y = 1500. For the initial set parameters x=412, y=1470, the accuracy of the solution is according to the equation: f(v0, v1) = $-8.881784197001252\cdot10^{-16}$ and by equation g (v0, v1) = $6.776263578034403\cdot10^{-19}$.

The accuracy of obtaining the output parameters: R0=1.8395174270280354 and R1=1.839517427028035 can be estimated up to 10^{-15}. None of the methods under study provides higher accuracy.

To improve the proposed method, it is necessary to apply the differentiation together in X and Y. In this case, you must use more than two unknown parameters.

The research carried out in this paper will allow us to develop and justify conceptual approaches to computer modeling of physical objects modified by gold nanoparticles based on the polarization characteristics of raman light scattering

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