Elimination of uncertainty in solving system of multidimensional differential equations in X for identification of silver nanoparticles on fibers

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Abstract. In the article, an increase of the sensitivity of identification of biologically active metal silver nanoparticles to cancer cells is considered to be based on the results of compiling a system of multidimensional differential equations with respect to X of the ellipses of probabilistic intersection of the spectra of a Raman polarization spectrometer. The nine main peaks of the spectrum of polyester fibers with silver nanoparticles and without them are analyzed with polarization along the X-transverse and Y-along fibers directions. The correlation matrices of the interconnection of peaks of the Raman spectrum are to be introduced into differential equations. During the solution of the system of equations, there is an intersection of the ellipses of the distribution of the statistical data of peak measurements. When checking the solution from the graphical estimation of the intersection of the ellipses of the data distribution of the Raman spectra, there was a 20% error detected in determining the radii of curvature R0 and R1. To eliminate the uncertainty, numerical additive $\Delta = +0.34342$ is introduced into the differential equation and when solving this system of differential equations with the additive, the accuracy is $(-1.42 \cdot 10^{-14} \div 1.94 \cdot 10^{-15})$ with the radius of curvature $R_0 = R_1 = 3.458112896121225$ at a sufficiently high accuracy of $10^{-14}$

1. Introduction

Nanoparticles of metallic silver can significantly affect (on) microorganisms, pathogenic microbes and viruses, improve the hygienic properties of products, combat various diseases (for example, cardiovascular and oncological), and affect (on) cancer cells in tumor formations. A small number of nanoparticles do not give a therapeutic effect, and a large number can adversely affect (on) healthy biological objects. It should be noted that silver ions in salts have a harmful effect on biological objects, even in very small quantities.

To estimate the concentration of silver metal nanoparticles, the most effective method is the Raman spectroscopy, which provides a giant Raman scattering of light (SERS), which increases the sensitivity by identifying metal silver nanoparticles by a factor of $10^7$, and it makes possible to detect on dielectric materials even several silver nanoparticles with a 5 - 10 nm. But it is difficult to obtain high sensitivity when identifying silver nanoparticles. For this, it is necessary to use special Raman polarization spectrometers and complex mathematical processing of all spectra simultaneously with polarization both along the X axis and along the Y axis and taking into account the correlation of the measurement data [1-3].
Identification of nanoparticles on polyester fibers is given in (works) [4, 5]. These methods do not provide sufficient accuracy of the solution and automatically do not allow solving the system of equations in determining the modes of applying nanoparticles to fibers and especially the change in the number of particles during operation. Because of the great complexity of manual preparation and the selection of values for the equivalent radii of distribution ellipses, the solution of the problem presents a great inconvenience and is very slow in time.

A method is used to generate multidimensional statistical correlation data for 9 peaks of Raman spectra simultaneously for fibers without silver nanoparticles and with nanoparticles.

If the estimation of the intersection of the ellipses of the distribution of statistical data is performed in a large range of the number of generated data (up to $10^7$), ellipses in this case will be described by a normal multidimensional distribution law for any nonlinear transformation and this greatly simplifies the use of fundamental correlation matrices. With the statistical generation of correlation polarization in X and Y data, the identification accuracy is $10^{-4}$-$10^{-5}$, it requires a lot of time and a lot of labor to detect nanoparticles.

In studies [4,5], an analytical solution of a system of multidimensional nonlinear equations for estimating the presence of nanoparticles was carried out. The accuracy of the solution is $(8.79 \div 9.99) \cdot 10^{-4}$ and the same accuracy of estimating the equivalent radii of distribution ellipses at the intersection point. This is not enough to detect nanoparticles and it takes a lot of time to solve the system of nonlinear equations because of the great preparatory work.

In this research, let us consider the possibility of increasing the number of equations for solving the system by using differentiation with respect to the unknown variables of the ellipses of the peak distribution of the Raman polarization spectrum when identifying silver nanoparticles on the surface of polyester fibers.

It is not possible to provide a solution of system of nonlinear quadratic equations with a number of parameters up to 9 in the (ordinary) analytic algebraic form because of the unwieldiness of the record. In this research, the authors used the method of compiling only quadratic differential correlation equations with two unknowns for solving the problem in a vector-matrix form with the possibility of moving to a system of equations with a large number of unknowns.

2. Materials and methods

Experiments on the measurement of random values were preliminarily carried out, the spectra of the PE fibers were obtained (Fig. 1), and correlation matrices and distribution parameters (1) were found (out) taking into account the polarization of the radiation in X and Y directions.

Figure 1 shows only spectrograms for PE with silver nanoparticles. Spectrograms without nanoparticles have an intensity almost 2 times smaller. This regularity can be seen from the mathematical expectations of the distribution parameters (1):

$$(\text{MENX}/\text{MENX0})^T = (1.767 \ 1.890 \ 1.803 \ 1.985 \ 1.919 \ 1.780 \ 1.664 \ 1.524 \ 1.476),$$

$$(\text{MENY}/\text{MENY0})^T = (1.244 \ 1.251 \ 1.236 \ 1.248 \ 1.390 \ 1.240 \ 1.326 \ 1.340 \ 1.302).$$

The relative change in the mathematical expectations for X - across the fibers and Y - along the fibers is significantly different. For X MENX / MENX0, there are significantly more changes in the presence of nanoparticles from 1.524 to 1.985, whereas for Y, the change in MENY / MENY0 is only from 1.240 to 1.390.

From the intensity of the spectral peaks, the spectrograms differ significantly for the polarization of the Raman radiation X - across the fibers and Y - along the fibers. In the X direction, across the fibers, the peaks have an intensity 2-3 times lower than in the Y direction along the fibers for both fibers without nanoparticles and for fibers with nanoparticles (1) and figure 1.

The central peaks in Y (4, 5, 6 and 7) are significantly higher than extreme peaks 1, 2, 3, 8 and 9 almost 20 times. The central peaks in X have practically the same intensity with extreme peaks. It is necessary to pay attention to the 8 and 9 peaks of X, which are comparable in intensity to the central peaks. And according to Y, peaks of 8 and 9 are less than even in X.
Analysis of the information showed that the correlation matrices have a wide range of values ranging from 0.812568 to -0.340895 without silver nanoparticles, and for fibers in the presence of nanoparticles the range is from 0.99868 to 0.24558. This indicates that silver nanoparticles increase the correlation.

![Spectrograms of Raman scattering](image)

**Figure 1.** Spectrograms of Raman scattering: a - polarization across PE fibers with silver nanoparticles; b - polarization along the PE fibers with silver nanoparticles

The distribution parameters (1), in particular the mathematical expectations, differ significantly in intensity of spectral peaks with polarization across fibers X and along Y fibers (Picture 1). Along the fibers, the intensity is much higher, even (in) several times, both for fibers without nanoparticles and for fibers with nanoparticles.

\[
\begin{align*}
\text{MEX}^T & = (698.207, 266.156, 384.805, 659.824, 661.551, 852.41, 849.92, 412.99, 796.091) \\
\text{MEX}^T & = (745.167, 457.096, 1196.862, 4023.14, 4073.14, 1775.226, 1780.878, 182.674, 196.222) \\
\sigma \Delta X^T & = (84.487, 50.527, 47.174, 73.693, 77.891, 89.624, 87.343, 19.679, 31.712) \\
\sigma \Delta Y^T & = (115.383, 74.971, 191.763, 626.399, 571.34, 270.561, 255.402, 29.143, 15.201) \\
\text{MENX}^0 & = (395.233, 140.846, 213.373, 332.365, 344.734, 478.977, 510.665, 270.989, 536.491) \\
\text{MENX}^0 & = (599.064, 365.357, 968.096, 3224.61, 2929.766, 1342.996, 136.366, 182.674, 150.694) \\
\sigma \Delta X^0 & = (60.722, 35.107, 27.743, 40.744, 55.448, 46.836, 65.836, 24.641, 50.471) \\
\sigma \Delta Y^0 & = (120.429, 74.806, 195.827, 612.321, 706.978, 273.1, 321.016, 32.016, 29.676)
\end{align*}
\]

(1)

Preliminary studies were carried out on the compilation and solution of the quadratic differential correlation equations for the random values of the distribution of Raman peaks by the revealed correlation matrices and distribution parameters, taking into account the polarization of the radiation along X-transversally and along Y-along the fibers simultaneously in one measurement.

During the solution of the system of differential correlation equations, an uncertainty was revealed that when checking a solution based on the graphical intersection of distribution ellipses without nanoparticles and with nanoparticles, two intersection points appeared. In this case, the equivalent radius of the ellipses was not equal to the radius found in solving nonlinear quadratic equations. The difference in these radii was significant, and the accuracy was 5%. Such accuracy for identifying silver nanoparticles is unacceptable. This accuracy can be used for preliminary results.

To compose a system of differential correlation equations, \( R \) is (used in) the radius of curvature of the intersection of distribution ellipses in vector-matrix analytic expressions along the coordinates of the points of intersection. In this research, let us consider a system of only two vector-matrix analytic expressions \( R^2 = X^T \Sigma^{-1} X \) for \( R^0 \) and \( R^1 \).
The analytical expression for differential correlation equation $g(x, y)$ is obtained by differentiating equation $g(x, y)$ with respect to $X$. It is necessary to choose addition $\Delta = + 0.34342$. The accuracy of the solution of the system of equations is high: $f(v_0, v_1) = - 1.42 \times 10^{-14}$ and $g(v_0, v_1) = 1.94 \times 10^{-15}$ (2). This shows a discrepancy in the accuracy of equivalent radii $R_0$ and $R_1$ to $10^{-14}$. But the accuracy of the coordinates of the intersection of the distribution ellipses depends on the choice of additive $\Delta$.

$$\begin{align*}
\sum 0 &= \begin{pmatrix} 1 & x_{XY0_{i,j}} \\ x_{XY1_{i,j}} & 1 \end{pmatrix}, \\
\sum 0 &= \begin{pmatrix} 1 & x_{XY1_{i,j}} \\ x_{XY1_{i,j}} & 1 \end{pmatrix}
\end{align*}$$

$$g(x,y) = \frac{dx}{d\Delta} = \begin{pmatrix} x - \text{MENX}_i \\ y - \text{MENY}_i \end{pmatrix} \sigma_{\Delta x_i} \sigma_{\Delta Y_j} \sum 0^{-1} \begin{pmatrix} x - \text{MENX}_i \\ y - \text{MENY}_i \end{pmatrix} \sigma_{\Delta x_i} \sigma_{\Delta Y_j}$$

$$f(x,y) = \begin{pmatrix} x - \text{MENX}_i \\ y - \text{MENY}_i \end{pmatrix} \sigma_{\Delta x_i} \sigma_{\Delta Y_j} \sum 0^{-1} \begin{pmatrix} x - \text{MENX}_i \\ y - \text{MENY}_i \end{pmatrix} \sigma_{\Delta x_i} \sigma_{\Delta Y_j}$$

$x := 400.0$ $y := 390.0$

Given

$$f(x,y) = 0 \quad g(x,y) = 0$$

$$v := \text{Find}(x,y)$$

$$v = \begin{pmatrix} 411.254471 \\ 385.08863 \end{pmatrix}$$

$$g(v_0,v_1) = 1.9428902930940237 \times 10^{-15} \quad f(v_0,v_1) = -0.000000000000001421$$

3. Results and Discussion

The curvature radii for the point of intersection of the ellipses of the intensity distribution of the reradiation spectra of the Raman spectra (4-5) are found (out) from the coordinates of ellipses $v (v_0, v_1)$:

$$\begin{align*}
R_{0_{i,j}} &= \begin{pmatrix} v_0 - \text{MENX}_i \\ v_1 - \text{MENY}_i \end{pmatrix} \sigma_{\Delta X_i} \sigma_{\Delta Y_i} \sum 0^{-1} \begin{pmatrix} v_0 - \text{MENX}_0 \\ v_1 - \text{MENY}_0 \end{pmatrix} \sigma_{\Delta X_0} \sigma_{\Delta Y_0} \\
R_{1_{i,j}} &= \begin{pmatrix} v_0 - \text{MENX}_i \\ v_1 - \text{MENY}_i \end{pmatrix} \sigma_{\Delta X_i} \sigma_{\Delta Y_i} \sum 0^{-1} \begin{pmatrix} v_0 - \text{MENX}_1 \\ v_1 - \text{MENY}_1 \end{pmatrix} \sigma_{\Delta X_1} \sigma_{\Delta Y_1}
\end{align*}$$

$$R_0 = 3.458112896121225 \quad R_1 = 3.458112896121227$$

The solution of the system of equations in this case will be: $R_0 = 4.055162413084189$ and $R_1 = 4.055162413084188$. The accuracy of solving the system of equations in this case will be: $-3.55 \times 10^{-15} + 9.15 \times 10^{-16}$.

For the control, a graphical evaluation of the intersection of the ellipses of the distribution of Raman spectra during the identification of nanoparticles during the polarization of $Y$ - along and $X$-
across the fibers was carried out at $\Delta = +0.34342$ (Fig. 2). The intersection of ellipses (is) occurred at one point.

**Figure 2.** Graphical estimation of the intersection of the ellipses of the distribution of Raman spectra in the identification of nanoparticles in the polarization of Y-along and X-across the fibers at $\Delta = +0.34342$: a - a general view; b - enlarged fragment of points of intersection

Also, for the control, an estimation was made in the intersection of the ellipses of the distribution of Raman spectra in the identification of nanoparticles during polarization of Y - along and X - across the fibers at $\Delta = 0.000$: a - a general view; b - enlarged fragment of points of intersection

**Figure 3.** Graphical estimation of the intersection of the ellipses of the distribution of Raman spectra in the identification of nanoparticles during Y-polarization and X - across the fibers at $\Delta = 0.000$: a - a general view; b - enlarged fragment of points of intersection
fibers at $\Delta = 0.0000$ (picture 3). The intersection of ellipses occurs at two points. The coordinates of one point of intersection give the solution of the system of equations (2-3), and it is not possible to obtain the coordinates of the second point even by selecting the initial values of X and Y for the solution. Selection of initial values was carried out at close initial values of X and Y to the second intersection point (Picture 5). The solution still gives the coordinates of the first point of intersection. This shows the high accuracy of the solution even for large deviations at the initial values of X and Y. Uncertainty arises in the solution of the system of differential equations due to the fact that the coordinates of the intersection of ellipses $v_0 = 410.77$ and $v_1 = 307.66$ (which) are obtained in the solution. For these coordinates, using (4) - (5), we obtain the radius $R_0 = R_1 = 4.055162413084188$ with an accuracy of $10^{-14}$, but the intersection of the ellipses occurs at two points, as it was shown at picture 5. The solution of the system of differential equations without additive has uncertainty in the error in determining the radius of intersection of ellipses 20%.

The error in determining the intersection coordinates will be: $\Delta v_0 = 0.12\%$ and $\Delta v_1 = 20.1\%$, which can only be used for preliminary results. Such identification is unacceptable for the identification of nanoparticles

4. Conclusion
In this research, the accuracy of solving equation $f(v_0, v_1) = 1.42 \times 10^{-14}$ and equation $g(v_0, v_1) = 1.94 \times 10^{-15}$ is found (out) in comparison with the accuracy of $10^{-4}$ used before the present research. The accuracy of obtaining parameters $R_0$ and $R_1$ is $10^{-14}$. The accuracy of calculating the uncertainty at the intersection of ellipses has 20% for the equations without the addition of $\Delta$, and depending on the accuracy of the addition $\Delta$, the accuracy of calculating the coordinates for solving the equations with the addition of $\Delta$ also depends.

The practical accuracy of the results depends on the necessary resolving power (sensitivity) of the proposed method for identifying silver nanoparticles. In order to ensure a resolution of 1-2% of the concentration of silver nanoparticles on fibers, it is necessary to calculate the results with an accuracy of (1-2) $\times 10^{-4}$, and the accuracy of obtaining the value of each parameter should be (1-2) $\times 10^{-9}$. To obtain a resolution of $10^{-6}$, it is necessary to provide an accuracy of $10^{-10}$ for each parameter.

It should be noted that when solving differential equations (2-3), uncertainty was revealed in the results, since there is an intersection of ellipses at two points (Picture 5) due to the increased radius of the ellipses of distribution of Raman spectra of polyester without nanoparticles and with silver nanoparticles. Hence, it becomes necessary to introduce additive $\Delta = 0.34342$. In this case, the ellipses intersect at one point (Figure 4) and the uncertainty disappears. However, this value of the additive is applied only for one particular solution of the system of equations for certain parameters. For other parameters, the value of the additive must be selected manually. It makes difficult to obtain results with high accuracy and with high speed. For 20% accuracy, the solution can be carried out without adding ($\Delta = 0.0000$) for any parameters of the system of differential equations and used for preliminary results. (The aim for further research: to conduct research on solutions of systems of differential equations together with the differentiation with respect to X and Y, to apply these methods on differentiation with respect to X and Y and at the same time to exclude the application of additive $\Delta$, and the solution of the system automatically).

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