Solution of multidimensional system with XY differentiation of probability density equations for identification of silver nanoparticles on fibers

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Abstract. The article presents the results of compiling and solving a system of multidimensional differential correlation equations of probability densities for identifying colloidal silver nanoparticles on polyester fibers with multidimensional correlation components of Raman polarization spectra. A method is proposed for increasing the accuracy and speed of identification of silver nanoparticles on polyester fibers, taking into account the longitudinal and transverse polarization of laser radiation over the entire range of the Raman spectrum with the analysis of two peaks sequentially and in order at the same time along the X-side and along the Y-side of the fibers. To implement the method, a program was developed in the Mathcad software. When solving the system using the nonlinear quadratic and differential equations with respect to XY, the probability density equations of distribution ellipses obtained very high accuracy $p_0$ and $p_1$ up to $10^{-16}$.

Keywords: polyester fiber, silver nanoparticles, Raman spectra, system of multidimensional equations, recognition accuracy, probability of intersection of distribution ellipses, accuracy of nanoparticle identification

1. Introduction
The current development of nanotechnology allows elaborating textile materials with improved hygienic and bactericidal properties. In the production of such products, the urgent task is to control the deposition of nanoparticles on the surface of materials, which in turn is impossible without the precise identification of nanoparticles [1–6]. To study nanostructured materials, microscopy and spectroscopy methods are used [7–8]. Multidimensional mathematical methods are used to recognize nanoparticles on the surface of textile materials. Development of methods for detecting nanoparticles on the surface of textile materials is impossible without the use of modern computer programs and the development of algorithms for the implementation of mathematical methods for identifying nanoparticles in applied mathematical programs. When solving the system of differential correlation equations, an uncertainty was revealed in the fact that when checking the solution for the graphic intersection of distribution ellipses without nanoparticles and with nanoparticles, two intersection points appeared. In this case, the probability densities of the intersection of ellipses, found when solving nonlinear quadratic equations, were not equal. The difference between these values was significant, and the accuracy was 23 %. Such accuracy for the identification of silver nanoparticles is unacceptable. The methods developed by the authors for identifying nanoparticles on the surface of textile materials with an
estimate of the probability density of the intersection of the distribution ellipses of the peaks of the Raman polarization spectrum are described in [9–10]. Moreover, in the proposed methods there are elements of manual selection of some components in the equations. The analytical expression of the differential correlation equation is obtained by differentiating the equation with respect to X. The accuracy is quite high at $10^{-15}$, but depends on the selection of additives in the equation.

To increase accuracy, it is necessary to develop a method for automatically determining the reliability of identification of nanoparticles.

2. Methods and materials

For the mathematical and software implementation of the method of identification of nanoparticles, Raman spectra were used, which were obtained at the regional center of nanotechnology of the South-Western State University in the study of polyester fibers (PE) upon deposition of silver nanoparticles on them from a colloidal solution of silver nanoparticles AgBion (TU 2499-003-44471019-2006, concern "Nanoindustry"). Using a scanning probe microscope (SPM) with a confocal Raman and OmegaScope™ fluorescence spectrometer, measurements were made at 5 points on each sample with polarization of the laser beam across X- and along Y-fibers. For analysis, 9 main peaks of Raman spectrograms were selected. Data processing was performed using the MathCad 15.

In this paper, we consider a possible increase in the number of equations for solving the system by using differentiation with respect to X and Y at the same time when estimating the probability density of the intersection of the ellipses of the peak height distribution of the Raman polarization spectrum when identifying silver nanoparticles on the surface of polyester fibers.

To compile a system of differential correlation equations, we use the p–densities of intersection probabilities of distribution ellipses in vector-matrix analytical expressions along the coordinates of the intersection points. In this paper, we consider a system of only two vector-matrix analytical expressions of probability densities $\ln(p)=X^T \cdot R^{-1} \cdot X$ and $\ln(p_{Ag})=X_{Ag}^T \cdot R_{Ag}^{-1} \cdot X_{Ag}$ for p and $p_{Ag}$ [14].

For the analytical estimation of probability densities (p and $p_{Ag}$) from the intersection points of distribution ellipses, in accordance with the method developed by the authors, vector-matrix expressions 1–5 are used.

$$R_{Ag} = \begin{pmatrix}
1 & r_{XYAg}
\end{pmatrix},
R = \begin{pmatrix}
1 & r_{XY}
\end{pmatrix}. \quad (1)$$
The following notation was used: $r_{XY}$, $r_{XYAg}$ are correlation matrices of the Raman polarization spectra of polyester fibers without silver nanoparticles and silver nanoparticles, respectively; $M_X$, $M_{XAg}$ are the mathematical expectation vectors of peak intensities of spectra with polarization across X fibers without silver nanoparticles and silver nanoparticles, respectively; $M_Y$, $M_{YAg}$ are the mathematical expectation vector of peak intensities of spectra with polarization along Y-fibers without silver nanoparticles and with silver nanoparticles, respectively; $\sigma_X$, $\sigma_{XAg}$ are the root-mean-square deviations of the peak intensities of the spectra with polarization across the X-fibers without silver nanoparticles and with silver nanoparticles, respectively; $\sigma_Y$, $\sigma_{YAg}$ are the root-mean-square deviations of the peak intensities of the spectra with polarization along the Y-fibers without silver nanoparticles and with silver nanoparticles, respectively; $i, j$ are the numbers of the peaks of the spectrograms, the
suppression of which is studied. Moreover, in the system of equations (2), the expression \( g(x, y) \) is the Jacobian double derivative (with respect to \( dx \) and with respect to \( dy \)), and there is no differentiation in the expression \( f(x, y) \). The analytical expression of the differential correlation equation \( g(x, y) \) is obtained by differentiating the equation \( f(x, y) \) with respect to \( X \) and \( Y \). In this case, the solution occurs automatically without manually selecting the values of the parameter \( p \).

3. Results

To solve the system of equations (2) using vector-matrix analysis, an algorithm was developed that was implemented using the built-in functions of the MathCad Enterprise Edition 15:

\[
\begin{aligned}
given
f(x, y) &= 0 \\
g(x, y) &= 0 \\
v := \text{Find}(x, y), 
\end{aligned}
\]

where \( v \) is the coordinate vector of the intersection of distribution ellipses with and without nanoparticles.

At the next stage, a software implementation of the solution of the system of equations (2) was carried out. So, when examining the intersection of 4 and 1 peaks:

\[
\begin{aligned}
f_{4-1}(v_{4-1}, v_{4-1}) &= -2.664535291003757 \times 10^{-15} \\
g_{4-1}(v_{4-1}, v_{4-1}) &= 1.0842021724855044 \times 10^{-17}
\end{aligned}
\]

To determine the recognition accuracy of nanoparticles, expressions (4–5) were proposed, where \( p \) is the identification accuracy for the equation without nanoparticles and \( p_{Ag} \) is the identification accuracy for the equation with silver nanoparticles.

\[
\begin{aligned}
P_{Ag} &:= \frac{1}{(2 \cdot \pi) \left[ \left( R_{Ag} \right)^{0.5} \right]} e^{-\frac{1}{2}} \left[ \begin{array}{c} v_0 - M_{xAg} \\ v_1 - M_{yAg} \\ \sigma_{xAg} \\ \sigma_{yAg} \end{array} \right] \left( R_{Ag} \right)^{-1} \left[ \begin{array}{c} v_0 - M_{xAg} \\ v_1 - M_{yAg} \\ \sigma_{xAg} \\ \sigma_{yAg} \end{array} \right] \\
P &:= \frac{1}{(2 \cdot \pi) \left[ \left( R \right)^{0.5} \right]} e^{-\frac{1}{2}} \left[ \begin{array}{c} v_0 - M_{x} \\ v_1 - M_{y} \\ \sigma_{x} \\ \sigma_{y} \end{array} \right] \left( R \right)^{-1} \left[ \begin{array}{c} v_0 - M_{x} \\ v_1 - M_{y} \\ \sigma_{x} \\ \sigma_{y} \end{array} \right]
\end{aligned}
\]

Reliability values \( p \) and \( p_{Ag} \) calculated from expressions (4–5) under the condition of simultaneous differentiation with respect to \( X \) and \( Y \) for the study of the intersection of peaks 4 and 1:

\[
\begin{aligned}
p_{Ag} &= 0.00082199604570955 \\
p &= 0.00082199604570954
\end{aligned}
\]

The analysis of the obtained values shows that \( p \) and \( p_{Ag} \) for the corresponding peaks are almost equal.

A graphical estimate of the intersection of distribution ellipses for various differentiation options is shown in Figures 1 and 2. If we solve the usual system of equations for the same peaks of the Raman spectrum, then the probability density will be:

\[
\begin{aligned}
p_{4-1} &= 0.00082188904657987 \\
p_{Ag4-1} &= 0.0008221540489625.
\end{aligned}
\]

When solving a system of equations with differentiation with respect to \( X \), we obtain for the same peaks of the Raman spectrum the probability density:
By solving the system of equations with differentiation with respect to \( Y \), we obtain the probability density for the peaks of the Raman spectrum:

\[
p_{(4-1)} = 0.00082199573106 \\
p_{Ag(4-1)} = 0.00082199573100
\]

Based on the solution of the system of equations (2), it is possible to determine the radii of the ellipses of the distribution of the radiation intensity of the Raman spectra from expressions 6–7. In this case, \( R \) is the radius of the ellipse for Raman spectra without nanoparticles; \( R_{Ag} \) is the ellipse radius for Raman spectra with silver nanoparticles.

**Figure 1.** A graphical estimate of the intersection of the ellipses of the distribution of Raman spectra and the results of solving the system of equations for identifying nanoparticles with polarization \( Y \)-along and \( X \)-across the fibers: a – general view; b – differentiation with respect to \( XY \) – ○ and general solution of the system of equations with respect to \( XY \) – □

**Figure 2.** Graphical estimate of the intersection of the ellipses of the distribution of Raman spectra and the results of solving the system of equations for identifying nanoparticles with polarization \( Y \)-along and \( X \)-across the fibers: a – differentiation with respect to \( XY \) – ○ and along \( X \) – ×; b – differentiation with respect to \( XY \) – ○ and with respect to \( Y \) – △
\[R_{Ag} = \begin{pmatrix} \frac{v_0 - M_{XAg}}{\sigma_{XAg}} & \frac{v_1 - M_{YAg}}{\sigma_{YAg}} \end{pmatrix} \begin{pmatrix} R_{Ag}^{-1} & \frac{v_0 - M_{XAg}}{\sigma_{XAg}} \\ \frac{v_1 - M_{YAg}}{\sigma_{YAg}} \end{pmatrix}. \]  
(6)

\[R = \begin{pmatrix} \frac{v_0 - M_X}{\sigma_X} & \frac{v_1 - M_Y}{\sigma_Y} \end{pmatrix} R^{-1} \begin{pmatrix} \frac{v_0 - M_X}{\sigma_X} \\ \frac{v_1 - M_Y}{\sigma_Y} \end{pmatrix}. \]  
(7)

The values of \(R_{Ag}\) and \(R\) for the distribution ellipses of the Raman spectra at the intersection of 4 and 1 peaks resulted in the following:

\[R_{Ag(4-1)} = 3.680765923137155 \]
\[R_{1(4-1)} = 3.275528794713935 \]

4. Conclusion

It should be noted that when solving the system of differential equations (2), high accuracy was revealed in the results with automatic numerical solution in a large range of initial parameters \(x = 50 \div 6000\) and \(y = 50 \div 5000\) with stable solution parameters.

The solution on the values of the coordinates of the intersection of distribution ellipses \(X = 398.4395417708532, Y = 371.1700822350267\) has high accuracy and does not depend on the initial value of the parameters \(x\) and \(y\) in the specified range.

The practically required accuracy of obtaining the results depends on the necessary resolution (sensitivity) of the proposed method for identifying silver nanoparticles.

In this paper, the accuracy of the solution by the equation \(f(v_0, v_1) = -4.440892098500626 \times 10^{-15}\) and by the equation \(g(v_0, v_1) = -3.9031278209478155 \times 10^{-18}\) for the initial given parameters \(x = 50, y = 400\) is revealed. With the initial given parameters \(x = 6000, y = 5000\), the accuracy of the solution is according to the equation: \(f(v_0, v_1) = -0.00000000000002398\) and according to the equation \(g(v_0, v_1) = 2.6020852139652106 \times 10^{-17}\).

The accuracy of obtaining the output parameters: \(p = 0.00082199604570954\) and \(p_{Ag} = 0.00082199604570955\) can be estimated up to \(10^{-16}\). Higher accuracy cannot be given by any of the investigated methods.

The objectives of further research are as follows. construct and solve a system of differential equations when differentiating along \(X\) and \(Y\) when compiling a system with the number of unknown parameters more than two, evaluate the increase in the reliability of increasing the sensitivity of identification of silver nanoparticles on polyester fibers using multidimensional differentiation by \(X\) and \(Y\) simultaneously with the study of two or more peaks spectrum.

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