Inverse problem of laser correlation spectroscopy for analysis of polydisperse solutions of nanoparticles

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Abstract. A new algorithm for the solution of the inverse problem of laser correlation spectroscopy is suggested. The algorithm allows one to analyse sizes of nanoparticles in polydisperse solutions. Experimental results demonstrating the efficiency of our approach are presented.

1. Introduction
Laser correlation spectroscopy (LCS) is one of few methods that allow a highly precise determination of nanoparticle sizes in solutions, which is important for the chemical and food industry and for medicine [1]. Other advantages of laser correlation spectrometers are their small sizes, a high speed, and low requirements to the conditions of measurements [2]. However, the commercially available laser correlation spectrometers are designed to analyze particle sizes only is one-component solutions and do not allow one to analyze solutions containing particles of several sizes. Determination of particle sizes in polydisperse solutions is a challenging task for the researchers. The complexity of identifying and accurately determining several particle sizes in polydisperse solutions is caused by the necessity to solve the inverse incorrect problem of LCS, and therefore the development of new algorithms for analyzing polydisperse solutions is highly important. The goal of our study was to develop an algorithm for solving the inverse problem of laser correlation spectroscopy aimed at determining particle sizes in polydisperse solutions.

2. Experimental
A typical scheme of a laser correlation spectrometer used in our investigations is presented in figure 1 [3–5].
The light from the laser scatters from particles of the solution of interest \((3)\). The scattered light which contains information on the velocity of particles is registered by a photomultiplier \((6)\). The signal from the photomultiplier is transmitted to a computer \((7)\) and is analyzed by using special software. Then the correlation analysis of the signal is carried out. The autocorrelation function can be approximated by \(6\)

\[
\int \frac{g^{(1)}(\tau)}{g} = \int_0^\infty F(\Gamma)e^{-\Gamma\tau}d\Gamma, \quad (1)
\]

where \(\Gamma\) is the diffusion broadening, and \(F(\Gamma)\) is the contribution of the radiation component scattered by particles of one size to the total intensity. The diffusion broadening is related to the diffusion coefficient \(D\) by

\[
\Gamma = Dq^2, \quad (2)
\]

where \(q = (4\pi n/\lambda)\sin(\theta/2)\) is the scattering vector, \(n\) is the refractive index of the medium, \(\lambda\) is the wavelength, and \(\theta\) is the angle of scattering.

By using the Stokes-Einstein formula

\[
D = k_b T / 6 \pi \eta R \quad (3)
\]

one can calculate the radius of the particles under study. Here, \(\eta\) is the viscosity of the medium, \(k_b\) is the Boltzmann constant, \(T\) is the temperature, and \(R\) is the particle radius.

Therefore, the solution of Eq. (1) and estimation of \(\Gamma\) are the main tasks in the mathematical processing of a scattered signal. Equation (1) is referred to as the Fredholm integral equation. Because of the presence of random noise in the experimental data, its solution belongs to the class of incorrect problems. This means that even a small error in the initial data will lead to the accumulation of errors in the course of solution, and the result will be incorrect.

3. The algorithm

There are a variety of methods for solving the Fredholm integral equation. The operation of modern spectrometers is typically based on the method of cumulants. This method allows one to estimate particle sizes with a high accuracy only for monodisperse solutions. There are also solutions relying on the Tikhonov regularization method which allow a more detailed analysis, and are more suitable for the determination of particle sizes in polydisperse solutions. So the Tikhonov regularization method was used as a basis for the algorithm design for the solution of the inverse problem of LCS.

In order to solve Eq. (1), it is presented in the form of a set of \(N\) points and, hence, we obtain a system of \(N\) equations which is written in the matrix form as

\[
A f = g. \quad (4)
\]

Since in practice only approximate values of the right-hand sides of system of equations (4) are known \(g \approx \tilde{g}\), it is necessary to solve the problem of the form

\[
||Af - \tilde{g}||^2 + \alpha \Omega(f) \rightarrow \min. \quad (5)
\]
where \( \alpha > 0 \) is the smoothing parameter, and \( \Omega(f) \) is the stabilizing functional which is selected for each task separately. The minimization of this type stabilizes the solution of the system, thereby improving its conditionality and increasing the accuracy of solution. The stabilizing functional was chosen as \( \Omega(f) = ||f||^2 \).

Below we present the implementation of the algorithm for solving the inverse problem of laser correlation spectroscopy based on the Tikhonov regularization method.

The algorithm is as follows:

1. set the initial (sufficiently high) value of \( \alpha \) equal to 1% of the maximum diagonal element of matrix \( A \);
2. solve system of equations (5) by the modified Gauss method and find the solution \( f \);
3. calculate the convergence \( ||Af - \tilde{g}||_i^2 \) (reduce \( \alpha \) by 90% after the first iteration and return to step 1);
4. compare \( ||Af - \tilde{g}||_i^2 < 0.1 \cdot ||Af - \tilde{g}||_{i-1}^2 \), if the answer is “yes”, reduce \( \alpha \) by 90% and return to step 1, if the answer is “no”, go to step 5;
5. check for the presence of negative components of solution \( f \). If \( f_i < 0 \) are present, take \( f_{\min} = 0 \) and return to step 1. The corresponding component is excluded from further calculations;
6. if \( f_i < 0 \) are absent, check the number of points at the function peak \( n > N \) (set prior to the solution), if the answer is “yes”, take \( f_{\min} = 0 \) and return to step 1, if the answer is “no”, the calculation is completed.

The last step is a modification suggested in our study. The aim of this modification is to provide determination of not only greatly differing but also slightly differing particle sizes.

Other important features of our algorithm which improve the accuracy of determining particle sizes are

- not only the points with the minimal values but also the points with the weakest influence on the convergence are removed from the signal (in contrast to the conventional method described in [7]);
- the procedure for setting and correcting the regularization parameter \( \alpha \) is described.

4. Discussion

The algorithm we suggested was tested on model signals from the particles with specified sizes of 48 nm (40% of particles in the solution), 46 nm (20% of particles in the solution) and 43.5 nm (30% of particles in the solution). A random noise from 1% to 10% was added to the model signals. Figure 2 a shows the result of calculations based on the algorithm suggested.
The solution of the inverse problem based on our algorithm resulted in a highly precise estimation of particle sizes in polydisperse solutions containing up to three components (the error was 6% at a confidence level of 95%). In addition, as one can see from Figure 2, the method we propose has a sufficiently high spatial resolution, owing to which the particle with the sizes differing by only 2.5 nm can be differentiated. The commercially available programs for LKS signal analysis do not allow one to distinguish between the particles with such close sizes.

The algorithm was also verified in experimental studies. Water solutions of latex microspheres, albumin and metal nanoparticles were investigated. The results of analysis were compared with the results of mathematical processing by “DynaLS”. “DynaLS” is a special program for a Photocor laser correlation spectrometer but it can also be used for a large variety of commercial laser correlation spectrometers. The mathematical tools of this program are also based on regularization methods.

Figure 3 shows the results of analysis of a polydisperse mixture of latex microspheres with three sizes calculated by our program and by “DynaLS”. We used latex microspheres with specified sizes of 30 nm, 45 nm, and 75 nm.
It is evident that the calculations based on our algorithm are characterized by a high accuracy, whereas the calculations employing the commercial program give incorrect results.

5. Conclusion
The algorithm for the solution of the inverse problem of laser correlation spectroscopy aimed at analysis of polydisperse solutions is suggested. The results obtained in our study have demonstrated a high efficiency of our algorithm for analysis of polydisperse solutions.

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