Development of optical diagnostic method for colloidal solutions based on elastic light scattering

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Abstract. The work is devoted to colloidal solutions diagnostics by the optical method based on elastic light scattering by particles of the dispersed phase. The scheme of the developed optical electronic complex for recording the intensity of radiation scattered by colloidal particles is presented. The experimental study results of the elastic scattering of laser radiation on spherical nanometer-sized aluminum oxide particles suspended in water are presented. A method for measuring the scattering indicatrix based on the registration of radiation scattered in various directions and subsequent computer processing has been proposed. A method for reconstructing the particle size distribution function of colloidal solution dispersed phase by comparing the measured scattering indicators and their computer models has been developed. The method has been tested, as a result of which the size distribution function of aluminum oxide nanopowder particles has been restored.

1. Introduction

Nanoscale structures of a substance with the size from 1 nm to 1000 nm have found wide application in various fields. The dispersed phase of colloidal solutions is an example of such structures. Various colloidal solutions are widely used in medicine, pharmacology and cosmetology. Another example of nanoparticles can be various nanopowders that are applied in electrical engineering, the creation of lubricating materials the production of composite materials and other types of industrial production. The continuous development of various nanotechnologies ensures the growth of their market availability, and the unique properties of nanoscale structures constantly expand the areas of their use.

Against the background of expanding the applications range of materials with a nanoscale structure in industrial, scientific, technical and other fields of human activity, the task of determining the properties and measuring their various parameters becomes relevant. In particular, the problem of measuring the size distribution function of colloidal particles is of significant importance. Currently, there are a number of methods for solving this problem.

For example, the nephelometry method [1] allows measuring the concentration of the dispersed phase in a colloidal system based on measuring the intensity of light scattered in it. The methods of optical [2] and electron [3] microscopy are used to determine the size and shape of nanometer-sized particles. The method based on dynamic light scattering also allows measuring the size of nanoparticles [4, 5]. To measure the size distribution function of colloidal particles, a combination of methods based on G. Mi scattering and analytical ultracentrifugation is used [6, 7].
This paper, which is a continuation of the work of [8] authors, presents the results of colloidal solution diagnostics of aluminum oxide based on the measurement of experimental scattering indicatrix on the developed optical electronic setup and their comparison with computer models of scattering indicatrix obtained within the framework of the theory of G. Mie.

2. Methodology

2.1. The experimental setup

The scheme of experimental setup for recording the angular distribution of the scattered radiation intensity is shown in figure 1. The laser module (1) has been used as radiation source. It consisted of a laser semiconductor diode with power driver and collimation optics. So three different modules with wavelengths $\lambda_1 = 650$ nm, $\lambda_2 = 515$ nm and $\lambda_3 = 450$ nm has been applied in experiment. These wavelengths belong to the red, green, and blue range of the visible region of the electromagnetic radiation spectrum. The output laser radiation of each module was predominantly linearly polarized. According to the laser module passport, the radiation power of each of them was 42 mW.

![Figure 1. The experimental setup scheme: 1 – laser module, 2, 3 – spherical lens, 4, 5 – cylindrical lens, 6 – polarizer, 7 – cylindrical vessel with the investigated medium, 8 – attenuating light filters, 9 – matrix photodetector.](image)

After the source, along the radiation direction, an optical system for generating probing radiation was installed on the optical bench. The system consisted of a short-focus spherical lens (2), a long-focus spherical lens (3), a short-focus cylindrical lens (4), a long-focus cylindrical lens (5) and a polarizer (6). The system of spherical lenses (2) and (3) was selected so that the transformed beam waist was in the measurement area. The collimation system of cylindrical lenses (4) and (5) ensured the formation of an almost non-divergent laser plane within the measurement area. The polarizer (6) was included in the probing radiation generation system to increase the degree of polarization and more accurately position the polarization plane relative to the scattering plane.
The study object was a physical model of a colloidal solution, which has been obtained by adding aluminum oxide $\text{Al}_2\text{O}_3$ nanopowder particles with known characteristics to distilled water. The shape of the nanoparticles was mainly spherical and the diameter of the particles corresponded to the range from 10 nm to 110 nm. The particle size distribution function provided by the nanopowder manufacturer is shown in figure 2. A cylindrical glass vessel with a colloidal solution of aluminum oxide (7) was installed in the measurement area. The direction of probing radiation was passed along the diameter of the cylindrical vessel, and the laser plane was oriented parallel to its axis.

The scattered radiation was recorded by a digital camera (9). The role of the receiving optical system was played by the camera lens, in front of which a holder with attenuating light filters has been installed (8). The recording system was installed on a separate optical bench, which was movable and had the ability to rotate. The rotation axis coincided with the axis of the vessel, thus it was possible to register radiation at different scattering angles in the range from $0^\circ$ to $165^\circ$. During the experiment, a Nikon 1 J5 digital camera was applied.

2.2. The experiment methodology
There are many factors that, in varying degrees, affect the results of measuring the angular distribution of the scattered radiation intensity. Therefore, in order to obtain correct experimental results, it was necessary to take into account those of them that have a significant impact.

The response of the digital camera to the recorded radiation depends non-linearly on the exposure. Thus even if the exposure time remains unchanged, it cannot be assumed that the pixels brightness in a digital image is directly proportional to the intensity of the incident light. In addition, the transfer function itself depends on the camera’s light sensitivity (ISO) setting. And if the purpose of recording radiation is to measure the intensity, then the exposure time should also be attributed to the parameters that affect the relation between the camera response and the intensity of the incident light. Therefore, it has been decided to experimentally measure the dependence of the pixels brightness in a digital image on the intensity of incident radiation and take into account the nonlinearity of the transfer function. It has been also decided to register the scattered radiation with the camera settings unchanged throughout the experiment, in order to exclude any change in the transfer function itself.

The scattered radiation intensity varies in a very wide range of values depending on the angle and position of the scattering plane. For this reason, it is impossible to measure the angular distribution of the scattered intensity and avoid obtaining images in conditions of excessive or insufficient exposure, using only the camera with unchanged recording parameters. To exclude excessive exposure of the camera matrix for certain scattering angles, attenuating light filters has been applied, which were glass plates made of neutral glass. These attenuators have been also used to experimentally determine the dependence of the pixel brightness in a digital image on the intensity of incident radiation.

Before carrying out an experimental study of scattering, the transmission coefficients of attenuating filters for the radiation of each laser module have been measured. The measurement results are presented in table 1.

At the next stage of preparation for the scattering study, the dependences of the average pixels brightness on the intensity of incident radiation for each color channel of the camera matrix were experimentally measured. The measurement results are shown in figure 2.

The experiment of the scattering indicatrix registration began from the preparation of the study object. To create a physical model of a colloidal solution, double-distilled water has been poured into the cylindrical glass vessel, and then aluminum oxide nanoparticles were placed. At the same time, only some particles remained suspended in the water and formed the dispersed phase of the solution. The remaining particles were combined into large clusters and fell to the bottom of the vessel in the form of sediment. Thus, after adding aluminum oxide powder to the water, the vessel with the solution has been placed in the probing area and was not subjected to any external disturbances for several hours. By the time of the experimental study, small particles remained suspended, indistinguishable to the naked eye, and large particles fell into the sediment.
Table 1. Attenuation coefficient of light filters.

| Filter number | Glass type | $\lambda = 650$ nm | $\lambda = 515$ nm | $\lambda = 450$ nm |
|---------------|------------|---------------------|---------------------|---------------------|
| 1             | NG-1       | 1.624               | 1.541               | 1.643               |
| 2             | NG-2       | 3.367               | 3.548               | 3.958               |
| 3             | NG-3       | 8.319               | 10.11               | 18.36               |
| 4             | NG-7       | 2.380               | 2.265               | 2.344               |
| 5             | NG-8       | 4.760               | 4.477               | 4.460               |
| 6             | NG-9       | 28.23               | 31.93               | 30.78               |
| 7             | NG-10      | 124.5               | 160.9               | 140.3               |
| 8             | NG-1       | 1.568               | 1.621               | 1.680               |
| 9             | NG-3       | 8.740               | 10.81               | 16.97               |
| 10            | NG-10      | 91.50               | 112.7               | 92.71               |
| 11            | NG-13      | 31.45               | 55.49               | 94.27               |

Figure 2. Plots of the dependences of the pixels average brightness in a digital image on the intensity of incident radiation for each color channel of the camera matrix: red channel (a), green channel (b), blue channel (c).

When the object of study has been prepared, the images of the probing laser plane were directly recorded in the scattered radiation at various angles. During one experiment, six series of images were recorded. So, two series of recordings were carried out with each laser module, which differ from each
other in the states of probing radiation polarization. In one case, the plane of polarization was oriented perpendicular to the scattering plane, in the other – parallel.

To register the first image in the series, the camera has been set to the scattering angle \( \theta = 5^\circ \). Each subsequent image in the series was recorded after the receiving system was rotated around the axis of the cylindrical vessel by an angle of 5° relative to the previous position. In each series, 33 images were obtained, which corresponded to the range of angles from 5° to 165°. Examples of the obtained experimental images are shown in figure 3. The registration of scattered radiation at all camera mounting angles was performed at the same recording parameters. The recording parameters were chosen so that the radiation scattered at an angle of 90° could be recorded without attenuation. At certain camera angles, one or more attenuating light filters were used to avoid excessive exposure of the camera matrix. Recording of experimental images has been carried out in RAW format in order to avoid correction of the signal received from the camera matrix due to built-in digital processing algorithms, as it happens when recording an image in JPEG format. At the same time, depending on the wavelength of the installed laser module, the signal received from only one of the three RGB radiation channels was considered informative.

![Figure 3](image)

**Figure 3.** Examples of experimental images, the laser plane in scattered light at different parameters: \( \lambda_1 = 650 \text{ nm}, \) horizontal polarization, \( \theta = 15^\circ \) (a), \( \lambda_1 = 650 \text{ nm}, \) vertical polarization, \( \theta = 30^\circ \) (b), \( \lambda_2 = 515 \text{ nm}, \) horizontal polarization, \( \theta = 45^\circ \) (c), \( \lambda_2 = 515 \text{ nm}, \) vertical polarization, \( \theta = 60^\circ \) (d), \( \lambda_3 = 450 \text{ nm}, \) horizontal polarization, \( \theta = 75^\circ \) (e), \( \lambda_3 = 450 \text{ nm}, \) vertical polarization, \( \theta = 90^\circ \) (f).

2.3. The experimental results processing
The correspondence of the camera mounting angle to the radiation scattering angle is possible only if the scattered radiation does not change the direction when passing through the glass vessel. So it is not refracted. This is true only for radiation that was scattered by the volume of the medium localized near the cylindrical vessel axis. In this case, the radiation scattered in the direction of the camera propagates along the radius of the vessel and falls normally on its surface. Therefore, when processing experimental images, pixels were taken into account, which were located in a small area corresponding to the image of a part of the probing laser plane in the vicinity of the cylindrical vessel axis.

The scattering indicatrix was constructed for each series of experimental images. To do this, first the average pixel brightness values in the informative area of each image in the series was calculated. The obtained average values of the pixel brightness level were reduced by an amount corresponding to the level of dark noise and compared with the scattering angles.
The next processing step was to take into account the nonlinearity of the camera matrix transfer function. For this purpose, the measured dependences of the average pixel brightness on the intensity of the incident radiation were used, the plots of which are shown in figure 2. For each average pixel brightness value, the corresponding radiation intensity, expressed in relative units was found. Plots of the dependences of the registered radiation intensity on the scattering angle are shown in figure 4.

Figure 4. The results of measuring the radiation intensity at different camera position angles: \( \lambda_1 = 650 \text{ nm} \), horizontal polarization (a), \( \lambda_1 = 650 \text{ nm} \), vertical polarization (b), \( \lambda_2 = 515 \text{ nm} \), horizontal polarization (c), \( \lambda_2 = 515 \text{ nm} \), vertical polarization (d), \( \lambda_3 = 450 \text{ nm} \), horizontal polarization (e), \( \lambda_3 = 450 \text{ nm} \), vertical polarization (f).

Then it was necessary to take into consideration that attenuating light filters has been used at certain camera mounting angles. Thus, the obtained intensity values were multiplied by the corresponding attenuation coefficients.
The number of particles scattering the radiation is another significant factor affecting the shape of the experimental scattering indicatrix. When the angular position of the receiving system changes, the number of scattering centers also changes. When the receiving system is installed at an angle of 90°, the number of particles scattering radiation in the direction of the camera is minimal, and when installed at an angle of 5°, it is maximum. It was determined that the number of centers scattering radiation in the direction of the receiving system is proportional to \( \sin^{-1}(\theta) \). In order to exclude the number of particles scattering radiation, which is recorded by the receiving system, from the number of factors affecting the shape of the scattering indicatrix, the intensity value obtained for each angle \( \theta \) was multiplied by \( \sin(\theta) \). The obtained scattering indicatrices are shown in figure 5.

2.4. The restoration of the particle size distribution function

When solving the inverse problem, it has been assumed that the particle size distribution function \( n(r) \) has the form of a modified gamma distribution (1)

\[
n(r) = a \cdot r^\alpha \cdot \exp(-b \cdot r^\gamma).
\]

(1)

The peculiarity of this distribution is that \( n(0) = 0 \) and \( n(\infty) \to 0 \), which corresponds to reality, since there are no particles of infinitely small and infinitely large size. As the argument \( r \) increases from zero, the function \( n(r) \) increases as a polynomial of order \( \alpha \), then reaches its maximum value at the value of the argument \( r = r_{max} \), which corresponds to the most probable particle size. With further growth of the argument \( r \), the function \( n(r) \) decreases, and the decay rate of the function is determined by the exponent \( \gamma \). Under the constancy condition of the values \( \alpha \) and \( \gamma \), the constant \( b \) is determined by the most probable particle size \( r_{max} \) in accordance with expression (2), and the constant \( a \) is determined by the concentration of particles \( N \) in accordance with expression (3)

\[
b = \frac{\alpha}{\gamma \cdot r_{max}^\gamma},
\]

(2)

\[
a = \frac{N}{\gamma^{-1} \cdot b^{-\frac{\alpha+1}{\gamma}} \cdot \Gamma \left( \frac{\alpha + 1}{\gamma} \right)},
\]

(3)

where \( \Gamma(\cdot) \) – is the gamma function.

The solution essence of the inverse problem was reduced to the selection of such parameters \( \alpha, \gamma \) and \( r_{max} \) of the particle size distribution \( n(r) \), at which the scattering indicatrix models best coincided with the experimental results. The mean square deviation of the relative scattered intensity values in the range of scattering angles from 40° to 120° was chosen as a criterion for the correspondence of experimental and theoretical scattering indicators. The justification for limiting the range of scattering angles at which the indicatrix comparison has been carried out is given below.

The computer modeling method of scattering indicatrix is based on the theory of G. Mie [9] and is considered in previous publications of the authors [10, 11]. For a correct comparison of experimental and model scattering indicators, it has been necessary to normalize them. The area under the scattering indicatrix plot in the considered angle range was chosen as the normalized parameter. Such a normalization parameter provides a smaller influence of the measurement error on the result of selecting the function \( n(r) \) parameters, than normalization by a single value of the radiation intensity scattered at a certain angle.

As a result of the comparison, it turned out that the smallest value of the standard deviation is equal to 0.036 rel. units for the following values of the function \( n(r) \) parameters: \( r_{max} = 5 \text{ nm}, \alpha = 2.4, \gamma = 0.3 \). Model and experimental scattering indicatrices for such parameters of the function \( n(r) \) are shown in figure 6. The plot of the restored function \( n(r) \) and the plot of the particle size distribution presented by the manufacturer are shown in figure 7.
**Figure 5.** The radiation scattering indicatrix on Al₂O₃ particles: \( \lambda_1 = 650 \text{ nm} \), horizontal polarization (a), \( \lambda_1 = 650 \text{ nm} \), vertical polarization (b), \( \lambda_2 = 515 \text{ nm} \), horizontal polarization (c), \( \lambda_2 = 515 \text{ nm} \), vertical polarization (d), \( \lambda_3 = 450 \text{ nm} \), horizontal polarization (e), \( \lambda_3 = 450 \text{ nm} \), vertical polarization (f).

3. **Discussions**

The reconstructed particle size distribution function does not necessarily have to correspond to the distribution presented by the manufacturer of the nanopowder. The fact is that nanoscale structures are
agglomerated in a liquid dispersed medium. The largest agglomerates fall to the bottom in the form of sediment, but it can’t be excluded that the agglomerates of several individual particles are small enough to remain suspended in a dispersed medium.

The range of angles considered when comparing model and experimental scattering indicators has been limited for a number of reasons. Figure 8 shows an image of a laser plane in scattered radiation at the camera mounting angle of 150°.

**Figure 6.** The radiation scattering indicatrix on Al₂O₃ particles (the points correspond to the experiment results, and the solid lines correspond to the simulation results): \( \lambda_1 = 650 \) nm, horizontal polarization (a), \( \lambda_1 = 650 \) nm, vertical polarization (b), \( \lambda_2 = 515 \) nm, horizontal polarization (c), \( \lambda_2 = 515 \) nm, vertical polarization (d), \( \lambda_3 = 450 \) nm, horizontal polarization (e), \( \lambda_3 = 450 \) nm, vertical polarization (f).
Figure 7. Particle size distribution: a solid line is a plot of the reconstructed function, the points correspond to the distribution presented by the manufacturer.

Figure 8. Experimental image of the probe laser plane in scattered radiation ($\lambda = 515$ nm), obtained at the camera installation angle $\theta = 150^\circ$.

In the image informative, in addition to scattered radiation in the direction of the receiving system, there is radiation scattered at a different angle and reflected from the far wall of the vessel. By the way the probing radiation is partially reflected from the outlet wall of the vessel and propagates in the medium in the opposite direction. The reflected radiation is also scattered on the particles of the colloidal solution, and if for scattered direct probing radiation the scattering angle is $150^\circ$, then for scattered reflected radiation the scattering angle is $30^\circ$. Of course, the intensity of the reflected radiation is only a few percent of the intensity of the direct probing radiation. But due to the fact that the particles scattering indicatrix is "stretched" forward, the scattered reflected radiation makes a significant contribution to the response value of the camera matrix. Thus, the results obtained at camera mounting angles exceeding $120^\circ$ were excluded when comparing the scattering indicatrix.

To create a colloidal solution physical model, double distillation water has been used. However, even as a result of the double distillation procedure, impurity particles that were visible to the naked eye remained in the water and were detected. The particles were detected when probing a vessel with water with a laser plane. The concentration of these particles was much less than the concentration of aluminum oxide nanoparticles, which were later, added to the water. But it is known that with an
increase in the particle size, the scattering indicatrix stretches in the forward direction. This means that at small scattering angles, impurity particles in a low concentration compared to the nanoparticles concentration can make a significant contribution to the intensity of radiation scattered at small angles. These considerations led to the fact that it has been decided to exclude the results that were obtained at camera installation angles less than 40°.

4. Conclusion

The developed optical electronic setup makes it possible to register radiation scattered by particles of the dispersed phase of a colloidal solution in the range of scattering angles from 5° to 165°. The developed method of the experiment and subsequent results computer processing allows measuring the scattering indicatrix by a colloidal particles ensemble.

The method for reconstructing the particle size distribution function by selecting the parameters of a given model based on a comparison of model and experimental scattering indicators has been developed. A modified gamma distribution has been chosen as a model of the particle size distribution function in this work. The selection of its parameters has been carried out according to the criterion of the smallest standard deviation of the relative scattered intensity in the model and experimental scattering indicatrices for three wavelengths. The particle size distribution function of the aluminum oxide nanopowder was restored, which showed a good correspondence to the distribution presented by the manufacturer.

To confirm the operability of the proposed method for diagnosing colloidal solutions, it is necessary in the future to develop a physical model of a polydisperse particles system, the parameters of which will be known with a sufficiently high degree of accuracy. This will allow taking into account experimental data on scattering at small angles when restoring information about the parameters of the medium under study.

Modification of the optical electronic setup in order to eliminate parasitic illumination of the matrix when registering radiation scattered at large angles is also a promising task. Its solution makes it possible to take into account experimental data on scattering at the mounting angles of the receiving system greater than 120°.

The proposed method for recovering information about the medium under study is also limited by the accepted model of the particle size distribution function and is not universal when solving the inverse problem.

These disadvantages show that it is necessary to carry out serious work so that the proposed method for diagnosing the colloidal solutions parameters could be used in solving scientific or industrial problems. However, the present work proves the validity of the scattering indicatrix as an informative measured parameter in the problems of colloidal solutions diagnostics, and the presented results of the application of the proposed method for determining the parameters of aluminum oxide nanopowder in water are correct.

References
[1] Jakmunee J, Udnan Y, Morrison R, Beckett R, McKinnon I and Grudpan K 2003 Analytical Sci. 19 1495–98
[2] Attota R, Kavuri P P, Kang H, Kasica R and Chen L 2014 Appl. Phys. Lett. 105 163105
[3] Boyd R D, Gunnarsson R, Pilch I and Helmersson U 2014 J. of Phys.: Conf. Series 522 012065
[4] Belicu I C M and Moraru C I 2009 J. of Dairy Sci. 92 1829–39
[5] Nobbmann U and Morfesis A 2009 Materials Today 12 52–54
[6] Mächtle W 1999 Biophysical J. 76 1080–91
[7] Lechner M D 2005 J. of the Serbian Chem. Society 70 361–69
[8] Saponov M V and Skornyakova N M 2019 J. of Phys.: Conf. Series 1421(1) 012017
[9] Mie G 1908 Ann. Phys. 25 377–445
[10] Saponov M V and Skornyakova N M 2017 Scientific Visualization 9(3) 42–53
[11] Saponov M V and Skornyakova N M 2019 Scientific Visualization 11(2) 28–38