Comparison of particle size measurements of some aqueous suspensions by laser polarimetry and dynamic light scattering

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Abstract. The results of the size distributions measurements of the particles of aqueous suspensions of ZnO, CuO, TiO_2, and $BaTiO_3$ by methods of laser polarimetry and dynamic light scattering are considered. These measurements are compared with the results obtained by electron microscopy. It is shown that a laser polarimetry method gives more accurate results for size parameter values more than 1–2.

1. Introduction

Laser techniques allow to determine the particle size of dispersed media remotely, efficiently, and with a high sensitivity [1]. Typically, the size determination is carried out on the assumption that the medium particles are spherical. Therefore, for media with irregular particles, data from these measurements are approximate. Measurement of the scattering matrix (4×4) whose elements are dependent on the refractive index, particle size and shape, in principle allows to determine the characteristic size of the particles considering their shapes. Accounting for the specific features of particle shape is a complex task requiring significant computing resources and practically difficult to realize. Research efforts are currently focused on finding the representative particles that are able to mimic real scattering properties of dispersed media and shape, which can be characterized by two or three parameters [2–5]. Spheroids (ellipsoids of revolution) are among these representative particle shapes. This paper presents the results of determination of particle size distributions of some suspensions obtained by laser polarimetry (LP) and dynamic light scattering (DLS).

2. Materials and equipment

Aqueous suspensions of ZnO, CuO, TiO_2, and $BaTiO_3$ were investigated, and the electron microscopy (EM) images of the particles are shown in figure 1. The effective area of the particles and the ratio of the transverse dimensions were determined from microphotographs. Histograms of particle size distribution are shown in figure 2 (dark bars), where r – radius of a circle with an area equal to the effective area of the particles. The values of the average radius (r_{av}) and standard deviation (σ), which characterizes the width of the distribution, were derived from the histogram. The values obtained are shown in table 1 (columns EM). CuO particles are characterized by strong absorption at a wavelength of 0.63 μm, and the absorption coefficient is $8.98 \cdot 10^4$ cm^{-1}. Particles in other suspensions do not absorb radiation.

The scattering matrices were measured by laser polarimeter [6], where a single-mode He-Ne laser with a wavelength of 0.63 μm and a power of 7 mW was used as a radiation source.

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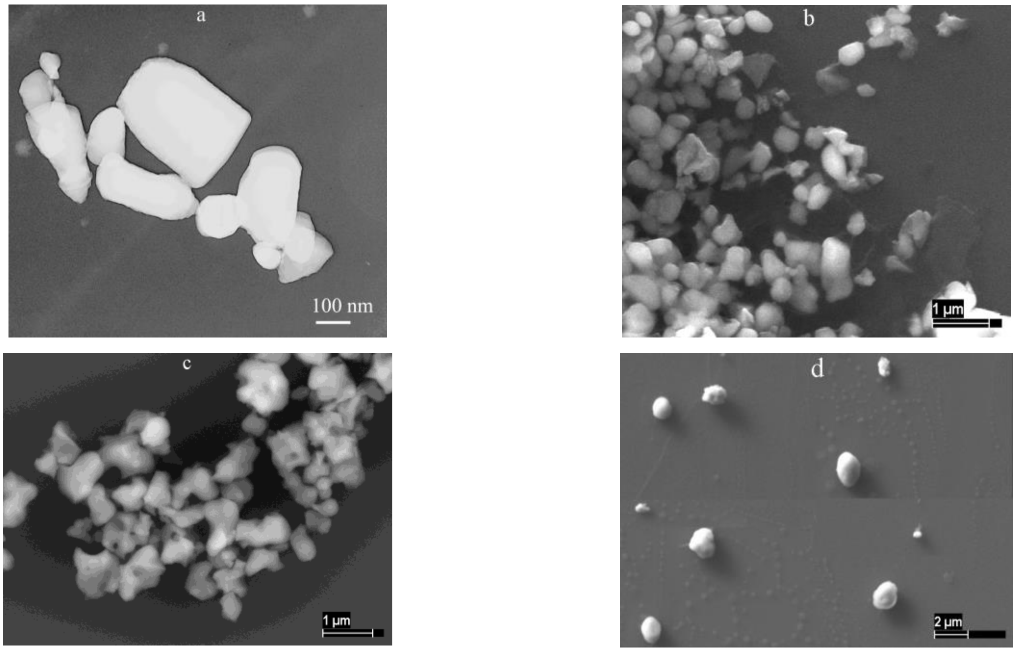

Figure 1. Microphotographs of particles of (a) ZnO, (b) CuO, (c) TiO_2, (d) $BaTiO_3$.

Measurements of the scattering matrices were carried out in the scattering angle range 10°–155°. For a macroscopically isotropic medium that contains identical numbers of randomly oriented scatterers and their mirror-symmetric counterparts, scattering matrix F(4 × 4) has a block-diagonal form [7]. In this case, elements F_{14}, F_{41}, F_{24}, F_{42}, F_{31}, F_{32}, F_{13}, and F_{23} are zero and $F_{12} = F_{21}$, $F_{34} = -F_{43}$. The dependence of element F_{11} on angle of scattering θ describes the scattering indicatrix of the nonpolarized radiation. The measured scattering matrix was represented as a weighted sum of the theoretically calculated scattering matrices of model (spheroidal) particles with different sizes and shapes (aspect ratio *a/b*). The values of the corresponding weights that ensured a minimum of mean square deviations of the theoretical and experimental data determined the sought particle size distribution. The scattering matrices of model particles were calculated using the program that is based on the T-matrix method developed by Mishchenko M I [7] for an ensemble of randomly oriented spheroids. The Levenberg–Marquardt algorithm was used to solve the optimization problem.

The NanoTrac particle analyzer (Microtrac company), whose operating principle is based on the dynamic light scattering method, was also used to determine the particle size distribution. Particle sizes are determined by measuring the spectral density width of the backscattered electric field. Heterodyne detection scheme is employed; radiation reflected from the optode tip is used as a reference.

3. Results of experiment

When recovering the particle size distribution of suspensions according to the measurement of the scattering matrix, best results were obtained by minimizing the sum of squared deviations of the theoretical values of the matrix elements from the experimental values for the diagonal elements, and not for all elements of a block diagonal matrix. Retrieved size distributions are shown in figure 2 (open bars), and the values of the average radius (r_{av}) and standard deviation (σ) are presented in table 1 (columns LP). The results for all except ZnO suspensions can be considered satisfactory. Average radius values are restored with an error not exceeding 30%, for both unimodal and bimodal distributions. The value of σ, which characterizes the width of the distribution, in the case of unimodal distribution is restored with an error not exceeding 10%, and in the case of a bimodal distribution – with an accuracy of 27%.

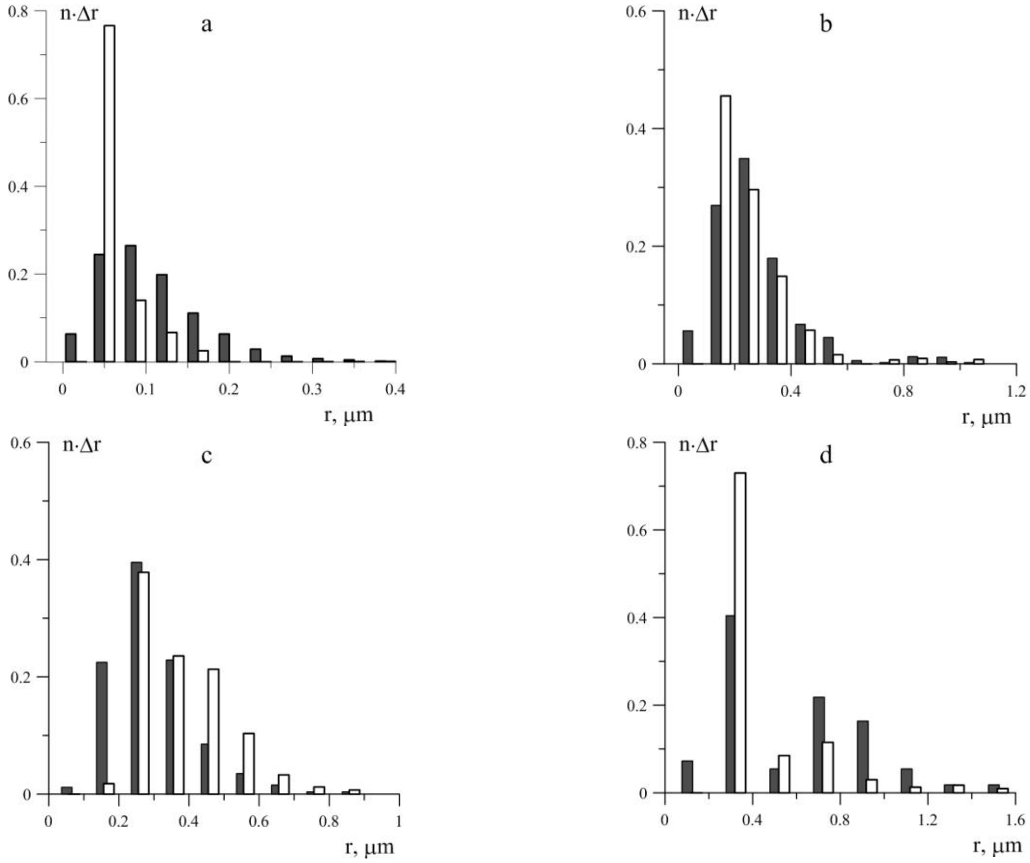

Figure 2. Histograms of particle size distribution in (a) ZnO, (b) CuO, (c) TiO_2, (d) $BaTiO_3$ suspensions. Dark bars are data obtained by EM. Open bars are data obtained by LP.

Table 1. The values of the parameters of the distributions.

Parameter	ZnO			CuO			TiO_2			$BaTiO_3$		
	EM	LP	DLS	EM	LP	DLS	EM	LP	DLS	EM	LP	DLS
r_{av}, μm	0.11	0.064	0.087	0.28	0.25	0.18	0.29	0.37	0.20	0.57	0.42	0.39
σ, μm	0.06	0.03	0.02	0.16	0.15	0.07	0.12	0.13	0.02	0.33	0.24	0.04
$(a/b)_m$	0.66	0.41	-	0.71	0.49	-	0.67	0.61	-	0.76	0.69	-

However, for the ZnO suspension, the distortions were observed in the retrieved distribution manifested in increasing the proportion of fine particles and reduction of the width of the distribution. Such distortions of the retrieved distribution are characteristic for the values of the size parameter $X = 2\cdot\pi\cdot r/\lambda$ smaller than 1–2. Firstly, this is due to the difference in the values of the element F_{11} for irregularly shaped particles and mixtures of spheroids, which can be most easily compensated by adding to the mixture of spheroids a relatively large number of particles of the fine fraction having a small scattering cross section and smooth indicatrix of scattering (dependence $F_{11}(\theta)$). Secondly, dependencies of the matrix elements F_{33}, F_{44} on the scattering angle for media with irregular particles are well enough approximated by the similar dependencies for a mixture of spheroids, while the $F_{22}(\theta)$ dependence is approximated worse. Under optimum conditions, the differences between the dependencies $F_{22}(\theta)$ for a mixture of spheroids and irregular particles are larger than the differences of $F_{33}(\theta)$, $F_{44}(\theta)$. Therefore, the main contribution to the sum of squared deviations of the theoretical and experimental values of the elements F_{22}, F_{33}, F_{44} will be given by a deflection of the element F_{22}. Decrease of particle size and increase of absorption result in F_{22} values approaching unity, in a decrease of the differences of this element for particles of different shapes, and hence in reducing the magnitude of this contribution. Note that the average ratio of the transverse dimensions $(a/b)_m$ is restored more accurately when the sum of squared deviations of the calculated and measured values of the element F_{11} is minimized. These values are 0.71, 0.53, 0.65, and 0.73 for suspensions of ZnO, CuO, TiO_2, and $BaTiO_3$, respectively.

Data obtained by the method of dynamic light scattering (table 1, columns DLS) indicate greater deviation of the average particle size from the size defined with microphotographs, compared with the method of laser polarimetry for all suspensions except ZnO slurry. The recovery of the particle size distribution based on the width measurements of the spectrum of the scattered light is an ill-conditioned mathematical problem. The noise level greatly affects the widths of the obtained distributions, therefore in the case of weakly scattering suspensions, only the position of the distribution maximum is reliably determined. Due to this fact, smaller values of the widths of the distributions are derived by the dynamic light scattering method. The ability to restore bimodal distribution with a particle size ratio corresponding to the maxima of the modes, 1:2, is a limit for this technique (for spherical particles) [1], therefore bimodality of the particle distribution in $BaTiO_3$ suspension was not detected in these measurements. The error in the size determination by dynamic light scattering method for spherical particles is rather low, not greater than 5–10% [1]. The measurement data even for ZnO suspension, which is characterized by the small size parameter value, indicate a greater error (18%). Possible reasons for these differences are related to the fact that the recovery of particle size distributions in the method of dynamic light scattering is carried out on the assumption that the particles are spherical. However, coefficients of translational and rotational diffusion, scattering cross sections, and backscattered intensity may be different for irregularly shaped particles and spherical particles that can change the field correlation function and the spectral density width of the scattered electric field. Trying to correct the data obtained from the ZnO suspension by dynamic light scattering by changing the diffusion coefficients, scattering cross sections, and the backscatter intensity for spherical particles, corresponding values for spheroids did not lead to significant changes in the distribution resulting from the small changes of these parameters. The asymmetry of the particles according to [3] for small size parameter (smaller than 2) also does not lead to a noticeable change in the scattering cross section and the backscattering intensity. Presumably, their change may be caused by the particle's surface roughness, which requires further research.

4. Conclusion

Use of the model of spheroidal scatterers to interpret the results of measurements of the scattering matrix of dispersive media containing non-agglomerated irregular particles allows to restore the particle size distribution for the values of the size parameter greater than 1–2 with satisfactory precision. At lower size parameter values, the restored distribution may exhibit the distortions due to increasing of the fine particle proportion. The dynamic light scattering method for small size parameter (smaller than 1–2) allows to determine the average size of suspension particles more accurately.

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