

Chapter 32

Estimation of Nanoparticles Sizes by Laser Correlation Spectroscopy Methods



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Abstract Analysis of nanoparticles sizes in suspensions is a dramatically important task nowadays because of mainstreaming of nano dispersed liquids. In this paper, we suggest the cross-correlation method and device for nanoparticle size estimating in monodisperse suspensions. It is based on dynamic laser light scattering modified by two-channel detection for reduction of multiple scattering noises. We obtained several experimental cross-correlation and autocorrelation functions for aqueous suspensions of latex microspheres of different diameters. The decay rate of the received cross-correlation functions coincides with the decay rate of autocorrelation functions and determines particles diameter in low-concentrated suspensions. Since the cross-correlation method, in contrast to the autocorrelation method, allows one to study turbid suspensions without dilution, that has great prospects for assessing the dispersion of liquid samples of different degrees of turbidity.

Keywords Cross-correlation · Autocorrelation · Particle size estimating

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32.1 Introduction

The method of dynamic light scattering is currently often used for dispersion analysis of solutions, suspensions, and other liquid media with small suspended particles [1–3]. The classical method of dynamic light scattering, based on the analysis of the autocorrelation function of the laser light scattering signal from the sample under study, allows one to estimate quickly the size distribution of particles in a liquid, the sizes of which can be from several nanometers to several microns [4–7].

The convenience of the dynamic light scattering method is explained by the fact that the optical system does not require calibration using model samples. These advantages of the method make it convenient for laboratory research, as well as for quality control of various areas of production [2, 8, 9].

With all the advantages of the dynamic light scattering method as a powerful tool for the dispersion analysis of liquid media with small particles, it cannot be used to study turbid samples with a high-volume concentration of particles [10]. This is due to the appearance of multiple scattering of light in the sample, that is, light that is scattered sequentially from two or more particles before leaving the cell with the sample and entering the photodetector. It is possible to get rid of the influence of multiple scattering on the measurement results by using the cross-correlation method [11].

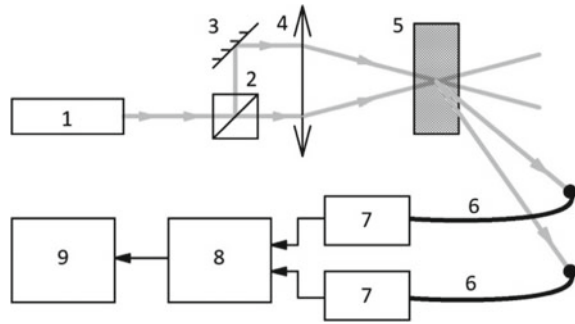
The cross-correlation method consists in simultaneously registering not one scattering signal from the sample, but two at once [12]. Due to the fact that the photodetectors are located very close to each other, the recorded signals have the same useful component created by single scattering, and different noise components created by multiple scattered light [4]. When calculating the cross-correlation function of such signals, the contributions from multiple scattering are suppressed and it is possible to extract a useful signal. Thus, the cross-correlation method allows one to explore turbid liquid samples without diluting them.

We developed an original scheme of a cross-correlation spectrometer, with which we estimated the particle size in a liquid monodisperse sample. Principles of operation of the spectrometer and the results obtained with it for aqueous suspensions with particles of known size are considered in this paper.

32.2 The Principle of the Cross-Correlation Spectrometer Operation

Figure 32.1 shows a cross-correlation spectrometer scheme. This spectrometer uses a two-beam scattering scheme, which implies the presence of two incident beams that intersect in the cell with the sample. Two beams are created by a helium-neon laser [13, 14] with a wavelength of 633 nm, a beam-splitting cube and a mirror, and a collecting spherical lens ensures the intersection of the beams inside the cell. We used a lens with a focal length of 30 cm.

Fig. 32.1 Cross-correlation spectrometer scheme. 1—laser, 2—beam splitter, 3—mirror, 4—collecting spherical lens, 5—cell with a liquid sample, 6—optical fiber, 7—photodetector, 8—analog-to-digital board, 9—computer



When laser radiation is scattered from a large number of particles randomly moving in a fluid, a speckle light field arises around the cell. The average size of single-scattering speckles depends on the laser wavelength, the distance from the scattering plane to the spectral observation plane, and on the size of the illuminated area. In our case, this size is the diameter of the beams inside the cell [15]. Moreover, the smaller the diameter of the illuminated area, the larger the speckle size [16, 17].

Light enters the input aperture of two multimode optical fibers with a core diameter of 50 μm and is detected by photodetectors [18–20]. An analog-to-digital scheme digitizes the scattering signals, after which they enter the computer and are processed.

The dynamic light scattering method uses one incident beam and one photodetector, so the size of speckles does not play a big role. Since both the dynamic light scattering method and the cross-correlation method, the incident beams are focused inside the cuvette, as a result of which a constriction is obtained there, a sufficiently large size of single-scattering speckles is provided for recording the scattering signal by one photodetector with high signal-to-noise ratio [21, 22]. But in the cross-correlation method, it is necessary that the same useful signal [10] gets to the input aperture of the optical fibers, that is, that one speckle falls directly into two optical fibers. Therefore, the size of speckles in the cross-correlation method plays a decisive role.

Optical fibers are arranged vertically one above the other in a plane perpendicular to the plane of the incident beams [23]. With a distance between the centers of the optical fibers of 100 μm [24], the average size of the single-scattering speckles in the vertical direction turned out to be 150 μm . To increase the level of the useful signal relative to the noise level [21, 25, 26], we placed a cylindrical collecting lens with a focal length of 14 cm close to the cell, which compresses the speckle field horizontally. We placed the optical fiber in the focus of this lens.

In other cross-correlation schemes, to record the intensity of the scattered light at two closely spaced points a translucent mirror is used. Next, one photodetector registers transmitted light, and the other—reflected. In such a scheme, a very accurate adjustment is required, which creates a problem when assembling a cross-correlation spectrometer. In our scheme, due to the use of a multi-fiber

patching cord, it is possible not only to receive light at two points at a distance of 100 μm from each other, but also to increase this distance, if necessary, in increments of 100 μm , using signals from other fibers of this patching cord.

In the presented cross-correlation setup, we refused to use the correlator. Thanks to the digitization of scattering signals by an analog-to-digital board and sending them to a computer, it becomes possible to improve the signal processing algorithms and change the counting frequency. In the future, this will help to choose the optimal counting frequency and calculation procedure.

32.3 Results

Figures 32.2 and 32.3 show the experimental autocorrelation and cross-correlation functions of scattering signals for four samples. Black color on the graphs indicate theoretical dependencies, which are described by the formula [11]

$$g(\tau) = Ae^{-2\Gamma\tau}. \quad (1)$$

Here $g(\tau)$ is the normalized temporal autocorrelation or cross-correlation function of scattering intensity, A is the proportionality coefficient, Γ is the quantity determined by the particle diffusion coefficient and the scattering vector module in accordance with the formula [4]

$$\Gamma = Dq^2, \quad (2)$$

where q is the modulus of the scattering wind defined by the formula [4]

$$q = (4\pi n/\lambda) \sin(\theta/2), \quad (3)$$

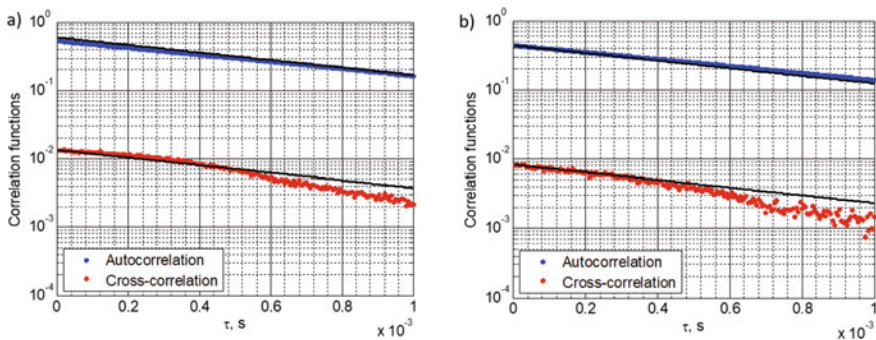


Fig. 32.2 Autocorrelation and cross-correlation functions for aqueous monodisperse suspensions of latex microspheres with a diameter 300 nm for the concentration of 5 mkl **a** and 1.25 mkl **b** of microspheres per 1 ml of water

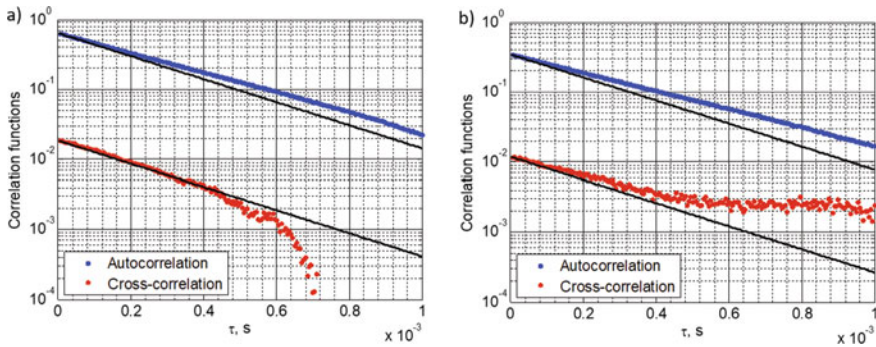


Fig. 32.3 Autocorrelation and cross-correlation functions for aqueous monodisperse suspensions of latex microspheres with a diameter of 100 nm for the concentration of 10 mkl **a** and 2.5 mkl **b** of microspheres per 1 ml of water

and D is the diffusion coefficient associated with the particle diameter d by the formula [4]

$$D = k_B T / (3\pi\eta d). \quad (4)$$

In Eqs. (3) and (4), n is the refractive index of the solvent, λ —is the wavelength of laser light, θ is the scattering angle of 90° , k_B —is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solvent.

In Figs. 32.2 and 32.3, we see that in the initial section, the autocorrelation and cross-correlation functions coincide with the theoretical ones, while the auto-correlation and cross-correlation functions for one sample coincide with the decay rate Γ . For samples of different concentrations with particles of the same size, the decay rates of the correlation functions coincide. At the same time, for samples with particles of different sizes, the decay rates of the correlation functions are different, which indicates the possibility of estimating the particle size in the sample by the decay rate of the autocorrelation or cross-correlation function using Eqs. (3)–(4).

The correlation functions obtained as a result of measurements with monodisperse samples can be approximated by smooth curves in accordance with Eq. (1) only for the delay time from 0 to about 0.2 μs ; then, as the delay time increases, noise begins to dominate more and more [30], which may be due to insufficient success matched parameters, such as the focal lengths of the lenses and the distance between the receiving optical fibers. In the future, it is planned to investigate this issue and select the parameters so that the correlation functions are less noisy.

In Figs. 32.2 and 32.3, one of the cross-correlation functions differs noticeably from the other three. This can be caused by the fact that the noise changes from implementation to implementation; therefore, for large values of the delay time τ , the behavior of the function is random. Nevertheless, in the initial section of the

curve, the cross-correlation function is weakly noisy and particle size can be estimated from it.

From the experimental results it turns out that the particle size in a monodisperse sample can be estimated from the decay rate Γ , having obtained its value by approximating the experimental function by a function of the form (1). Moreover, the value of Γ in cross-correlation should depend on the average particle size and should not depend on their concentration, which makes the cross-correlation method the most preferable among optical methods of analysis of variance. With its help, highly turbid samples can be examined without dilution.

32.4 Conclusion

The difference between the developed scheme and other similar ones is that the receiving scattered radiation system is simplified, and instead of the correlator, an analog-to-digital board and a computer are used. Due to these changes, we tried to improve the cross-correlation scheme, significantly reducing the sensitivity of the receiving system to the accuracy of positioning of elements and making the signal processing block more universal.

Due to the fact that the cross-correlation function is used in the cross-correlation method, the contributions from multiple scattering in the sample, which creates noise, are excluded from consideration [27]. In the presence of multiple scattering, the dynamic light scattering method cannot be used due to incorrect results, while the cross-correlation method can be used [11]. This gives the cross-correlation method a great advantage in the study of turbid liquid media without dilution.

The results obtained showed the fundamental possibility of estimating particle size by the methods of autocorrelation and cross-correlation. In the future, it is planned to identify those limits of application of the cross-correlation method in size and concentration when autocorrelation is unsuitable for analysis of variance, while cross-correlation can be successfully applied. This task is quite complicated, but its solution will reveal the area of the most effective application of the method.

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