Design and metrological characteristics of native analyzers Photocor for measuring the particle size and zeta-potential of nanodispersed systems

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Abstract. Particle size and zeta potential analyzers Photocor have been developed and are mass-produced by the Russian company Photocor. The principle of operation of the analyzers is based on the dynamic light scattering method. Photocor instruments have a certificate of type approval of measuring instruments and are included in the Russian Federal Information Fund for Ensuring the Uniformity of Measurements.

1. Introduction
For several decades, nanoparticles have been increasingly studied and used in a wide variety of scientific and industrial fields. Obviously, some of the main parameters that determine the properties of nanodispersed systems are their geometric characteristics (size and shape), concentration, interaction characteristics, as well as the stability and resistance of such systems to external influences. In this regard, instruments that allow measuring these parameters are becoming more and more in demand both for scientific research and for solving technical and production problems. Methods of static and dynamic light scattering are ideal for creating corresponding measuring instruments on their basis. It should be noted that the first research institution in Russia was the Federal State Unitary Enterprise All-Russian Scientific Research Institute of Physicotechnical and Radio Engineering Measurements (FSUE VNIIFTRI) where, already in 1971, the country's first dynamic light scattering device was created [1]. The actual successor to the research carried out at that time is the Limited Liability Company Photocor (Photocor company), which today occupies a prominent place in the market of such devices.

2. Physical foundations of the dynamic light scattering method
The first devices operating on the basis of the dynamic light scattering method appeared in 1961. Synonyms for the name of the method - photon correlation spectroscopy and quasi-elastic light scattering - are used less frequently. Dynamic light scattering is also used to measure the flow rates of liquids and gases. Traditionally, this variant of the method is called laser Doppler anemometry (LDA). In particular, this configuration of the dynamic light scattering (DLS) method is used to measure the electrophoretic mobility of nanoparticles, from which the zeta potential is calculated.

The physical foundations of the method are quite simple and beautiful [2]. As an example, consider the diffusion of monodisperse nanoparticles dispersed in a liquid. Chaotic Brownian motion of dispersed particles leads to microscopic fluctuations of their local concentration and corresponding local inhomogeneities of the refractive index of the medium. When a laser beam passes through such a medium, some of the light will be scattered by these inhomogeneities. The fluctuations in the scattered light intensity will correspond to fluctuations in the local concentration of dispersed particles.

Information on the particle diffusion coefficient is contained in the time-dependent correlation function of intensity fluctuations. The time autocorrelation function, according to the definition, has the following form:

\[ G(\tau) = \langle I(0)I(t-\tau) \rangle = \lim_{\tau \to -\infty} \frac{1}{\tau} \int_0^{\tau} I(t)I(t-\tau)dt \] (1)
where the intensity $I$ has different values at times $t$ and $(t-\tau)$. $t_m$ is the integration time (accumulation time of the correlation function). Obviously, at $\tau = 0$, the autocorrelation function is equal to the rms scattering intensity $<I^2>$. For infinite time, there is no correlation, and the autocorrelation function is equal to the square of the average scattering intensity:

$$G(\tau) = \langle I(0)I(t-\tau) \rangle = \langle I(0) \rangle \langle I(t-\tau) \rangle = \langle I \rangle^2$$

(2)

According to Onsager's hypothesis, the relaxation of microscopic fluctuations of concentration to an equilibrium state can be described by Fick's first law (diffusion equation):

$$\frac{\partial c(r,t)}{\partial t} = -D \nabla c(r,t)$$

(3)

where $c(r,t)$ is the concentration and $D$ is the diffusion coefficient of particles.

It can be shown that in such a system the autocorrelation function of the light scattering intensity decays exponentially with time, and the characteristic relaxation time is uniquely related to $D$. The correlation function of the scattered light intensity (for the case of square-law detection) has the form:

$$G(\tau) = a \exp\left(-\frac{2\tau}{t_c}\right) + b$$

(4)

where, in accordance with the solution of the diffusion equation, the inverse correlation time is:

$$\frac{1}{t_c} = D_q^2$$

(5)

The amplitude of the wave vector of light scattered by concentration fluctuations is described by the expression:

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

(6)

In expressions 4-6: $a$ and $b$ are experimental constants, $n$ is the refractive index of the liquid where disperse particles are suspended, $\theta$ is the scattering angle, $\lambda$ is the wavelength of laser light.

The $t_c$, $a$ and $b$ values can be found by approximating the measured correlation function with a theoretical exponential function. For spherical noninteracting particles, their size can be calculated using the Einstein-Stokes formula:

$$D = \frac{k_B T}{6\pi \eta R}$$

(7)

where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $\pi$ is mathematical constant, equal to 3.14159, and $\eta$ is the shear viscosity of the liquid where particles with radius $R$ are suspended.

It is clear from the Einstein-Stokes formula that dynamic light scattering can be used to solve the problem of measuring the viscosity of a liquid. For the case of light scattering by dispersed particles of a known size, the measured characteristic time of fluctuations makes it possible to calculate the viscosity.
of the liquid. Moreover, in this case, we can talk about the micro-rheological viscosity, which, in principle, may differ from the viscosity measured on a macroscopic scale.

The problem of approximating experimental data is simple for the considered case of light scattering by monodisperse spherical particles. For polydisperse samples, the interpretation of experimental data becomes more complicated. For a really achievable measurement accuracy, only two or three parameters of a monomodal particle size distribution can be obtained: the average particle size, width and distribution asymmetry. For multimodal polydisperse systems, we can talk about the average particle size of each component and the relative contribution of each component to the scattering intensity. It is important to note that two close particle sizes of a polydisperse system will be resolved as separate components only if their sizes differ from each other by at least 1.5–2 times.

The great advantage of light scattering techniques is that they are absolute. During the measurement, the diffusion coefficient of Brownian particles is directly determined, which is uniquely related to the size of these particles. Thus, light scattering methods do not require any preliminary calibration to obtain a measurement result. Such methods allow obtaining high measurement accuracy and can be a good basis for creating reference instruments.

3. Design features of dynamic light scattering instruments.

In the operation of an instrument using the dynamic light scattering method, the most important is the method of measuring the spectrum of the scattered light. So far, there are no optical spectrum instruments with sufficient resolution that would allow measuring narrow spectra of scattered light fluctuations. Therefore, the decisive finding in the practical implementation of the dynamic scattering method was the use of light heterodyning methods. In this case, the envelope of the scattered light spectrum is transferred from the optical frequency to the low-frequency region, where there are analyzing instruments with sufficient resolution. A necessary condition for effective heterodyne conversion of the optical spectrum is to ensure the coherence of the scattered light with a sufficient signal-to-noise ratio of the received optical signal.

To fulfill these conditions, the aperture of the photodetector is chosen very small, the characteristic linear size of the scattering volume is usually 50 ... 100 µm. As a result, for effective reception of such low scattered light intensities, it is necessary to use a photodetector operating in the photon counting mode and a multichannel signal correlator. The correlator measures an auto- or cross-correlation function, which in terms of the information received is equivalent to a spectral function.

The most suitable light source is a gas or diode semiconductor laser. The laser beam is easily focused into the scattering volume and allows the required scattering intensity to be obtained.

The measurement result is the second-order correlation function - the correlation function of the scattered light intensity fluctuations. To calculate the characteristic relaxation time of fluctuations and then calculate the diffusion coefficient and particle size, it is necessary to find the initial correlation function of the first order, i.e. solve the inverse scattering problem. The solution to the inverse problem is trivial only for the monodisperse case, when light was scattered by particles of only one size. In the case of a polydisperse particle size distribution, the inverse problem becomes incorrect.

Ill-posed problems have a non-unique and unstable solution. This instability takes place in relation to even small input disturbances, to small measurement deviation. Minor deviation in the measurement of the correlation function can lead to different resulting distributions. To solve such problems, special regularization methods are used.

A noticeable limitation of light scattering methods is the need for sufficient transparency of the test object for the light used. In some cases, this limitation can be overcome. Firstly, this can be done by choosing a light source with a wavelength for which the transparency of the research object is sufficient to obtain correct measurement results. Secondly, it is possible to use special measurement geometries, for example the so-called backscatter geometry. The scattered light is collected from the near-wall region of the entrance of the laser beam into the liquid under study. For correct measurements, a laser beam penetration depth of about 0.1 mm is sufficient. This method is successfully applied in many studies of opaque systems, such as dyes, solutions of asphaltenes, oil, etc. The backscattering geometry
significantly improves the quality of particle size measurements under conditions of high level of multiple scattering.

4. Photocor instruments.

The Photocor company develops and manufactures equipment for the analysis of dispersed particles in liquids using dynamic and static light scattering methods. The instruments allow the determination of particle size, zeta potential and molecular weight in the nanometer and submicron range of sizes. These parameters are relevant both for fundamental and applied research in various fields of science, and for the control and management of technological processes in modern industries [3].

Photocor instruments are designed and manufactured in Russia. The originality of technical solutions and copyright for manufactured instruments are protected by a number of patents [4-10]. The instruments fully comply with modern standards for the dynamic light scattering method. The instruments allow measurements by static and dynamic light scattering methods in a wide range of scattering angles. The instruments are effective for traditional physical and chemical research, as well as for applications in nanotechnology, biochemistry, and biophysics. Two models from the manufactured range of instruments are shown in Fig. 1. In this case, the analyzing instrument must work in real time. From the point of view of a simpler technical implementation, a digital multichannel signal correlator is used as an analyzer.

The compact rigid design of the Photocor instruments makes it possible to dispense with the use of a special optical table. The main technical characteristics of the instruments are shown in Table 1.

![Figure 1. Pictures of Photocor Complex (a) and Photocor Compact (b) instruments](image)

**Table 1. Technical characteristics of the Photocor instruments.**

| Measuring range          | Particle diameter: 0.5 nm to 10 μm  
|                         | Diffusion coefficient: $10^{-5} \ldots 10^{-10}$ cm²/s  
|                         | Molecular weight: 1000 Da \ldots 1000 MDa  
| Methods for measuring zeta potential | Electrophoretic light scattering (ELS), Phase Analysis Light Scattering (PALS)  
| Sample volume          | Particle size measurement: 50 μl to 10 ml  
|                         | Zeta potential measurement: 1 ml to 2 ml  
| Scattering angles      | $10^° \ldots 150^°$, deviation $0.01^° / 20^°, 90^°, 160^°$, 
|                         | fine adjustment of the scattering angle is provided  
| Photodetector          | A high sensitive photon counting system based on an avalanche photodiode. It is possible to measure various polarizations of the scattered light.  

5. Metrological support of instruments Photocor

The dynamic light scattering method is supported by Russian and international standards [11-15]. Photocor analyzers have a certificate of type approval of measuring instruments and are included in the Russian Federal Information Fund for Ensuring the Uniformity of Measurements. Type approval tests were carried out at the FSUE VNIIFTRI, which also provides services for the primary and periodic verification of Photocor instruments.

The choice of a dispersion system for calibration and verification of instruments for measuring nanoparticle sizes by dynamic light scattering is not an easy task. Integral characteristics of a dispersed system, such as the average size and numerical concentration, give a correct idea of the dispersion system only if it is a system of particles of the same shape, composition and size. If this is not the case, then for a correct description of such a system, it is necessary to obtain the distribution over the corresponding parameter. In this case, the distribution can be numerical, mass or volumetric. It is often difficult to obtain the exact shape of the distribution, but at the same time it is possible to describe the distribution not only by the position of the maximum, but also by the value of the variance and asymmetry.

Obviously, for verification of DLS instruments, it is desirable to use monomodal spherical particles dispersed in dust-free liquids at concentrations that provide single scattering of light. Monodisperse polystyrene latexes dispersed in bidistilled water are good enough reference for checking DLS instruments.

All manufactured instruments are verified in the Photocor laboratory using certified reference materials, additionally controlled by the Malvern ZETASIZER instrument available in the laboratory. As an example, Fig. 2 shows the results of the initial verification of the Photocor Compact-Z, serial number 195243, by successive particle size measurements of certified monodisperse polystyrene latex reference materials supplied by Thermo Scientific: 3040A (40 nm), 3050A (50 nm), 3450A (450 nm).

![Figure 2. Results of measurements of certified reference materials on the instrument Photocor Compact-Z, serial number 195243](image-url)
The Figure 2 shows the relative deviations of the measured values of the diameters of three certified reference materials for 10 successful measurements for each reference.

6. Conclusion
Over the past quarter century of the existence of the Photocor company, more than 200 dynamic light scattering instruments have been produced. These instruments have been successfully used in laboratories around the world and shown their high reliability and simplicity of use. Currently, the company is working on the development of new light scattering instruments. One type of them will be a nanoparticle size and zeta potential devices using a promising method of real-time optical analysis of nanoparticle tracks. Other type will be a universal multispectral fluorescent device for monitoring biological particles in liquids and gases.

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