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THE HIGH-PERFORMANCE LASER ELS METHOD FOR ANALYZING THE AGGREGATION STABILITY IN COLLOIDAL SOLUTIONS OF NANOPARTICLES

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Abstract. In the paper, modification of the electrophoretic light scattering (ELS) method for improving an accuracy of determining the electrophoretic mobility and zeta potential of nanoparticles in colloidal systems has been put forward. The modification included the creation of an original experimental setup operating in the heterodyne mode using a multimode fiber at the input of the recording unit, an increase in the signal-to-noise ratio of the system, and also an expansion of ranges of nanoparticles' key parameters: sizes, electrical conductivity, concentration in solution. The theoretical substantiation for processing the scattering signal of polydisperse colloidal solutions of nanoparticles and calculating the electrophoretic mobility and zeta potential of colloidal systems was given. The high accuracy of the measured parameters was achieved, in comparison with the data obtained from the ZetaSizer Nano commercial device.

Keywords: zeta potential, electrophoretic mobility, electrophoresis, dynamic light scattering, heterodyne mode, colloids, nanoparticles

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ВЫСОКОЭФФЕКТИВНЫЙ МЕТОД ЛАЗЕРНОГО ЭЛЕКТРОФОРЕТИЧЕСКОГО РАССЕЯНИЯ СВЕТА ДЛЯ АНАЛИЗА АГРЕГАЦИОННОЙ УСТОЙЧИВОСТИ КОЛЛОИДНЫХ РАСТВОРОВ НАНОЧАСТИЦ

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Аннотация. В работе предлагается модификация метода лазерного электрофоретического рассеяния света для повышения точности определения электрофоретической подвижности и дзета-потенциала наночастиц в коллоидных системах. Модификация включает создание оригинальной экспериментальной установки, работающей в гетеродинном режиме с применением многомодового волокна на входе регистрирующей части, увеличение отношения сигнал/шум системы, а также диапазонов ключевых параметров наночастиц: их размеров, электропроводности и концентрации в растворе. Приводится теоретическое обоснование для обработки сигнала рассеяния полидисперсных коллоидных растворов наночастиц, а также расчета электрофоретической подвижности и дзета-потенциала коллоидных систем. Достигнута высокая точность параметров, измеренных на созданной установке, по сравнению с результатами, полученными на коммерческом приборе ZetaSizer Nano.

Ключевые слова: дзета-потенциал, электрофоретическая подвижность, динамическое светорассеяние, гетеродинный режим, коллоидный раствор, наночастица

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Introduction

The stability of colloidal nanoparticle solutions is an important issue for consideration in colloidal chemistry [1–3]. In particular, it is crucial to accumulate data on the aggregation and sedimentation properties of gold and copper nanoparticles used in catalysis, optical, sensor and electronic devices [2]. Furthermore, copper and gold nanoparticles have bactericidal and antimicrobial properties, so they have potential for applications as therapeutic nanomedicines; data about the sizes of nanoparticles, their surface charge, stability and behavior during agglomeration should be obtained to develop these medicines.

The zeta potential depending on the properties of the initial system is used to characterize the stability of colloidal nanoparticle solutions [4]. This parameter can be calculated based on the existing theoretical models using the measured value of electrophoretic mobility. The values of the zeta potential are obtained using various methods: optical, electrokinetic and acoustic. The most widespread method is laser-Doppler electrophoretic light scattering (ELS), making it possible to obtain the parameters of an object quickly and noninvasively.

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However, the laser devices commercially available as zeta potential analyzers generally have a number of drawbacks:

as electrolytic process evolves in the dispersive medium with sufficiently high magnitudes of the electric field (over 150 V/cm), gas bubbles appear near the electrodes; they can then enter the scattering volume and distort the results;

the accuracy of the results can be considerably reduced because there are no procedures for monitoring the temperature and the viscosity of the given solution;

polarization of electrodes under prolonged exposure to an electric field can also produce errors; mono- and polydisperse solutions with high electrical conductivities (over 4 mS/cm) are characterized by large measurement errors (over 50%);

because such parameters such as applied voltage, number of measurements and particle size distribution cannot be adjusted, it is difficult to control the stability of colloidal particles.

In view of these drawbacks, the existing laser-Doppler ELS method should be further refined to increase the measurement accuracy for electrophoretic mobility and zeta potential of mono- and polydisperse colloidal nanoparticle solutions.

The goal of this study consisted in describing and validating a more effective technique for laser Doppler electrophoretic light scattering we have developed, allowing to analyze the aggregation stability of mono- or polydisperse colloidal nanoparticle solutions.

The technique was modified by introducing an original experimental setup operating as a heterodyne detector with multimode fiber at the input to the detector. As a result, the signal-to-noise ratio of the system is increased, providing wider distribution ranges for particle size, electrical conductivity of the samples and particle concentration in the solution.

Analysis of electrokinetic parameters of nanoparticles using autocorrelation functions

Colloidal nanoparticles in an electric field move from one electrode to another with a certain velocity. As these nanoparticles are exposed to laser radiation, a dynamic speckle pattern appears. If we register the dynamics of changes in the intensity of the speckle pattern formed, then it becomes possible to draw Conclusions about the electrokinetic properties of nanoparticles can be drawn by monitoring the variations in the intensity of the speckle pattern produced.

The dynamics of fluctuating colloidal systems can be traced by analyzing the frequency spectrum $\langle \Delta E_s(\omega) \rangle$, i.e., the fluctuations of some scattering signal $E_s(t)$ (ω is the frequency of the fluctuations in the photocurrent signal).

Correlational analysis is used to analyze the photocurrent spectrum, calculating the time-dependent autocorrelation function (ACF) of signal fluctuations with the following form:

$$G^{(1)}(\tau) = \langle E_s(0)E_s(\tau) \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T E_s(t)E_s(t+\tau)dt, \quad (1)$$

where τ , s, is the range of the correlation characterizing the fluctuations in the system; t , s, is the time; T , s, is the time range for which the signal was recorded.

The field of a scattered light wave is generally written as

$$E_s(t) = \sum_j A_j e^{i\varphi_j} e^{-i\omega_0 t}, \quad (2)$$

where A_j , V/cm, is the amplitude of the field scattered by the j th diffuser; ω_0 , rad/s, is the frequency of the laser radiation source; φ_j , rad, is the corresponding phase of the field.

Substituting the magnitude of the field to the ACF, we obtain:

$$G^{(1)}(\tau) = \left\langle \sum_j A e^{-i\mathbf{q}r_j(0)} \sum_j A e^{i\mathbf{q}r_j(\tau)} \right\rangle, \quad (3)$$

where \mathbf{q} is the scattering wavevector.

If there is no interaction between the particles, the ACF is written as

$$G^{(1)}(\tau) = N|A|^2 \left\langle e^{-iq(r_j(\tau) - r_j(0))} \right\rangle = N|A|^2 \int P(r, \tau) e^{iqr\tau} d^3r, \quad (4)$$

where N is the number of particles, $P(r, \tau)$ is the probability of finding a particle at position r and in the correlation range τ .

The correlation function of intensity fluctuations in the experiment on dynamic light scattering follows the expression

$$G^{(2)}(\tau) = \langle I(t)I(t + \tau) \rangle. \quad (5)$$

The relationship between the autocorrelation functions of intensity and field takes the form:

$$I(\omega) = \frac{1}{2\pi} \int_0^\infty G(\tau) e^{-2\pi i \omega \tau} d\tau, \quad (6)$$

In this case, the frequency spectrum $I(\omega)$ and the correlation function are related by a Fourier transform formulated as

$$I(\omega) = \frac{1}{2\pi} \int_0^\infty G(\tau) e^{-2\pi i \omega \tau} d\tau, \quad (7)$$

where ω , rad/s, is the fluctuation frequency of the photocurrent signal.

The correlation function $G(\tau)$ is described by the following expression:

$$|G^{(1)}(\tau)| = ae^{-\Gamma\tau} + b, \quad (8)$$

where a , b are constants; Γ , s^{-1} , is diffusion broadening of the spectrum.

If we approximate expression (8), we obtain the formula

$$g^{(1)}(\tau) = \int_0^\infty F(\Gamma) e^{-\Gamma\tau} d\Gamma, \quad (9)$$

where $F(\Gamma)$ is the contribution from the component of the radiation scattered by particles of the same size to the total intensity [6]; on the other hand,

$$\Gamma = \frac{1}{t_c} = Dq^2, \quad (10)$$

where D , m^2/s , is the diffusion coefficient.

Thus, the ACF for scattered light takes the form

$$G(\tau) = Ae^{-q^2 D \tau}. \quad (11)$$

The heterodyning technique is applied to detect the particle velocity. The scattered radiation is mixed with a reference laser beam in this mode. Then the total field amplitude is expressed as

$$E(t) = E_l(t) + E_s(t) = E_0 e^{-i\omega_0 t} + E_s(t). \quad (12)$$

The concentration fluctuations are taken as equivalent to the probability density of the particle position within the dynamic light scattering approach, and can be described by Fick's first law [6]:

$$\frac{\partial P(r, \tau)}{\partial \tau} = D \nabla^2 P(r, \tau). \quad (13)$$

The probability of finding a particle at position r in the correlation range τ with an electric field applied can be calculated using the following expression [7]:

$$\frac{\partial P(r, \tau)}{\partial \tau} = D \nabla^2 P(r, \tau) \pm v \frac{\partial P(r, \tau)}{\partial x}. \quad (14)$$

The second term in this expression can be either negative or positive, depending on the direction of the particle's motion in the electric field. Eq. (14) is solved using the Fourier transform, yielding a Gaussian distribution function [7]:

$$P(r, \tau) = \left(\frac{1}{4\pi D\tau} \right)^{3/2} e^{-\left[\frac{(x \pm \mu E\tau)^2 + y^2 + z^2}{4D\tau} \right]}, \quad (15)$$

where μ , $\mu\text{m}\cdot\text{cm}/(\text{V}\cdot\text{s})$, is the electrophoretic mobility; E , V/cm , is the intensity of the electric field applied.

If we substitute expression (15) into equality (4) and take into account that particles in an electric field move with the following velocity to an oppositely charged electrode [8]:

$$v = \mu E, \quad (16)$$

then it is possible to calculate the ACF [9], which takes the form

$$G^{(1)}(\tau) = N |A|^2 e^{-i\omega_0\tau} e^{-iqv\tau \cos \theta / 2} e^{-q^2 D\tau}. \quad (17)$$

The correlation function in an electric field (see expression (17)) is modulated by a cosine function whose period is determined by the electrophoretic mobility (EPM) of particles. The latter can be calculated for a monodisperse solution by applying a simple expression

$$\mu = \frac{2\pi}{E\Delta t q \cos \theta / 2}, \quad (18)$$

where Δt , s, is the period of ACF fluctuations; θ , deg, is the detection angle of scattering.

After the EPM is obtained, it can be converted to zeta potential by the formula

$$\zeta = 3 \frac{\mu\eta}{2\varepsilon\varepsilon_0 f(\kappa R)}, \quad (19)$$

where κ , nm^{-1} , is the inverse screening length; R , nm, is the particle radius; $f(\kappa R)$ is the Henry function (the product κR is called the equivalent radius, or Debye number); η , $\text{Pa}\cdot\text{s}$, is the viscosity; ε is the permittivity; ε_0 , F/m , is the vacuum permittivity.

Notably, the value $f(\kappa R \rightarrow \infty) = 3/2$ correspond to particles larger than 200 nm suspended in water, while $f(\kappa R \rightarrow 0) = 1$ for particles smaller than 200 nm suspended in strong electrolytes.

The electrophoretic mobility and zeta potential of polydisperse solutions were estimated by an algorithm developed earlier, allowing to calculate the power spectral density of the photocurrent via fast Fourier transform. The power spectral density of the photocurrent for polydisperse systems follows the expression

$$I(\omega) = \sum_{i=1}^n N A_i^2 \frac{D_i R^2}{(\omega - \omega_0 \pm q v_i)^2 + (D_i q^2)^2}, \quad (20)$$

where i is the number of the diffuser; A_i , V/cm , is the amplitude of the field scattered by the i th diffuser, D_i , m^2/s , is the diffusion coefficient of the i th diffuser, v_i , m/s , is the velocity of the i th diffuser.

This spectrum takes the form of a Lorentzian curve shifted from zero frequency to $\Delta\omega$, where the shift is expressed as

$$\Delta\omega = 2\pi\Delta f = q\vec{v} = qv \cos \theta / 2. \quad (21)$$

Knowing this value, we can calculate the particle velocity with an electric field applied:

$$v = \frac{2\pi\Delta f}{q \cos \theta / 2}. \quad (22)$$

The corresponding EPM value can be calculated by Eq. (16):

$$\mu = \frac{\Delta f \lambda_0}{2\pi n E q \cos \theta / 2}. \quad (23)$$

Improved setup for laser-Doppler electrophoretic light scattering

Fig. 1 shows our modified measurement setup for electrophoretic light scattering with improved efficiency.

Radiation source 1 is a laser module with distributed feedback; it has the following parameter values:

$\Delta f < 300$ GHz,

RIN (relative intensity noise) is less than 150 dB/Hz

a distributed Bragg reflector laser EYP-DBR-0633-00010-2000- BFW01-0000 with a power of 10 MW and a wavelength of 630 nm is used.

The wavelength of laser radiation in the selected band was chosen so that its absorption by the given samples was minimal.

The radiation from source 1 passes through aperture 2 to narrow the laser beam and is divided into incident and reference beams using corner cube 3 to implement heterodyne reception. Collecting lens 5 is used to focus the incident radiation into cuvette 6 containing the colloidal system, where platinum electrodes are placed. A DC voltage from source 7 is supplied to the electrodes (the current can be varied). The reference beam passes through fiber modulator 4, mixes with scattered radiation and is recorded by photomultiplier tube (PMT) 9.

An important characteristic of the setup is that the measurement system uses multimode optical fiber 8 for transmitting scattered radiation to the PMT, making detection much simpler (as there is no need to configure a system of lenses, mirrors and holes to direct radiation to the entrance aperture of the PMT).

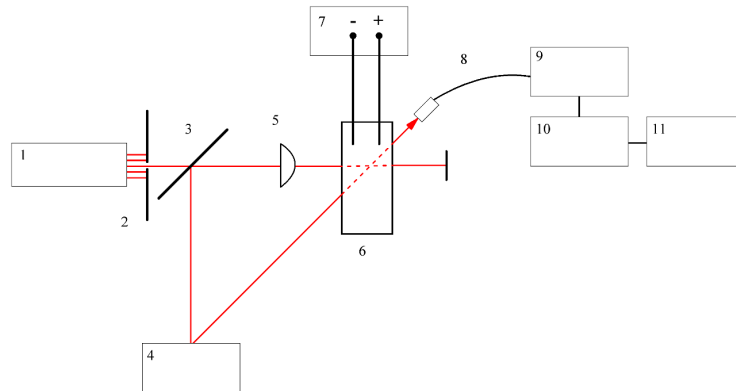


Fig. 1. Measurement setup for laser-Doppler electrophoresis:

laser module 1; aperture 2; corner cube 3; fiber modulator 4; collecting lens 5; cuvette 6 with colloidal system; DC power source 7; multimode fiber 8; PMT 9; ADC 10; computer 11; the path of the laser beam is marked by a red line

As a coherent laser beam probes the colloidal solution, light is scattered by an ensemble of particles, with a speckle pattern simultaneously appearing in the far field, where the coefficient D_1 should be much greater than unity [10].

This value of D_1 follows from the formula

$$D_1 = \frac{\lambda z}{d^2}, \quad (24)$$

where λ is the incident radiation wavelength, z is the distance between the scattering plane and the observation plane, d is the size of the illuminated surface area.

The distance from the scattering region to the entrance aperture of the fiber connected to the PMT was 7 cm (calculated result based on the parameters of the setup and the elements used); the scattered signal was recorded at an angle of 7° .

The scattered radiation entered the Hamamatsu H10723-20 PMT with a spectral sensitivity of 5 kA/W (for $\lambda = 635$ nm), the control voltage was 0.7 V, the maximum dark current was 10 nA, the maximum output current was 100 Ma. Power was supplied to the PMT from stabilized source 6. Next, the detected signal was transmitted from the PMT to analog-to-digital converter 10 (ADC), and then to computer 11, where the ACF of the photocurrent signal was calculated.

Calculated estimation of signal-to-noise ratio for the measuring system developed

The measurement accuracy depends on the duration of the procedure and sampling, amplitude-frequency distortions of the signal, the resolution of the device, statistical error and noise characteristics of the setup elements. Let us estimate the SNR of the measuring system for the expected scattering parameters of the colloidal system, which is calculated as the ratio of the RMS deviation (RMSD) of useful signal to the RMSD of the noise from the radiation source, PMT and ADC.

We carry out a theoretical assessment of the noise value for each element in the setup.

The noise of laser radiation generally consists of frequency and power fluctuations. The greater the fluctuations in the power and frequency of the laser, the less contrasted the speckle pattern. The fluctuations in laser power associated with thermal drift can be assumed to be rather slow. They affect the mean scattering intensity and are monitored during calibration measurement. In this case, the laser power drift does not contribute to the measurement error, since its magnitude is greater than the characteristic time for measuring one run, equal to 30 ms. Power fluctuations over frequency can be calculated by the following expression [11]:

$$\langle \sigma_{U,laser} \rangle = RINP_0^2 \Delta f, \quad (25)$$

where P_0 , W, is the mean optical power of laser radiation; the RMSD of frequency noise was $0.1 \mu\text{W}$.

The PMT is characterized by different types of noise, including thermal and shot.

The shot noise of the useful scattering signal is calculated as follows [11]:

$$\langle \sigma_{U,n.phm} \rangle = [2eR^2SP_s\Delta f]^{1/2}, \quad (26)$$

where e , C, is the electron charge ($e = 1.6 \cdot 10^{-19}$ C); S , A/W, is the radiant sensitivity accounting for the gain of the PMT; P_s , W, is the radiant flux; R , Ohm, is the load resistance; Δf , Hz, is the frequency band of the photodetector ($\Delta f = 1$ MHz).

The corresponding peak load voltage for shot noise was 4.85 mV for the signal power $P_s \approx 10$ MW.

The signal conversion errors are associated with the sampling error of the ADC, which in turn depends on the bit depth of the converter used. In this case, the bit depth n was $n = 14$ bits. The measurements were carried out in the voltage range of ± 2.5 V. The RMSD of quantization noise can be calculated by the formula

$$\langle \sigma_{U,converter} \rangle = \frac{\Delta U}{2^n \sqrt{12}}. \quad (27)$$

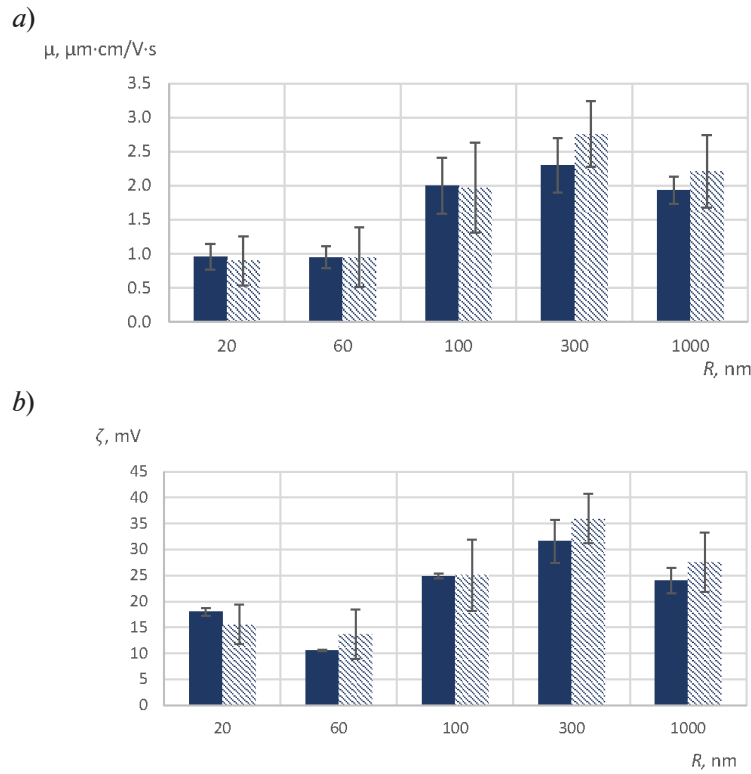


Fig. 2. Electrophoretic mobility (a) and zeta potential (b) as functions of microsphere size in solution obtained with the modified setup (blue bars) and with the commercial ZetaSizer Nano analyzer (crosshatched bars)

The RMSD of quantization noise for the selected elements was 0.025 mV. The ADC also has intrinsic noises whose RMSD is equal to 0.60 mV. The total RMSD of ADC noise was 0.61 mV and the RMSD of the measuring system was 0.77 mV.

The experimental SNR value for a colloidal solution with microspheres with the diameter $d = 60$ nm was 64.9. The obtained SNR value allows to apply the developed setup for analyzing the electrokinetic parameters of colloidal systems. We intend to establish below that the measurement error is less than 10% for this SNR value.

Results and discussion

The modified setup was tested through measurements of electrophoretic mobility and zeta potential in solutions with carboxyl latex microspheres of different sizes. Similar measurements were carried with the commercial ZetaSizer Nano analyzer for comparison. The values obtained for the quantities measured by both devices are shown in Fig. 2.

Evidently, the results are in good agreement. The experimental error (calculated from the data on the spread in the calculated parameter values for the number of experiments $n = 10$) generated during measurements with the developed setup turned out to be less than that obtained with commercial device in all cases. Therefore, we can conclude that the setup and the data processing technique used are even more effective.

The lower bound of the size range allowing to find the electrokinetic parameters is determined by the scattering power required to achieve an SNR exceeding 10 (as discussed in our earlier studies on dynamic light scattering [12]). In turn, the scattering power with fixed parameters of the setup is determined by the concentration and size of the scatterers. It is preferable to impose the following condition to find the lower bound of the particle size range available for analysis (all other things being equal): the intensity of scattering by the particles considered should be at least 10 times higher than the intensity of scattering by the molecules of the medium (solvent). Considering an aqueous solution where the typical molecule sizes are 0.32 nm [12], we can establish based on scattering theory (i.e., scattering by the particle should be directly proportional to the sixth power of scatter size) that the minimum possible particle diameter to be determined is about 0.5 nm.

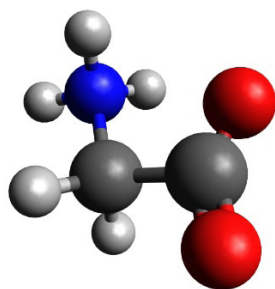


Fig. 3. Structural model of glycine molecule constructed in the Avogadro program: red atoms correspond to oxygen, blue to nitrogen, black to carbon, gray to hydrogen

The capabilities that the setup offers for estimating the parameters of particles with the sizes near the lower bound of the given range were tested experimentally for aqueous solution of glycine molecules (Fig. 3).

The maximum size of glycine in aqueous solution reaches 0.46 nm [12]. The hydrodynamic radius of this molecule lies in the range from 0.5 to 0.7 nm. The values of electrophoretic mobility and zeta potential for glycine solution, calculated using the developed measuring system, amounted to, respectively,

$$\mu = 3.00 \pm 0.74 \mu\text{m}\cdot\text{cm}/\text{V}\cdot\text{s}, \zeta = 5.60 \pm 1.38 \text{ mV}.$$

These values correspond to the literature data for glycine [13], so we can conclude that the setup operates correctly for the lower bound of the given size range.

The setup was further tested by measuring and calculating the values of electrophoretic mobility and zeta potential in microspheres with sizes of 320 and 970 nm in polydisperse solution. The difficulty in this case was separating the contributions from particles with different sizes and mobilities to the experimental ACF. Therefore, the parameters μ and ζ in polydisperse solutions were quantified based on the algorithm developed to estimate the power spectral density of the photocurrent using the fast Fourier transform. Data processing consisted of selecting the spectral window $W(f)$, constructing modified periodograms for each recorded file, and subsequently calculating the electrophoretic mobility and zeta potential for polydisperse solution at the corresponding frequencies. A DC electric field of 3.5 V/cm was applied to the system during the experiment. The measurement results are presented in Table 1.

Table 1

Electrophoretic mobility and zeta potential of polydisperse solution with polystyrene microspheres of two sizes

Size, nm	Parameter value	
	$\mu, \mu\text{m}\cdot\text{cm}/\text{V}\cdot\text{s}$	$ \zeta , \text{mV}$
320	5.40 ± 0.95	67.00 ± 3.56
970	7.03 ± 0.32	87.00 ± 5.45

The data given in the table confirm that the calculation errors for electrophoretic mobility and zeta potential in polydisperse colloidal solutions do not exceed 10%. The difference between the calculated values and the experimental data shown in Fig. 2 is explained by the differences in the parameters of the given particles (microspheres in the experiments had different coatings, which affected their mobility).

We can conclude from the above experimental data that our ELS method makes it possible to analyze the aggregation stability of mono- and polydisperse colloidal solutions in the range from 0.5 to 1000 nm with an error of no more than 10%.

Next, we measured the values of the zeta potential in the case when sodium chloride added to the microsphere solution. It proved impossible to analyze similar solutions with high electrical conductivity (3.9 mS/cm) using the commercial ZetaSizer Nano device; a possible explanation for this is that applying strong electric fields may induce heating of the sample, subsequently modifying its properties (the voltage in the electrodes cannot be regulated for samples of different types). On the other hand, solutions with high electrical conductivity are often used in medicine (for example, solutions of various electrolytes). The magnitude of the external electric field in our experiments did not exceed 10 V/cm with sodium chloride added to the solution. The values of electrophoretic mobility and zeta potential for a solution with carboxyl latex microspheres with the sizes of 60 nm and concentrations $C_{\text{NaCl}} = 0.5 \text{ mmol/l}$ were $1.54 \pm 0.55 \mu\text{m}\cdot\text{cm}/\text{V}\cdot\text{s}$ and



28.72 ± 7.45 mV, respectively. The increase in the absolute value of the zeta potential with added NaCl is associated with the variation in the thickness of the electrical double layer (EDL). The diffusion of counterions in the solution slows down, as the concentration difference between the diffuse layer and the solution decreases. Accordingly, the number of ions in the diffuse region of the EDL also decreases, a larger number of counterions accumulates in the dense layer, which leads to an increase in the absolute value of the zeta potential.

Thus, the experiment proved that the setup is well applicable for solutions with high electrical conductivity if the field strength can be regulated.

The thresholds of the electrostatic field strength acceptable for the experiments were found by analyzing the behavior of a solution with carboxyl latex microspheres with the size of 300 nm. For this purpose, we calculated the dependence of the EPM on the strength of the field applied to the electrodes (Fig. 4).

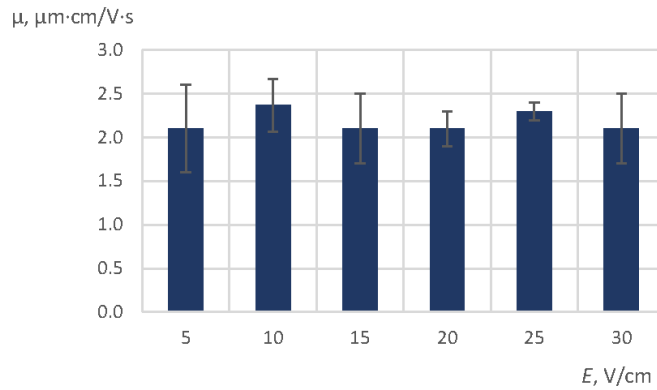


Fig. 4. Calculated dependence of electrophoretic mobility for solution with 300-nm microspheres on the strength of the electric field applied to the electrodes

Minor fluctuations observed in the EPM parameter upon variation in the electric field lie within the measurement error, proving that the setup and the measurement technique are stable. No significant contribution of thermal effects and electro-osmosis could be detected in the measuring volume. The measurement results obtained with our setup and with the commercial Zetasizer Nano device are in good agreement (see Fig. 2). The mean EPM measured with our setup was 2.3 ± 0.4 $\mu\text{m} \cdot \text{cm} / \text{V} \cdot \text{s}$, while measurements of the same glass microspheres (in an electrostatic field with the strength of 150 V/cm) with the Zetasizer Nano device yielded an average value of 2.5 ± 0.5 $\mu\text{m} \cdot \text{cm} / \text{V} \cdot \text{s}$. The voltages applied vary from 5 to 30 V/cm in our setup. Directional particle motion was not observed at voltages below 5 V/cm, and the value of 30 V/cm was sufficient to observe electrophoretic phenomena in all conducted experiments; no further increase in the electric field strength was required.

In addition to the above restrictions imposed on particle sizes, electrical conductivity of the solution and strength of the applied field, the concentrations of the samples considered should also be maintained within certain acceptable thresholds. The scattering volume should contain at least 500 particles to correctly calculate the electrophoretic mobility and zeta potential of particles in colloidal solution. The number of particles in the scattering volume V can be calculated by the formula [12]:

$$N = \frac{3C_0V}{4\pi R^3}, \quad (28)$$

where C_0 , g/l, is the volume fraction of particles in the sample of colloidal solution, V , l, is the scattering volume, R , nm, is the mean particle size.

The recommended concentration values for particles of different sizes are given in Table 2.

We carried out experimental studies on the dependence of EPM on the concentration of scatterers in the solution considered. Fig. 5 shows an example of such a dependence for microspheres with a diameter of 20 nm versus their mass concentration in solution, in the range of recommended concentrations (see Table 2).

Table 2

Recommended concentrations for particles of different sizes in colloidal solutions

Particle size, nm	Concentration		Density of colloidal systems, g/cm ³ , at maximum concentration (condition)
	Minimum, g/l	Maximum, wt%	
<10	0.5	Concentration is limited only by particle interactions	
10–100	1.0	5	1
100–1000	0.01	1	

Note. The recommendations are for the case of a cuvette with immersed electrodes.

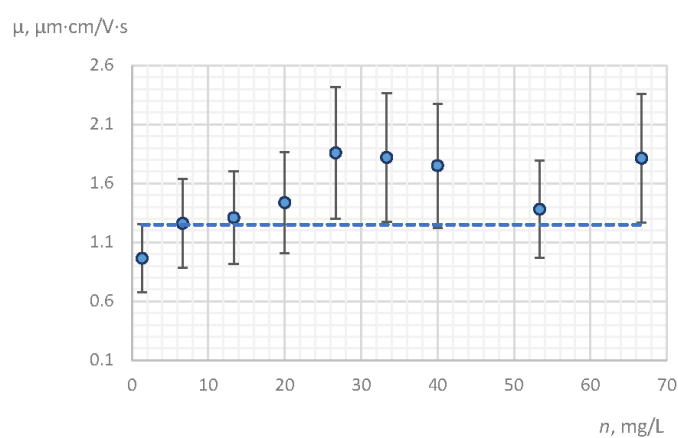


Fig. 5. Dependence of electrophoretic mobility on mass concentration of the sample for microspheres 20 nm in diameter

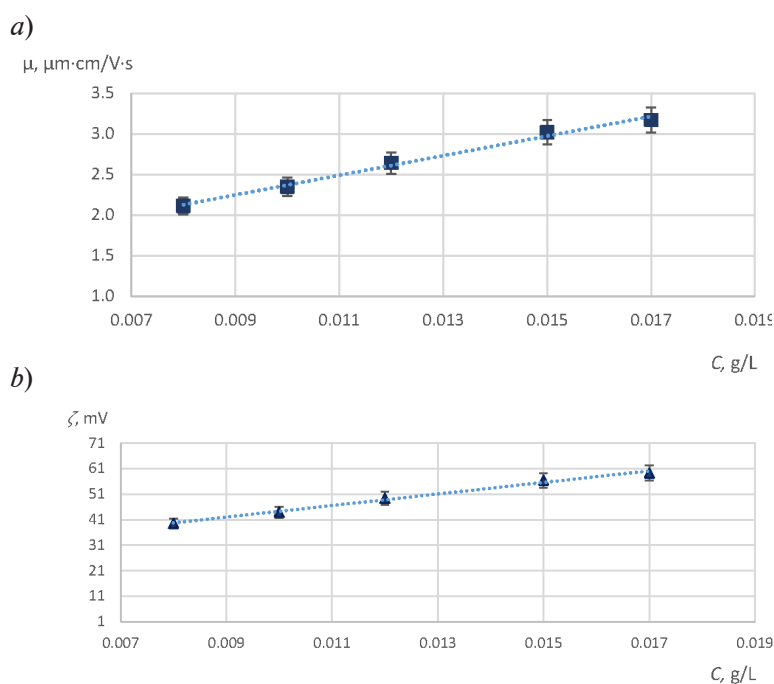


Fig. 6. Dependences of electrophoretic mobility (a) and zeta potential (b) on the concentration of colloidal copper nanoparticles in solution

The EPM varied in the range of 1.00–1.89 $\mu\text{m}\cdot\text{cm}/\text{V}\cdot\text{s}$ with varying concentration. The mean value of the EPM was 1.25 $\mu\text{m}\cdot\text{cm}/\text{V}\cdot\text{s}$, which corresponds to the results obtained with the Zetasizer Nano device (see Fig. 2).

Copper nanoparticles were also used in the study to test the developed setup. Since such particles, widely used in medicine and cosmetology, absorb (to some extent) radiation at the selected wavelength, we also separately tested the performance of the setup for analysis of these particles.

The values of EPM and zeta potential for copper nanoparticle solution depending on the concentration, obtained with the developed measuring system, are shown in Fig. 6.

One of the key factors influencing the magnitude of the zeta potential is the concentration of the colloidal system [14]. As evident from the figures, the zeta potential increases with increasing concentration of copper nanoparticles due to adsorption of ions from the surface of the dispersed phase. The absolute value of the zeta potential, equal to 30 mV, acts as a conditional boundary for separating liquid colloidal systems into stable ($|\zeta| > 30$ mV) and unstable ($|\zeta| < 30$ mV) [15]. Therefore, we can conclude that copper nanoparticles are resistant against aggregation processes. This property is also reported by the manufacturer of these nanoparticles, since they are coated with polyvinyl alcohol.

Thus, the improved technique for electrophoretic light scattering in heterodyne mode that we developed allows analyzing the electrokinetic parameters of monodisperse nanoparticle solutions partially absorbing laser radiation; the measurement error does not exceed 5%. The particles can be thus deemed to possess aggregation stability based on this analysis.

Conclusion

The improved technique for electrophoretic light scattering in heterodyne mode allows to study the aggregation stability of mono- and polydisperse solutions with particle sizes ranging from 0.5 to 1000 nm. The technique is highly efficient as several parameters can be measured at once, also offering significant detection rate (the time it takes to obtain the measured parameters does not exceed 1 min) and compact size. This makes it possible to analyze sample solutions with concentrations of 1 mg/l and electrical conductivities over 4 mS/cm.

The measurement accuracy for the parameters of mono- and polydisperse colloidal nanoparticle solutions has been increased to 90% thanks to the modifications introduced into the measuring setup. We analyzed the setup in detail, specifically evaluating the signal-to-noise ratio achievable for the given configuration. The obtained SNR value, equal to 64.9, allows to use the setup for analyzing the electrokinetic parameters of colloidal systems.

Testing the developed ELS technique, we found that the measurement accuracy offered by the setup for particle sizes in monodisperse solutions is on par with commercial spectrometers (Zetasizer Nano ZS and Photocor) [4]; moreover, a broader range of data can be obtained for solutions with high electrical conductivities compared to any equivalents so far as we are aware. The results obtained for determining the zeta potential of nanoparticles are compared with a threshold value of 30 mV for stable suspensions; this information lead us to conclude that nanoparticles have high aggregation stability, showing promise for applications in therapeutic nanomedicines.

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