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**THE ELECTROKINETIC POTENTIAL MEASUREMENTS  
OF BIOCOLLOIDS PARTICLES**

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There the ways of measurements of an electrokinetic potential (zeta-potential) of colloid particles and, in particular, a problem associated with use of the classical electrophoresis are briefly discussed in the article. The methods and devices based on measurements of a light scattering of particles and became a frequent practice now are analyzed most extensively. It is shown that the Doppler spectroscopy of the light scattered by particles is accompanied by difficulties not only by the analyze of particle sizes, in particular, for polydisperse colloids, but also, first of all, while measuring the zeta-potential because it is defined not so much by the size, as totality of peripheral parameters of the particles. The way of measurement near to a classical electrophoresis is offered, where the sign-variable electric field is used, the drift length of the particles and a difference of electric potentials are minimized.

*Keywords:* zeta-potential, electrophoresis, dynamic light scattering, modified electrophoretic method

**INTRODUCTION**

The research on the boundary potentials determined by presence or absence of charged and/or polarizable groups on interacting surfaces has a long history. This is especially true for aqueous colloidal systems and, particularly, for the systems containing biogenic particles (for example, live-alone bacterial cells, body fluids particles or numerous model elements, for example, liposome from small ( $0.02 \div 0.05 \mu\text{m}$ ) to giant ( $5 \div 100 \mu\text{m}$ ) [1]. Various fundamental parameters of these systems are determined by electrical properties of water and aqueous electrolytes [2, 3]. It is sometimes said [4] that colloidal dispersion study is one way to research a condensed state of matter (soft matter).

The surface potentials of particles can be electropositive at the expense of protonation or electronegative as a result of surface radicals dissociation. The maximum density of the electronegative surface-bound charge (for example, for the bilayer on basis of phosphatidylserine) determining the surface potential is assessed [1] in magnitude of  $0.1 \div 0.2 \text{ C} \cdot \text{m}^{-2}$  that corresponds to the micronic particle surface charge that is approximately equal to  $10^7 e$ . The free charge determining zeta-potential is significantly smaller. Surfactant micelles (for example, of sodium dodecyl sulfate) can bear as many as 60 elementary charges at the ex-

pense of  $\text{Na}^+$  cations dissociation [4]. Such electrical parameters as the membrane dipole potential, the surface potential or the double layer potential are generally not accessible to direct measurement. The exception is the electrokinetic potential (zeta-potential) though that is also not accessible to direct measurement but can be calculated by the measured velocity value of particle motion in an electric field.

The accuracy of the size and zeta-potential measurements of biological suspensions particles has also a diagnostic value, for example, in case of inflammatory and tumour lung diseases [5].

Finally the measurement task of zeta-potential is of current interest to research glass surfaces or medical polymers [6], which used, for example, in designs of jet or stream microfluidic moduli.

**MEASUREMENT TECHNIQUES**

To measure the parameters of dispersed phase particles, that is the sizes, charge and electrokinetic potential, some technologies can essentially be used. These include numerous types of electrophoresis, beginning with Tiselius cell, the electrical audibility methods and crop of new methods based on the measurement of colloids light scattering.

The particle drift length is too large, that adds to the time in the clinical electrophoresis. Consequently quite a high voltage (to 1000 V) is required to increase electric field strength. The typical values of the parameters describing the process: the electric current density  $j = 1 \text{ A} \cdot \text{m}^{-2} = 0.1 \text{ mA} \cdot \text{cm}^{-2}$ ; the suspension conductivity  $\sigma = 0.2 \text{ } (\Omega \cdot \text{m})^{-1}$ ; the electric field strength  $E = 0.05 \text{ V} \cdot \text{cm}^{-1}$ ; the drift (electric) mobility of erythrocytes as the ratio of the motion speed to the electric field strength [7]

$$\mu_{\text{er}} = (0.87-1.35) \text{ } (\mu\text{m/s})/(\text{V/cm}).$$

The zeta-potential of the submicron zeolite particles in the suspension based on distilled water was measured with the use of electroacoustic technology by applying the device ZetaProbe Analyzer (Colloidal Dynamic Inc., USA) [8].

The ways of ultrasound application [9] to measure a size and an electrokinetic potential of colloid particles were described.

The way to use the electro-optic cell for direct measurement of a motion speed of the previously dyed particles in an alternating-sign field and for calculations of the electrokinetic potential of the particles was offered [10]. Theanilino-naphthalenesulfonate (1,8-ANS) was used for dyeing. The critical weakness was that dye adsorption has altered the surface potential and the particle charge, and therefore the electrokinetic potential.

In recent decades a set of dynamic light scattering methods (Doppler spectroscopy, optical-mixing spectroscopy, photon correlation spectroscopy, quasielastic light scattering spectroscopy, laser correlation spectroscopy (LCS) et al.) has become more widely implemented to analyze size-consist as well as to measure zeta-potential of particles of different nature, including biomedical colloid systems.

It is rightly considered [11, pp. 38–40] that so-called "optical tweezers", i. e. laser photon impact (with a wavelength 500 nm) on the micron colloid particle is easily realized, where as the possibility of applying "acoustic tweezers" of 2 MHz frequency (a wavelength is near  $10^6$  nm) is much more complicated.

However, with respect to dynamic light scattering there has been reported [12] that "the end result had not been related to employed algorithm of achievement of this result in the commercially available devices". In other cases there has been noted [4, 5], that

there had not been calculated relations to make possible to evaluate experimental results in the LCS methodology. As a whole, in spite of mass use of devices of this type, advantages and disadvantages of the methods based on dynamic light scattering are not described with enough authority. For example, there have been reported [13] the following advantages: short duration of the measurement (from units of seconds to a few minutes); the wide range of measured particle sizes (from 0.001 to few microns); commercial availability; extremely small sample (probe) amount necessary for analysis. It is also believed that this technique is absolute, namely, it does not require calibration based on known (standard) distributions.

Among the disadvantages are noted: low resolution in order of size (1:1000) in comparison with a particle counter and microscopy (1:10); absence of the controlled parameters used for calibration.

Some basic factors which underlie the method are discussed below.

#### ANALYSIS OF THE DYNAMIC LIGHT SCATTERING METHODS

The main effect of light scattering consists in producing the Doppler frequency shift determined by diffusion particle displacement on exposure to monochromatic (laser) radiation on the suspension. These frequency shifts are determined, in the first place, by the kinetic parameters of the particles which are movement speed, mobility and diffusion coefficient, and in the presence of an electric field – by charge and potential of the particles.

To analyze the frequency shifts of a host of the light scattering particles it was historically needed first of all to write the autocorrelation function of the particle position (coordinates) and then in accordance with the Wiener—Khinchin—Kolmogorov fundamental theorem to obtain the spectrum for scattering radiation, using the Fourier representation.

To describe particles random shuffle in statistical mechanics there has been used (see for example [14]) autocorrelation function of type:

$$G(\vec{r}, t) = \left( \frac{m}{2\pi t^2 k_B T} \right)^{3/2} \cdot \exp \left( -\frac{m(|\vec{r}|^2)}{2t^2 k_B T} \right),$$

expressing, per unit of volume, likelihood that the particle being at  $t = 0$  at a point of space after the period  $t$  will be found at the point being separated by a distance  $|\bar{r}|$  from the starting point. Here  $|\bar{r}|$  should be understood as module of the average value for the three-dimensional motion of a particle. This expression for the autocorrelation function exactly corresponds to Maxwell velocity distribution function accepted in the kinetic-molecular theory of gases:

$$f(\bar{V}) = \left( \frac{m}{2\pi t^2 k_B T} \right)^{3/2} \cdot \exp \left( -\frac{m|\bar{V}|^2}{2k_B T} \right),$$

where  $\bar{V} = |\bar{r}|/t$  — the mean value of module of particle velocity.

The Fourier transform of the autocorrelation function yields the representation closed to Gaussian one for the spectral density of the scattered radiation that is:

$$S(|K|, \Delta\omega) = \left( \frac{m}{2\pi |K|^2 k_B T} \right)^{1/2} \cdot \exp \left( -\frac{m\Delta\omega^2}{2|K|^2 k_B T} \right),$$

where  $|K|$  — module of the difference between the wave vectors of the downward and scattered radiation;  $\Delta\omega$  — the difference of circular frequencies of the downward and scattered light dependent on rate of motion of the scattering particles.

Inclusion (incorporation) of the scattering particles diffusion coefficient into analysis, formally speaking, is equivalent to the substitution in the last expression that is based on the equation  $\Delta\omega^2/|K|^2 = D \cdot \Delta\omega$ , where  $D$  — diffusion coefficient of the particles. Stokes—Einstein formula  $D = k_B T / (6\pi r \eta) = k_B T \cdot \mu_m$  for the diffusion coefficient determines mechanical motion of a particle  $\mu_m$ , multiplying it by particle charge magnitude, we obtain the electric mobility, and the next multiplying by field strength gives us the value of the particle motion velocity  $V = Q_p \mu_m E$ . Note that the particle mechanical mobility is determined just by the sizes, the form and the medium viscosity whereas the charged particle motion velocity is determined by the particle charge and by electric field intensity. Cummins and co-authors do

not specify the origin, character and the magnitude of the electric field strength in their article [15, 16] that has become the initial one for development of technique for dispersion analysis based on dynamic light scattering. It is considered that thermal fluctuation of the particle velocity not only generates the Doppler shift and the corresponding scattering spectrum changes but also reflects the values of mobility, charge and electrokinetic potential of the particle contained therein.

Integration of thermal fluctuation theory formalism and exact solutions in the Mie scattering theory which is thought to produce the best results [17] for liquid colloidal suspensions as well as for atmospheric colloids allowed obtaining of the expression for the spectral distribution of scattered light in the form of the Lorenz curve which is suitable for practical use [14]:

$$S(|K|, \Delta\omega) = \frac{1}{2\pi} \cdot \frac{2|K|^2 \cdot D}{\Delta\omega^2 + |K|^4 \cdot D^2},$$

where  $|K|^2 \cdot D$  — diffusion spectral broadening of scattering light.

Similar in form ratios [18] for autocorrelation function and spectral density are used in laser correlation spectroscopy which is widely employed in biological studies and, in particular, in nephelometry:

$$G(\tau) = A \exp(-\Gamma \cdot \tau);$$

$$S(\omega) = (A \cdot \Gamma / \pi) / \left[ (\omega_0 - qV)^2 + \Gamma^2 \right],$$

where  $A$  — range of light scattering fluctuations, which corresponds to diffusion broadening of the  $\Gamma$  spectrum;  $\tau = 1/(2D_i q^2)$  — correlation radius that is time within which particles behavior is statistically independent;  $\omega_0$  — impinging light frequency;  $qV$  — the Doppler shift of the impinging light frequency on the particles migrating during translation diffusion ( $q$  — wave number;  $V$  — particle velocity). The diffusion broadening is determined by the product  $\Gamma = D_i \cdot q^2$ , where the translation diffusion coefficient  $D_i$  is determined by the given above Stokes—Einstein formula  $D_i = k_B T / 6\pi \eta R_h$  ( $R_h$  — particles hydrodynamic radius). The wave number  $q$  is determined by the ratio  $q = (4\pi n / \lambda) \sin(\Theta/2)$ ,

where  $\lambda$  — wave length of impinging laser light;  $n$  — refractive index of a medium;  $\Theta$  — angle of observation of scattered light near to  $\pi$  (back scattering). The expression for diffusion coefficient allows calculate the particle mobility from the equation  $D_t = k_B T \cdot \mu$  and further to calculate zeta-potential on the basis of equality (the Smoluchowski formula)  $\mu = (2\varepsilon\varepsilon_0/3\eta)\zeta$ .

Yankovsky and co-authors [12] solved the inversed spectral problem with method of regularization (matrix solution of incorrect problems in linear algebra). This problem first of all comes down to finding a function of dispersed particles size distribution and then it may be used to find diffusion coefficient, charge and electrokinetic potential of the particles. The authors note that "even when quality of device component of hardware—software complex is high", which provides low noise and hum (presence of frequencies not belonging to the impinging and scattering light spectra, for example, at the expense of the light scattering on solvent molecules), it is hard enough to restore the details of multimode particle size distributions in colloidal solutions. This is especially the case with biological compound solutions (particularly, blood serum) containing very plenty of components. For this reason, as the authors of the article note, majority of producers of nanosizers are limited to employment of cumulants (most often average value and dispersion, but also asymmetry coefficient and kurtosis). Thus, it succeeds (comes off), as the same authors note, to describe reliably the trivial distribution of the particles of the same size or the distribution consisting of no more than two modes widely separated. But it has been noted in earlier assessments [19] of LCS appropriateness for dispersive analysis that light scattering spectra processing for polydisperse systems is the inverse problem of the spectrum analysis with a "badly specified matrix".

#### STATISTICAL ASSESSMENT OF THE METHOD DYNAMIC LIGHT SCATTERING

Let us adduce some additional considerations to evaluate light-scattering methods. The average square of the one-dimensional electrodiffusion shift of a particle is determined by ratio [20, pp. 166–169]:

$$\overline{(x - x_0)^2} = V_d^2 t^2 + 2Dt,$$

where drift (electrophoretic) velocity is determined by production of mobility and velocity of the particle  $V_d = \mu E$ , and diffusion coefficient is determined by Stokes—Einstein formula  $D = k_B T / (6\pi\eta r)$ . Mobility, as already has noted above, is determined by the ratio  $\mu = (4\pi\varepsilon\varepsilon_0\zeta / 6\pi\eta) f(ka)$ , where the production  $4\pi\varepsilon\varepsilon_0\zeta = Q_p$  determines a particle charge;  $k$  — Debye length;  $a$  — colloid sphere radius;  $f(ka)$  — Henry function of electrolyte concentration and ion radius. While  $ka \rightarrow 0$   $f(ka) \rightarrow 1$  (Huckel—Onsager limit) is met, and if  $ka \rightarrow \infty$  condition  $f(ka) \rightarrow 3/2$  (Helmholtz—Smoluchowsky limit) is met. In the second case ( $f(ka) = 3/2$ ) mobility is given by the expression already noted above  $\mu = (2\varepsilon\varepsilon_0/3\eta)\zeta$ .

Therefore, root-mean-square velocity of electrodiffusion shift of a particle equals:

$$\begin{aligned} \frac{\sqrt{\overline{(x - x_0)^2}}}{t} &= \sqrt{V_d^2 + \frac{2D}{t}} = \\ &= \sqrt{\left(\frac{2\varepsilon\varepsilon_0\zeta f(ka)E}{3\eta}\right)^2 + \frac{2k_B T}{6\pi\eta r t}}. \end{aligned}$$

From the obtained ratio directly follows that velocity diffusion constituent is determined by the observation time  $t$ , whereas the drift velocity is only determined by the medium parameters (viscosity, polarizability, field strength) and by the parameters of moving particle (size, charge and zeta-potential). It is clear that for assessment of the drift velocity it is necessary to neglect the subduplicate addend on the right side of the expression, in other words, to consider observation time being sufficient as it is in a practical electrophoresis.

In measuring practice of light scattering an interval of measurement time, as noted above, is a time from some seconds to some minutes, which in itself is a big advantage for the method as compared with electrophoresis. However, this time is not considered as a necessary condition for measurement process performance, and the measurements themselves not directly related to the described parameters (size, charge, electric mobility and particle electrokinetic potential).

Formalism of the laser correlation spectroscopy contains no set of parameters determining the electrokinetic potential, i. e. the nature of the electrolyte of the incubation medium, viscosity of this medium, the double electrical layer structure, the particle surface nature, including polarizability which is exactly the property that determines the Mie scattering. Though the diffusion broadening of the scattered light spectrum without doubt reflects all properties of colloidal system, it is hard directly to put it into formalism of the Gouy—Chapman—Stern theory. It is therefore understandable the noted above comment of Yanowski and co-authors [12] that the measurement results don't related to the algorithm for the result generation.

It has been long enough shown for aerodispersive colloids (aerosols) [20, pp. 166–169] that an error when particles sizes are determined by Brownian motion can be ten times more than when these are determined on speed of a directed movement (for example, sedimentation), and just for very small particles ( $< 0.1 \mu\text{m}$ ) Brownian velocity fluctuations can be used to access particles sizes. The error appeared to be even more in measurements of charged particle motion velocity in a strong electric field. The conclusions are apparent, since to small particles the velocity of such fluctuations comes well over an ordered motion velocity and increases quickly with the size reduction.

It may be assumed that these errors are even greater for liquid colloids because Brownian particle displacements are still less and, consequently, more difficult to measure.

Nondiffusion mode of motion under very low times has taken an interest comparatively for a long time as regards not only gaseous molecules but also scattering light colloid particles [21]. Most recently a ballistic (not Brownian) single particle motion in the nanosecond interval for the first time was directly seen in the optical trap with the passband 75 MHz as the article authors claim [22]. During these studies the particle place was measured with precision of Angstrom units.

In general, light scattering measurements as well as their underlying diffusive drift of the light scattering particles have the statistic nature and give the median results in any case, while the size, the charge, the zeta-potential and the other determined parameters of the certain kind particles can be accurately measured in principle.

### PROPOSED MEASUREMENT TECHNIQUE

The method of measuring the particle sizes and electrokinetic potential, which is related to electrophoresis, is considered in the article. This method is based

on direct measuring the particle velocity in an electric field.

We use the kinetic relaxation time as the key parameter characterizing the establishing durability of the particle steady motion in a viscous fluid under an electric force. For the charged particle bearing the electric charge  $Q_p$  steady drift velocity  $V_d = \mu E$  ( $\mu$  — mobility of the particle) in the electric field of the strength  $E$  is given by the Stokes ratio  $6\pi r\eta V_d = Q_p E$ , that does not however contain the time in an explicit form. Since kinetic parameters don't depend on nature of the force acting upon the particles, the kinetic relaxation time  $\tau_k$  may be determined if we use mechanical analogies  $\mu E \rightarrow g\tau$  and  $Q_p E \rightarrow mg$ , where  $g\tau$  and  $mg$  mean the rate of sedimentation and the weight of the particle with density  $\rho$  respectively. Then the kinetic relaxation time will be determined by the formula  $\tau_k = (2r^2\rho/(9\eta))$  widely used in the aerosol mechanics. For example, in respect of the particle of radius  $r = 1 \mu\text{m}$  density  $\rho = 10^3 \text{ kg}\cdot\text{m}^{-3}$  (water), moving in the medium with viscosity  $\eta = 10^{-3} \text{ Pa}\cdot\text{s}$  (water), this time is equal to  $\tau_k \cong 0.2 \mu\text{s}$ . The production  $l_i = V_0 \cdot \tau_k$  determines particle inertial run after electric force action has finished. For the micron particle holding zeta-potential  $\zeta = 30 \text{ mV}$  and the charge  $Q_p = 2000e$  and moving in electric field of intensity  $E = 2 \text{ V}\cdot\text{cm}^{-1}$  with velocity about  $V = 3 \mu\text{m}\cdot\text{s}^{-1}$  the inertial run reaches no more than  $0.01 \text{ \AA}$ .

Note also, that Debye relaxation time  $\tau_d = 4\pi\eta^* a^3 / (k_B T)$  determining the particle polarization rate is defined by Debye formula  $\tau_d = 4\pi\eta^* a^3 / k_B T$ , where  $\eta^*$  — microviscosity of dispersion medium;  $a$  — radius of a spherical dipole molecule. It has been experimentally demonstrated that Debye relaxation time ( $10^{-12} \div 10^{-9} \text{ s}$ ) substantially less than the kinetic relaxation time and, in addition, is determined by the macroscopic value of viscosity [23].

The setting elements, which is intended for method realization, and measuring techniques are described later.

The differential cell, containing two closely set cylindrical canals, their diameter and length respectively were equal to  $d_k = 7 \text{ mm}$ ;  $l_k = 40 \text{ mm}$ , was used. Both canals were filled by the electrolyte (NaCl) and included as two adjacent shoulders in the measuring bridge, their scheme is shown in the fig. 1. The bridge was fed by impulse voltage (fig. 2).

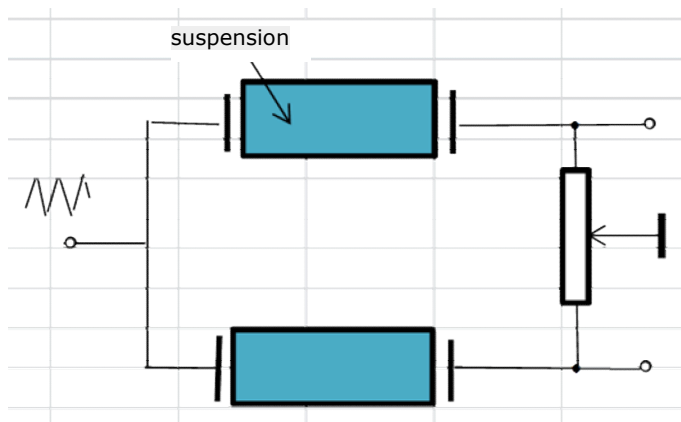


Fig. 1. Simplified the measuring bridge connection

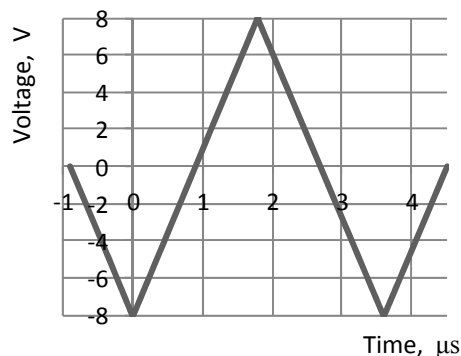


Fig. 2. The form and the parameters of voltage feeding the measuring bridge connection; pulse length  $\tau_u = 3.6 \mu\text{s}$ ; amplitude  $U_m = 8 \text{ V}$

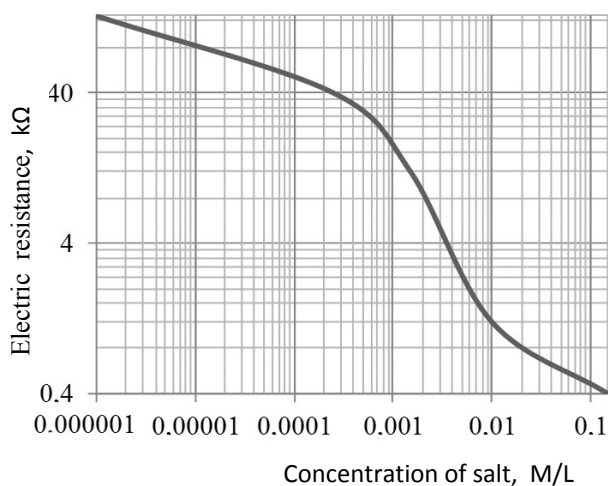


Fig. 3. The impulsive electric resistance (kΩ) of the conducting channel for the aqueous electrolyte NaCl depending on salt concentration; the concentration upper limit ( $0.15 \text{ M}\cdot\text{L}^{-1}$ ) corresponds to the physiologic saline and to the least channel resistance; the lower limit approximately corresponds to distilled water; pulse length ( $\tau_u = 3.6 \mu\text{s}$ ) pulse amplitude  $U_m = 8 \text{ V}$ . The channel diameter and length  $d_k = 7 \text{ mm}$ ;  $l_k = 40 \text{ mm}$  respectively

Two another adjacent shoulders represent a low-resistance potentiometer ( $50 \Omega$ ) with a grounded mid point, which was used to balance the bridge. Practically, bridge balancing could be perform accurate to voltage no more than  $1 \text{ mV}$  measured in the bridge diagonal. The dependence of electric resistance (impedance) on NaCl level is in fig. 3.

Thus, small resistance of the bridge-balancing potentiometer allows good balancing even when channel resistance is the least (physiologic saline). After balancing the investigated suspension was added in one of channels (fig. 1).

The linear varying voltage  $U(t) = k_u \cdot t$  presenting the antiperiodic function of time  $U(t + T/2) = -U(t)$ , amplitude  $U_m = 8 \text{ V}$  and period  $T = \tau_u$  with proportionality constant equal to  $k_u = U_m / (\tau_u / 4)$  was imputed

to the bridge feed diagonal. The form and the parameters of the power voltage are shown in the fig. 2. Fourier spectrum of this signal represents as the sum

$$f(t) = \frac{8U_m}{\pi^2} \sum_{k=1}^{\infty} (-1)^{\frac{k-1}{2}} \frac{\sin k\omega t}{k^2} (k=1,3,5,\dots; \omega = 2\pi/T)$$

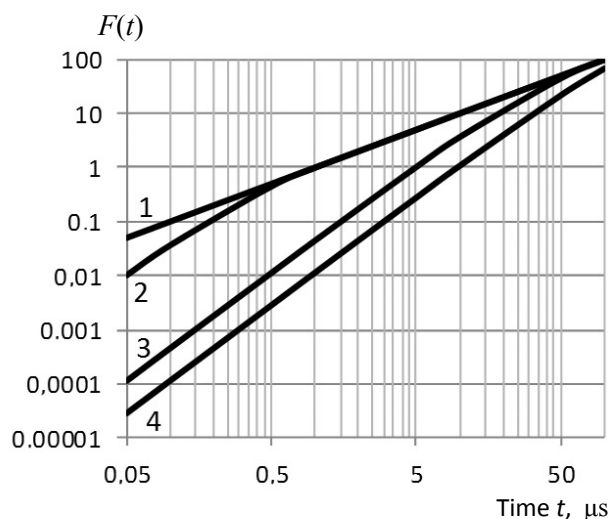
and contains sign-changing uneven sin harmonic components, which rapidly decreases in amplitude (in ratios  $6.48 : 0.72 : 0.26 : 0.13 : 0.08$  and etc.). For comparison we note, that for meander with Fourier spectrum

$$f(t) = \frac{4U_m}{\pi} \sum_{k=1}^{\infty} \frac{\sin k\omega t}{k} (k=1,3,5,\dots; \omega = 2\pi/T)$$

the higher harmonic content is much higher. The power generator  $U_{num}$ . presented self-excited loop de-

sign containing series of a regenerative element (Schmitt trigger) and an integrator, which were carried out on basis of high-speed ( $V_u \geq 50$  V/ $\mu$ s) operational amplifiers.

Inertial deceleration of a charged particle and its actual displacement velocity under pulse action of an electric field  $U(t) = k_u \cdot t$  is determined by the time-dependent exponential factor  $[1 - \exp(-t/\tau_k)]$ , so that initial velocity of motion at  $t = 0$  (field strength jump in the pole reversing) is zero, and a power-series expansion at small times ( $t \ll \tau_k$ ) provides near-linear velocity rise. The multiplier  $[1 - \exp(-t/\tau_k)]$  obtained by integration of the exponent  $\exp(-t/\tau_k)$  is common to many processes. The production  $F(t) = t[1 - \exp(-t/\tau_k)]$  defines delayed in time response of system (i. e. particle moving in electric field), that is equivalently to autocorrelation function (convolution) dependent on time of field strength which determines the actual motion velocity. One can easily estimate that it takes the time interval  $(4 \div 5)\tau_k$  to achieve the steady velocity at given (as ratio of potential difference to channel length) field strength. Thus the triangular pulse of the length  $\tau_u = 1.8 \mu$ s (fig. 2) should be seen as optimal for particles with a radius of  $r \approx 1.5 \mu$ s. Fig. 4 displays the autocorrelation functions depending on particles radius. It appears, in particular, from this figure that the pulse length of electric field must be not less  $1 \mu$ s for micronic particle investigation and not less  $100 \mu$ s for particles of ten microns. Fig. 4 also shows that high resolution for relatively large particles (1–20)  $\mu$ m is obtained in time line less than  $100 \mu$ s and for submicron particles (0.1–1)  $\mu$ m — in time line not exceeding  $1 \mu$ s. As reported below, for averaging (that is necessary for calculations) of electric field strength the condition  $(\tau_u/4) \geq (4 \div 5)\tau_k$  has to be met. So both conditions hold for equality  $(\tau_u/4) = (4 \div 5)\tau_k$ .



**Fig. 4.** Dependence of autocorrelation function  $F(t) = t[1 - \exp(-t/\tau_k)]$  for the particles with a radius of  $r$ .

1 —  $r = 0.1 \mu\text{m}$  ( $\tau_k = 2.2 \cdot 10^{-3} \mu\text{s}$ ),

2 —  $r = 1 \mu\text{m}$  ( $\tau_k = 0.22 \mu\text{s}$ ),

3 —  $r = 10 \mu\text{m}$  ( $\tau_k = 22 \mu\text{s}$ ),

4 —  $r = 20 \mu\text{m}$  ( $\tau_k = 88 \mu\text{s}$ )

Oscillation motion of a particle is determined by power voltage sign (fig. 2). During positive half-period the field voltage and the particle velocity first rise from zero to maximum value, after which these fall and come to zero by the beginning of negative half-period when fulfilling the condition  $(\tau_u/4) \geq (4 \div 5)\tau_k$ . Then similarly accelerated motion begins in the reversed direction.

To assess mean values of the potential difference and the field strength accordingly it is enough to integrate for half ( $0 \leq t \leq \tau_u/4$ ) the positive half-period of the power voltage:

$$U_{\text{mtr.}}^{\text{cp.}} = \frac{U_m}{(\tau_u/4)^2} \int_0^{\tau_u/4} t [1 - \exp(-t/\tau_u)] dt.$$

The result of integration is written as:

$$U_{\text{mtr.}}^{\text{cp.}} = U_m \left[ \frac{1}{2} - \left( \frac{\tau_k}{\tau_u/4} \right)^2 \left( 1 - e^{-\tau_u/4\tau_k} \left( \frac{\tau_u}{4\tau_k} + 1 \right) \right) \right].$$

This expression shows that the average voltage monotonous approach to the predictable level of (1/2) maximum one, when the pulse length is raising. The table below provides the mean coefficient values depending on the ratio  $\tau_u/\tau_k$  and the averaging errors in percentage terms.

This table shows, for example, that when a short pulse acts on relatively heavy particle ( $\tau_u = 0.5\tau_k$ ), effective-field strength is small (0.04 from mean), and the contribution of particles of this kind to electrophoretic current is also small and can be done even less. These considerations are becoming important when analyzing polydisperse colloids.

Therefore, steady particle motion at fixed relaxation time  $\tau_k(r)$  in the electric field with steady (averaged) intensity conforms to condition  $(\tau_u/2) \geq (4 \div 5)\tau_k$ . We note once more that this condition must be compared with the opposite in sense condition  $(\tau_u/2) \leq (4 \div 5)\tau_k$ , in order to retain good resolving ability, and consequently the equality  $(\tau_u/2) = (4 \div 5)\tau_k$  follows from this. The condition is directly looking through in the fig. 4.

Order of measuring and calculation of electrokinetic potential for the most easy case of a monodisperse colloid solution is brought to the following. When the bridge was balanced and the investigated suspension was added, the nonzero potential difference in the measuring diagonal of the bridge  $U_d$  is just determined by an electrophoretic current of particles  $I_{\text{ef}}$  that runs through the proper arm of the balancing resistor  $R_0$ . The current is determined by the ratio  $I_{\text{ef}} = U_d / (R_0 / 2)$  and the proper current density is determined by the ratio  $j_{\text{ef}} = 2U_d / (R_0 S_k)$  ( $S_k$  — the area of a channel cross-section). Further, there is the formula (Ohm law in differential form)  $j_{\text{ef}} = \sigma_k \cdot E$  ( $E = U_{\text{mtr.}} / l_k$  — electric field intensity in the channel) from which the channel conductivity  $\sigma_k = 2U_d \cdot l_k / (R_0 \cdot S_k \cdot U_{\text{mtr.}})$  should be found.

The current density can also be determined to use a single particle charge  $Q_p$  and a concentration of charged particles  $n$  on the basis of the equality  $j_{\text{ef}} = Q_p \cdot n \cdot \mu_{\text{ef}} \cdot E$  where the production  $\mu_{\text{ef}} \cdot E$  gives velocity of particle motion, and the production  $Q_p \cdot n$  — gives a volume charge density of moving particle. The equality

$$\frac{2U_d \cdot l_k}{R_0 \cdot S_k \cdot U_{\text{mtr.}}} = \zeta^2 \left[ 4\pi (\varepsilon \varepsilon_0)^2 \cdot r \cdot n \cdot (1/\eta) \right]$$

allows to calculate the electrokinetic potential value for a monodisperse colloid solution with known particle radius:

$$\zeta = \left( \frac{2U_d l_k \eta}{4\pi (\varepsilon \varepsilon_0)^2 R_0 S_k U_{\text{mtr.}} r n} \right)^{1/2}.$$

Values of the averaging coefficient and error of averaging depending on the normalized duration of electrical pulse

$\tau_u/\tau_k$	0.5	1	2	4	8	16	24	32	40
Mean coeff.	0.040	0.076	0.139	0.236	0.351	0.443	0.473	0.484	0.490
Averaging errors, %	96.0	92.4	36.1	26.4	14.9	5.7	2.7	1.6	1.0



For the parameter set  $l_k, \eta, \varepsilon, \varepsilon_0, R_0, S_k, U_{\text{max}}$  it is reasonable to introduce the proportionality coefficient

$$k_\zeta = 2l_k\eta / 4\pi(\varepsilon\varepsilon_0)^2 R_0 S_k U_{\text{num}} \quad [\text{V}\cdot\text{m}^2]$$

using the accepted earlier designations. Yet three parameters, i. e. the measured potential difference  $U_d$ , known values of particle radius  $r$  and of volume particle concentration  $n$  define the multiplier  $U_d/rn$  dimensional  $[\text{V}\cdot\text{m}^2]$ . Thus, a particle electrokinetic potential formula takes the form:

$$\zeta = \sqrt{k_\zeta \cdot U_d / (r \cdot n)}.$$

Analysis of polydisperse colloids, in particular, if constituent fractions have similar sizes, presents significant difficulties as usual. Technically it is the most ordinary to use the methods and calculations hereinabove for several successive (carrying out simultaneously) measurements, increasing by discrete steps the pulse repetition cycle and the pulse length of power voltage respectively. The limits of these steps must be overlapped. The number of the steps as well as the quantization intervals are determined by fractional structure of a colloid, if it is known, or these can be equal. Increasing of the electrophoretic current in every step of this process is determined by weighted contributions of all the colloid constituents and these deposits as it is noted above, can be estimated in advance. Furthermore, to give adaptivity to the measuring system, when increasing current, the quantization interval has to be decreased, and the more the current rises the faster interval decreases. To algorithmize the process it is reasonable to use such correlation methods as "overlap-add" [24], which employed in many kinds of applications, for example, to measure radio signals against the background noise or to determinate signals in nervous systems.

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## THE ELECTROKINETIC POTENTIAL MEASUREMENTS OF BIOCOLLOIDS PARTICLES

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There the ways of measurements of an electrokinetic potential (zeta-potential) of colloid particles and, in particular, a problem associated with use of the classical electrophoresis are briefly discussed in the article. The methods and devices based on measurements of a light scattering of particles and became a frequent practice now are analyzed most extensively. It is shown that the Doppler spectroscopy of the light scattered by particles is accompanied by difficulties not only by the analyse of particle sizes, in particular, for polydisperse colloids, but also, first of all, while measuring the zeta-potential because it is defined not so much by the size, as totality of peripheral parameters of the particles. The way of measurement near to a classical electrophoresis is offered, where the sign-variable electric field is used, the drift length of the particles and a difference of electric potentials are minimized.

*Keywords:* zeta-potential, electrophoresis, dynamic light scattering, modified electrophoretic method

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