

Effectiveness of the Simultaneous Application of Capillary Zone Electrophoresis and Static Light Scattering in the Study of Volcanic Ash Nano- and Submicroparticles

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Abstract—An advantage of using capillary zone electrophoresis and static light scattering is demonstrated on an example of suspensions containing nano- and submicroparticles of volcanic ash under the condition of simultaneous studies using the same aqueous suspensions. We found the dependences of the electrophoretic mobility and the zeta potential of nano- and submicroparticles on size by comparing electropherograms with diagrams of size distributions. These dependences can be used for the satisfactory estimation of weight-average particles size in the newly prepared suspensions.

Keywords: capillary zone electrophoresis, static light scattering, nanoparticles, submicroparticles, volcanic ash

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Currently, despite the development of direct instrumental methods of analysis, the study of polydisperse environmental samples remains an urgent task in analytical chemistry. It is known that the properties of particles depend on their size; therefore, particle separation methods play a fundamental role in the detailed study of complex polydisperse environmental samples, such as soil, dust, and ashes [1–3]. It should be noted that nano- and submicroparticles (NSP) are of the most considerable scientific interest because of their unique physical and chemical properties [4]. For example, it has recently been shown that the NSP of urban dust and volcanic ash can preconcentrate toxic elements and thus serve as their carriers in natural atmospheric and aquatic systems [5, 6].

Aquatic systems are among the main reservoirs of the environmental NSP, where their migration directly depends on aggregation and sedimentation stability [7]. The zeta potential and size of NSP are among the essential characteristics that make it possible to evaluate the stability of NSP in aquatic systems. Thus, the problem of the separation of NSP and the study of surface properties depending on their size are significant analytical problems.

There are various methods for the separation and characterization of particles in liquid media [8]. Dynamic light scattering, for example, is widely used to study particle size distribution and to evaluate their zeta potential by laser Doppler velocimetry. However,

it is not a separation method and, therefore, does not ensure the correct determination of the zeta potential of particles, the electrophoretic mobility of which depends on size, in polydisperse systems. Such a problem can be solved only after the preliminary separation of particles.

Numerous examples of using capillary zone electrophoresis (CZE) to separate particles that differ in size and zeta potential are known [9–13]. The electrophoretic mobilities corresponding to different particle size ranges can be determined by the position of the peaks in electropherograms (EPGs). However, the correct calculation of the zeta potential requires, as a rule, the knowledge of not only the electrophoretic mobility but also of particle size. In this sense, a combination of CZE with methods of the dynamic or static light scattering (SLS) of particles [14–21] is promising, which enables not only obtaining the particle size distribution but also evaluating their surface properties (charge sign, zeta potential) based on the study electrophoretic behavior.

The purpose of this study was to develop a comprehensive approach to the separation and determination of the size and zeta potential of the environmental NSP, based on a combination of capillary zone electrophoresis and static light scattering, using volcanic ash particles as an example. The study of the volcanic ash NSP is of great practical importance, since such particles are toxic and extremely mobile in the envi-

ronment [5, 22]. These particles (in contrast, for example, to the soil and dust particles) are mainly pseudospherical in shape and form suspensions being quite stable over time, which makes it possible to obtain reproducible results of parallel experiments and simplifies calculations.

EXPERIMENTAL

Samples and reagents. The studies were carried out using an ash sample from the Klyuchevskoy volcano (Kamchatka, Russia), collected after the eruption in February 2015.

Reagents of analytical grade and ultrapure water (Type I, ASTM D1193) with a resistivity of 18.2 M Ω cm (Millipore, France) were used at all stages of this study.

Isolation of the fraction of nano- and submicroparticles of volcanic ash. The NSP fraction was isolated from the bulk volcanic ash sample by field-flow fractionation in a rotating coiled column (RCC) according to a previously developed procedure [23]. The isolated NSP fraction of ash (15 mL) was deposited on membrane filters of mixed cellulose esters with a pore size of 50 nm (Vladipor, Russia) using a filtration cell (Millipore, France) at a pressure of 3.5 bar. Then, the NSP deposited on the filters were redispersed in 7.5 mL of a 2.5 mM phosphate buffer solution (pH 8.4) in a Bandelin DT52 ultrasonic bath (Germany). The resulting suspension of volcanic ash NSP was further investigated by static light scattering, scanning electron microscopy (SEM), and capillary zone electrophoresis.

Study of volcanic ash nano- and submicroparticles using static light scattering and scanning electron microscopy. To assess particle size distribution, the isolated fractions were characterized by static light scattering using a Shimadzu SALD-7500nano analyzer (Japan) in the range of 7 nm to 800 μ m. Particle size and morphology were studied by SEM with a Tescan MIRA LMU microscope (Czech Republic). The test suspension was applied to a cleaned, polished silicon wafer, which gave a better contrast in observing individual particles.

Study of volcanic ash nano- and submicroparticles by capillary zone electrophoresis. The ash NSP fractions were analyzed using a Capel-105M capillary electrophoresis system (Lumex, Russia), equipped with a spectrophotometric detector with variable wavelength (190–380 nm). A quartz capillary 75 μ m in inner diameter, 60.0 cm in total length, and 50.0 cm in length to the detector was used. Experiments were performed at temperature 25°C and wavelength 220 nm with a source of high voltage of positive polarity. Benzyl alcohol served as a marker of electroosmotic flow (EOF). The capillary was washed between the measurements with a background electrolyte (a 2.5 mM phosphate buffer solution with pH 8.4) for 2 min; the

degree of purification was monitored by an electropherogram. The results of experiments were processed using the Elforan software. The electrophoretic mobility of particles was determined by the difference between the observed and electroosmotic mobilities.

Fractionation of nano- and submicroparticles of volcanic ash. The fraction of volcanic ash particles not exceeding 400 nm in size was isolated from suspensions by centrifugation (Elmi CM-6M, Latvia). The centrifugation time for the deposition of particles of more than 400 nm was calculated according to the Stokes equation, based on the average density of volcanic ash particles 2600 kg/m³. Fractionation was performed at a relative centrifugal acceleration of 2000 *g* for 5 min; then, the supernatant was decanted and studied by CZE.

RESULTS AND DISCUSSION

Capillary zone electrophoresis. The electrophoretic behavior of the suspensions of volcanic ash NSP was studied at a voltage of 25 kV. Depending on the sample, the shape of the electropherogram can change; however, the range of changes in electrophoretic mobility remains constant. Figure 1a shows an electropherogram of suspension 1 as an example. Here, in addition to the peak of the EOF marker, three partially resolved peaks of ash particles are recorded, the positions of the tops of which indicate a negative charge of the particles and correspond to electrophoretic mobilities of -28.1×10^{-5} , -31.8×10^{-5} , and -35.6×10^{-5} cm²/(V s). The presence of several peaks in the electropherogram indicates the discreteness of particle size distribution, that is, the existence of intervals including sizes most widespread for particles in suspension. The electropherogram of suspension 2 (Fig. 1c), in addition to the peak of the EOF marker, contains a broad peak with a shoulder on the right slope. The position of the peak top corresponds to electrophoretic mobility of -29.8×10^{-5} , and the shoulder is located at -35.9×10^{-5} cm²/(V s). A comparison of these two electropherograms shows that the position of the peak top in the second electropherogram (Fig. 1c) is intermediate with respect to the first and second peaks in the first electropherogram (Fig. 1a), and the position of the shoulder in the second electropherogram (Fig. 1c) practically coincides with the position of the third peak in the first electropherogram (Fig. 1a). The observed differences in the shape of the zones are probably because of a change in the relative concentration of particles of different sizes depending on the sample being analyzed.

With an increase in the background electrolyte concentration to 5.0 mM, the absolute value of electrophoretic mobility decreases by $(1.2\text{--}1.4) \times 10^{-5}$ cm²/(V s). With a decrease in the background electrolyte concentration to 1.25 mM, the peaks slightly, by 0.5×10^{-5} cm²/(V s), shift toward higher

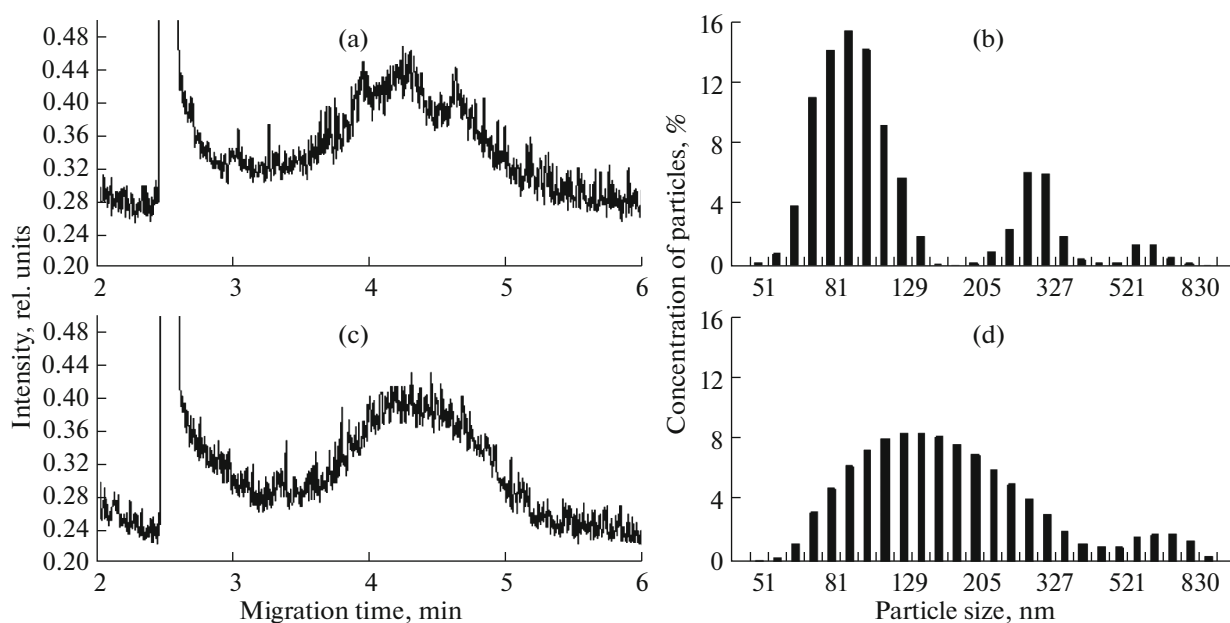


Fig. 1. Electropherograms and size distributions of volcanic ash particles in (a, b) suspension 1 and (c, d) suspension 2; dispersion medium and supporting electrolyte, 2.5 mM phosphate buffer, pH 8.4.

absolute values of electrophoretic mobility. The observed dependence of electrophoretic mobility on the background electrolyte concentration at constant pH is due to a decrease in the absolute value of the zeta potential with an increase in the ionic strength of the solution.

Static light scattering. To assess a possibility of using SLS for attributing peaks in the electropherograms to specific particle size ranges, we studied the size distributions of the fractions of ash NSP. It is important to note that the determination of particle sizes by SLS and the study by CZE were carried out almost simultaneously, using the same suspensions. Figures 1b and 1d show the size distribution diagrams of volcanic ash particles in suspensions 1 and 2, respectively.

The distributions differ in the numbers of recorded peaks (Fig. 1); however, the ranges of particle size changes generally coincide in both suspensions and amount to 45–830 nm. The full particle size range in the distribution diagram of suspension 1, including the size ranges of the first (45–130 nm) and second (180–400 nm) peaks, entirely coincides with the particle size range (45–400 nm) of the first peak in the distribution diagram of suspension 2. Large submicroparticles of the same size (400–830 nm) make up the third peak in the distribution diagram of suspension 1 and the second peak in the distribution diagram of suspension 2. It should be noted that the first peak in the distribution diagram of suspension 1 characterizes mainly the presence of nanoparticles, and the second peak is for submicroparticles with sizes of 180–400 nm. To compare the two distributions, the size range in the distribution

diagrams was conditionally divided into three ranges (45–100, 100–400, and 400–830 nm), which enabled us to estimate the relative concentration of nanoparticles, small submicroparticles, and large submicroparticles in both suspensions (Fig. 2). It was 69 and 31, 27 and 61, and 4 and 8% for suspensions 1 and 2, respectively. Thus, particles are present in both suspensions, the size range of which is the same, but the relative concentrations of nano- and submicroparticles differ. Different relative concentrations of particles of different sizes in suspensions are probably the reason for the appearance of different numbers of peaks on their electropherograms and size distribution diagrams.

The data obtained by static light scattering are in good agreement with the results of electrophoretic studies of suspensions. The number of peaks recorded in the electropherograms of suspensions is the same as their number observed on the size distribution diagrams. The attribution of the peaks in the electropherograms to the weight-average particle sizes, corresponding to the positions of the peaks in the size distributions, makes it possible to obtain the dependence of the electrophoretic mobility on the particle size (Fig. 3a). This dependence can be used to estimate the weight-average particle size in newly prepared suspensions. It should be noted that in the particle size range of 80–200 nm, where the strongest dependence of the electrophoretic mobility on the size is observed and the resolution of the peaks improves, the shape of the recorded peak is complex, as it is the result of superposition of several peaks.

Zeta potential of particles. The experimentally determined decrease in the absolute value of the elec-

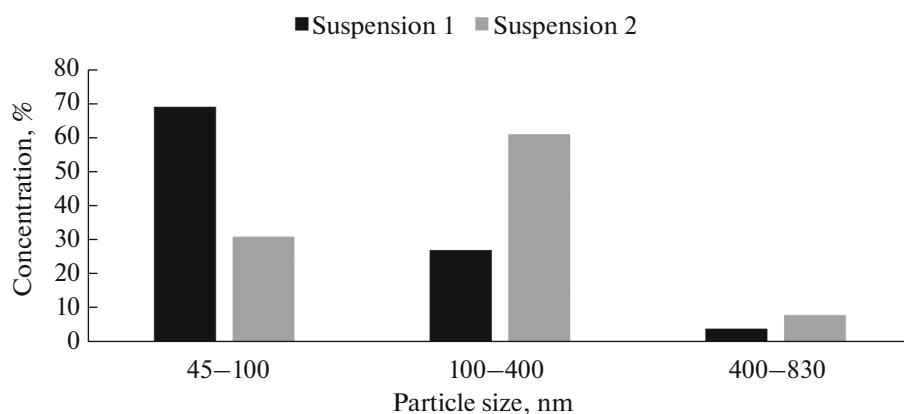


Fig. 2. Particle size distribution of volcanic ash in suspensions 1 and 2.

trophoretic mobility of particles with an increase in the background electrolyte concentration shows that the values of the zeta potentials of ash NSP are not located at the maximum on the curve of the dependence of the electrophoretic mobility on the zeta potential, where there is no effect of the zeta potential on the electrophoretic mobility of the particle. Also, these values are not located in the region where two values of the zeta potential correspond to the same magnitude of electrophoretic mobility [24]. In addition, the studied volcanic ash particles do not conduct electric current and generally have a pseudo-spherical shape, as evidenced by SEM micrographs (Fig. 4). Thus, the necessary conditions are met for using the values of electrophoretic mobility in calculating the zeta potential of particles. In order to select an analytical expression that satisfactorily describes the dependence of electrophoretic mobility on the zeta potential, it is necessary to estimate the zeta potential (ζ) and calculate the products kR , where k is the Debye–Hückel parameter, the reciprocal of the thickness of the double electric layer, and R is hydrodynamic radius of a particle. The Debye–Hückel parameter was calculated by the equation

$$k = \sqrt{\frac{e^2 N_A \sum_i z_i^2 c_i}{\epsilon_r \epsilon_0 k_B T}} = \sqrt{\frac{2e^2 N_A \sqrt{I}}{\epsilon_r \epsilon_0 k_B T}}$$

where e is the electron charge, z is the number of charges, c is the molar concentration of ions, N_A is the Avogadro number, ϵ_0 is the electric constant, ϵ_r is the relative dielectric constant, k_B is the Boltzmann constant, T is the thermodynamic temperature, and I is the ionic strength of the solution. It is found that the kR values corresponding to the selected experimental conditions vary in the range of 11–80. To evaluate the zeta potential, we plotted the dependences of electrophoretic mobility on particle size at three different values of the zeta potential: 40, 45, and 50 mV (Fig. 3). A comparison of these curves with the experimental

dependence of the electrophoretic mobility on the size of volcanic ash particles (Fig. 3) shows that the zeta potential of the particles in the suspensions does not exceed 50 mV. Under these conditions, we can neglect the relaxation effect (the concentration polarization of the double electric layer caused by the distortion of the ionic atmosphere of the particle during its movement in the electric field) to evaluate the zeta potential and use the Henry equation [24]. The calculated values of the zeta potential were in the range of 43–48 mV, i.e., were close to the limit value. To evaluate the relaxation effect, we used the approximate analytical expression proposed by Ohshima [25] and modified by Pyell et al. [18]. This equation takes into account the relaxation effect and the stronger effect of the counterion of the background electrolyte on the electrophoretic mobility of particles, that is,

$$\mu = \frac{2\epsilon_r \epsilon_0 \zeta}{3\eta \zeta} \times \left[f_1(kR) - \left(\frac{ze\zeta}{k_B T} \right)^2 f_3(kR) - m \left(\frac{ze\zeta}{k_B T} \right)^2 f_4(kR) \right],$$

where μ is the electrophoretic mobility, ζ is the zeta potential, and η is the dynamic viscosity of the medium.

It should be noted that the first term of this equation corresponds to the Henry equation. For comparison, we present the curves of the dependence of electrophoretic mobility on particle size at three different values of the zeta potential, calculated by the Henry equation and using the analytical expression proposed by Ohshima (Fig. 3b). Under the selected experimental condition, a slight effect of the relaxation effect on the electrophoretic mobility is observed. The zeta potential of particles with sizes up to 300 nm does not change and is –45 mV. At the same time, the absolute value of the zeta potential of larger particles is higher and amounts to 48 mV. The revealed effect of particle size on the zeta potential may be due to a change in the surface charge of the particles, which, in turn, may be

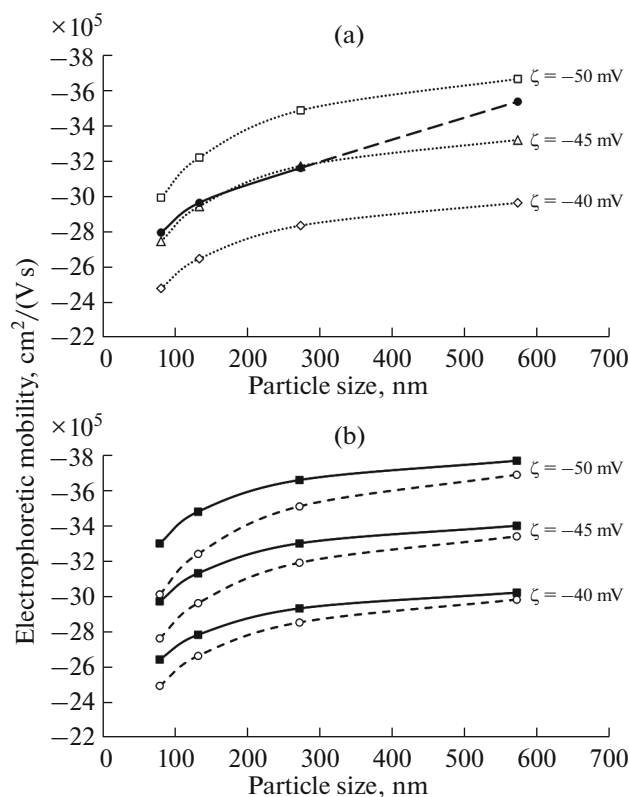


Fig. 3. Effect of size and zeta potential on the electrophoretic mobility of volcanic ash particles: (a) dependence of the electrophoretic mobility of volcanic ash particles on size, (●) experimental dependence; (b) dependences of the electrophoretic mobility of volcanic ash particles on size at zeta potentials of 40, 45, and 50 mV, obtained (■) by the Henry equation and (○) using the analytical expression proposed by Ohshima.

due to the presence of particles of different mineral composition in volcanic ash. Additional studies are needed to explain this phenomenon.

Fractionation of suspensions. To confirm the correctness of peak attribution in the electropherograms to specific sizes or size ranges of particles in suspension, the volcanic ash NSP were fractionated by centrifugation. The size of the particles to be settled was determined by the peak in the electropherogram of the initial suspension, corresponding to the maximum particle size. As an example, Fig. 5a shows an electropherogram, the peak in which corresponds to a particle size of 400 nm. To attribute the peak, the previously obtained dependence of the electrophoretic mobility on the particle size was used. After centrifugation, this peak disappears from the electropherogram (Fig. 5b), which indicates a possibility of a satisfactory estimation of the particle size from the calculated values of their electrophoretic mobility.

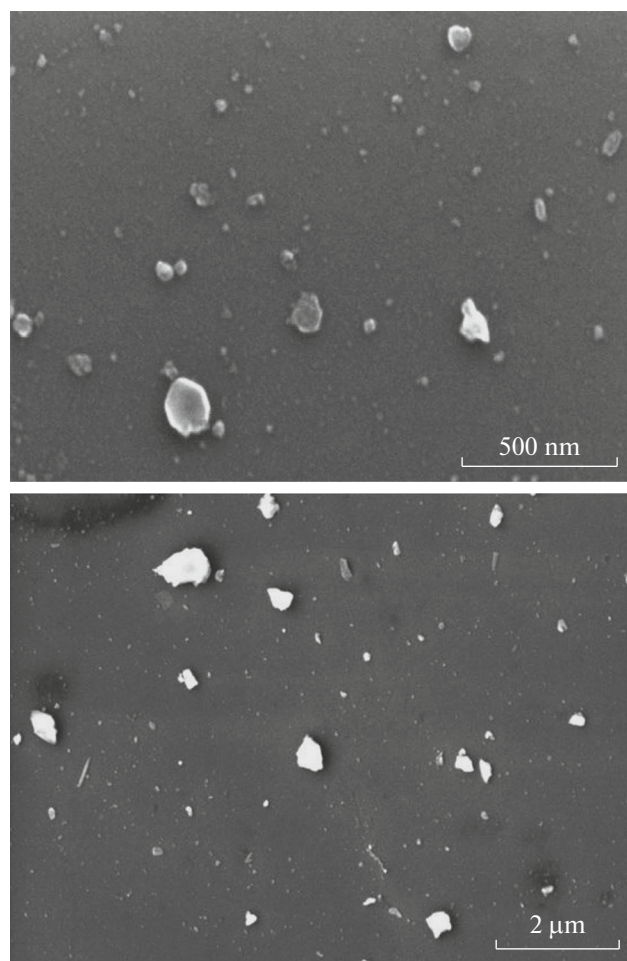


Fig. 4. SEM micrographs of nano- and submicroparticles of volcanic ash.

CONCLUSIONS

Thus, the study of the same suspensions simultaneously by capillary zone electrophoresis and static light scattering yields additional information on the properties of particles. Only under these necessary conditions, the obtained SLS distributions correspond to the particle size distribution of the suspensions studied by CZE. This is especially true for suspensions containing aggregation-prone inorganic particles. Moreover, by comparing the diagrams of SLS distributions and electropherograms, it becomes possible to attribute peaks in the electropherogram to specific particle size ranges, which, in turn, makes it possible to estimate the effect of particle size on the electrophoretic mobility and zeta potential. Such dependencies could not be found using each method individually. Thus, because of the simultaneous use of CZE and SLS, a synergistic effect arises, expanding the capabilities of both methods.

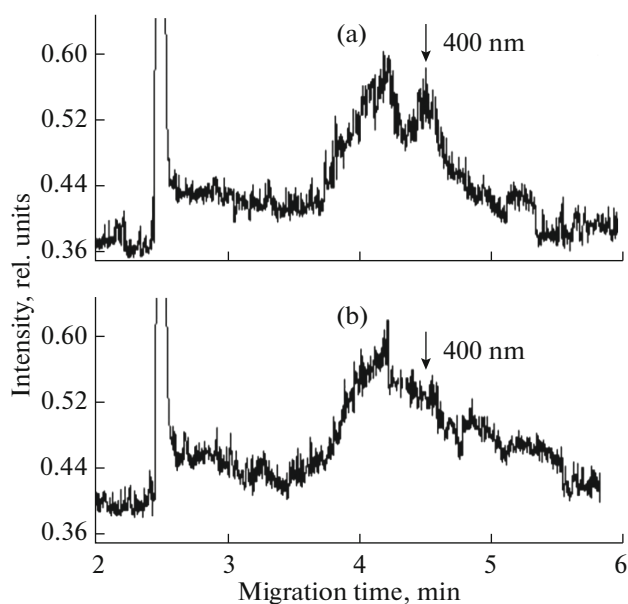


Fig. 5. Electropherograms of suspensions of volcanic ash particles (a) before centrifugation and (b) after centrifugation; dispersion medium and supporting electrolyte, 2.5 mM phosphate buffer, pH 8.4.

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