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Colloidal systems — Methods for zeta-potential determination —

Part 2: Optical methods

Systèmes colloïdaux — Méthodes de détermination du potentiel zêta —

Partie 2: Méthodes optiques

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 13099 was prepared by Technical Committee ISO/TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Particle characterization*.

ISO 13099 consists of the following parts, under the general title *Colloidal systems — Methods for zeta-potential determination*:

— *Part 1: Electroacoustic and electrokinetic phenomena*

— *Part 2: Optical methods*

The following part is under preparation

— *Part 3: Acoustic methods*

Introduction

Zeta-potential is a parameter that can be used to predict the long term stability of suspensions and emulsions and to study surface morphology and adsorption on particles and other surfaces in contact with a liquid. Zeta-potential is not a directly measurable parameter. It can be determined using appropriate theoretical models from experimentally determined parameters, such as electrophoretic mobility. Optical methods, especially electrophoretic light scattering, have been widely used to determine electrophoretic mobility of particles or macromolecules in suspension or in solution. The purpose of this part of ISO 13099 is to provide methods for measuring electrophoretic mobility using optical means and for calculating zeta-potential.

Colloidal systems — Methods for zeta-potential determination —

Part 2: Optical methods

IMPORTANT This part of ISO 13099 shall be read in conjunction with ISO 13099-1, which gives a comprehensive overview of the theory.

1 Scope

This part of ISO 13099 specifies two methods of measurement of electrophoretic mobility of particles suspended in a liquid: video microscopy and electrophoretic light-scattering. Estimation of surface charge and determination of zeta-potential can be achieved from measured electrophoretic mobility using proper theoretical models, which are described in detail in ISO 13099-1.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 13099-1, *Colloidal systems — Methods for zeta-potential determination — Part 1: Electroacoustic and electrokinetic phenomena*

ISO Guide 30: *Terms and definitions used in connection with reference materials*

3 Terms, definitions and symbols

3.1 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1.1
Brownian motion
random movement of particles suspended in a liquid cause by thermal movement of medium molecules

3.1.2
Doppler shift
change in frequency and wavelength of a wave for an observer moving relative to the source of the wave

3.1.3
electric surface potential
difference in electric potential between the surface and the bulk liquid

NOTE Electric surface potential is expressed in volts.

3.1.4
electrokinetic potential
zeta-potential
ζ-potential
ζ
difference in electric potential between that at the slipping plane and that of the bulk liquid

NOTE Electrokinetic potential is expressed in volts.

3.1.5
electroosmosis
motion of liquid through or past a charged surface, e.g. an immobilized set of particles, a porous plug, a capillary or a membrane, in response to an applied electric field, which is the result of the force exerted by the applied field on the countercharge ions in the liquid

3.1.6
electroosmotic velocity
υ_{eo}
uniform velocity of the liquid far from the charged interface

NOTE Electroosmotic velocity is expressed in metres per second.

3.1.7
electrophoretic mobility
μ
electrophoretic velocity per electric field strength

NOTE 1 Electrophoretic mobility is positive if the particles move toward lower potential (negative electrode) and negative in the opposite case.

NOTE 2 Electrophoretic mobility is expressed in metres squared per volt second.

3.1.8
electrophoretic velocity
υ_e
particle velocity during electrophoresis

NOTE Electrophoretic velocity is expressed in metres per second.

3.1.9
slipping plane
shear plane
abstract plane in the vicinity of the liquid/solid interface where liquid starts to slide relative to the surface under influence of a shear stress

3.2 Symbols

a particle radius

D diffusion coefficient

E electric field strength

k_B Boltzmann constant

I light intensity

N_A Avogadro's number

n medium refractive index

R_{cap} capillary radius

$S(\omega)$ frequency power spectrum of scattering

Γ characteristic Lorentzian half peak width

ε medium permittivity

ζ electrokinetic potential (zeta-potential)

η_0 medium viscosity

θ angle between incident light and scattered light

θ' angle between two cross-beams

κ reciprocal Debye length

λ wavelength

μ electrophoretic mobility

μ_{eo} electroosmotic mobility of liquid

ν frequency

ξ angle between scattered light and electric field direction

τ delay time in autocorrelation function

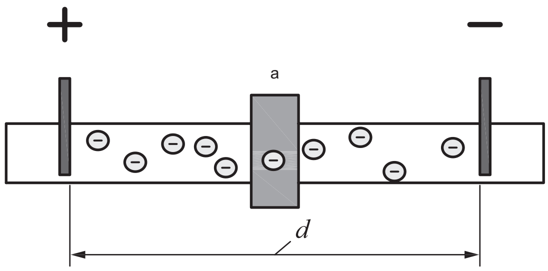
φ volume fraction

ω rotational frequency ($= 2\pi\nu$)

4 Principles

A suspension of particles having a given electrokinetic charge is placed in a cell which has a pair of electrodes placed some distance apart (Figure 1). This cell can be in the form of either a cylindrical or rectangular capillary with electrodes at either end, or a pair of electrodes at a known fixed distance apart that are dipped into a cuvette or other vessel. A potential is applied between the electrodes. Due to the process of electrophoresis, particles carrying a net negative charge are drawn towards the electrode of opposite sign and vice versa. In addition, if the capillary walls are charged, then an effect called electroosmosis causes the liquid to stream along the capillary walls. The direction and velocity of this flow depends on the sign and magnitude of the wall charge. The resulting velocity of the particle in the frame of references associated with the cell is superposition of the electrophoretic velocity and the velocity of electroosmotic flow. Here it should be noted that the time taken for the particle to reach the terminal electrophoretic velocity after the application of the electric field is much shorter than the period of time needed to fully establish the electroosmosis flow throughout the whole cell. This difference is exploited in some implementations. The velocity of the particles measured at a specific position can be determined using either video microscope or electrophoretic light scattering through a laser Doppler arrangement. Both the velocity and the direction of the moving particles in the frame of references associated with the cell are determined. Provided that the distance between the electrodes is known together with the applied electric potential, then the electrophoretic mobility can be established, from which a zeta-potential can be calculated using established theories. Alternatively, calibration with particles having a known zeta-potential can be used to eliminate the need to determine the unknown cell constant of a particular cell.

There are two distinctively different approaches to monitor particle motion in the electric field. Historically, the first deals with particle images observed through a microscope. It is referred to as the “microscopic method”, or alternatively as “microelectrophoresis”. The second relies on measuring light scattered by particles and extracting information on electrophoretic mobility from the Doppler frequency shift of the scattered light. This method is called the “electrophoretic light-scattering method”. For optical techniques, a cell constant for many types of cells has to be determined, through either calculation or measurement of a solution of known conductivity.



Key

d distance

a Measurement zone.

Figure 1 — Schematic diagram of electrophoresis measurement

5 Microscopic methods

The main principles of these methods can be traced back over two centuries (Reference [1]) following the development of microelectrophoresis. A light source illuminates particles migrating under the influence of a d.c. or a.c. electric field. The illuminated particles can be observed due to scattering. This illumination can be arranged either as a bright field or as a dark field or both (Reference [2]). The contrast afforded by the bright field illumination is inadequate to illuminate particles with sizes smaller than about 0,2 µm. Dark field illumination is suitable for capturing images of moving nano-particles with sizes down to nanometre scale.

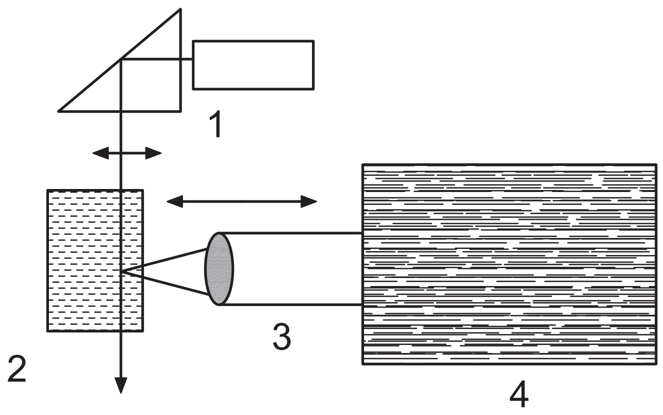
There are several approaches to the treatment of microscopic images of the moving particles. Depending on the degree of operator involvement, it can be classified as manual, semi-automatic and automatic. Manual methods track the movement of one or several individual particles by eye and a stopwatch and therefore are typically time consuming, tedious to employ and inaccurate.

In the semi-automatic methods, particles are tracked through a microscope manually while the apparatus either scans the illuminating light or moves a prism reflecting the illuminated image of particles. When the light-scanning velocity or prism-moving velocity is semi-automatically adjusted so that the particle image as viewed in the microscope is static, such a velocity is the electrophoretic velocity of particles (References [3][4]). These methods are only applicable to samples having a homogeneous electrophoretic mobility.

There are designs combining the manual microscopic observation with automatic electrophoretic light-scattering signal analysis to measure samples of polydisperse electrophoretic mobility (References [5][6]).

The appearance of modern charge-coupled devices (CCD) and computers has made it possible to capture images, transfer the images sequentially to a computer, and then using sophisticated image analysis to reconstruct trajectories of particles moving under the influence of an electric field from the time-stamped video frames. Only particles confined to video visibility can be measured. In order to record accurate moving distances, from the time duration between frames and the distance each particle moved, the velocity of each particle is calculated and combined with the applied field strength, and its electrophoretic mobility is obtained. Dark field illumination extends this method to nano-particles. This method allows application of electric field for very short periods of time, which resolves the problems of thermal convection and electrochemical contamination. Concentration of particles shall be very low in order to track individual particles.

A 90° laser scattering device is a typical optical arrangement of modern instruments. The laser serves as the illumination of the microscope focal plane. Both laser beam and microscope axis are perpendicular to the electric field. In Figure 2, the field direction is perpendicular to the plane of the drawing. Laser illumination and microscope require alignment with the stationary layer to avoid electroosmosis, which is explained in Annex A. It is necessary precisely to locate this position in order to accurately measure the electrophoretic motion of particles (Reference [7]).



Key

1 laser

2 cell channel cross-section

3 microscopic objective

4 video camera

Figure 2 — A typical electrophoresis video microscope

6 Electrophoretic light-scattering (ELS) method

6.1 General

Electrophoretic light scattering (ELS) is an indirect ensemble method for measuring electrophoretic mobility via the Doppler shifts in scattered light. In an ELS experiment, coherent incident light illuminates dispersed particles in a liquid that are subjected to an applied electric field. Charged particles move towards either the anode or the cathode, depending on the sign of their net charge. Because of the motion, the frequency of scattered light from particles is shifted due to the Doppler effect. From the frequency shift distribution, the particle electrophoretic mobility distribution can be determined. ELS provides rapid, accurate, automatic, and highly reproducible electrophoretograms of complex particulate samples suspended in either aqueous or non-aqueous media without the need to use standard particles for calibration (Reference [8]).

6.2 Cell design

Many designs of measurement cell have been employed. All cells have at least three functions: holding the sample containing the particles to be measured; supplying an electric field to the sample; and providing an entrance and an exit for the incident light and scattered light, respectively. Some cells are designed with liquid flow capability so that automatic titration can be performed with an additional device. In some implementations, special cell designs, e.g. utilizing a transparent electrode and multiple refraction for both incident and scattered light (Reference [9]), have been implemented to facilitate measurements of electrophoretic mobility at moderate concentrations. The electric field at the place of measurement shall be stable, homogenous, and parallel. To achieve that, either the two electrodes have to be placed very close to each other, in the case of cuvette cells, or the field path has to be confined, in the case of capillary cells. The voltage applied to the electrodes induces a current in the liquid if ions are present. This current can well be sufficiently high to cause Joule–Thompson heating of the liquid and lead to electrolysis at the electrodes. Therefore, choosing an appropriate type of cell and electrode material, sufficiently prompt temperature control, and properly applied field duration and field strength are all important factors to ensure correct and reproducible results.

To reduce polarization on the electrodes and maintain homogenous distribution of particles in the sample, the applied field direction is regularly reversed with an intervening off-time to minimize heating effects. In capillary cells, because of electroosmosis of liquid caused by charges on the walls, particles do not move in a static liquid. The liquid moves in a parabolic form across the closed capillary. Measurements are therefore taken at the so-called stationary layer where there is no liquid movement or multiple measurements are taken across the capillary to separate the liquid movement from the electrophoretic motion of the particles. Some implementations offer disposable cells.