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Methods for zeta potential determination — Streaming potential and streaming current methods for porous materials

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Contents

Foreword

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Introduction

There are several different types of porous materials, such as porous monoliths, porous particles, deposits of solid particles, etc. Each of these different types can require a special sample handling system. This document covers only those aspects of the measurement and interpretation of electrokinetic and electroacoustic phenomena that are common for all these types of porous materials.

The determination of the zeta potential in wetted porous materials is complicated by the fact that this parameter is not a directly measurable quantity. It is calculated from the measured electric signal (either current or potential) that is generated in the wetted porous material by the liquid moving under the influence of an applied pressure gradient. The theories used in the calculation will not be discussed in detail.

There are a number of situations where electrokinetic and electroacoustic measurements, without further interpretation, provide extremely useful and unequivocal information for technological purposes. The most important of these situations are:

a) identification of the isoelectric point by titration of the zeta potential against a potential determining ion (e.g. pH titration);

b) identification of the isoelectric point by titration with other reagents such as surfactants or polyelectrolytes;

c) identification of a saturation plateau in the adsorption indicating optimum dosage for a dispersing agent;

d) relative comparison of various porous materials with regard to their electric surface properties.

Methods for zeta potential determination — Streaming potential and streaming current methods for porous materials

1 Scope

This document specifies methods for the zeta potential determination in porous materials that are saturated with a liquid where the pores are readily accessible. There is no restriction on the value of the zeta potential or on the porosity of the porous material. A pore is assumed to be on the scale of hundreds of micrometres or smaller without any restriction on pore geometry.

This document covers the applications of alternating current (AC) and direct current (DC) methods using aqueous media as wetting liquids.

This document is restricted to linear electrokinetic effects.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

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

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1 Terms related to the electric double layer and the zeta potential

3.1.1
Debye length
κ^{-1}
characteristic length of the *electric double layer* (3.1.2) in an electrolyte solution

Note 1 to entry: The Debye length is expressed in metres.

[SOURCE: ISO 13099-1:2012, 2.1.2, modified — In the Note to entry, "nanometres" has been changed to "metres".]

3.1.2
electric double layer
spatial distribution of electric charges that appears on and at the vicinity of the surface of an object when it is placed in contact with a liquid

3.1.3
electric surface charge density

σ

charges on an interface per area due to specific adsorption of ions from the liquid bulk, or due to dissociation of the surface groups

Note 1 to entry: Electric surface charge density is expressed in coulombs per square metre.

[SOURCE: ISO 13099-1:2012, 2.1.6]

3.1.4
electrokinetic charge density

σ_{ek}

effective charges at the slipping plane (shear plane) per area due to partial compensation of the *electric surface charge density* (3.1.3) by the accumulation of oppositely charged solutes in the bulk liquid phase

Note 1 to entry: Electrokinetic charge density is expressed in coulombs per square metre.

3.1.5
isoelectric point

condition of liquid medium, usually the value of pH, that corresponds to zero *zeta-potential* (3.1.7)

[SOURCE: ISO 13099-1:2012, 2.1.10]

3.1.6
surface conductivity

K^{σ}

excess electrical conduction tangential to a charged surface

Note 1 to entry: Surface conductivity is expressed in siemens.

[SOURCE: ISO 13099-1:2012, 2.2.11]

3.1.7
electrokinetic potential
zeta-potential
ζ-potential

ζ

difference in electric potential between that at the slipping plane and that of the bulk liquid

Note 1 to entry: Electrokinetic potential is expressed in volts.

[SOURCE: ISO 13099-1:2012, 2.1.8]

3.2 Terms related to electrokinetic and electroacoustic phenomena

3.2.1
colloid vibration current
CVI

alternating current generated between two electrodes, placed in a dispersion, if the latter is subjected to an ultrasonic field

[SOURCE: ISO 13099-1:2012, 2.3.1, modified — The admitted term I_{CVI} has been removed; the note has been removed.]

3.2.2
electrokinetic phenomena

phenomena associated with tangential liquid motion adjacent to a charged surface

3.2.3
electroacoustic phenomena

phenomena arising from the coupling between the ultrasound field and electric field in a liquid that contains ions

Note 1 to entry: Either of these fields can be primary driving force. Liquid can be a simple Newtonian liquid or complex heterogeneous dispersion, emulsion or even a porous body. There are several different electroacoustic effects, depending on the nature of the liquid and type of the driving force.

3.2.4
seismoelectric current
SEI

I_{see}

non-isochoric *streaming current* (3.2.5) that arises in a porous body in liquid when an ultrasound wave propagates through

Note 1 to entry: A similar effect can be observed at a non-porous surface, when sound is bounced off at an oblique angle.

Note 2 to entry: Seismoelectric effect is expressed in amperes.

3.2.5
streaming current

I_{str}

current through a porous body in liquid resulting from the motion of the liquid under an applied pressure gradient

Note 1 to entry: Streaming current is expressed in amperes.

[SOURCE: ISO 13099-1:2012, 2.2.8]

3.2.6
streaming current coupling coefficient

$I_{\mathrm{str}}/\Delta P$

electrokinetic phenomenon (3.2.2) determined by the slope of the linear dependence of the measured *streaming current* (3.2.5) on an applied pressure gradient

Note 1 to entry: Streaming current coupling coefficient is expressed in amperes per pascal.

3.2.7
streaming potential

U_{str}

potential difference at zero electric current, caused by the flow of liquid under a pressure gradient through a capillary, plug, diaphragm or membrane

Note 1 to entry: Streaming potentials are created by charge accumulation caused by the flow of countercharges inside capillaries or *pores* (3.3.5).

Note 2 to entry: Streaming potential is expressed in volts.

[SOURCE: ISO 13099-1:2012, 2.2.10]

3.2.8
streaming potential coupling coefficient

$U_{\mathrm{str}}/\Delta P$

electrokinetic phenomenon (3.2.2) determined by the slope of the linear dependence of the measured *streaming potential* (3.2.7) on an applied pressure gradient

Note 1 to entry: Streaming potential coupling coefficient is expressed in volts per pascal.

3.3 Terms related to porous materials

3.3.1
deposit of solid particles

accumulation of individual *particles* (3.3.4) by sedimentation from a *dispersion* (3.3.2) on a solid support

3.3.2
dispersion

multi-phase system in which discontinuities of any state (solid, liquid or gas) are homogeneously distributed in a continuous phase of a different composition or state

Note 1 to entry: This term can also refer to the act or process of producing a dispersion, but in this context the term "dispersion process" shall be used.

Note 2 to entry: If solid *particles* (3.3.4) are dispersed in a liquid, the dispersion is referred to as a suspension. If the dispersion consists of two or more immiscible liquid phases, it is termed an emulsion.

[SOURCE: ISO/TS 22107:2021, 3.7]

3.3.3
monolith

solid porous object with size on scale of a few millimetres or larger

3.3.4
particle

minute piece of matter with defined physical boundaries

Note 1 to entry: A physical boundary can also be described as an interface.

Note 2 to entry: A particle can move as a unit.

[SOURCE: ISO 26824:2013, 1.1, modified — Note 3 to entry has been removed.]

3.3.5
pore

cavity or channel which is deeper than it is wide, otherwise it is part of the material's roughness

[SOURCE: ISO 15901-1:2016, 3.5]

3.3.6
pore size

internal *pore* (3.3.5) width, which is a representative value of various sizes of vacant space inside a *porous material* (3.3.8)

EXAMPLE Diameter of a cylindrical pore or the distance between the opposite walls of a slit.

[SOURCE: ISO 15901-1:2016, 3.13, modified — Part of the definition has been moved to an example.]

3.3.7
porosity

ratio of the volume of the accessible *pores* (3.3.5) and voids to the bulk volume occupied by an amount of the solid

[SOURCE: ISO 15901-1:2016, 3.27]

3.3.8
porous material

materials with cavities or channels which are deeper than they are wide

3.3.9
powder

porous or nonporous solid composed of discrete *particles* (3.3.4) with maximum dimension less than approximately 1 mm

Note 1 to entry: Powders with a particle size below approximately 1 µm are often referred to as fine powders.

[SOURCE: ISO 15901-1:2016, 3.4, modified — Part of the definition has been moved to a Note to entry.]

4 Symbols

a	pore radius
a_i	radius of particles building sediment
c	electrolyte concentration in the bulk
c_i	concentration of the *i*-th ion species
t_{cr}	time to reach first maximum of the electroacoustic signal
z_i	valence of the *i*-th ion species
$z_{\pm}$	valences of cations and anions
D_{eff}	effective diffusion coefficient of the electrolyte
F	Faraday constant
I	ionic strength
I_{see}	streaming current in high frequency AC mode (seismoelectric current)
I_{str}	streaming current in DC mode
K	electric conductivity
K_{m}	electric conductivity of the dispersion medium or liquid
K_{s}	electric conductivity of the wetted porous material
P	pressure
R	ideal gas constant
T	absolute temperature
U	voltage
U_{str}	streaming potential
$\dot{V}$	volume flow rate
ε_0	vacuum permittivity
ε_{m}	relative permittivity of the medium
η	dynamic viscosity
φ	volume fraction of solids
φ_{sed}	volume fraction of solids in sediment
κ^{-1}	Debye length
ρ_{m}	liquid density
ρ_{p}	particle density

ρ_s	density of the dispersion
σ	electric surface charge density
σ^d	electric charge density of the diffuse layer
ω	circular frequency
ζ	electrokinetic potential, zeta potential
Ω	porosity

5 Streaming current and streaming potential

5.1 General overview

The phenomena of streaming current and streaming potential occur in porous materials that are wetted with a liquid. The pore walls of such porous materials are covered with electric charges that are generated either by the dissociation of surface functional groups or by the specific adsorption of solutes at the solid-liquid interface. These surface and interfacial charges are screened by stationary and diffuse layers of accumulated ions forming a structure known as the "electric double layer" (EDL). Different types and models of EDLs applicable to porous materials are described in Annex A.

The application of a pressure gradient on wetted porous materials generates a flow of liquid passing through the pores. This liquid flow, in turn, causes an electric response, either current or potential, depending on the method of its measurement. This electric response occurs due to the motion of the diffuse layer that is dragged by the liquid flow tangentially to the pore-liquid interfaces. This response is referred to as the "streaming current" or the "streaming potential".

The AC and DC modes of the streaming current and streaming potential require different measuring techniques and different instrumentation. The applicability of AC and DC techniques for the calculation of the zeta potential is determined by the pore size of the porous material. The threshold between the two methods may be defined in terms of the pore size. This critical pore size is approximately 10 µm, where the AC mode is applicable below and the DC mode above this threshold size. There is a certain size range around 10 µm where both AC and DC methods are applicable. Due to the different applicable size ranges, the AC and DC methods are discussed separately below.

There is another justification for a separate presentation of AC and DC techniques. The generation of liquid flow with a DC pressure gradient is possible only for porous materials with a sufficiently high hydrodynamic permeability. Decreasing either pore size or porosity leads to a decrease of the permeability and eventually blocks liquid flow. This means that a DC pressure can be applied for generating streaming current and streaming potential only for sufficiently large pores and porosity. In contrary, an AC pressure gradient at high frequency (MHz) can penetrate only into porous materials with small pores and limited porosity.

This differentiation indicates different application ranges for the DC and AC streaming current and streaming potential measurements. The DC mode is applicable to materials with large pores and high porosity, the AC mode to materials with small pores and low porosity.

5.2 Streaming potential in DC mode

5.2.1 General

The streaming potential depends strongly on the distribution of the electric potential inside the pores. Figure A.1 illustrates possible space distributions of this potential including two extreme cases:

a) isolated thin double layers;

b) homogeneous, completely overlapped double layers.

There are analytical theories of the streaming potential that correspond to these two extreme cases.

Smoluchowski[5] developed the theory for the streaming potential in case of isolated thin electric double layers. This theory yields the following expression [Formula (1)] for the electric potential difference ΔU_{str} generated by a pressure difference ΔP:

$$\Delta U_{\mathrm{str}} = \frac{\varepsilon_{\mathrm{m}} \varepsilon_0 \zeta}{\eta K} \Delta P \tag{1}$$

where

ε_{m} is the dielectric coefficient of the liquid;

ε_0 is the vacuum permittivity;

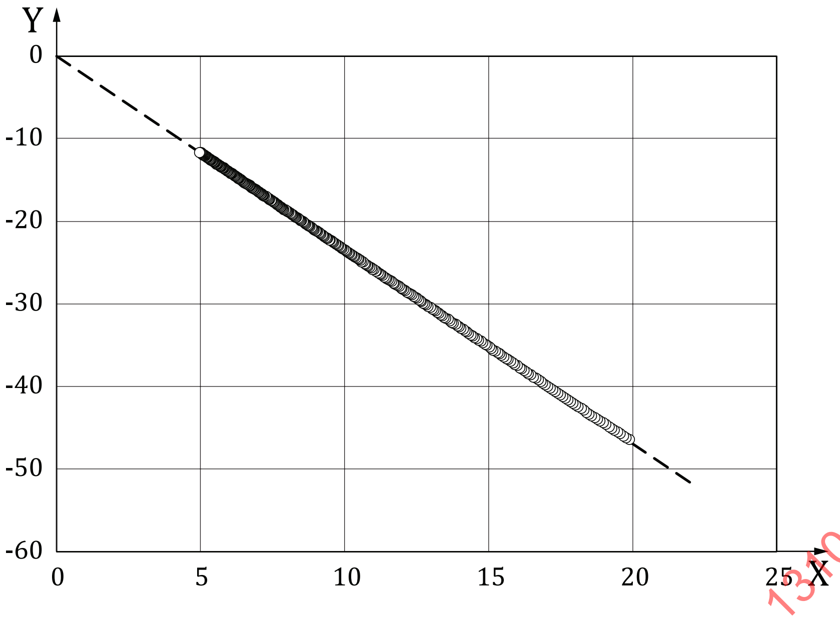
ζ is the electrokinetic potential (zeta potential) of the pore surface;

η is the dynamic viscosity of the liquid;

K is the electric conductivity inside a capillary flow channel.

5.2.2 Measurement of the streaming potential coupling coefficient

The streaming potential and alternatively the streaming current are the electrical responses to the flow of a test liquid through a capillary or a capillary network driven by a pressure gradient that is applied between both ends of this capillary (capillary network). According to Formula (1), the streaming potential is strongly dependent on the applied pressure gradient. For the sake of measurement reproducibility and independence of the instrument design and operation conditions, the zeta potential is related to the streaming potential coupling coefficient $\mathrm{d}U_{\mathrm{str}}/\mathrm{d}\Delta P$. The streaming potential coupling coefficient is calculated by referring the measured streaming potential to the applied pressure gradient. Figure 1 shows the result of a streaming potential measurement in DC mode during a continuously decreasing pressure gradient.



Key

X pressure difference (kPa)

Y streaming potential (mV)

NOTE polyether ether ketone, particle size 80 µm, 0,001 mol/l KCl, conductivity 0,014 S/m, pH 5,36, $\zeta = -43{,}76$ mV.

Figure 1 — Measurement result of the streaming potential at a continuously decreasing pressure gradient in DC mode

5.2.3 Calculation of the zeta potential

The calculation of the zeta potential at the particle-liquid or pore-liquid interfaces from the measurement of the streaming potential coupling coefficient is derived from Formula (1).

For a sufficiently large distance between adjacent particles in the sample plug or a sufficiently large pore size at a sufficiently high ionic strength of the test liquid, the conductivity term K in Formula (1) may be replaced by the conductivity of the bulk liquid phase K_m. After re-arrangement of Formula (1), we obtain Formula (2):

$$\zeta = \frac{\mathrm{d}U_\mathrm{str}}{\mathrm{d}\Delta P}\frac{\eta}{\varepsilon_\mathrm{m}\varepsilon_0}K_\mathrm{m} \qquad (2)$$

for the zeta potential determined from a streaming potential measurement. The application of Formula (2) is valid if the inter-particle distance in a plug of a particulate sample or the wall-to-wall distance of a porous material is large in comparison with the extension of the electric double layer at the solid-liquid interface, which is a function of the ionic strength according to Formula (A.1). If the condition of $a >> \kappa^{-1}$, where a is either the average distance between particles in a plug of a particulate sample or the average pore radius of a porous material, is not fulfilled by the properties of the corresponding sample, Formula (2) delivers a zeta potential result that is too low in magnitude and commonly denoted an apparent zeta potential. Formula (2) is also not applicable to determine the true zeta potential if the material bulk or the material surface are electrically conductive even if the boundary condition of $a >> \kappa^{-1}$ is fulfilled.

Alternatively, the zeta potential is determined from the streaming current coupling coefficient $\mathrm{d}I_\mathrm{str}/\mathrm{d}\Delta P$ according to Formula (3):

$$\zeta = \frac{\mathrm{d}I_\mathrm{str}}{\mathrm{d}{''}P}\frac{\eta}{\varepsilon_\mathrm{m}\varepsilon_0}\frac{L}{A} \qquad (3)$$

where

L is the length of the flow channel;

A is the cross-section of the flow channel;

The application of Formula (3) requires the knowledge of the ratio L/A. For a plug of a particulate sample or a porous material, the voids inside the particle plug and the pores of the porous material, respectively, determine the geometry of the flow channel. The exact length and cross-section of these networks of capillaries cannot be determined quantitatively and therefore makes Formula (3) not applicable for the zeta potential analysis of a plug of particles or a porous material.

5.3 Streaming current in AC mode

Ultrasound at high frequency is the driving force for the generation of the streaming current in the AC mode of measurement. Frenkel[6] introduced the term “seismoelectric effect”. Liquid becomes compressible at a frequency in the MHz range, and, consequently, the corresponding electrokinetic effects become non-isochoric.[7][8]

Frenkel used the theory of Smoluchowski for the streaming current in DC mode to derive the equation for the seismoelectric current, which is also limited to EDLs that are isolated and thin compared to the pore size. The seismoelectric current I_{see} is related to the zeta potential by Formula (4)[9][10]:

$$I_{\text{see}} = \frac{\varepsilon_{\text{m}}\varepsilon_0\zeta}{\eta}\left(1-\frac{\rho_{\text{m}}}{\rho_{\text{s}}}\right)\frac{K_{\text{s}}}{K_{\text{m}}}\nabla P \qquad (4)$$

where

ρ_{m} is the density of the liquid;

ρ_{s} is the density of the wetted porous material;

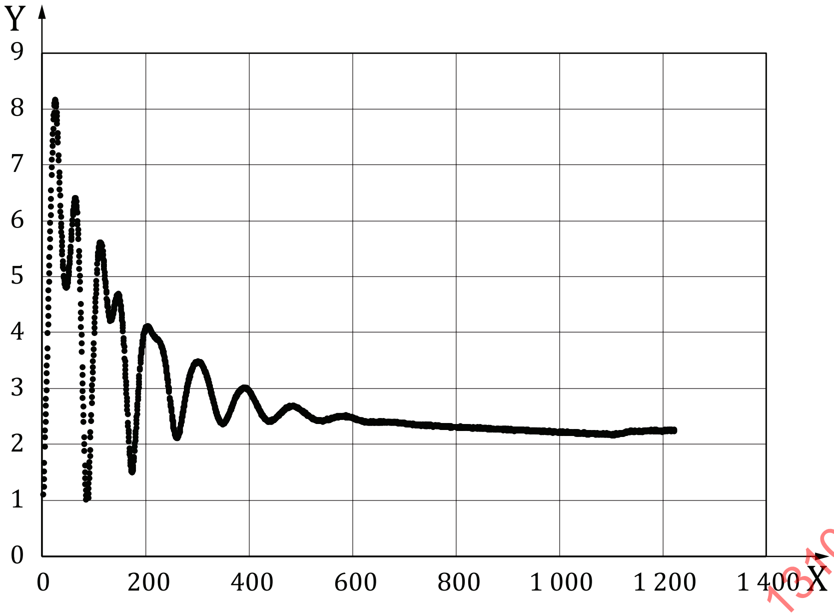
K_{m} is the electric conductivity of the liquid;

K_{s} is the electric conductivity of the porous material.[11]

An alternative theory for smaller pores is also available.[12]

The measurement of the seismoelectric current is demonstrated by an example of silica particles with a median diameter of 1,5 µm, which were used for building up a sediment as a model of a porous body. A dispersion of these particles was prepared at a weight/volume percentage concentration of 10 % dispersed in distilled water at pH 10. Sonication was applied for 5 min for dispersing particles in this solution.

Each of the sedimentation experiments with the silica particles consisted of 3 000 continuous measurements of the electroacoustic signal generated by silica particles sedimenting to the surface of the electroacoustic probe. Each experiment took approximately 20 h to complete. All the particles settled on the probe surface during this time.



Key

X time (min)

Y electroacoustic magnitude [10^7 mV·(s/g)$^{1/2}$]

Figure 2 — Time dependence of the measured seismoelectric current generated by the gradual build-up of the sediment on the face of the electroacoustic probe

Figure 2 shows the evolution of the magnitude of the electroacoustic signal with time. The particle dispersion is thoroughly mixed before pouring into the cup on the face of the electroacoustic probe. Initially, particles are therefore homogeneously distributed. The first measurement reflects the colloid vibration current (CVI) signal from such homogeneously dispersed particles. As time passes by, particles start settling on the surface of the probe. As a result, their concentration in the vicinity of the surface of the probe increases. The CVI signal increases as well because it is proportional to the particle volume fraction. This increase continues until particles fill a layer with the thickness of the half wavelength of the sound. After that, particles begin filling the second half wavelength layer where the direction of the pressure gradient of the ultrasound wave reverses. Consequently, particles start moving to the opposite direction, which leads to the reversal of the CVI signal generated by these particles. This contribution to the CVI signal will be subtracted from the CVI signal caused by the particles in the first wavelength layer. As a result, the total CVI signal starts dropping. This is reflected in Figure 2 as the signal of the electroacoustic magnitude reaches the first maximum.

The growing deposit of particles becomes more and more dense due to the ongoing sedimentation. At some point, the electroacoustic phenomenon switches from CVI mode (particles moving relative to a steady liquid) to seismoelectric current (SEI) mode (liquid moves relative to densely packed particles). Apparently, the first minimum in the curve in Figure 2 corresponds to this transition. A small increase in the signal occurs due to the larger magnitude of SEI compared to CVI for the same number of particles. The decline after the second maximum reflects the continuing filling up of the second wavelength layer. Afterwards, the signal starts growing again when the third half wavelength layer begins to be filled with settling particles.

The amplitude of these oscillations decays because of ultrasound attenuation. It eventually reaches saturation after the particles have filled approximately 10 wavelength layers. The thickness of each layer depends on the ultrasound frequency. At a frequency of 3,3 MHz, which corresponds to a wavelength of approximately 450 µm, the electroacoustic signal reaches saturation when the particles fill a roughly 4,5 mm thick layer on top of the probe.

There are two important parameters that characterize the curve in Figure 2.

The first one is the time required for the electroacoustic signal to reach the first maximum. This number, t_{cr}, can be used to determine the porosity of the sediment Ω or, alternatively, the volume fraction of silica in the sediment φ_{sed} (see Annex C), using Formula (5):

$$\varphi_{sed} = 1 - \Omega \tag{5}$$

The second parameter is the final magnitude of the electroacoustic signal after it reaches saturation at the end of the experiment. This parameter can be used to calculate the zeta potential in the sediment using the derived seismoelectric theory.

The final magnitude of the electroacoustic signal, which is obtained when reaching saturation at the end of the experiment, is identical to the magnitude of the electroacoustic signal for the particle dispersions measured through the colloid vibration current. A dispersion usually fills a layer that is thicker than 450 µm. The calibration constant determined with a certified reference material corresponds to this saturated value. It means that the final magnitude of the electroacoustic signal can be used to calculate the ζ-potential of particles in a sediment by assuming the same calibration constant.

Application of Formula (4) for the calculation of the zeta potential requires information on the ratio of conductivities of the liquid and the sediment. Instead of measuring them, a calculation can be employed based on the Maxwell-Wagner theory.[13][14] It gives an expression for conductivity in heterogeneous systems, which is rather simple in the case of a negligible surface conductivity, as indicated by Formula (6):

$$\frac{K_s}{K_m} = \frac{1 - \varphi_{sed}}{1 + 0{,}5\varphi_{sed}} = \frac{\Omega}{1{,}5 - 0{,}5\Omega} \tag{6}$$

Substituting the ratio of conductivities in Formula (4) by Formula (6) and expressing the ratio of densities of the liquid and the sediment though the porosity Ω of the sediment and the particle density ρ_p, Formula (7) is obtained for the seismoelectric current generated by the propagation of ultrasound through the sediment:

$$I_{see} = \frac{\varepsilon_0 \varepsilon_m \zeta}{\eta} \left(1 - \frac{1}{\Omega + \dfrac{\rho_p}{\rho_m}(1 - \Omega)} \right) \frac{\Omega}{1{,}5 - 0{,}5\Omega} \nabla P \tag{7}$$

A result of the zeta potential calculated using Formula (7) is shown in Table 1. The zeta potential for the silica particle dispersion at a mass fraction of 10 % was determined by the measurement of the colloid vibration current as ζ = −61,2 ± 0,2 mV. There is rather close agreement between ζ potential values for dispersion and for sediment.

Table 1 — Zeta potential for a dispersion and for a sediment of silica particles

Sample	Zeta potential mV	Experimental condition
Silica particle dispersion	−61,2 ± 0,2	Dispersion at 4,8 % vol. Mixing. Inertia size related correction, CVI theory[a]
Silica particle sediment	−57,9 ± 0,9	Sediment with 62 % volume fraction, porosity 38 %, seismoelectric theory, Formula (7)[b]

[a] Determination using the measurement of the colloid vibration current (CVI). Data sourced from Reference [15].

[b] Determination using the seismoelectric current (conductivity 0,03 S/m, pH 7,3).

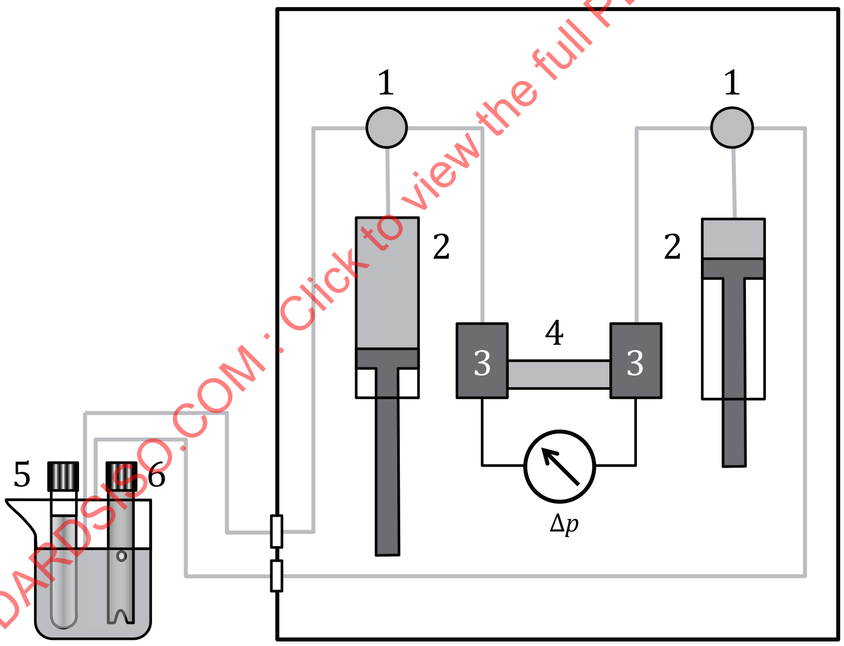
6 Measurement of DC streaming potential for porous materials

6.1 Operational procedures

The main components of an instrument for DC streaming potential/streaming current measurement comprise a sample holder for the solid sample, a container for the test liquid, a set of electrodes for the measurement of streaming potential and streaming current, a supply of pressure (either a mechanical pump or a pressurized gas reservoir), a pressure sensor for recording the pressure difference, an electrometer with the capability to measure streaming potential (that requires an electric circuit with a high internal impedance of the electrometer) and streaming current (that requires an electric circuit with a low internal impedance of the electrometer), and a conductivity probe for the measurement of the bulk electric conductivity of the test liquid. When using an aqueous solution as the test liquid a significant dependence of the zeta potential on the pH of the aqueous solution is commonly observed. The equipment of the instrument for streaming potential and streaming current measurement with an integrated pH probe for a continuous monitoring of the pH of an aqueous test solution is therefore recommended.

A granular or powder sample is prepared as a porous plug and the voids between granular particles are filled with a test liquid. A condensed porous material provides a network of pores, which are again filled with the test liquid. A pressure gradient is applied between the ends of the plug of the granular sample or between the ends of the porous material, which are soaked with the test liquid. The pressure gradient provokes liquid flow and the transport of the diffuse layer of the electric double layer at the solid-liquid interface, which contains ions that compensate the electrokinetic charge density. The moving ions in the diffuse layer generate an electric current (a DC current, which is called the streaming current). At a sufficiently high impedance of the electrometer (voltmeter), the streaming current is compensated by a back-current through the conductive pathway of the test liquid. At the equilibrium of streaming current and back-current, the electric potential between the ends of the plug of the granular sample or between the ends of the porous material (a DC voltage, which is called the streaming potential) is measured. Alternatively, the streaming current is measured directly by using a low impedance of the electrometer (amperemeter).

Figure 3 shows the schematic drawing of a typical setup for the streaming potential and streaming current measurement in DC mode.



Key

1	3-way valve	4	sample holder
2	syringe pump	5	pH probe
3	electrodes, pressure sensors	6	conductivity probe

Figure 3 — Schematic drawing of an experimental setup for the streaming potential/streaming current measurement in DC mode[16]

The streaming potential (streaming current) is measured by a set of electrodes, which are located at both ends of the plug of the particle sample or of the porous material. Reversible electrodes such as silver-silver chloride (Ag|AgCl) electrodes are recommended to suppress the effect of electrode polarization, i.e. an offset of the measured voltage different from 0 V in the absence of flow of the test liquid (see 6.8.5).

The streaming potential coupling coefficient (streaming current coupling coefficient) may be determined by different methods.

- A single-point measurement of the streaming potential (streaming current) at a given pressure difference applied between the ends of the plug of the particulate sample or of the porous material enables the calculation of the quotient $\Delta U_{\mathrm{str}}/\Delta P$ ($\Delta I_{\mathrm{str}}/\Delta P$). This approach can be subject to a significant error if the assumption of a negligible electrode polarization does not hold (see 6.8.5).
- The measurement of streaming potential (streaming current) at a single pressure difference, where pressure is applied alternatively on either end of the plug of the particulate sample or of the porous material, eliminates the contribution of any electrode polarization to the calculation of the quotient $\Delta U_{\mathrm{str}}/\Delta P$ ($\Delta I_{\mathrm{str}}/\Delta P$).
- A series of streaming potential measurements (streaming current measurements) at a series of individual pressure differences shall present a linear dependence of the streaming potential (streaming current) on the applied pressure difference. A fit of the set of streaming potential (streaming current) and pressure difference data by a linear regression gives the differential quotient $\mathrm{d}\Delta U_{\mathrm{str}}/\mathrm{d}\Delta P$ ($\mathrm{d}\Delta I_{\mathrm{str}}/\mathrm{d}\Delta P$) and eliminates the contribution of any electrode polarization.
- The measurement of streaming potential (streaming current) simultaneously to a continuously changing pressure gradient enables the recording of a large set of streaming potential (streaming current) and pressure difference data for a fit by a linear regression with improved measurement statistics. Preferably the pressure difference is varied without the action of a mechanical pump in order to eliminate pressure fluctuations.

6.2 Instrument location

The instrument for streaming potential and streaming current measurement in DC mode should be located in a clean environment. Conveniently, the instrument is placed next to a water purification unit for the dispense of ultrapure water for the preparation of the aqueous test solutions and for cleaning of the wetted parts of the instruments. It is also convenient to place the instrument next to a sink for disposing the used measuring and cleaning solutions.

Sources of mechanical vibration nearby the instrument do not harm the measurement; however, the instrument should not contact any device that generates such vibrations.

The influence of temperature on the zeta potential is negligible in the range of 20 °C to 30 °C, however, the temperature dependences of the electric conductivity, the dynamic viscosity and the dielectric permittivity of the test solution need to be considered. It is common practice to record the electric conductivity and the temperature of the test solution simultaneously to the streaming potential or streaming current, and to use tabulated values for the temperature dependence of viscosity and dielectric permittivity of the solvent for the calculation of the zeta potential according to Formula (2) and Formula (3). The viscosity and dielectric permittivity values for the solvent are a suitable substitute for the corresponding parameters of the aqueous solution especially at low and medium ionic strength of $I < 0{,}1$ mol/l.

6.3 Sample holder

A variety of different sample holders are required to cover the wide range of solid materials with different size and shape. For particulate samples and porous materials, the sample is accommodated in a sample holder with a cylindrical compartment. A suitable diameter of the cylindrical compartment is in the range of 10 mm to 20 mm in order to provide a cross-section of the plug of granular media or of the porous material for a sufficiently high volume flow rate of the test liquid at the applied pressure gradient. The cylindrical jacket of the compartment shall fully seal the particulate plug or porous material sample to avoid any bypass of the test liquid. At both ends of the sample plug or porous material, perforated disks support the sample thereby enabling the permeation of the test solution without adding an additional pressure gradient. For a condensed porous material, support disks with coarse holes of 1 mm to 2 mm diameter are suitable. For sample plugs prepared from particles, additional support is required, e.g. by covering the ends of the particle plug with filter disks with a mesh that is sufficiently dense to prevent leakage of particles as well as sufficiently loose to let the test liquid permeate without any additional pressure drop across the filter disk.

The compartment of the sample holder enables the adjustment of a flexible volume to accommodate different amounts of the particulate sample or different lengths of the cylindrically shaped porous material. Furthermore, the sample holder contains a mechanism for a continuous adjustment of the compression of the plug of particles.

6.4 Sample preparation

In the DC mode of the streaming potential and streaming current method for the zeta potential analysis, the solid and liquid phases are initially separated from each other (different to the particles dispersed in a liquid for the measurement of the electrophoretic mobility, the colloid vibration current, or the electrosonic amplitude). Although the solid material (consolidated plug of particles or porous material) is commonly considered as the “sample”, the test solution also requires some attention (see 6.8).

The preparation of a granular or powder sample requires the formation of a compacted plug with focus on the hydraulic permeability towards the flow of the test solution. Since the test solution permeates the porous plug of granular powder for recording the streaming potential signal, this approach is referred to as the permeation mode of measurement. The starting material is usually available as a dry powder. The permeability of the particle plug is determined by the powder mass and the plug compression. For rigid particles, the plug formed inside the cylindrical recess of the sample holder is hardly compressible and its permeability is therefore mainly determined by the powder mass. The mass used for the formation of the permeable plug of the granular media depends on the particle size and is estimated empirically. The smaller the particle size, the lower is the required sample mass. Typical sample weights and the height of the cylindrical column of the plug-shaped sample are given in Table 2 for a series of particle size ranges. Besides the particle size, the wettability of the particle sample determines the permeability. When testing the zeta potential of granular media in the presence of an aqueous solution, the hydrophilicity of the particle surface and the propensity to swelling reduce the required mass for the formation of the sample plug.

Table 2 — Relation between particle diameter and particle mass for the formation of a sample plug with a suitable permeability for the streaming potential and streaming current measurement in DC mode

Particle diameter d µm	**Particle mass** m mg	**Plug height** mm	**Porosity** %
$\approx 10 < d < 100$	$50 < m < 100$	1	50 – 75
$100 < d < 500$	$200 < m < 500$	10	75 – 90
$500 < d < 1\,000$	1 000	20 – 40	75 – 88
$1\,000 < d < 2\,000$	5 000	100	75

The preparation of a consolidated porous material for the streaming potential and streaming current measurement requires the complete removal of air inside sample pores. Soaking of a porous material in the test solution for a sufficiently long time (12 h – 24 h) prior to the measurement is required to establish an equilibrium between the pore surface and the surrounding liquid phase. As for a plug of granular media, the hydraulic permeability of the porous material determines the applicability of the permeation mode of the streaming potential and streaming current measurement. For a porous material the permeability is determined by the pore size and porosity and the thickness of a cylindrically shaped sample. The wettability of the pore surface by the solvent of the test solution is of secondary importance.

The permeability of a plug of granular media or of a porous material is described by the ratio of the volume flow rate $\dot{V}$ and the applied pressure difference ΔP between both ends of the sample. Commercial instruments for the streaming potential and streaming current measurement offer an adjustable pressure to accommodate a wider range of sample permeabilities. The applied pressure difference has to generate a minimum volume flow rate of approximately 2×10^{-8} m^3/s (approximately 1 ml/min) to avoid any drift in the streaming potential and streaming current signals. On the other hand, the permeability coefficient $\dot{V} / \Delta P$ should not exceed 4×10^{-11} $\text{m}^3 \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ to avoid a deviation from a linear flow profile of the test liquid,[17] which is a condition of the Smoluchowski theory for the zeta potential analysis by the streaming potential and streaming current method in DC mode.

If the hydraulic permeability of a porous material is too low such that the volume flow rate does not exceed the minimum threshold of 1 ml/min even at the highest applicable pressure difference, the permeation mode of streaming potential and streaming current measurement fails and may be replaced by the tangential mode of measurement. In this approach, the flow of the test solution is directed through a single capillary channel, formed by the solid sample, and tangential to the surface of this sample. The tangential mode of streaming potential and streaming current measurement is applicable to solid samples with a flat surface but is not discussed in this document.

6.5 Test solution

The composition of the test solution that is used for probing the solid sample is important for the interpretation of the zeta potential results. Streaming potential and streaming current measurements are commonly performed in the presence of an aqueous solution.

For the preparation of an aqueous test solution, ultrapure water with a resistivity of 18,2 MΩ·cm[18] shall be used. Preferably the test solution shall be prepared prior to the measurement to avoid a degradation of the quality of the ultrapure water during storage.

The ionic strength of the aqueous solution shall be adjusted reproducibly by weighing the correct amount of the selected salt. The type of salt depends on the purpose of the zeta potential analysis and on the surface chemistry of the granular media or the porous material. Commonly, a monovalent electrolyte (NaCl, KCl) is used to prepare an aqueous test solution at a certain ionic strength. Monovalent ions do not show any specific interaction (such as adsorption, complexation, precipitation) with the majority of solid material surfaces and enable the calculation of the electrokinetic charge density from the zeta potential.[19]

To prevent the dissolution of carbon dioxide (CO_2) from ambient air in the dilute aqueous solution of a monovalent electrolyte it is recommended to purge the aqueous test solution with inert gas such as nitrogen of high purity.

The determination of the isoelectric point requires the adjustment of pH in the test solution and at the solid material-water interface, respectively. For a reliable adjustment of a pH change at the solid-water interface, a sufficiently high volume of the test solution shall pass the permeable plug of granular media or the pores inside a porous material before proceeding with the zeta potential analysis.

6.6 Verification

A calibration of an instrument for streaming potential and streaming current measurement in DC mode is not required. However, different instrument components such as all wetted parts (see 6.8.1) and the measuring electrodes (see 6.8.5) can contribute to an erroneous determination of the zeta potential. A verification of the instrument condition prior to a sample analysis is therefore recommended.

At the time of publication of this document, a certified material for the zeta potential analysis by the streaming potential and streaming current method is not yet available. For the verification of the instrument for streaming potential and streaming current measurement, it is therefore recommended:

- to select a specific material, either granular or porous, for the application of the permeation mode of measurement, with a reproducibly determined zeta potential;
- to follow the recommendation of the instrument manufacturer of a suitable material for verification measurement. A cotton fabric conforming to ISO 105-F09 is an example of such a suitable material for verification measurement.

6.7 Repeatability and reproducibility

The main contribution to the repeatability of the zeta potential determined from streaming potential and streaming current measurement arises from instability of the solid material-water interface. Both the solid surface as well as the composition of the bulk aqueous solution can alter during a series of repetitive analyses. The partial dissolution of the bulk solid material, the delamination of a surface coating, and the swelling of surface or bulk material cause temporal changes in the zeta potential that contribute adversely to the measurement repeatability. The composition of the test solution can further change due to contamination by the dissolution of carbon dioxide from the ambient atmosphere in water. A contamination of the test liquid can cause a temporal drift in the recorded zeta potential due to its accumulation at the solid-water interface and its adsorption on the solid surface.

The reproducibility of the zeta potential is primarily determined by the sample surface heterogeneity. Although the zeta potential determined by streaming potential and streaming current measurement is a parameter that averages the electrokinetic charge density across a relatively large surface area, heterogeneous sample surfaces introduce a higher variance. A thorough preparation of the solid material, achieved by selecting a proper method for sample conditioning and rinsing the sample for a sufficiently long time with the test solution prior to the streaming potential measurement, to establish reliably an equilibrium at the solid-liquid interface, contributes to a significant improvement of the measurement reproducibility.

The repeatability and the reproducibility of the zeta potential are best reported by the standard deviation in millivolts (mV) for a series of at least six (6) streaming potential measurements of the same sample and of different batches of the sample, respectively. The repeatability of the zeta potential using the DC mode of the streaming potential measurement is ± 3 % with a minimum of ± 0,5 mV. The reproducibility of the zeta potential is ± 10 % with a minimum of ± 1 mV.

6.8 Sources of measurement error

6.8.1 Contamination of the current sample by the previous sample

The magnitude but even the sign of the zeta potential can be affected by different artefacts that can be introduced by the solid sample, the test solution and some instrument components. Knowing the different sources of such artefacts assists in the problem-solving process. Preventing these artefacts will enhance the reliability of the streaming potential and streaming current measurement and the zeta potential calculation thereof.

The zeta potential at the material-liquid interface is sensitive to the chemistry at the outermost surface of the solid sample. At the solid-liquid interface the chemistry is determined by the material surface composition and by the possible contamination of the sample surface due to the adsorption of volatile components when storing the sample in ambient air or of contaminants dissolved in the test liquid. The contamination of a freshly prepared test solution can occur by the desorption of compounds from any of the wetted parts of the instrument for streaming potential and streaming current measurement, that have been released from a previously measured solid material. Especially for samples with a small surface area (usually not applicable to granular media and porous material) and for materials with a hydrophobic surface, the zeta potential analysis can be affected by contaminants in solution already at a concentration of a few parts per billion (ppb).

Rigorous cleaning of wetted parts of the instrument for streaming potential and streaming current measurement with ultrapure water or appropriate and highly pure organic solvents prevents the risk of cross-contamination. The use of detergents or individual surfactants for cleaning the container for the test liquid, commonly a laboratory glass beaker, is not recommended. The cleanliness of the wetted parts of the instrument is verified by a zeta potential analysis of a reference sample (see 6.6).

6.8.2 Inappropriate sample preparation procedure

The conditioning of the solid material and the correct alignment of the sample in the sample holder of the instrument for streaming potential and streaming current measurement are fundamental for a reliable and reproducible determination of the zeta potential.

Granular media exhibit a large surface area. This property offers the benefit of an enhanced reproducibility of the streaming potential and streaming current measurement but also the drawback of a longer time for equilibration of the solid-water interface compared to samples with a planar surface. Consolidated porous materials require a thorough filling of the pores with the test solution or at least with water prior to the measurement. Reactive material surfaces of both granular media and porous samples, especially those of mineralogical origin, frequently cause partial dissolution of crystalline lattice ions and demand a significantly longer time for equilibrating the solid-water interface.

The packing density of a sample plug made of granular media needs monitoring to eliminate an adverse effect on the determination of the zeta potential (see 6.7). Similarly, the pore size, porosity and height of the cylindrically-shaped porous material determine the applicability of the streaming potential and streaming current measurement. The effects of a packing density of a sample plug of granular media or of a permeability of a porous material outside of the applicable range of hydraulic permeability for the streaming potential and streaming current measurement become visible by a nonlinear deviation of the dependence of streaming potential or streaming current on the pressure gradient. The observation of such a nonlinear dependence of streaming potential or streaming current on the pressure gradient is possible provided that the streaming potential or streaming current is measured at a series of multiple pressure differences (see 6.4).

6.8.3 Inappropriate test solution

The properties of the test solution that determine its applicability for the zeta potential analysis by the streaming potential and streaming current method are the viscosity, the dielectric permittivity, the electric conductivity and the purity. For aqueous solutions, the pH needs an additional consideration. For commonly used diluted aqueous solutions, the solution viscosity and dielectric permittivity are in the appropriate range for liquid transport and charge formation, and adverse effects of these parameters on the zeta potential are thus eliminated.

The electric conductivity remains the most important restriction for a reliable zeta potential analysis by the streaming potential measurement. The lowest possible conductivity in aqueous solutions occurs for ultrapure water with a resistivity of 18,2 MΩ·cm (corresponding to an electric conductivity of $5{,}6 \times 10^{-6}$ S/m).[18] At a medium and high applied pressure gradient ($\Delta P > 10$ kPa) the streaming potential evolving in ultrapure water can thus exceed the specified limit of a high-end voltmeter that is integrated in commercial instruments for the streaming potential and streaming current measurement. The measurement of streaming current is not restricted at an extremely low electric conductivity.

At a high ionic strength of an aqueous solution the electric conductivity introduces another limitation of the streaming potential measurement. The model of the electric double layer predicts the dependence of the zeta potential on the ionic strength, i.e. the magnitude of the zeta potential for a certain material-water interface decreases with an increasing ionic strength of an aqueous test solution of monovalent ions. According to the Smoluchowski limit for the calculation of the zeta potential from the streaming potential measurement (Formula (2)), the streaming potential coupling coefficient $\mathrm{d}\Delta U_{\mathrm{str}}/\mathrm{d}\Delta P$ is even stronger affected by an increase in the electric conductivity K_{m} than the zeta potential. For instance, for a given material and a pressure gradient of $\Delta P = 30$ kPa, the streaming potential ΔU_{str} can assume −20 mV at an ionic strength of 0,001 mol/l but less than −200 µV at an ionic strength of 0,1 mol/l (the corresponding zeta potential can read $\zeta_{I = 1\ \mathrm{mM}} = -50$ mV and $\zeta_{I = 100\ \mathrm{mM}} = -15$ mV).

6.8.4 Air bubbles

The presence of air that is remaining inside the tubing of the electrolyte circuit and especially inside the voids of a packed granular sample or inside the pores of a porous material affects the resistivity of the test solution. A thorough rinsing of the complete liquid transport system of the instrument for streaming potential and streaming current measurement and an appropriate conditioning of the solid sample are required for a complete removal of air. Preferably the instrument for streaming potential and streaming current measurement offers the possibility to measure and to display information about the resistivity of the test solution, e.g. by the measurement of the electric resistance by respective measuring electrodes and the corresponding electronic circuit.

6.8.5 Faulty electrodes

Different types of measuring electrodes may be employed for the analysis of the zeta potential by the streaming potential and streaming current measurement in DC mode. Most commonly, electrodes made of silver|silver chloride (Ag|AgCl) as a representative of electrodes of the second kind are preferred for their superior performance, high reversibility and larger surface area (compared to a metal electrode). Ag|AgCl electrodes are prepared by the deposition of a AgCl coating on a silver substrate such as a silver wire or a tubular support. Ag|AgCl electrodes become faulty if the adhesion of the AgCl coating on the silver support fails and the coating gets peeled off. To prevent such a failure, the use of an appropriate geometry of the silver support needs to be considered, i.e. a tubular support is preferred to a silver wire.

Ag|AgCl electrodes require the presence of chloride ions in solution to show a reliable performance. The use of chloride ion-generating salts is therefore recommended. For a zeta potential analysis at the pristine material-water interface, monovalent electrolytes such as NaCl or KCl shall be used (see 6.5).

If the presence of chloride ions in the test solution has to be omitted, a metal electrode (electrode of the first kind) may substitute the Ag|AgCl electrode. Electrodes made of gold or platinum are available. The higher polarizability of electrodes of the first kind, especially in the absence of the corresponding metal ions in solution, further limit the applicable range of the ionic strength of the test solution (see 6.8.3).

A faulty electrode performance is recognized by the measurement of the DC voltage by the voltmeter of the instrument for the streaming potential measurement in the absence of any flow of the test solution (i.e. in the absence of a pressure gradient, $\Delta P = 0$ Pa). The deviation of the measured voltage from $U = 0$ mV shall remain within the range of -1 mV $\leq U \leq +1$ mV (note that the deviation depends on the ionic strength of the test solution and on the type of the used electrode). Alternatively, the streaming potential shall be recorded in an appropriate range of the applied pressure gradient using a dilute aqueous solution (e.g. 0,001 mol/l KCl) and a non-conductive solid material (see 6.6). A strictly linear dependence of streaming potential on the pressure difference and an extrapolated voltage of less than ± 1 mV at $\Delta P = 0$ Pa confirm a reliable electrode performance.

6.8.6 Limitation of the Smoluchowski approximation

The Smoluchowski approximation for the calculation of the zeta potential from streaming potential measurement by Formula (2) was derived for a planar solid-liquid interface with an infinite extension of the solid surface. Despite the obvious deviation from this boundary condition for a plug of granular media or a porous material, Formula (2) is also applicable for such sample with a complex geometry of the flow channel. However, any contribution of the material-liquid interface or of the bulk material to the electric conductance inside the capillary flow channel is not represented by the measured conductivity K_m of the bulk aqueous solution. Sources for such contribution are:

- the interfacial conductance (aka as the surface conductance) due to the higher ion concentration at the material-liquid interface compared to the bulk liquid. The inter-particle distance in a plug of granular media or the pore diameter in a porous material and the ionic strength of the test solution determine the effectiveness of a contribution of the interfacial conductance;
- the ionic conductance carried by the aqueous solution inside pores of granular particles or a porous material especially if these pores are interconnected. The contribution of pore conductance depends on the ionic strength of the test solution;
- the ionic conductance carried by the aqueous solution that penetrates a solid material upon swelling;
- the electronic conductance of the bulk material, which is applicable to conductive samples.

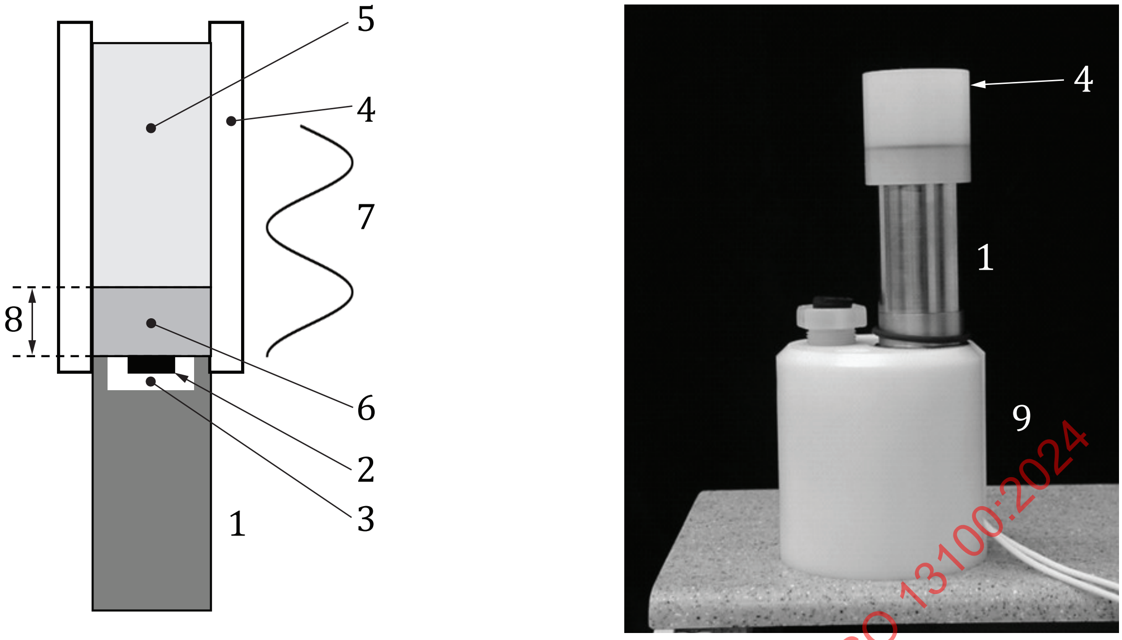
Especially for the cases of samples with a significant swelling propensity and conductive samples, the sample contribution to the conductance inside the flow channel cannot be compensated by the bulk electrolyte conductivity, and Formula (2) gives a zeta potential which is determined too low in magnitude. Such zeta potential result indicates the correct sign of the surface and interfacial charge but provides a too small estimate of the charge density and is commonly denoted an apparent zeta potential.

7 Measurement of AC streaming current for porous materials

7.1 Instrument setup for particle deposits

Solid particles of a sufficiently large size can exist in liquid in two different states: either as a homogeneous dispersion when the liquid is stirred, or as a deposit after stirring is turned off. In the second case, the deposit of solid particles forms a model porous material.

Figure 4 shows the setup of the sample handling system, which allows using the electroacoustic device for characterizing porous bodies.



a) Schematic drawing of an exemplary setup for the measurement of the seismoelectric current

b) Example of an electro-acoustic probe with sample handling system for the measurement of particle deposits and porous bodies

Key

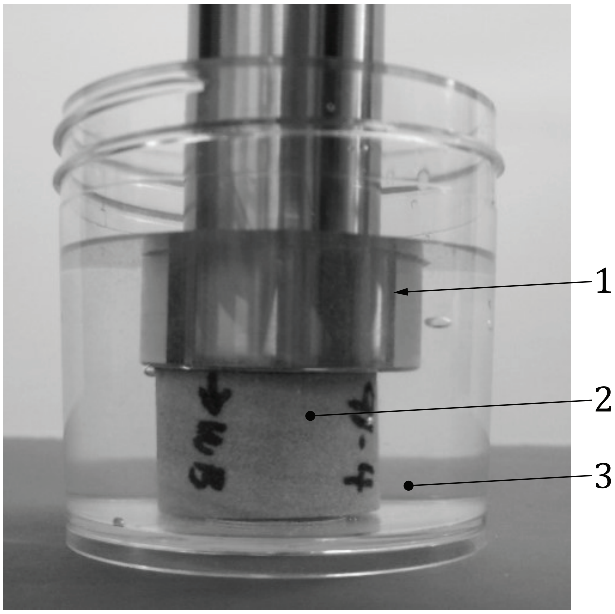
1	electroacoustic probe
2	gold electrode
3	plastic separator
4	plastic cup
5	particle dispersion
6	particle deposit
7	ultrasound pressure wave
8	height of the particle deposit
9	pedestal

Figure 4 — Arrangement of an electro-acoustic probe for the measurement of the seismoelectric current

The electro-acoustic probe is placed vertically in a suitable stand that orients it such that the face of the probe with the gold electrode is on top. A cylindrical fixture around the top of the probe creates a cup with the probe face serving as a bottom of the cup. This cup can be filled with liquid and a porous material can be placed in this liquid in contact with the gold electrode. Ultrasound pulses generated by the electro-acoustic probe enter the liquid phase through the gold electrode, whereupon they enter the porous material that is placed on top of the gold electrode. The sound wave generates a seismoelectric current as it propagates through the porous material and is sensed as an alternating current between the gold electrode (2) and the stainless-steel electroacoustic probe (1). The electronics measure and process these current pulses in a manner similar to the electro-acoustic pulses generated by dispersed particles.

7.2 Instrument setup for consolidated porous materials

The measurement of the seismoelectric current requires a close contact between the sensing probe and the surface of the consolidated porous material (porous monolith), as shown in Figure 5. The size of the flat area on the monolith surface shall be at least 2 cm in diameter.



Key

1	electroacoustic probe
2	monolith sample
3	test solution

Figure 5 — Example of an experimental setup for measuring the seismoelectric current of a geological core sample, representing a porous monolith material

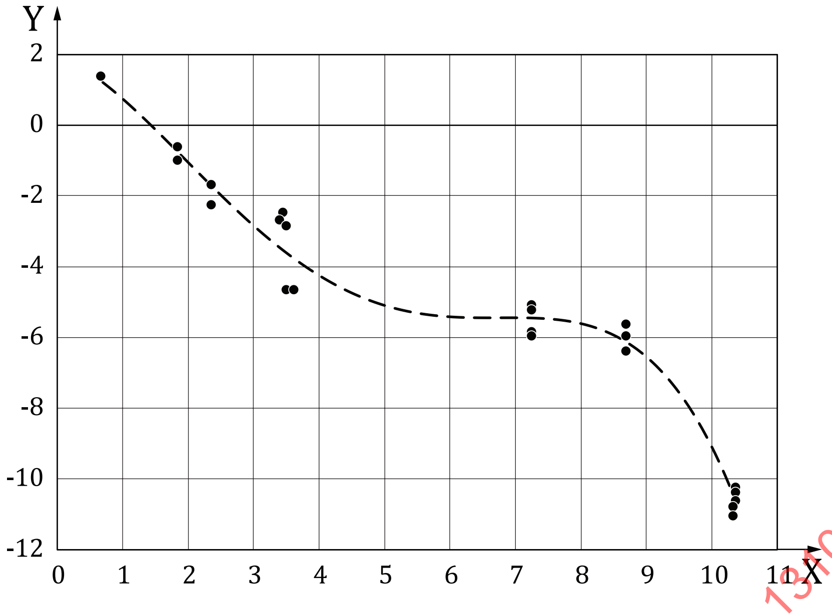
This method yields the zeta potential of the local spot on the flat surface of the monolith. Some variation in monolith composition is possible. In such case, measurement would reveal varying value of the zeta potential. The higher spread in such reading, the less homogeneous is the monolith. Therefore, such method can be used for characterizing the homogeneity of porous monolithic bodies, such as ceramic tiles, concretes, geological cores, etc.

Prior to the measurement, it is important to achieve equilibrium between the monolith and the surrounding liquid. Such an equilibration for a monolith (5.3) requires approximately 10 hours. The equilibration can be accelerated by stirring the liquid that surrounds the monolith.

The monolith shall be properly placed during the equilibration process by soaking the complete monolith sample. The flat parts shall be exposed to the test liquid.

The equilibration process can be monitored with a pH probe placed in the liquid surrounding the monolith. The stabilization of pH with time serves as an indicator that the interior of the monolith has reached an equilibrium condition with the surrounding liquid.

The monolith can be equilibrated with the liquid at different pH values by adding either acid or base to the surrounding liquid. This is analogous to an equilibrium pH titration for porous material. The main purpose of conducting such titration is to determine the isoelectric point of the monolith, which characterizes the chemical composition of the pore surface. The determination of the isoelectric points does not require a conversion of the seismoelectric current into the zeta potential. Plotting the electroacoustic magnitude versus pH is sufficient to determine the isoelectric point (this approach is the same for other electrokinetic effects, such as the electrophoretic mobility, the colloid vibration current, and the streaming potential coupling coefficient, that transfer into a zeta potential). An example of such titration curve is shown in Figure 6. The main indicator of the isoelectric point is a shift of the current phase by 180 degrees driven by the change in the sign of the surface charge.



Key

X pH

Y electroacoustic magnitude [10^5 mV·(s/g)$^{1/2}$]

Figure 6 — Dependence of the seismoelectric current magnitude on pH for a Berea sandstone core to determine the isoelectric point (at pH 1,3)[9]

7.3 Sample requirements

The thickness of the porous material sample shall exceed 10 wavelengths of the applied ultrasound. In case of ultrasound with a frequency of 3 MHz, this critical thickness amounts to 4,5 millimetres.

The knowledge of the porosity is required for calculating the zeta potential from the measured seismoelectric current. It can be calculated from the conductivity ratio by Formula (5) or from the critical time t_{cr} of the electroacoustic signal by Formula (C.1). The porosity of the sample shall be above 1 %.

7.4 Calibration and verification

7.4.1 Reference materials

Electroacoustic instruments perform better for systems with a higher density contrast. This is why traditional latex standards are not appropriate for calibrating, validating or verifying electroacoustic instruments.

A certified reference material (CRM) for electrophoretic mobility[21] is used for the calibration of the electroacoustic instrument and for instrument validation.

Reference materials for verification shall be used with every measurement series to ensure a correct performance of the instrument. This control is most suitably done using quality control charts. Reference materials for this purpose shall be homogeneous and stable, but are not required to have a metrologically valid assigned value.[22]

Different reference materials are therefore used for calibration and for daily quality control.

7.4.2 Calibration

A calibration of the electroacoustic device is required for determining the geometrical factor that characterizes the distribution of the electric field lines. Calibration of the electroacoustic instrument that is employed for measuring seismoelectric current can be conducted with certified reference materials for particulates.[21] These materials shall be used to either calibrate the instrument or to validate the trueness of the measured results.

The distribution of the electric field lines remains the same when a homogeneous deposit of solid particles is built on the face of the electroacoustic probe. Therefore, the calibration constant can be used for measuring the seismoelectric current generated by the particle deposit.

7.4.3 Verification

The verification procedure for the seismoelectric effect is based on determining the zeta potential of certain particles in the dispersed and sediment states.[22] The zeta potential results shall be identical since the sedimentation of particles does not change the electrochemical equilibrium.

Methods for the zeta potential characterization of particles in dispersions are described in ISO 13099-2 and ISO 13099-3. The convenient way of verifying the AC streaming current method is an electroacoustic device for characterizing the zeta potential in concentrated dispersions by measuring the colloid vibration potential (CVP) or the colloid vibration current (CVI) described in ISO 13099-3.

7.5 Repeatability and intermediate precision

To achieve the desired repeatability of an electroacoustic measurement, the following steps need to be followed.

- Set up the instrument adequately, select the proper settings for operating conditions and allow all parts sufficient warm-up time.
- Follow the measurement protocol given for the material.
- Perform at least six consecutive measurements with the same aliquot.

An instrument is considered to meet the requirement of this document if the coefficient of variation for the mean electrophoretic mobility value of six measurements for a reference material is less than 3 % if the absolute value of the reference material mobility is higher than 10^8 $m^2 \cdot V^{-1} \cdot s^{-1}$.

The test of intermediate precision shall follow the procedure for the repeatability except that six different sample aliquots at an appropriate concentration shall be used.

An instrument is considered to meet the requirement of this document if the coefficient of variation for the mean electrophoretic mobility value of six measurements for a reference material is less than 4 % if the absolute value of the reference material mobility is higher than 10^8 $m^2 \cdot V^{-1} \cdot s^{-1}$.

7.6 Sources of measurement error

The main source of errors in the reported value of the zeta potential are errors in the input parameters, such as porosity, densities, viscosity and dielectric permittivity of the liquid. High values of the calculated zeta potential exceeding ± 100 mV in magnitude occur due to the assumption of a too low or a too high porosity, a too low difference in solid and liquid densities, a too low dielectric permittivity for the liquid, or a too high viscosity for the liquid.

Formula (4) for calculating the zeta potential is limited to solid skeletons with elastic properties. Furthermore, Formula (4) is applicable to the case of isolated electric double layers or a ratio of the pore size and the Debye length of $a/\kappa^{-1} >> 1$ (refer to Formula (A1) in Annex A for a calculation and to Annex B for an experimental estimation of the Debye length).

The measured signal can drift in time in case the equilibrium has not been established. This is especially important for monolith samples.