STABINO ZETA: Fingerprint method for the comprehensive characterisation of the particle charge

CHARGE DISTRIBUTION AT THE INTERFACE WITH THE SURROUNDING LIQUID: THE ELECTRICAL DOUBLE LAYER

This White Paper provides a brief overview of the STABINO ZETA measuring principle and its most important features for practical use. The same laws apply regardless of whether the interface is a flat, particle or molecule surface. A charged surface attracts oppositely charged excess ions from the liquid environment, which shield the charge from the outside. In aqueous media, the extent of the charge cloud, the so-called double layer, is approximately between 0.5 and 20 nm. At high conductivity, it is less extended than at low conductivity. In contrast to the simple model of a smooth surface and monovalent surrounding ions shown below, it can also become very complex. The following considerations are useful in practice, even when dealing with uneven surfaces, porous particles, and elongated macromolecules or fibres.

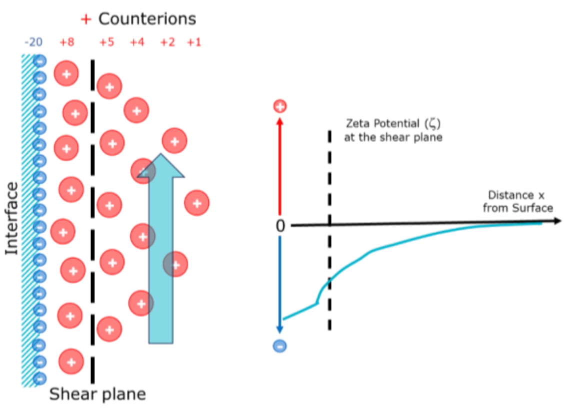


Fig.1: *Anionic interface with cationic charge cloud that balances the charge to the outside.*

At the shear plane, the outer, loosely bound excess ions can be sheared off. The graph shows a simplified potential profile at the interface. For practical purposes, only the measurable potential after shearing at the shearing plane is important: the zeta potential ζ.

In an aqueous medium, cations and anions, such as Na^+ and Cl^-, are evenly distributed. At an anionically charged interface, a cloud of ions with a cationic excess forms to neutralize the charge of the interface towards the outside (***Fig. 1***). The first and subsequent cation layers are fixed, while those further away from the interface are loosely bound. This electric charge cloud is called the "double layer". The loosely bound ions can be sheared off by an electric field (electrophoresis) or by mechanical forces (flow, ultrasound). The course of the net charge can be represented as a potential profile (Fig. 1). Of practical interest is only the potential exposed and measurable at the shearing plane, the so-called zeta potential. The potential profile within the shear plane is not experimentally detectable and is therefore of theoretical interest at best. In the following, the mechanical flow principle is discussed, which was practically implemented in the STABINO ZETA analyzer.

THE ZETA STREAMING POTENTIAL PRINCIPLE

When a liquid is set in motion in a capillary, the excess charge cloud shifts in the direction of the flow (***Fig. 2***). The more charge there is at the shearing plane, the greater the amount of shifted charge. The amount of sheared excess charge depends on the zeta potential, which in turn depends on the ionic strength of the surrounding solvent. An electric potential difference, the "flow potential" $\mathbf{U_r}$, is tapped with the help of electrodes **El1** and **El2** along the flow. According to Helmholtz-Smoluchowski, the streaming potential is proportional to the zeta potential $\boldsymbol{\zeta}$ and the dielectric permittivity $\boldsymbol{\varepsilon_0}$, and inversely proportional to the viscosity $\boldsymbol{\eta}$. The higher the applied flow pressure, the higher the flow potential can build up. Therefore, the pressure difference $\mathbf{\Delta p}$ between the electrodes is included in the formula. The conductivity of the medium $\mathbf{K_m}$ counteracts the generated flow potential. The measurement of the pH dependence of the zeta potential and the determination of the surface charge provide important information about the type and number of functional groups of carbon compounds.

$$\Delta U = \frac{\Delta p \cdot \varepsilon \cdot \varepsilon_0 \cdot \zeta}{\eta \cdot K_m}$$

Helmholtz Smoluchowski (1)

In this way, the zeta potential of surfaces can be determined.

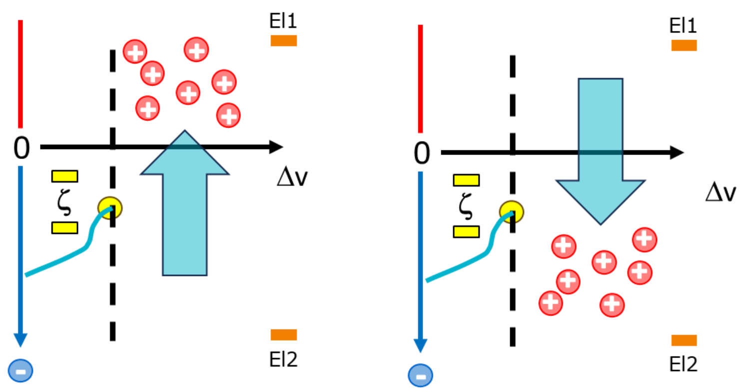


Fig. 2: *By applying a flow pressure in a narrow gap, the medium flows past the interface and shears off the counterions. The flow potential is tapped between the electrodes El1 and El2.*

The previous text is very important for understanding how the STABINO ZETA works. Because this method is used in the STABINO ZETA in only a slightly modified way.

THE ZETA STREAMING POTENTIAL OF PARTICLES IN THE STABINO ZETA

Macromolecules and particles attach to surfaces so that they remain in a stationary. It is then possible to generate a streaming potential on them. The streaming potential is caused in the STABINO ZETA is caused by the zeta potential of particles adhering to a Teflon wall and a forced flow with velocity Δv.

The functional sketch ***in Fig. 3*** looks similar to the one in ***Fig. 2***. The surface of the interface is drawn slightly enlarged to show the attachment of the particles. In contrast to streaming potential devices for smooth surfaces, the flow in the STABINO ZETA has an oscillatory character. This has several practical reasons, which are discussed below.

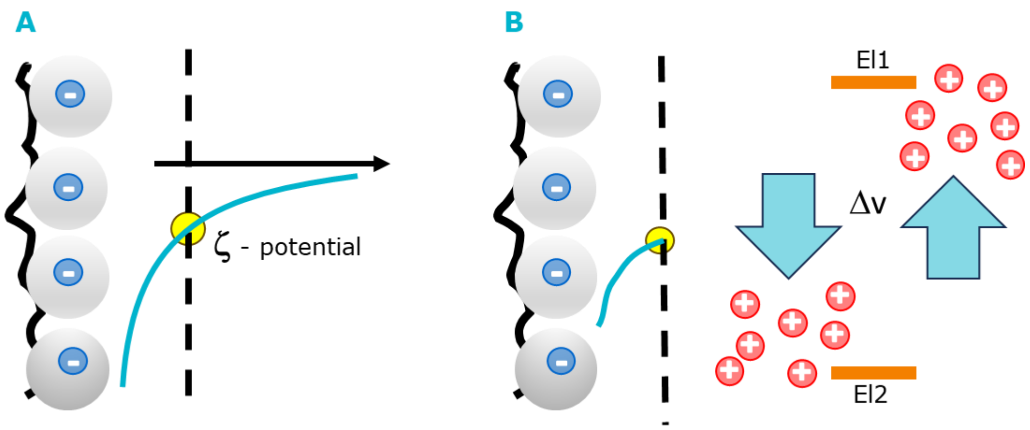


Fig.3a*: Teflon - surface of the measurement cell covered with particles. Potential curve without streaming. The zeta potential is at the potential shear plane.*

Fig.3b: Shear of the free positive counter ions by the streaming liquid with velocity Δv. Interrupted potential gradient at the shear plane.

The streaming potential U is measured between an upper (El 1) and a lower electrode (El2). The polarity of the streaming potential changes according to the direction of flow.
The pressure cannot be easily measured. Instead, the flow velocity can be calculated from the cell dimensions and the oscillation frequency. The frequency is constant, the velocity is adjustable. The above Helmholtz - Smoluchowski - formula can be written as follows:

$$\Delta U = \frac{0.5\rho \cdot \varepsilon \cdot \varepsilon_0 \cdot \zeta}{\eta \cdot K_m}$$

Smoluchowski (2)

Δp was modified to $0.5\rho(\Delta v_{max})^2$.

ZETA POTENTIAL - STREAMING POTENTIAL

The zeta potential can be derived from the measured raw streaming potential. If always measures under the same conditions and in strong polar liquides like aqueous systems, can simplify the formula (2):

$U_r = k^{-1} \cdot \zeta$ OR $\zeta = U_r\, k$ (3)

The constant k is a calibration constant (device constant) which easily can be done.

$$k = 0.5\rho \cdot (\Delta V_{max})^2 \cdot (\frac{\varepsilon \cdot \varepsilon_0}{\eta \cdot K_m}) \qquad (4)$$

MEASUREMENT SETUP OF STABINO ZETA

The up and down movement of a Teflon plunger in a measuring cylinder made of Teflon creates a high liquid flow in the narrow gap between the plunger and the cylinder (***Fig.4***). This causes an oscillating flow potential as described above.

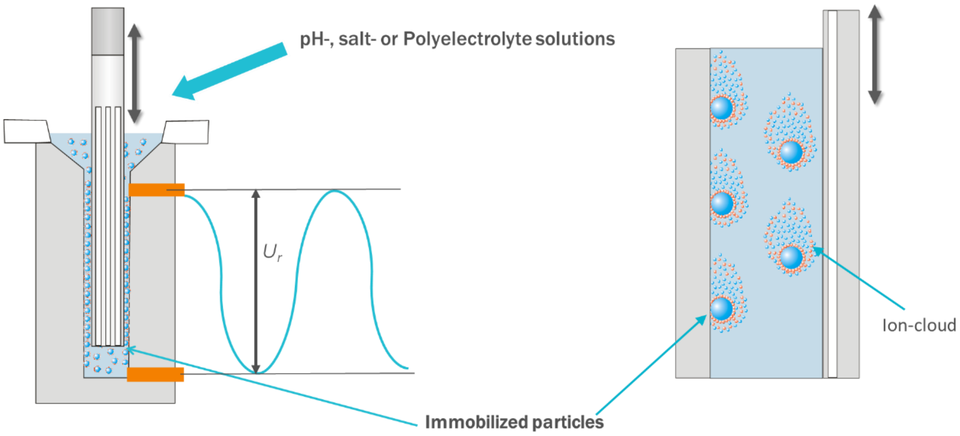


Fig.4: Measuring cell (10 ml, 3 ml or 1 mL sample volume), piston and the electrodes at which the oscillating raw potential U_r is taken. The corresponding titrant solutions (pH, polyelectrolyte or salt solution) can be added from above in a minimum 10 µl minimum step.

- Due to the plunger movement
  - the measuring signal is generated in 1 second.
  - the sample is kept homogeneous.
  - the sample is mixed immediately.
  - There are no convection problems.
  - The method is about 30 times faster compared to optical methods.
- The electrical signal is not influenced by color or transparency.
- The measuring principle is applicable from 0.3 nm to 300 µm. It is therefore suitable for macromolecules (polyelectrolytes) as well as for powder suspensions.
- The gap deepness can be adjusted by four different pistons with different gaps sizes to the measurement problem:
  - For high viscosities (50 - 100 mPa.s) with a wide gap.
  - For high conductivities (5 - 50 mS/cm) with a narrow gap. This increases the sensitivity of the signal is increased
- Calibration in zeta potential

Derived from the above properties, the overall system is tailor-made for efficient charge titrations. In order not to have to change the titration vessels too often, two titration paths and pumps are built into the system. Over all: the STABINO ZETA is more suitable than any other instrument for formulation work as a "charge mapping tool".

APPLICATIONS IN GENERAL

In addition to comparative potential measurements, the most common applications are:

- pH – titrations
- Polyelectrolyte titrations
- For charge zero determination

- For quantitative determination of functional ionic end groups
- Determination of stable and unstable zones
- Kinetics of the interfacial potential

The fields of application are manifold and range from chitosan, proteins, beverages, nano- and microcoating to algae and geological samples. More about applications can be found in the special application notes.

pH – Titration

As an example for a pH – Titration a forth and back titration of an Alumina is shown in Fig. 5. Here it is very interesting to the the hysteretic effect and shift in the isoelectric point. The titration are countinues titrations and one direction will takes between 5 and 10 minutes.

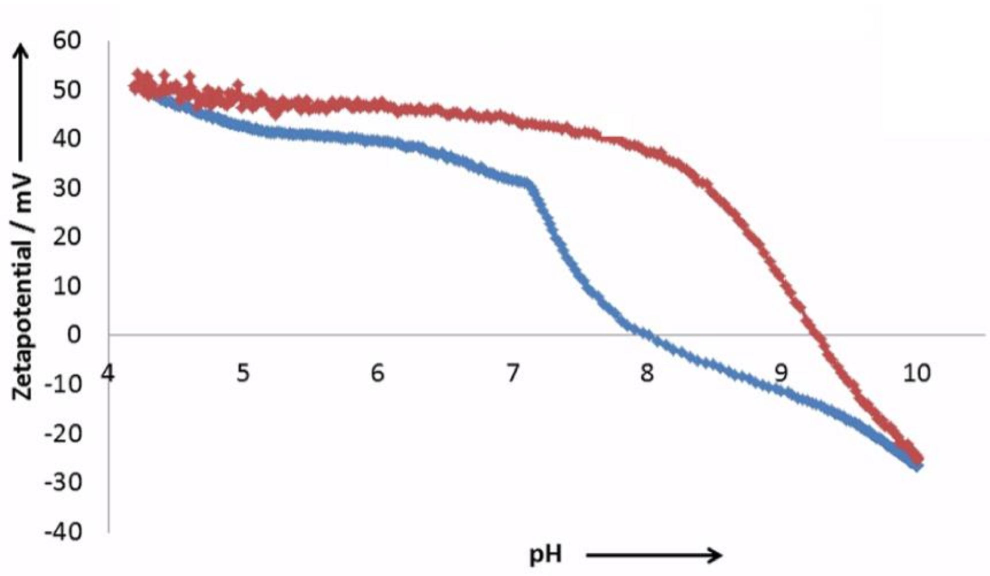
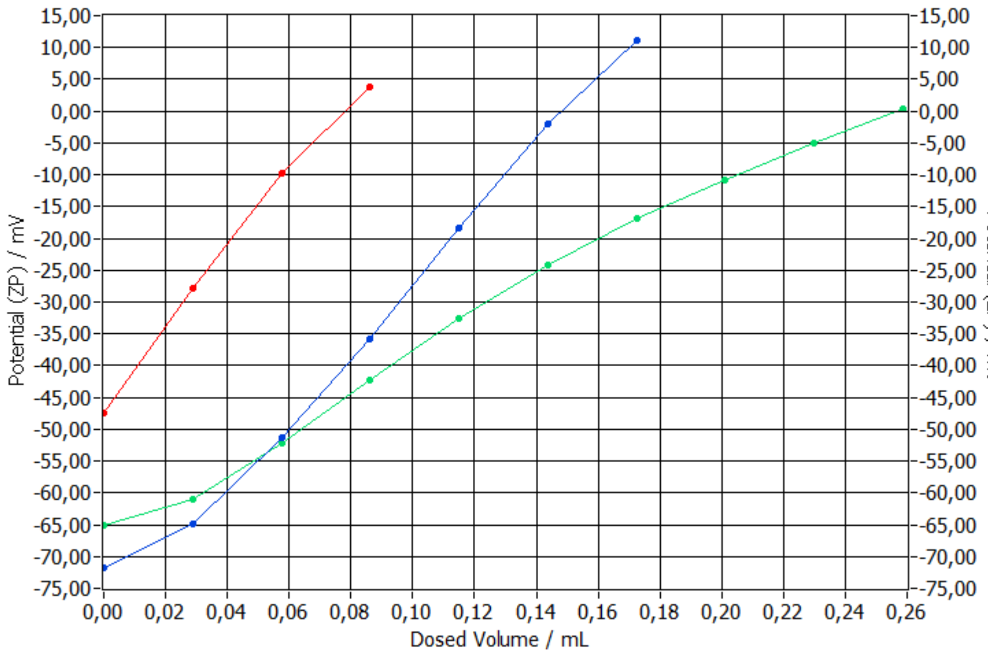


Fig. 5: *pH – titration of Al_2O_3 from pH 4 to 10 (blue) and from pH 10 to 4 (red).*

Polyelectrolyte titration

This type of titration is less known, but the information getting from this titration are very useful for behavior of the formulation. In this case much more detailed information about the surface chemistry is obtained by determining the surface charge density.

During the titration Poly-DADMAC adsorbs on the particle surface and neutralizes the charge In addition to the quantification of the adsorption sites or coordination sites, polyelectrolyte titration is also suitable for quality control. The combination of both methods, i.e. the measurement of the surface charge density at different pH values, enables the functional surface groups to be differentiated on the basis of their acid strength (***Fig. 6***).



Sample	Titrant	Volumen mL	Charge / C g^{-1}	Charge/ µeq g^{-1}
Graphite pH 11	P-DADMAC	0.257	0.155	1607
Graphite pH 9	P-DADMAC	0.148	0.089	966
Graphite pH 7	P-DADMAC	0.078	0.047	488

Fig. 6: *Charge determination of graphite at different pH values*

Polyelectrolyte titration provides information about the charge conditions at different pH values. By difference formation the amount of charge can be assigned to the different functional groups.

Influence of salts in the surrounding solution

The high signal-to-noise ratio of the electrically measured streaming potential is used to be able to carry out measurements even at high salt contents (***Fig.7***).

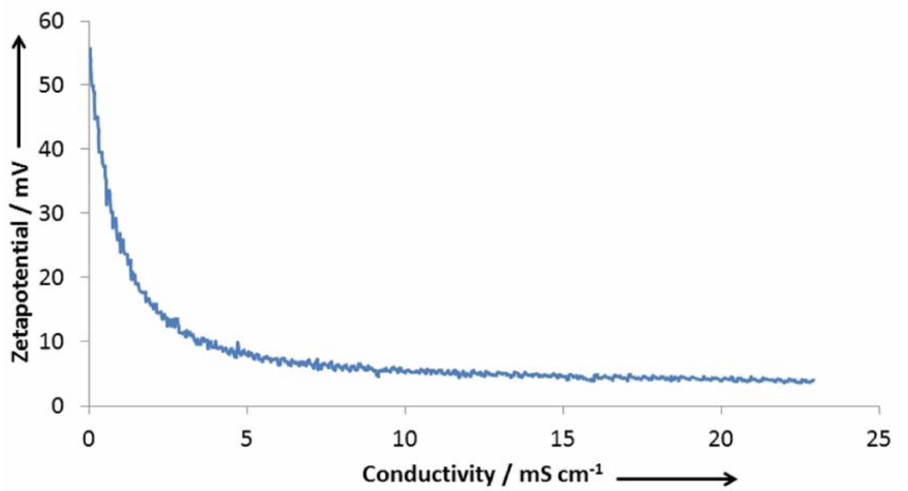


Fig. 7: *Salt titration of Al_2O_3 at pH 4 with KCl to increase the conductivity.*
By increasing the conductivity the zeta potential decreases dramatically and runs asymtotically towords a zeta potental of zero.

REPEATABILITY AND REPRODUCIBILITY

The repeatability and reproducibility are 10% in the potential level due to the accuracy of the standard, electronically it is much better (2 %). The reproducibility the titration will approx. 6% for the consumption of titrant solution, provided that a titration requires a consumption of more than 3 ml (= 30% of the sample volume presented). The reproducibility depends also on the cleaning of the measurement cell and the piston. The motor frequency of the piston is constant. Although the potential changes with the gap deepness of the piston, the amount of titrant consumed during a titration does not.

CONCENTRATION AND VISCOSITY

The optimal concentration is 0.1 to 40%. Because of the risk of viscosity increase at zero charge, an upper limit of 20% is recommended for titrations. The strong viscosity increase that often occurs there thereby hinders the mixing of the sample with the plunger.

ADDITIONAL PARTICLE SIZE MEASUREMENT

Since the most applications work with nanoscale samples, the system can additionally be equipped with the NANOTRAC FLEX a 180° heterodyne DLS size measurement system. The combination of STABINO ZETA and NANOTRAC FLEX is shown in ***Fig 8*** a NANOTRAC Flex is a highly flexible Dynamic Light Scattering (DLS) analysers that provides information on particle size, concentration, and molecular weight. The innovative design of the NANOTRAC Flex allows faster measurements with reliable technology, higher precision, and better accuracy. The unique external probe design allows to convert nearly every vessel into a measurement cell. It also allows measurement of samples over a wide concentration range, monomodal or multimodal samples, all without prior knowledge of the particle size distribution.

A

B

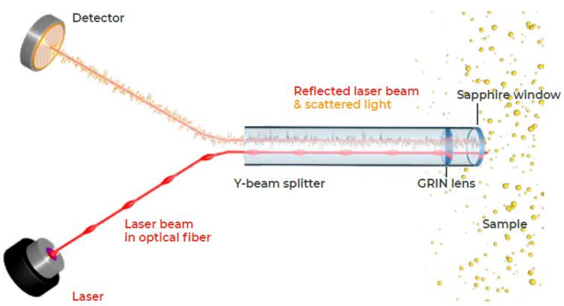


Fig 8 a: Combination of STABINO ZETA and NANOTRAC FLEX. **Fig 8 b**: optical setup of the Nanotrac Flex

The optical bench of the NANOTRAC FLEX is a probe containing an optical fibre coupler with a Y splitter. Laser light is focused on a volume of sample close to the interface of the probe window and the dispersion. The high reflectivity sapphire window reflects a portion of the laser beam back to a photodiode detector. The laser light also penetrates the dispersion and the particles' scattered light reflects at 180 degrees back to the same detector. The setup is shown in ***Fig. 8b***.

CONCLUSION

The wide size range of the STABINO ZETA enables novel applications The speed of the method invites to perform a titration sooner than with the classical zeta potential - titration. This makes the STABINO ZETA ideally suited to determine the stability of various samples which can be compared very quickly with a very high reproducibly. The determination of the charge density is a unique tool of the System and allows a quick quantification of the functional groups on the surface or the stability of a sample. Beside also classical pH – titrations are possible to get quick and precise information about the isoelectric point.