# C06 - Particle Charge Titrations on cationic SiO$_2$- and Al$_2$O$_3$- Suspensions

In many cases, the stability of colloids is dependent on the electrostatic repulsion between particles. Ionic groups at the particle interface play the main role. Is the repulsion zero, Van der Waals attraction may lead to coagulation and subsequent separation of the particles and the liquid phase. By chemical modification of the particles interface it is possible to control their repulsing force. Environmental situations such as pH, conductivity, presence of polymers have to be taken in account. In such systems, instabilities can be predicted by the value of the repulsing potential and by the particle size distribution. To optimize stability and dispersability a lot of formulation work is needed. Stabino® is a very efficient assistant to the stability researcher. In water recycling, destabilization of such dispersions is induced by flocculation or emulsion breaking. This is achieved by bringing the ionic charge near to zero. The dosing of flocculates can be easily controlled with the Stabino®.

In this measurement report the focus is on the charge control of metal oxides.

Stabino®   **NANO-flex**
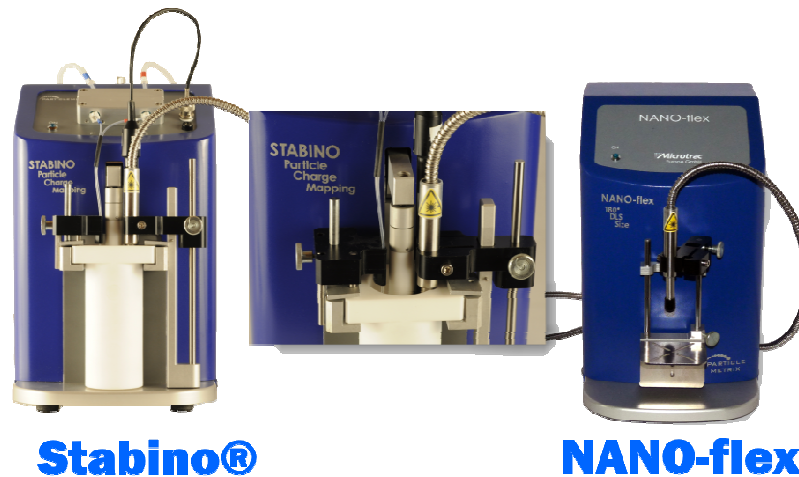
The Measurement Principle

A **size distribution measuring module** can be incorporated. The right picture shows the NANO-flex particle size probe. The technique is based on the 180° DLS dynamic heterodyne back scattering method of light, applicable from 0.3 to 6.5 µm at sample concentrations up to 40%. For more information on the sizing method, the brochure is recommended. The **charge measurement principle** of the Stabino® is described in detail in other company literature. Only a few principals are cited here:

The sensing signal for the **particle interface potential** (PIP) is an electrical voltage originating from shearing the ionic cloud around of particles in the thin gap between the measurement cylinder and the oscillating piston. (on the left).

- The effect of chemicals or salt to the particle interface is quantitatively determined by titrations with pH, polyelectrolyte or salt solutions.
- The optimum sample concentration is between 0.1 and 10% v/v. Below 0.1% the sensitivity may be too low, above 10% or even lower the high viscosity is the limit.
- The method is applicable in an overall size range from 0.3 nm to 300 µm.

individual particle processing
size – concentration – zeta potential
> 20 nm size distribution
10^8 to 10^{16} particles/mL concentration
zeta potential stability parameter
patented image sharpness stability

Focus on Charge Titration

The measurement of the PIP and mixing of the sample and titrand are undergoing in the same measurement cylinder. Chemical transformations which may take place after making up a fresh sample may be much slower than the titration which is often a matter of minutes. Due to this charge titration efficiency many experiments per day can be performed allowing screening work. Following studies are frequently performed with the Stabino®:

- pH – titrations to find the isoelectric point pH (0mV) and the stable region(s).
- Polyelectrolyte - titrations to the point of zero charge and the consumption of a polyelectrolyte solution of known concentration of elementary charges in „V (0mV) [mL]". The consumption gives answer to following questions:
  - What is the total charge of unknown polyelectrolytes?
  - How many functional ionic end groups per gram sample are covering the surface of the particles in the dispersion?
- Quantification of the stoechiometry of polyelectrolyte reaction partners
- Sequence of two automatic titrations. Two titration systems serve for this purpose and for the ease of titrand handling. The titration program reacts dynamically to the progress of measurement signals. Was the change of the PIP or the pH value too high after adding the last portion of titrand, in the next step less titrand will be added, and vice versa. This saves time without sacrificing precision.
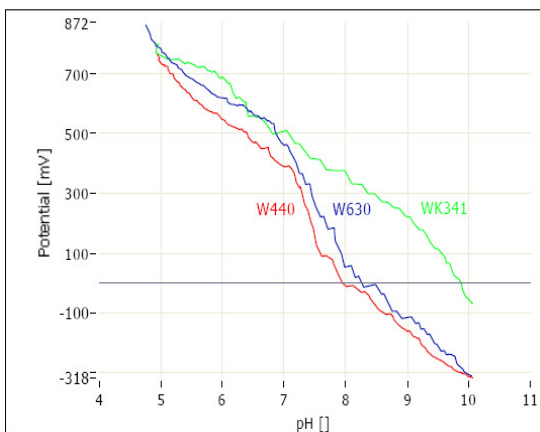
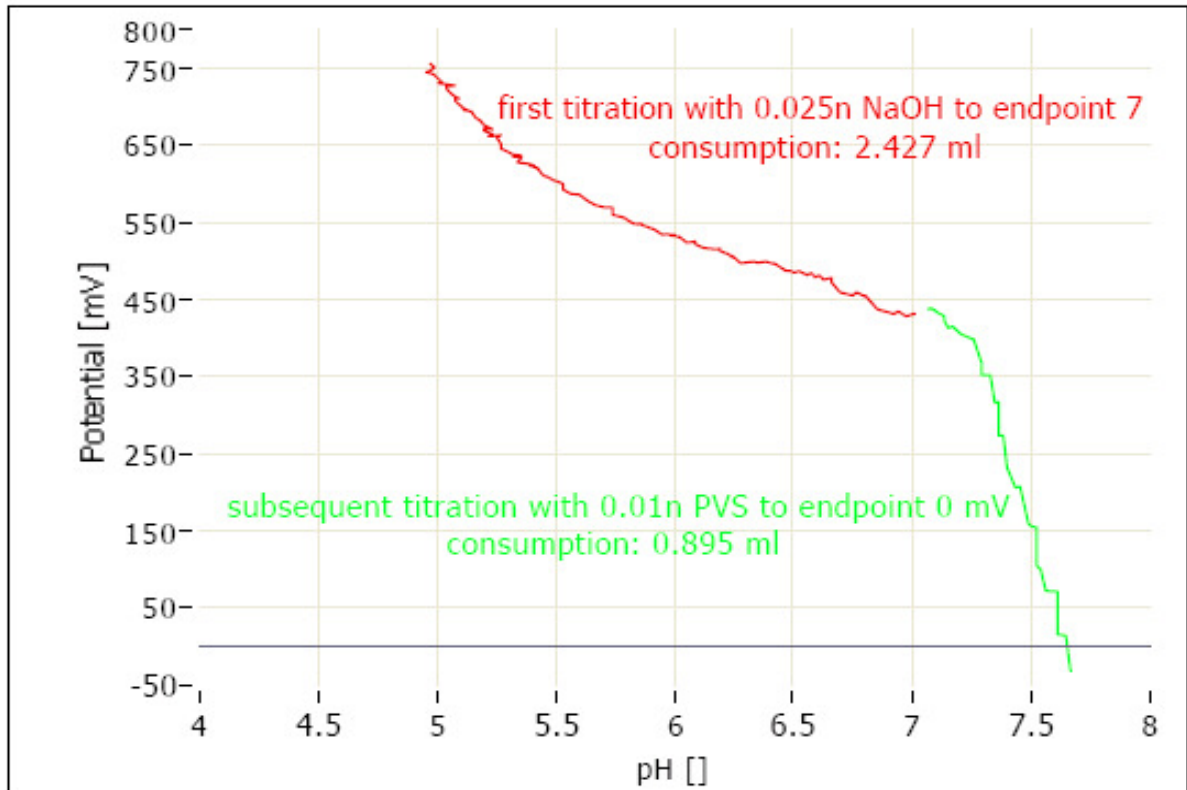|	pH (0 ml)	pH (0 mV)	P (0 ml) [mV]	V (0 mV) [ml]
7	4.944	7.947	766	3.020
8	4.759	8.263	863	2.216
9	4.973	9.874	799	1.118
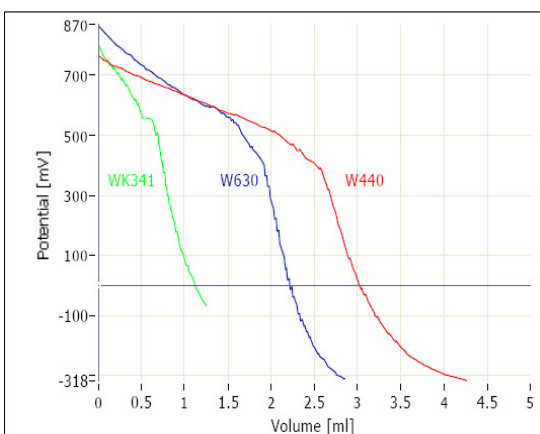
The examples on the left demonstrate the **efficiency of the Stabino®** system. The selected samples are very stable suspensions of pyrogenically produced SiO_2 or Al_2O_3 powders from Evonik Degussa. They are delivered in 30 – 40% w/v concentration. The surface of the particles was modified in a way to have a wide pH range, where the products stay stable and cationic. One of the applications is for the coating of inkjet - paper.

Starting from pH of 4.5, three dispersions of 1% (w/v) and of 10 ml each, were titrated with 0.025n NaOH solution up to pH 10. The isoelectric points (IEP) of the 3 curves can be found in the table in the column „pH (0mV)". The consumption of titrand up to the isoelectric points is given as "V (0mV) [mL])". The same titrations can be graphically presented in different ways. Y- and x- axis may be pH, volume or time, respectively. The example on the left shows the potential versus volume presentation. For some applications, it is interesting to know the value of the potential at given points of the titration. In this example it was the potential at the starting point "P (0 mL) [mV]". The selection of characteristic parameters and results for the table is user defined. A full exportable table and curve is also available. The reproducibility is such that the potential reading of comparable sample classes can be used as a stability parameter. Under similar measurement conditions, the value of the streaming potential may then be correlated to the zeta potential.

It is very useful to do two titrations in a sequence. Starting from a low pH, a given pH can be obtained in a controlled way. A subsequent polyelectrolyte titration delivers the total charge of the suspension at this pH.

In the following example of a 1% w/v W440 suspension, a titration up to pH of 7 is programmed as the first step, followed by a 0 mV polyelectrolyte titration as the second step. This delivers the total charge of the suspension at that pH 7.

	pH (0 ml)	pH (0 mV)	P (0 ml) [mV]	V (0 mV) [ml]
3	4.973	NaN	757	NaN
4	7.063	7.651	437	0.895

To present the 2 titrations the potential versus pH was chosen. This offers the possibility to see the shift of the pH due to the addition of anionic PVS – solution during the polyelectrolyte titration to the zero point. The consumption of 0.01n PVS @ pH = 7.06 is 0.895 mL. This tandem titration was repeated through the whole pH range. The result is presented below.

W 440 in 100 µS/cm KCl: Spezific Charge
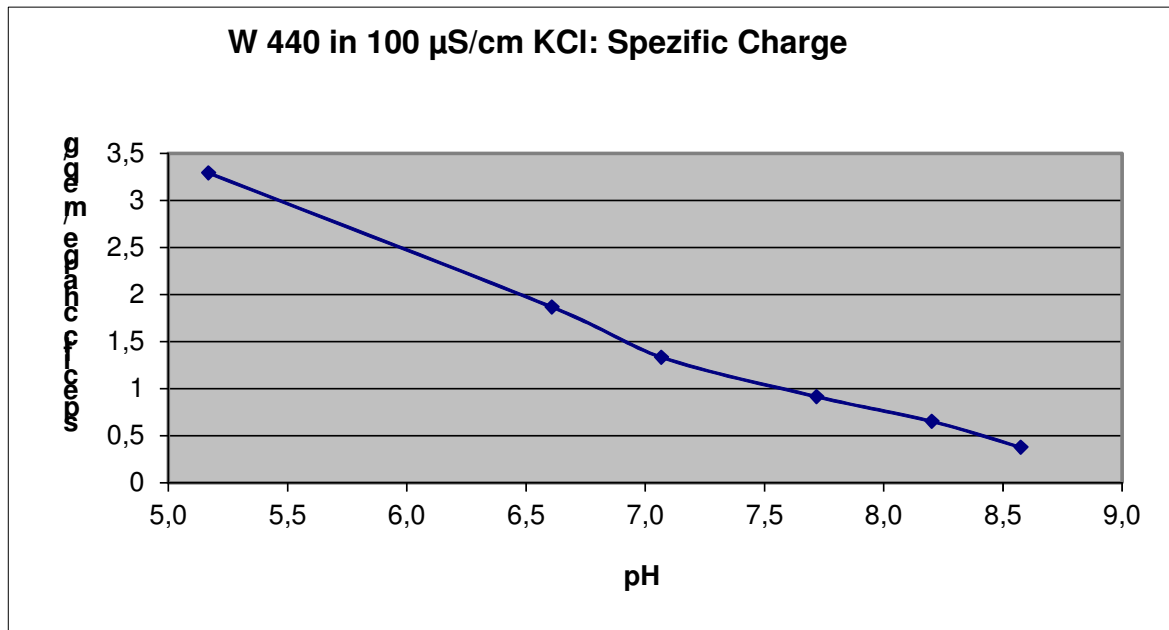
Astonishingly, the charge density vs pH does not follow the corresponding potential curve. The reason for that is not known. But this shows that charge content is not always proportional to potential.

Final Remark

Stabino® opens the way to develop stable dispersions and colloidal materials in an efficient way. This is achieved with the integrated double titration automate, good repeatability, short analysis durations and comfortable handling.

Another publication on similar metal oxide dispersions shows the influence of the pH to size and zeta potential distribution.

For more information contact:

analytikLtd (UK and Ireland Distributor)
Barn B, 2 Cygnus Business Park, Middle Watch, Swavesey, Cambridge, CB24 4AA
T: +44 (0)870 991 4044 F: +44 (0)870 135 2488 E: info@analytik.co.uk **www.analytik.co.uk**