Methods for charge and size characterization colloidal systems
Content

• **General Basics**

• **Stabino®**
  – Measurement basics
  – Applications

• **NANO-flex**
  – Measurement basics
  – Applications

www.particle-metrix.de
Nanoparticles

Bulkphase of gold

gold nanoparticle in water
size: 5 – 10 nm

www.particle-metrix.de
What are Colloids?

- Macromolecules in solution
  - < 1nm – 10 nm
- Particles dispersed in liquids
  - < 1 nm – 10 µm
- > 20 nm → turbid

`wwwparticle-metrix.de`
Colloids

www.particle-metrix.de
Colloids

- are substances in solution and not membrane permeable
- be divided into continuous and disperse phase
- disperse phase is dispersed in the continuous phase
- continuous phase = dispersant
How do colloids behave?

- General tendency to agglomerate
  - dipole - dipole interaction (Van der Waals)
  - Adhesions forces

- Stability is guaranteed by having a repulsive surface
Stabilization of nanoparticles

- (A) electrostatic stabilization → we can measure
- (B) steric stabilization
- (C) electrosteric stabilization → we can measure

Any charged surface of an object – macromolecule, particle, wall – has the potential to attract or repulse other charges

www.particle-metrix.de
Slurry dispersion
(stabilization, liquefaction)

- Particle in water
- Sedimentation
- Electrically charged particles
  no sedimentation
  slurry "stable"

www.particle-metrix.de
Charges, colloid interfaces interact with **ALL** ions from the surrounding liquid

- Charges stabilize
- Charges interact with ions from the liquid environment
- A change in chemical environment can cause stability to be better or worse.
Interaction partners in liquids

1. **Smallest ions (pH & salt)**
   \[ H^+, \text{OH}^-, \text{Na}^+, \text{Cl}^-, \text{Ca}^{2+} \ldots \]

2. **Poly – electrolytes (PE)**
   = charged macromolecules, 100 to 1000 times bigger

3. **Particles**

4. **Big surfaces**
   (glass with negative ions)

ALL – that is the difficulty!!!

[Further information available at www.particle-metrix.de]
Repulsion / Attraction

- Ionic charges on every surface have the POTENTIAL to repulse or attract charges.
- Depending on the polarity of the interaction partner, there is repulsion or attraction.

Required for stability
How strong is ...?

- Repulsion or attraction depends on the amount of charges per surface area.
How to measure the strength of repulsion or attraction?

1. The magnitude of Zeta potential
2. The consumption of calibrated polyelectrolytes for the Total Charge determination

**In general**, the higher Zeta potential and the consumption of polyelectrolytes → the better is the stability
Creating zeta potential - Closer look

Mobile counter ions

Moving force:
Electric field (common)
Fluid stream

Shear plane = location of the zeta potential
Measurement methods for Zeta Potential

• Electrophoretic mobility
  – Particles in an electric field \( \mu_e = vE^{-1} \)
  – zeta potential (ZP, \( \zeta \)) calculated \( ZP \sim \mu_e \)

• streaming zeta potential (SZP)
  – Liquid moves, particles immobilized (more details later)

• colloid vibration current (cvi)
  – Movement of the liquid with ultra sound

www.particle-metrix.de
Difficulties reported

- ZP Measurements not **repeatable**
  → chemical environment changes
- Problems with **bubbles**
- Problems with the **optical properties** of the sample
- Problems with **dilution**
- Titrations very **slow and complicated** – therefore avoided
Stabino®  NANO-flex  ZETA-check

DUO-S  DUO-Z

www.particle-metrix.de
Combination of Stabino® & NANO-flex

Remote controled form Stabino Software

www.particle-metrix.de
Transport boxes

- Easy and save transport in special boxes
- Possible to take it in a plane and store it in the overhead bin

www.particle-metrix.de
Specifications

- no optical and form parameters of the particles
- potential measurement in 1 sec
- mixing in 2 sec
  - \textit{Titration in 5 min possible}
- Measurement range
  - charge: 0.3 nm to 300 \(\mu\)m
  - size: 0.8 nm to 6.5 \(\mu\)m (with NANO-flex)
  - Concentrations: 0.01 to 40 vol.%
- 1 mL or 10 mL sample volume

www.particle-metrix.de
Immobilized particles at a plane Teflon® - surface

„plane“ surface
Surface coated with particles
shear plane „Zeta“ plane
Double layer with zeta potential

www.particle-metrix.de
Shearing at interface

Fluid stream → Streaming zeta potential (SZP)

Electric field → Electrophoresis zeta potential
Producing an oscillating streaming potential

Changing the environment of the particles by defined addition of pH-, salt- or Polyelectrolyte solutions

\[ SP = k \cdot ZP \]

\[ ZP \sim \text{measured potential} \]

\[ SP = \text{streaming potential} \]

\[ K = \text{system constant} \]

\[ ZP = \text{zeta potential} \]
Stabino® setup

Titrant 1 & 2 =
- Acid
- Base
- Polyelectrolyte (anionic or cationic)
- Salt solution

power connection

PC connection

Titrant 1

Titrant 2

P1 = Pump 1
P2 = Pump 2

Streaming & Zeta potential + Conductivity

pH temperature

NANO-flex connection for in situ size measurement

www.particle-metrix.de
Producing an oscillating streaming potential

Changing the environment of the particles by defined addition of von

**SP** = k · **ZP**

**ZP** ~ (measured potential)

**SP** = streaming potential

**K** = system constant

**ZP** = zeta potential

pH-, salt- or Polyelectrolyte solutions

www.particle-metrix.de
Calibration of the potential with suspensions and polyelectrolytes

- Zeta Potential (ZP) with a standard suspension of known Zeta potential
- Streaming potential (SP) with a standard polyelectrolyte solution of known streaming potential

During a measurement, ZP / SP are displayed simultaneously

www.particle-metrix.de
Application

- pH Titrations
  - Isoelectric Point Measurements
  - Stable pH Areas

- Poly Electrolyte Titration
  - Coatings with polyelectrolytes
  - Stability measurements of dispersions
  - Ionic activity / Charge density

- Salt titrations
  - Conductivity measurements

www.particle-metrix.de
Application (pH)

pH – Titration of Al₂O₃ from pH 4 to pH 10 and pH 10 to pH 4

Zetapotential / mV

pH
Application (pH): 3D Plot of $\text{Al}_2\text{O}_3$ (W630)
Application (pH): Al₂O₃ with size measurement
Application (pH): characterization of ceramic raw materials

Forth titration: From pH 3 → pH 11
Back titration: From pH 11 → pH 3

Iso electric point: pH 5.5 - 6
Application (pH): Titration of Lysozyme
Application (PE): 1% carbon nanotubes

Carbon Nanotubes (1 %) with coating
Carbon Nanotubes (1 %) without coating
Application (PE): polyelectrolyte titration
Application (PE): oil in water emulsion
Application (PE): stability of filtered beers

Stability against becoming turbid


www.particle-metrix.de
Application (PE): stability study of rice milk
Application (salt)
Benefits

- Zeta potential and streaming potential in one measurement
- Conductivity is measured at every measurement point
- 3D Plots
- Size range for charge: 0.3 nm to 300 µm
- Macromolecules to big particles
- Total charge
- Charge mapping tool for formulation
- Hi concentration 0.01 to 40 vol.%
- Potential at hi conductivity
- NANO-flex - DLS inside as option

www.particle-metrix.de
NANO-flex
Methods of Light Scattering (LS)

**Static LS (SLS):**
The information on size is in the angle function

**Dynamic LS (DLS):**
The information on size is in the fluctuation of the scattering signal (Brownian motion)
180° heterodyne back scattering (DLS)

- Highest possible concentration
- From transparent to carbon black
- No multiple scattering

Size & concentration

0.01 – 40 vol%
Signal at the detector

Log intensity

heterodyne

homodyne

Noise

time

www.particle-metrix.de
Different ways of measurement

- drop
- in nearly every vessel
- online
- with Stabino®

www.particle-metrix.de
Specifications

- size 0.8 nm (0.3 nm) – 6.5 µm (10 µm)
- Concentration up to 40 vol.%
- Minimum sample volume 10 µL
- Molecular weight by Debye Plot dn/dc
- Online or inline Measurements are possible
- Cuvettes
- Zeta potential option with Stabino® / ZETA-Check
NANO-flex Applications

- protein
- drinks
- lysozyme
- liposome
- humic acid
- fullerene
- diamond
- CNT's

- quantum Dots
- emulsion
- metal oxide
- polymer dispersions
- printing ink
- coatings
- and much more
**Application: three modal latex beads mixture**

<table>
<thead>
<tr>
<th>Dia / nm measured</th>
<th>Vol % measured</th>
<th>Dia /nm theoretical</th>
<th>Vol % theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>83.9</td>
<td>11.7 %</td>
<td>95.6</td>
<td>33.74 %</td>
</tr>
<tr>
<td>711</td>
<td>76.8 %</td>
<td>746</td>
<td>63.22 %</td>
</tr>
<tr>
<td>3790</td>
<td>11.5 %</td>
<td>4760</td>
<td>3.04 %</td>
</tr>
</tbody>
</table>

![Size Distribution Diagram](Image)
Application: high resolution and differentiation

Particle Size Distribution

- 200 nm
- 100 nm

www.particle-metrix.de
## Sensitivity in a mix of 20 & 100 nm PS

### Mode Summary

<table>
<thead>
<tr>
<th>d(nm)</th>
<th>Pct</th>
<th>Width</th>
<th>C(I)</th>
<th>C(V) cm³/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.51</td>
<td>96.19</td>
<td>1.04E-02</td>
<td>1.04E-01</td>
<td>1.34E-03</td>
</tr>
<tr>
<td>211.2</td>
<td>3.81</td>
<td>4.12E+00</td>
<td>4.12E-03</td>
<td>1.11E-07</td>
</tr>
</tbody>
</table>

5 drops 20 nm PS in 1 mL water

<table>
<thead>
<tr>
<th>d(nm)</th>
<th>Pct</th>
<th>Width</th>
<th>C(I)</th>
<th>C(V) cm³/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.90</td>
<td>1.905</td>
<td>4.74E-01</td>
<td>4.74E-02</td>
<td>1.71E-03</td>
</tr>
<tr>
<td>91.67</td>
<td>98.09</td>
<td>2.44E+00</td>
<td>2.44E+09</td>
<td>3.51E-14</td>
</tr>
</tbody>
</table>

5 drops 20 nm PS in 1 mL water + 1 drop 100 nm PS

<table>
<thead>
<tr>
<th>d(nm)</th>
<th>Pct</th>
<th>Width</th>
<th>C(I)</th>
<th>C(V) cm³/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.98</td>
<td>12.26</td>
<td>3.32E+02</td>
<td>3.32E-01</td>
<td>4.72E-03</td>
</tr>
<tr>
<td>96.70</td>
<td>87.74</td>
<td>2.38E+03</td>
<td>2.38E+00</td>
<td>3.05E-04</td>
</tr>
</tbody>
</table>

20 drops 20 nm PS in 1 mL water + 1 drop 100 nm PS

<table>
<thead>
<tr>
<th>d(nm)</th>
<th>Pct</th>
<th>Width</th>
<th>C(I)</th>
<th>C(V) cm³/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.20</td>
<td>13.20</td>
<td>3.26E+02</td>
<td>3.26E-01</td>
<td>5.33E-03</td>
</tr>
<tr>
<td>92.50</td>
<td>86.80</td>
<td>2.14E+03</td>
<td>2.14E+00</td>
<td>3.09E-04</td>
</tr>
</tbody>
</table>

25 drops 20 nm PS in 1 mL water + 1 drop 100 nm PS

www.particle-metrix.de
Application: ceramics

50 w% ceramic slurry with a liquid agent at pH 9

50 w% ceramic slurry with a liquid agent at pH 1

www.particle-metrix.de
Application: Filtration control

Comparison: red = unfiltered, green = filtered

Filtered: Concentration index = 0.0136
Unfiltered: Concentration index = 0.0351

www.particle-metrix.de
Application: Gushing inducing particles

**red**: gushing; **green**: tendency to gushing; **blue**: no gushing

Haffmans ISD INPACK 200
SAMPLING DEVICE

www.particle-metrix.de
Application: ONLINE in-situ size measurement

www.particle-metrix.de
Benefits

- Hi concentration
- Organic and aqueous solution in one cell
- Online Measurement
- Cuvettes possible
180° DLS Silver
1nm + 35 nm

Particle Size Distribution

Number
Intensity

www.particle-metrix.de
Summary

• DUO of collective and single particle analysis → full picture in nano
• High and low concentrations
• High dynamics with collective (DLS) particle analysis
• Volume concentration and particle concentration results
Specifications

- **Measurement range**
  - size: 20 nm – 3 µm
  - size for zeta potential: 20 nm–50 µm
  - zeta potential: -150 mV to + 150 mV
  - 15 – 55°C

- **Concentration**
  - Minimum 10⁶ particles pro cm³
  - Maximum 1000 ppm at 150 nm particle size

- **Laser**
  - red: 650 nm
  - blue: 405 nm with *Cut-Off* filter for fluorescence

www.particle-metrix.de
Multiparameter NTA with the Laser Scattering Video Microscope

Counting

Zeta potential

Size distribution

Laser

Dispersed nanoparticles

ZetaFocus

Microscope

Cell channel cross section

Video Camera

www.particle-metrix.de
Applications: size of proteins

size ≈ 150 nm

www.particle-metrix.de
Applications: zeta potential of proteins
Applications: zeta potential distribution

Latex Mix cationic & anionic
-8 mV & +45 mV

www.particle-metrix.de
Benefits

- Multiparameter NTA provides **zeta potential**, **concentration** and **sizing** in one measurement (i.e. on the same sample)

- Zeta potential distribution

- **Auto-alignment** and **autofocus** after cell change

- Multiple positions (up to 11) for statistic validity

- Full control by „seeing is believing“ principle
180° DLS
Size range 0.8 – 6500 nm

90° NTA
20 nm - 1000 nm

Medium to high concentration

Lowest concentration: > $10^5$ cm$^{-3}$
Summary

The diagram illustrates the capabilities of different particle analysis tools:

- **Stabino® ZETA-check**
- **Nanotrac® Wave NANO-flex**
- **ZetaView® Particle Tracking Analyser**

Properties:
- **Charge only**
- **Size only**
- **Charge and Size**
- **Zeta Potential Agglomerates**

Concentration K:
- Medium to high
- 1 Mio P/mL to 1000 ppm

The diagram categorizes particle sizes from 0.3 nm to 300 µm, highlighting the areas where each tool is most effective.
All 3 Methods in one?

Unpossible $\rightarrow$ lot of Compromises!

NO!

www.particle-metrix.de
MANY THANKS FOR YOUR ATTENTION