Review:

ISO 13099 Colloidal systems — Methods for zeta potential determination

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ISO 13099-1:2012

Colloidal systems -- Methods for zeta-potential determination -- Part 1: Electroacoustic and electrokinetic phenomena

ISO 13099-2:2012

Colloidal systems -- Methods for zeta-potential determination -- Part 2: Optical methods

ISO/NP 13099-3

Methods for zeta potential determination -- Part 3: Acoustic methods

Standards under development

Outline

- ISO standards
- Zeta potential background
- Cells
- Operational and dilution procedures
- Reference materials
- System verification

ISO TC 24/SC 4 Published Standards

TC 24/SC 4 - Particle characterization
32 standards published so far

ISO 9276:1998 **Representation of results of particle size analysis**
Part 1: Graphical representation
Part 2: Calculation of average particle sizes/diameters and moments from particle size distributions
Part 3: Adjustment of an experimental curve to a reference model
Part 4: Characterization of a classification process
Part 5: Methods of calculation relating to particle size analyses using logarithmic normal probability distribution
Part 6: Descriptive and quantitative representation of particle shape and morphology

ISO 9277:2010 **Determination of the specific surface area of solids by gas adsorption**
-- BET method

ISO 13099-1:2012 **Colloidal systems -- Methods for zeta-potential determination**
Part 1: Electroacoustic and electrokinetic phenomena
Part 2: Optical methods

ISO TC 24/SC 4 Published Standards

ISO 13317-1:2001: **Determination of particle size distribution by gravitational liquid sedimentation methods**
Part 1: General principles and guidelines
Part 2: Fixed pipette method
Part 3: X-ray gravitational technique

ISO 13318-1:2001: **Determination of particle size distribution by centrifugal liquid Sedimentation methods**
Part 1: General principles and guidelines
Part 2: Photocentrifuge method
Part 3: Centrifugal X-ray method

ISO 13319:2007 **Determination of particle size distributions -- Electrical sensing zone method**

ISO 13320:2009 **Particle size analysis -- Laser diffraction methods**

ISO 13321:1996 Particle size analysis -- **Photon correlation spectroscopy**

ISO 13322-1:2004Particle size analysis -- **Image analysis methods**
Part 1: Static image analysis methods
Part 2: Dynamic image analysis methods

ISO TC 24/SC 4 Published Standards

ISO 14488:2007 Particulate materials -- **Sampling and sample splitting for the determination of particulate properties**

ISO 14887:2000 Sample preparation -- **Dispersing procedures for powders in liquids**

ISO 15900:2009 Determination of particle size distribution -- **Differential electrical mobility analysis for aerosol particles**

ISO 15901-1:2005 **Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption**
Part 1: Mercury porosimetry
Part 2: Analysis of mesopores and macropores by gas adsorption
Part 3: Analysis of micropores by gas adsorption

ISO 20998-1:2006 **Measurement and characterization of particles by acoustic methods**
Part 1: Concepts and procedures in ultrasonic attenuation spectroscopy

ISO TC 24/SC 4 Published Standards

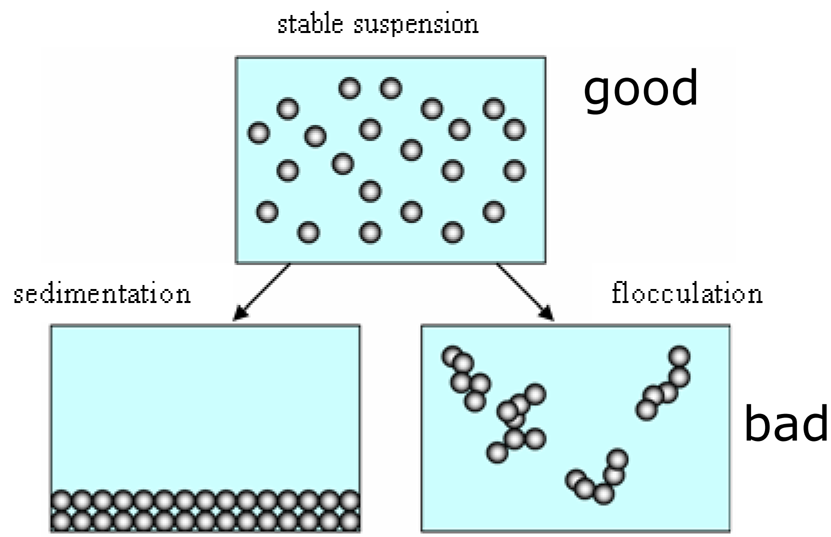
ISO 21501-1:2009 **Determination of particle size distribution Single particle light interaction methods**

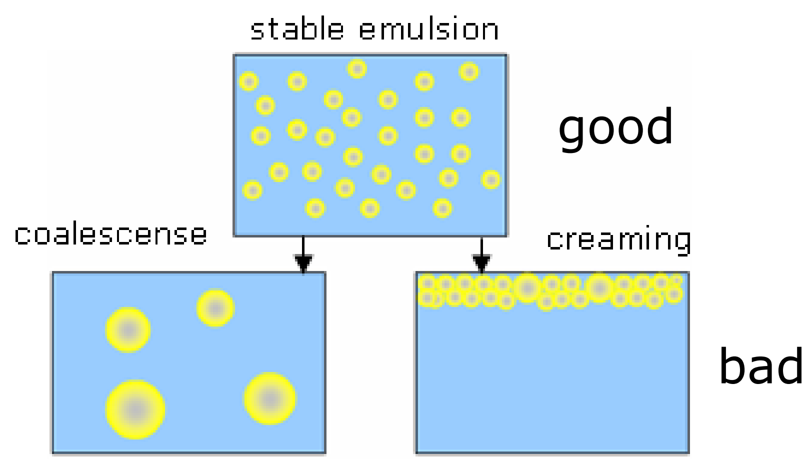
Part 1: Light scattering aerosol spectrometer
Part 2: Light scattering liquid-borne particle counter
Part 3: Light extinction liquid-borne particle counter
Part 4: Light scattering airborne particle counter for clean spaces

ISO 22412:2008 **Particle size analysis -- Dynamic light scattering (DLS)**

Why Colloidal Systems?

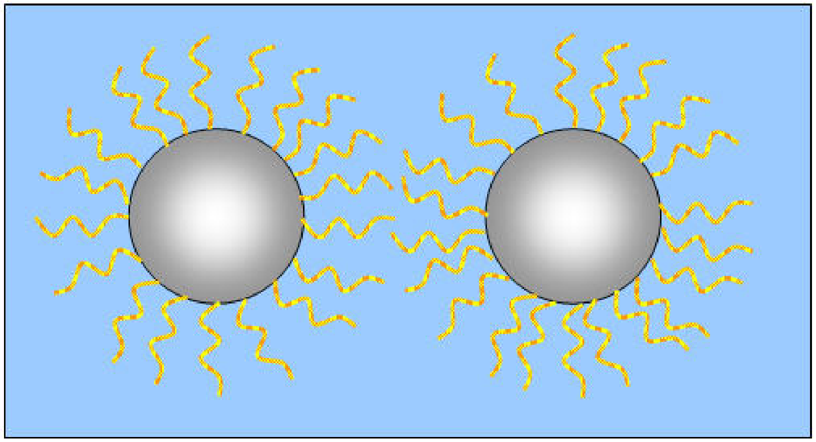
- Zeta potential often used in colloidal stability studies
- Want stable dispersion
- Suspensions sediment & flocculate
- Emulsions phase separate, creaming or coalescence



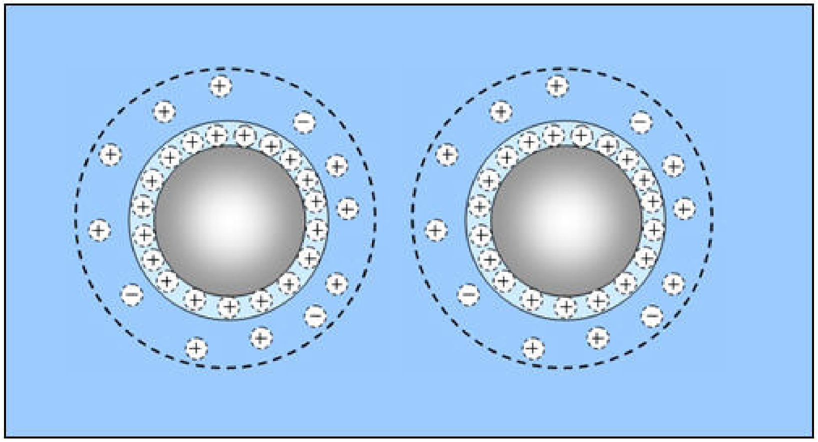


Stabilization

- Steric stabilization: coat surface with polymers
- Particles can’t touch so they don’t interact

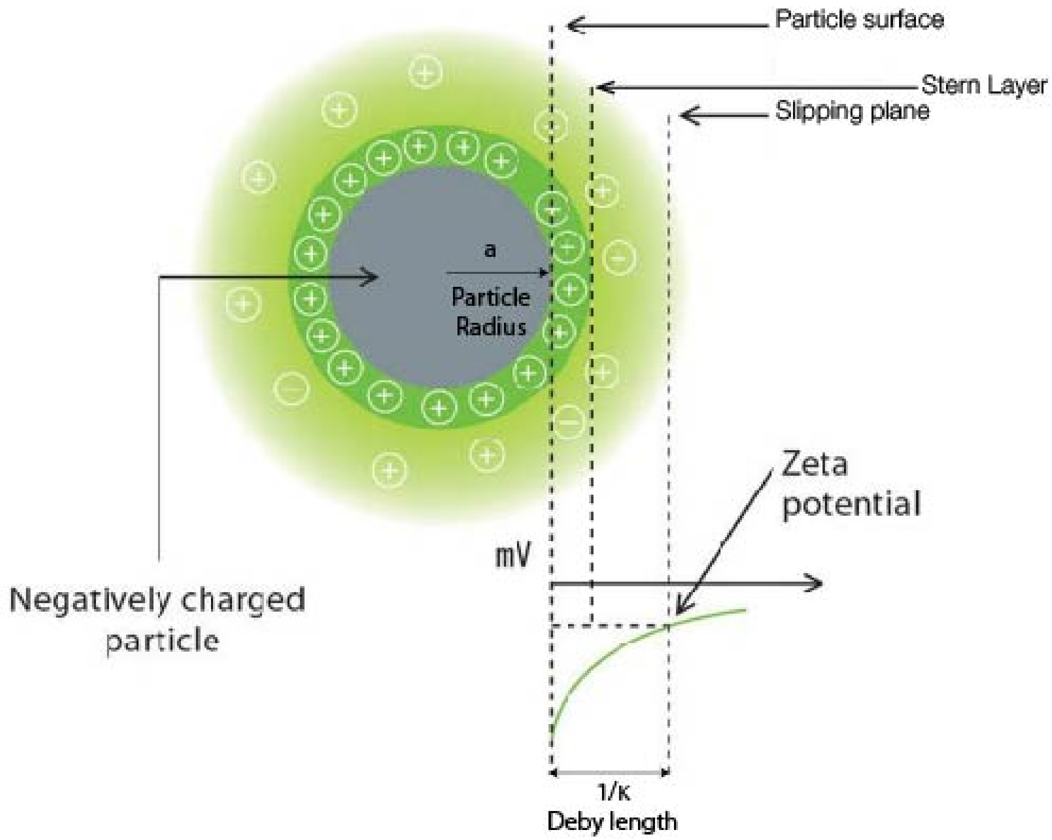


- Electrostatic stabilization: alter surface chemistry to put charge on particle surface
- Repel like magnets



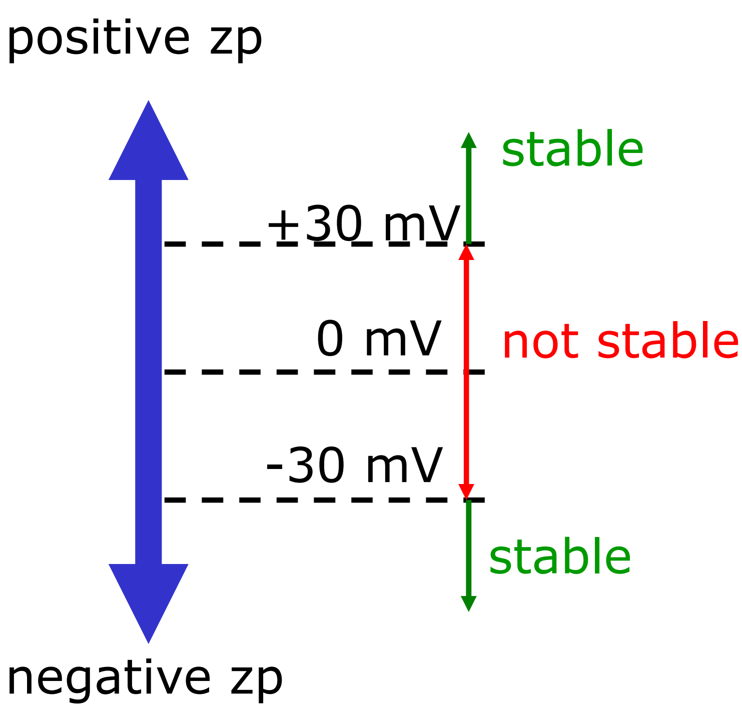
Zeta Potential

- If surface has - charge, then + ions attracted to surface
- - ions attracted to + ions, builds electric double layer
- Slipping plane: distance from particle surface where ions move with particle
- ZP = potential (mV) at slipping plane



Zeta Potential Predicts Stability

Different guidelines



Sample Dependency

- Oil/water emulsions > 10 mV
- Polymer latices > 15 mV
- Oxides > 30 mV
- Metal sols > 40 mV

Zeta Potential: Emulsion Isoelectric Point (IEP)

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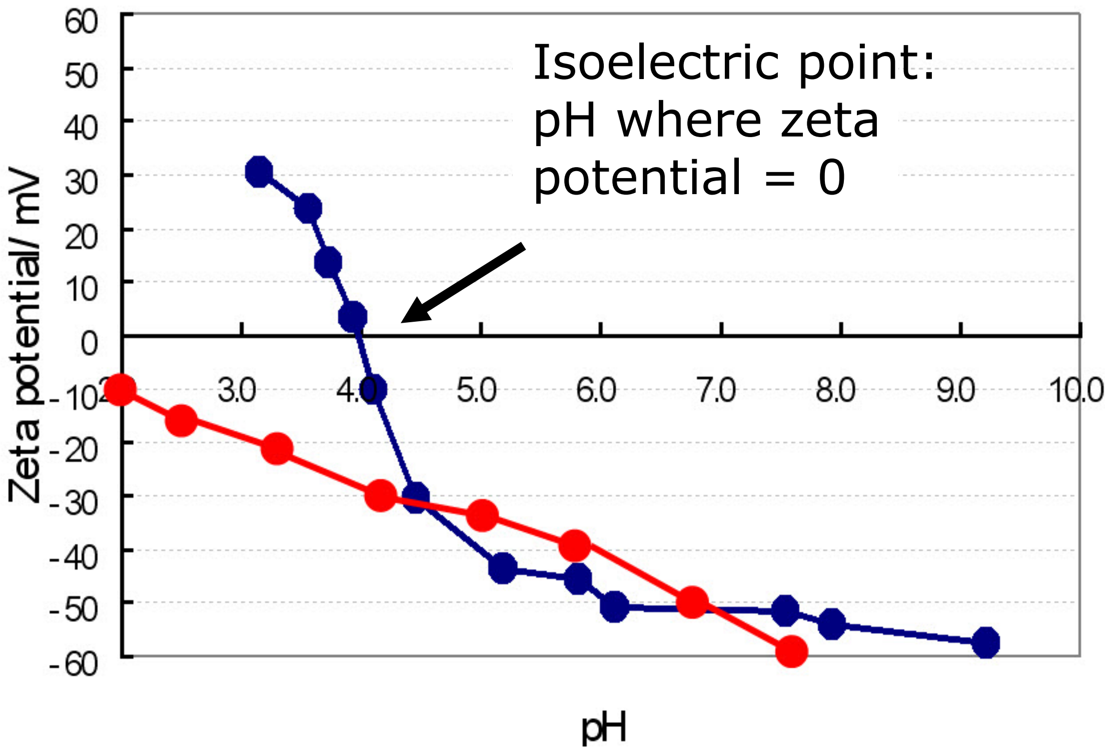
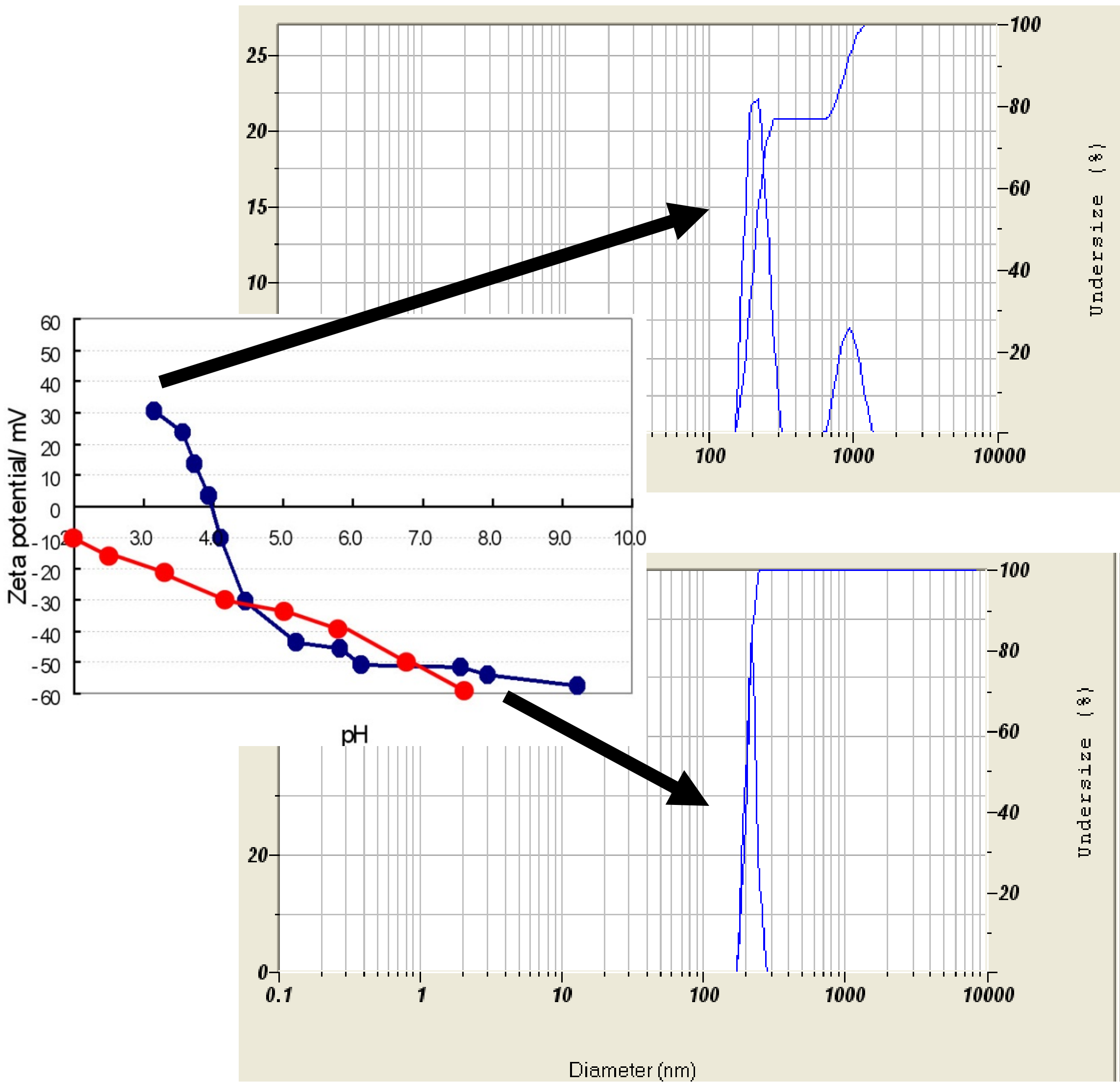


Automate IEP studies with auto titrator

Emulsion IEP Study: Stability



coffee mate pH 3 zeta cell_0107.nsz

Measurement Results

Date : mardi 3 avril 2012 15:59:41
Measurement Type : Particle Size
Sample Name : coffee mate pH 3 zeta cell
Scattering Angle : 173
Temperature of the holder : 24.8 °C
Run duration : 30 Seconds
Representation of result : Scattering Light Intensity
Count rate : 1420 kCPS

Calculation Results

Peak No.	S.P.Area Ratio	Mean	S. D.	Mode
1	0.77	201.6 nm	28.9 nm	201.9 nm
2	0.23	889.7 nm	128.2 nm	885.8 nm
3	---	--- nm	--- nm	--- nm
Total	1.00	362.9 nm	299.1 nm	201.9 nm

Cumulant Operations

Z-Average : 1282.7 nm
PI : 0.516

coffee mate pH_8 zeta cell_0094.nsz

Measurement Results

Date : mardi 3 avril 2012 15:34:25
Measurement Type : Particle Size
Sample Name : coffee mate pH_8 zeta cell
Scattering Angle : 173
Temperature of the holder : 24.8 °C
Run duration : 60 Seconds
Representation of result : Scattering Light Intensity
Count rate : 1309 kCPS

Calculation Results

Peak No.	S.P.Area Ratio	Mean	S. D.	Mode
1	1.00	203.1 nm	16.1 nm	202.8 nm
2	---	--- nm	--- nm	--- nm
3	---	--- nm	--- nm	--- nm
Total	1.00	203.1 nm	16.1 nm	202.8 nm

Cumulant Operations

Z-Average : 640.8 nm
PI : 0.500

Zeta Potential: Measurement

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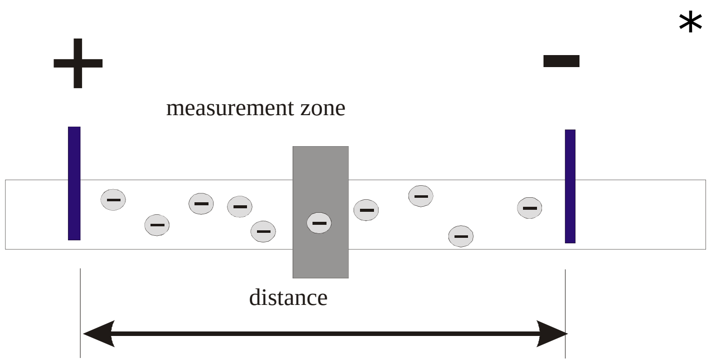
- Optical
  - Microscope

  - Electrophoretic light scattering
    - (ELS)
- Acoustic

Zeta Potential: ELS Measurement

- Apply electric field
- Measure particle motion
- Direction tells + or –
  - + particles move to –
  - - particles move to +
- Speed tells amplitude
  - Get speed from frequency shift from motion of particles



* Figure 1, part 2

Optical Configuration

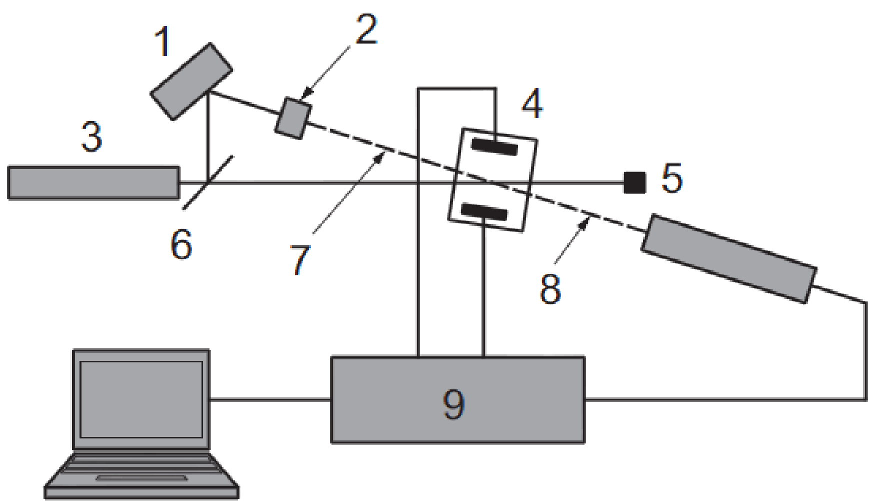
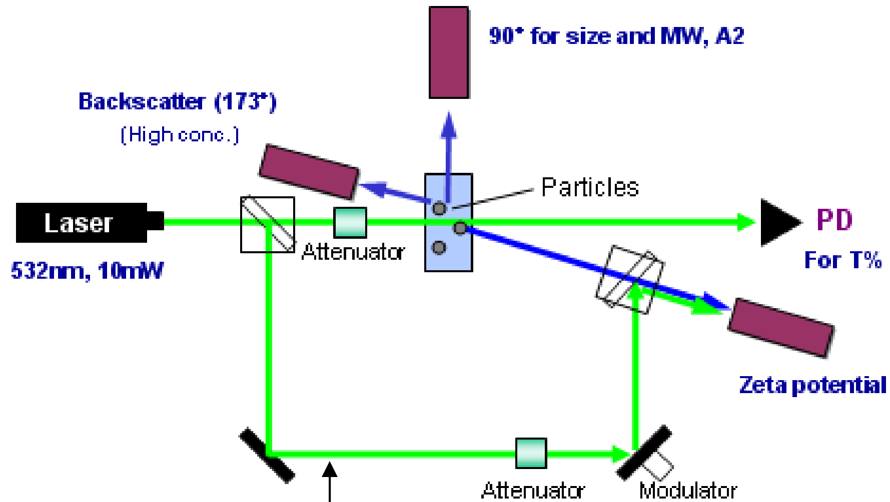


Figure 3 from 13099-2*



SZ-100 optics

Reference beam
Heterodyne @ 17°

* Figure 3, part 2

Zeta Potential Measurement

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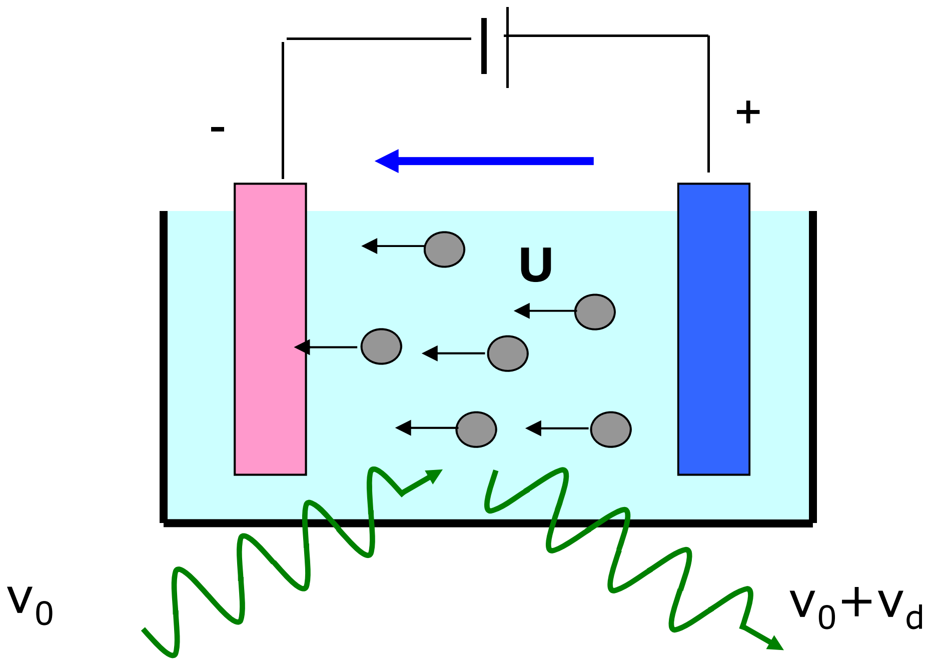

Mobility*

$$\mu = \frac{\Delta\omega\lambda_0}{4\pi n E \sin(\theta/2)\sin[(\theta/2)+\xi]}$$

Zeta potential*

$$\mu = \frac{2\zeta\varepsilon}{3\eta_0} f(\kappa a)$$

Particle motion causes Doppler shift

Frequency ⟶ mobility

Mobility ⟶ zeta potential

μ	electrophoretic mobility
$\Delta\omega$	Doppler frequency shift
λ_0	laser wavelength
n	medium refractive index
E	electric field strength
Θ	angle between incident & scattered light
ζ	zeta potential
ε	dielectric permitivity
ηo	medium viscosity
$f(\kappa a)$	ratio of the particle radius to the EDL

* Equations 1 and 2, part 2, section 6.6

Thin vs. Thick Double Layer

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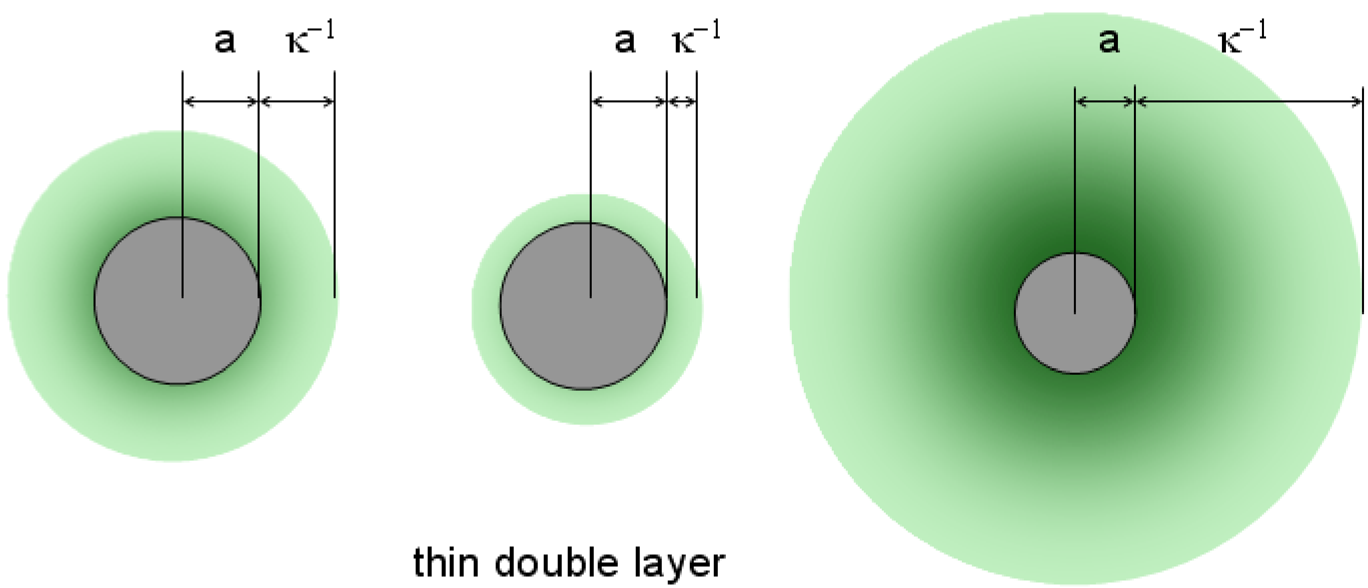
$$\mu = \frac{2\zeta\varepsilon}{3\eta_0} f(\kappa a)$$

Debye length = κ^{-1}
Particle radius = a
Viscosity = η
Dielectric permitivity = ε



Huckel
$F(\kappa a) = 1.0$

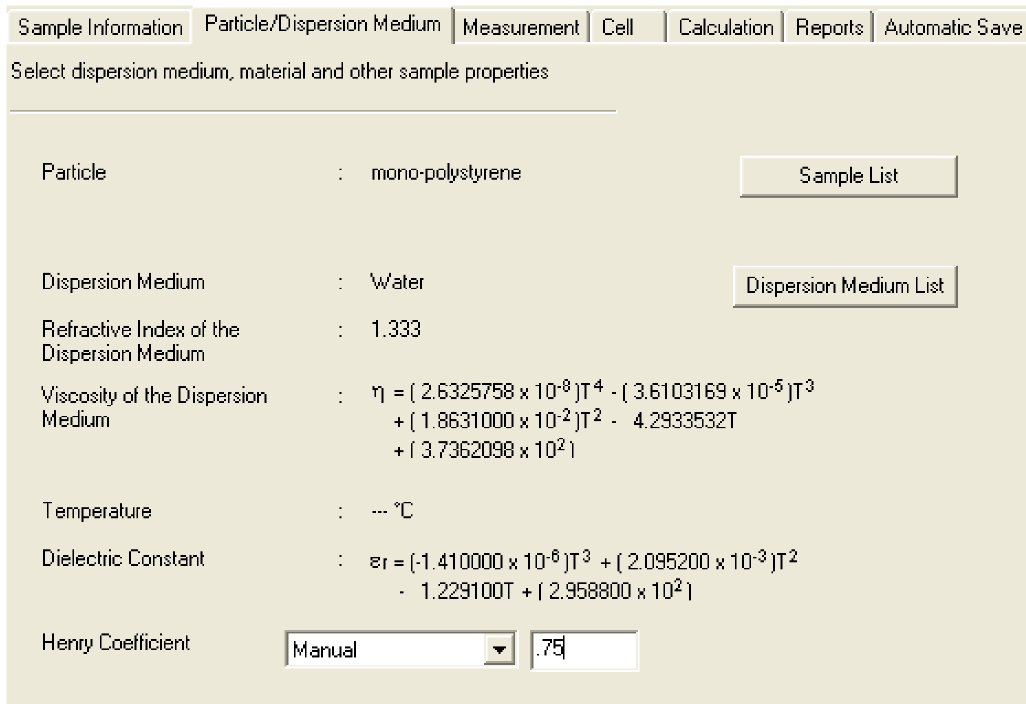
thin double layer
Smoluchowski
$F(\kappa a) = 1.5$
$\kappa a >> 1$

thick double layer

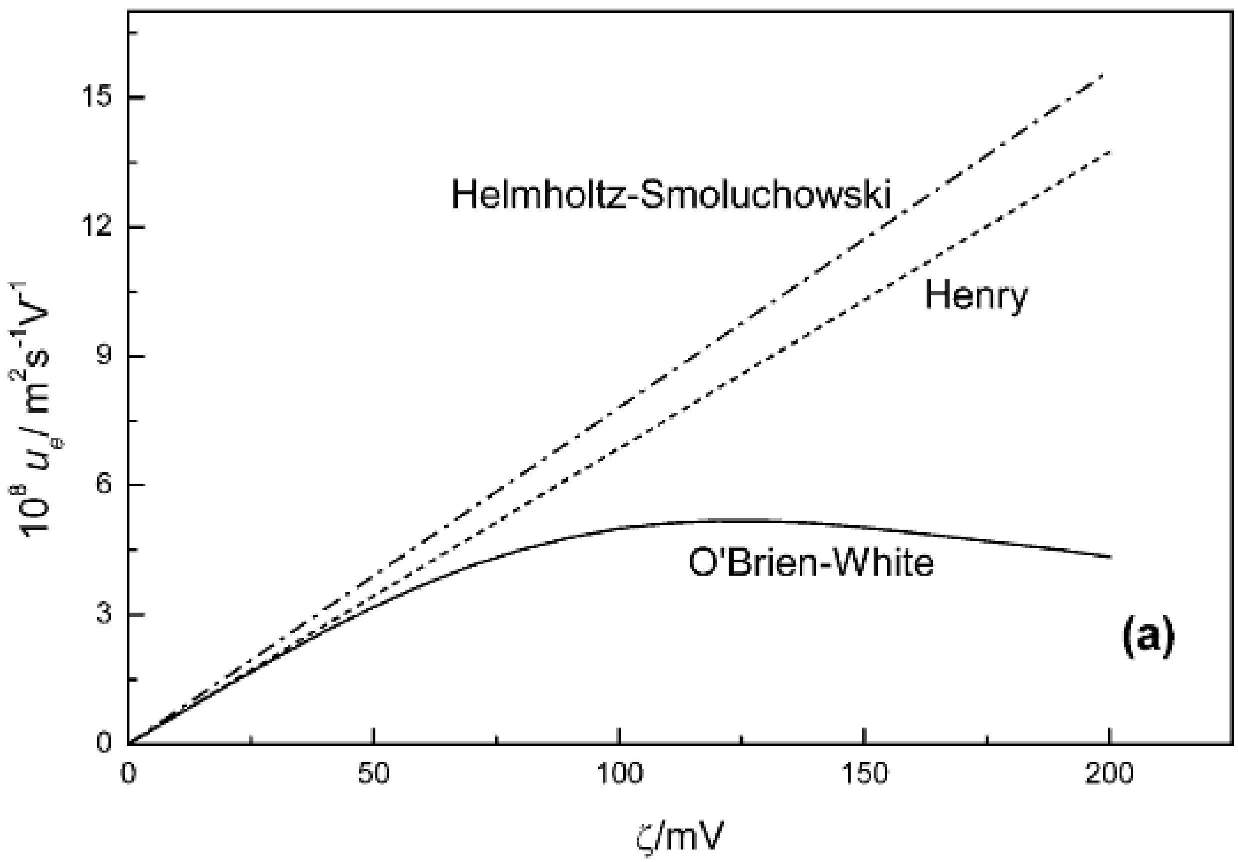
$\kappa a << 1$

SZ-100 Software

- Default is Smoluchowski
- Selection for Huckel
- Or enter manually for other model



Advanced Theories*



* Discussed in part 1, but graph from IUPAC technical report **MEASUREMENT AND INTERPRETATION OF ELECTROKINETIC PHENOMENA** *Pure Appl. Chem.*, Vol. 77, No. 10, pp. 1753–1805, 2005

Measurement Details

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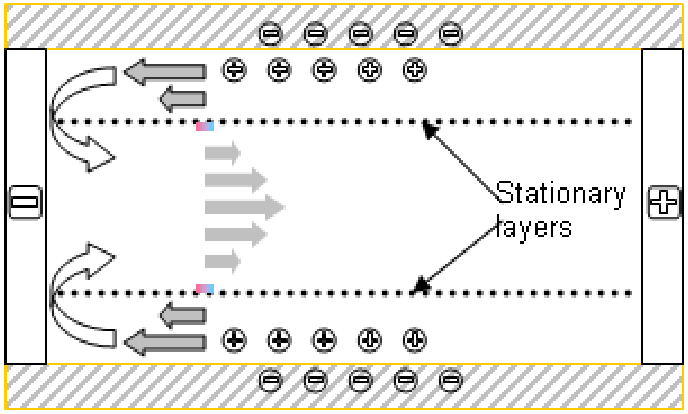
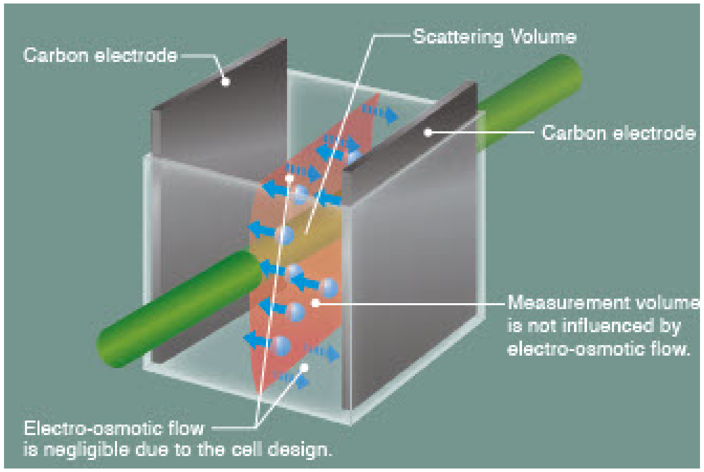
- First measure conductivity
- Then decide applied electric field
  - Auto or manually
- Reverse electric field to avoid polarization & electroosmosis
- To avoid electroosmotic effect near cell walls
  - “Uzgiris” type cells avoid this problem

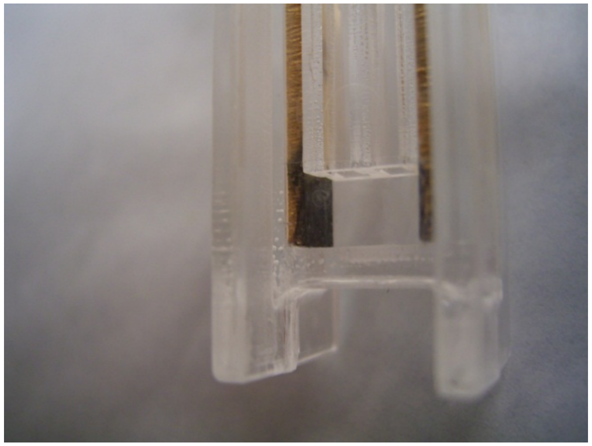
*





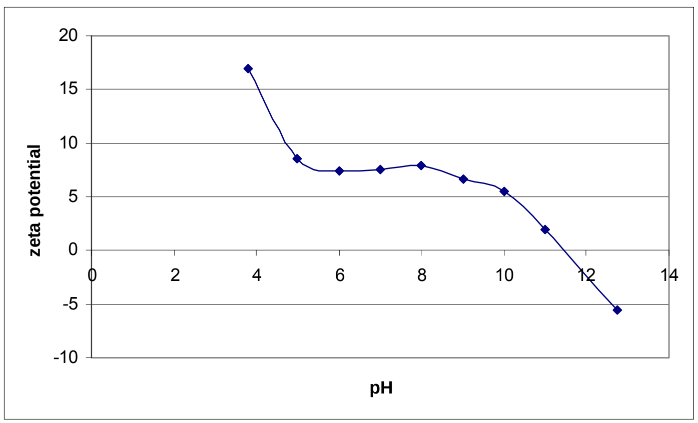
* Figure 6, part 2

Zeta Potential Cells

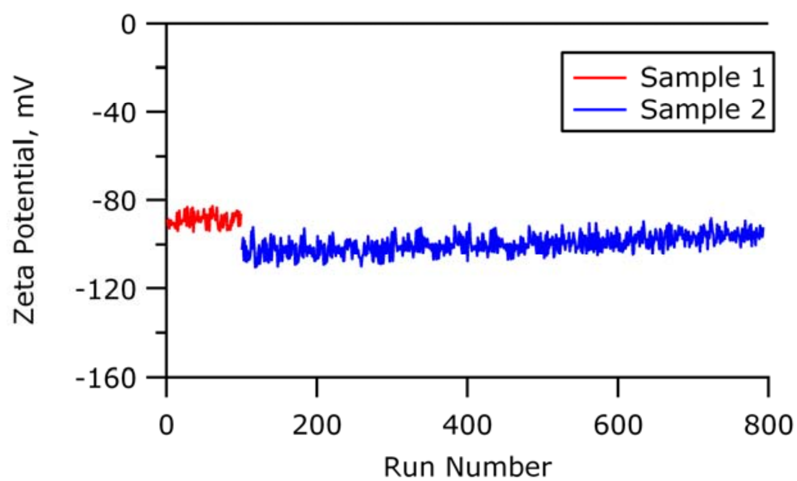


Gold coated electrodes (ruined)

Carbon coated electrodes



IEP 3.4 nm protein



800 measurements with one cell

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Section 8 Operational Procedures

- Instrument location Place the instrument in a clean environment on a surface without vibration
- Dispersion liquids Ensure chemical compatibility between the medium and the cell
- Measurement cell Clean cells that have been previously used, control the temperature
- Sample inspection Look for sedimentation, if visible then the measurement is questionable

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Section 8: Dilution

- Try to avoid dilution
- Don't dilute with DI water
  - No ions, changes surface chemistry & ZP
- Best: equilibrium dilution with same liquid as sample, but with no particles
  - Us supernatant after sedimentation or centrifugation

- Otherwise, dilute with 0.01 M KCL solution

Section 8.2: Verification

- 8.2.1 reference Materials
- Be sufficiently homogeneous and stable for the stated time and temperature range
- The accepted electrophoretic mobility value was obtained by several operators and rigorously proven.
- The material should be well documented in terms of sampling procedure, dilution, if required, and measurement protocol.

Section 8.2: Verification

- 8.2.2 **Repeatability**
- Prepare sample following provided procedure
- Measure same portion three times
- Pass if mean value CV <10%
  - Assuming $2 \times 10{-}8\ m^2/V \cdot s$
- Note: expect most customers to use zeta potential values

Section 8.2: Verification

- 8.2.3 **Intermediate Precision**
- Same procedure as 8.2.2 but using <u>different portions</u> of sample
- Pass if Repeatability; CV <15%
  - Assuming $2 \times 10-8\ m^2/V \cdot s$
- Doubt this is done often
- In pharmaceutical industry intermediate precision implies multiple systems, multiple operators, different days

Section 8.2: Verification

- 8.2.4 **Trueness** (accuracy)
- Prepare, measure same portion 3 times
- Pass if mean value within 10% of published electrophoretic mobility value, assuming > 2 × 10−8 m2/V•s.
- Note: when calculating pass/fail criteria it is OK to include the uncertainty of the sample
- Note: most customers use the zeta potential value, not the mobility

NIST SRM1980 on SZ-100

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Pass criteria:
Mean within 10% of reference value
COV<10%

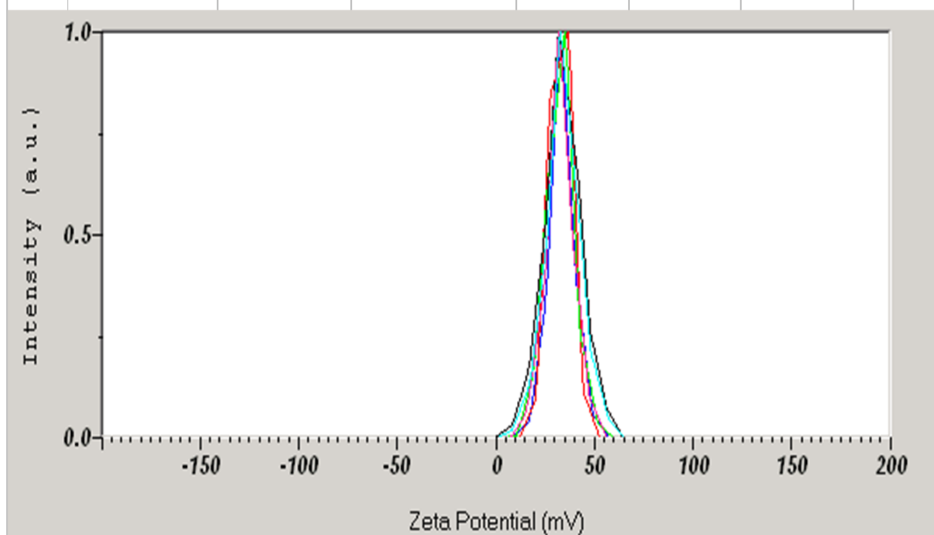
Reference value
2.53 µm·cm/V·s ± 0.12 µm·cm/V·s

Upper limit:
(2.53 + 0.12)*1.1 = 2.92

Lower limit:
(2.53 – 0.12)* 0.9 = 2.17

Pass

No.	Sample Name	Zeta Potential(mV)	Electrophoretic Mobility(cm2/Vs)
17	NIST SRM1980	33,4	0,000257
18	NIST SRM1980	32,7	0,000252
19	NIST SRM1980	32,5	0,00025
20	NIST SRM1980	33,9	0,000261
21	NIST SRM1980	32,7	0,000252
22	NIST SRM1980	34,2	0,000263
Mean		33,2	0,000256
S. D.		0,7	0,000005
COV		2,11	1,95



Section 8.3: Sources of Error

- Contamination from previous sample
- Poor sample preparation
- Inappropriate sample
- Inappropriate liquid medium
- Poor temperature stabilization
- Condensation on the illuminated surfaces
- Too large a potential applied

Section 8.3: Sources of Error

- Particles, fingerprints or scratches on the optical surfaces
- Incorrect entry of parameters by the operator
- Air bubbles
- Cell coating damage
- Inappropriate theory for calculating zeta-potential from the measured electrophoretic mobility

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Summary

- ISO 13099 part 1 and 2 useful for chemists new to zeta potential
- Some theoretical background
- Some operational advice
- Agreed upon pass/fail verification
  - But most customers use zeta potential, not electrophoretic mobility
- How we suggest you comply: use an SZ-100 from HORIBA
  - Best cells, lower cost of ownership

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Thank-you