Measure and Modify Colloidal Stability

Featuring the SZ-100 Nanoparticle Analyzer

Mark Bumiller
mark.bumiller@horiba.com
www.horiba.com/particle

Colloids Definition

Two phases:

- **Dispersed phase** (particles)
- **Continuous phase** (dispersion medium, solvent)

May be solid, liquid, or gaseous

Size range 1 nm – 1 micron

High surface area creates unique properties

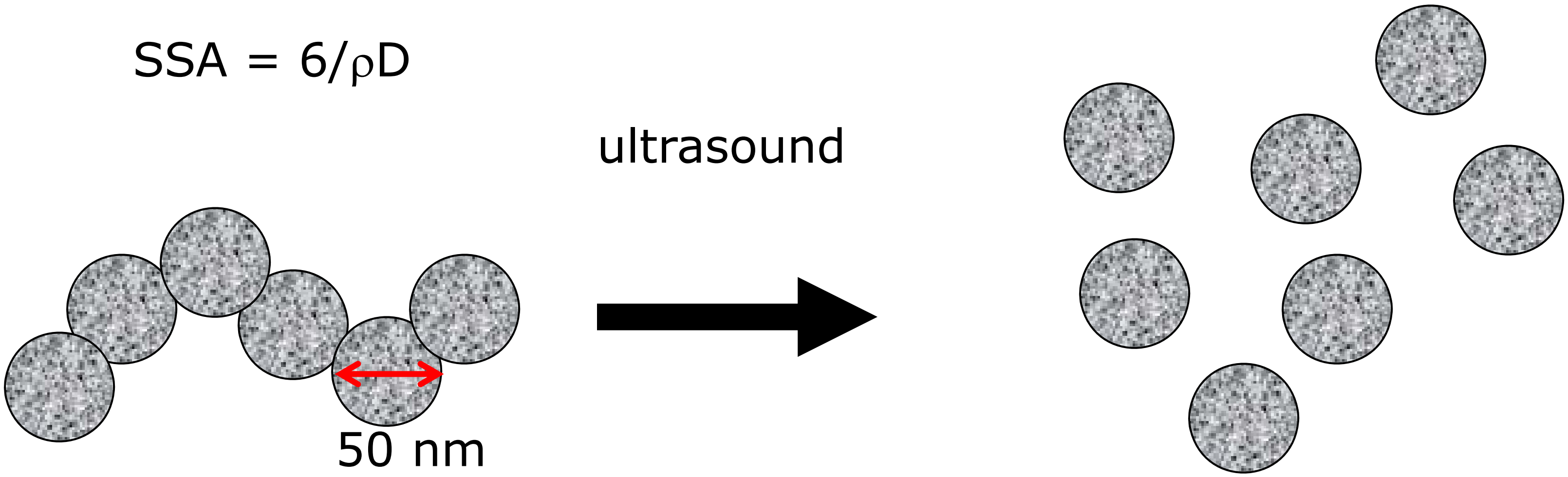
		Dispersed Medium		
		Gas	Liquid	Solid
Continuous Medium	Gas	**NONE** (All gases are mutually miscible)	**Liquid Aerosol** Examples: fog, mist, clouds	**Solid Aerosol** Examples: smoke, air particulates
	Liquid	**Foam** Examples: whipped cream	**Emulsion** Examples: milk, mayonnaise, hand cream	**Sol** (suspension) Examples: paint, pigmented ink
	Solid	**Solid Foam** Examples: aerogel, styrofoam, pumice	**Gel** Examples: gelatin, jelly, cheese, opal	**Solid Sol** Examples: cranberry glass, ruby glass

Colloid or Nanoparticle?

- Colloid: 1 nm – 1 µm
- Nanoparticle: 1 – 100 nm
- So a suspension of 50 nm gold particles in water: colloid or nanoparticle?
- Both, mostly terminology
- Also hear “nanocolloid, nanoparticle colloid…” (<100 nm)

Nanoparticle or Not?

$SSA = 6/\rho D$

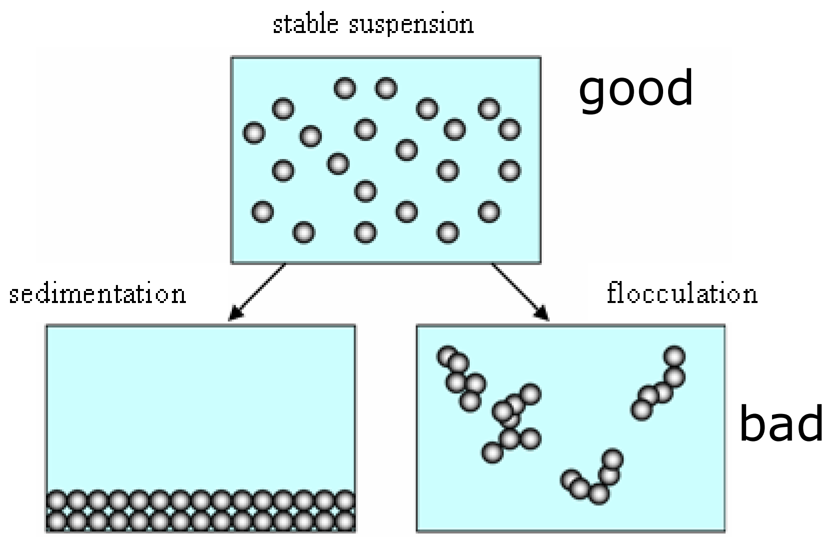


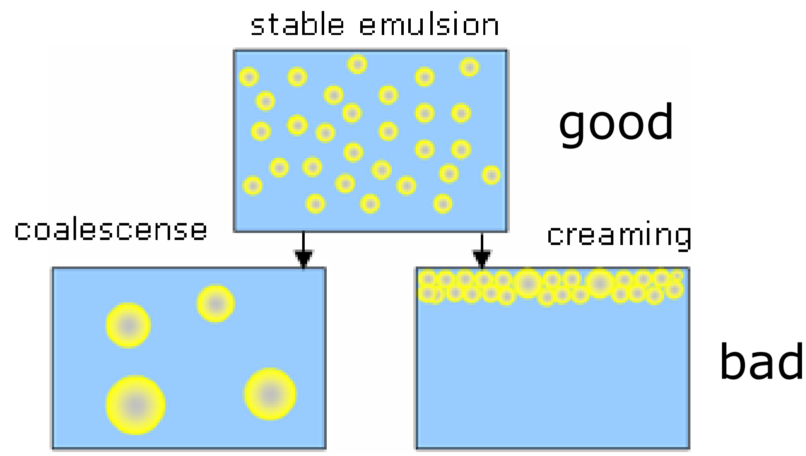
D from SEM ~50 nm
D from SSA ~60-70 nm
D from DLS ~250 nm
So: is this a nanoparticle?

Used ultrasound to disperse to primary particles or use weak acid to break bonds
D from DLS ~50 nm

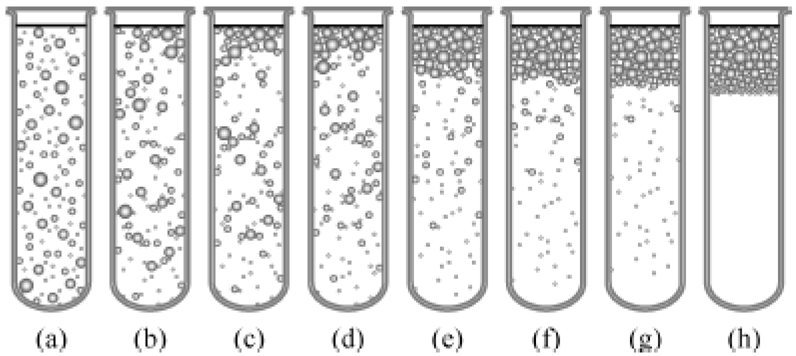
Stability

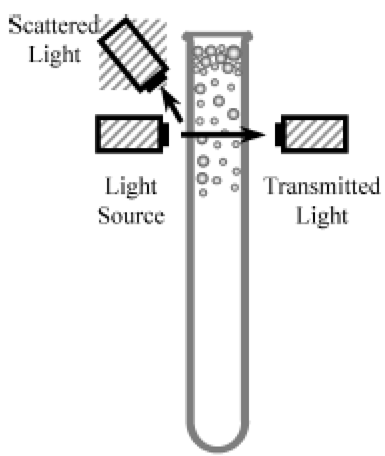
- Want stable dispersion
- Either suspensions or emulsions
- Suspensions sediment & flocculate
- Emulsions phase separate, creaming or coalescence

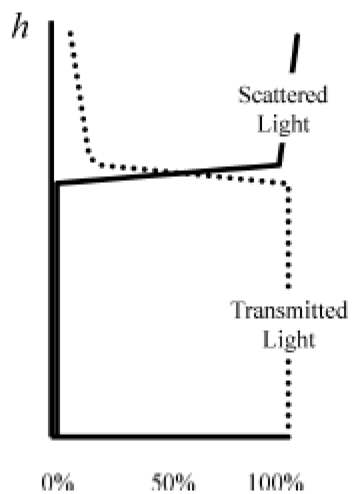


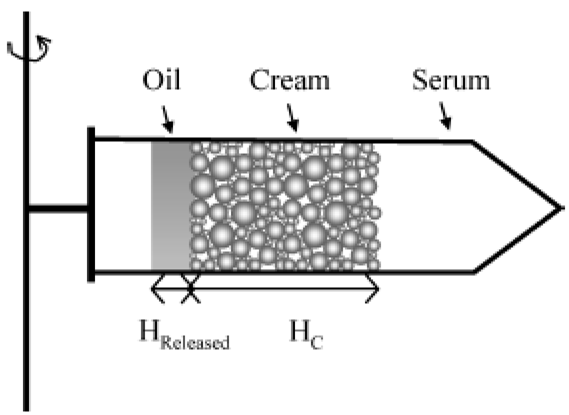


Measuring Stability



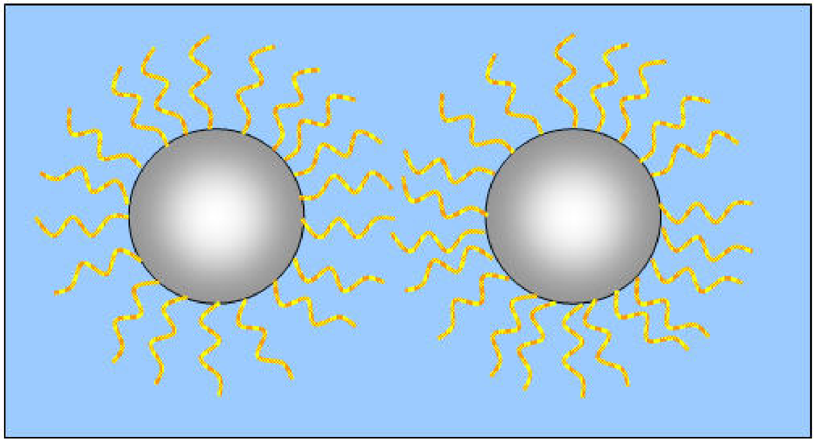




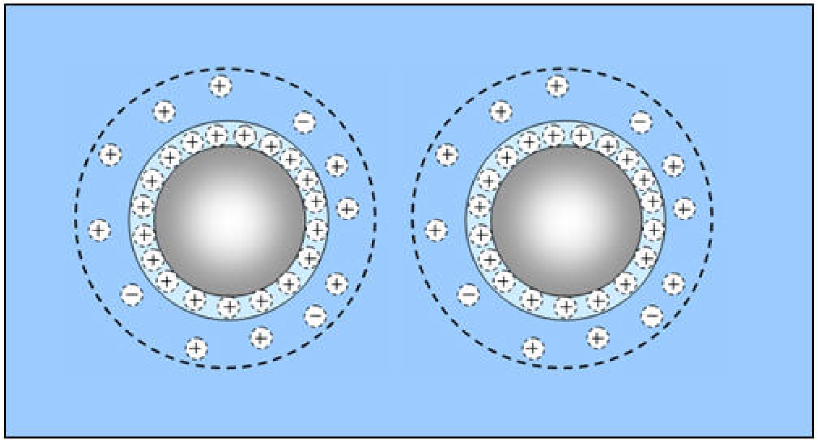


Stabilization

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

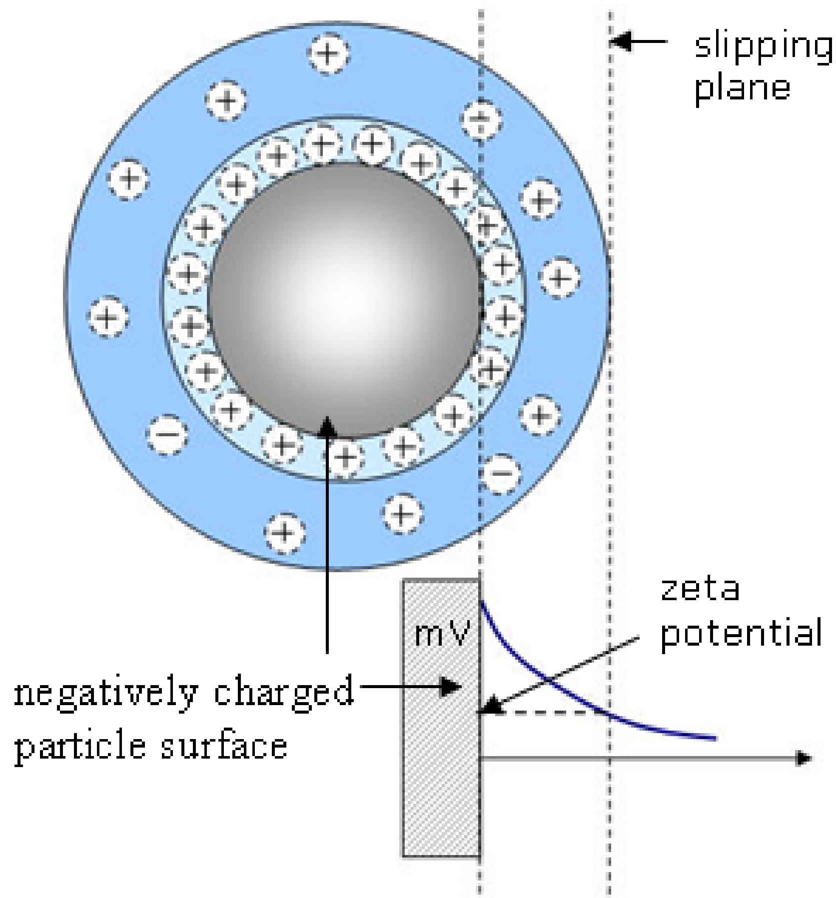


- Electrostatic stabilization: alter surface chemistry to put charge on particle surface
- Repel like magnets

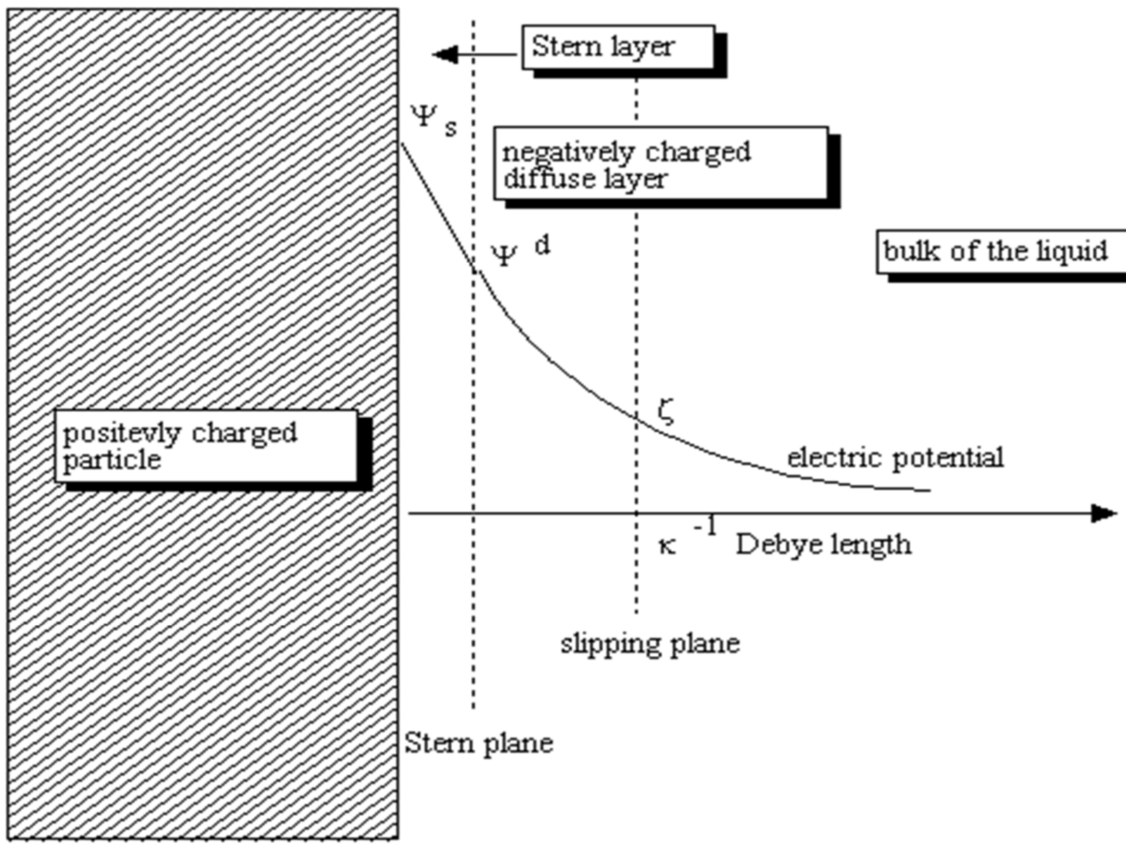


Zeta Potential

- 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



Stability Theory

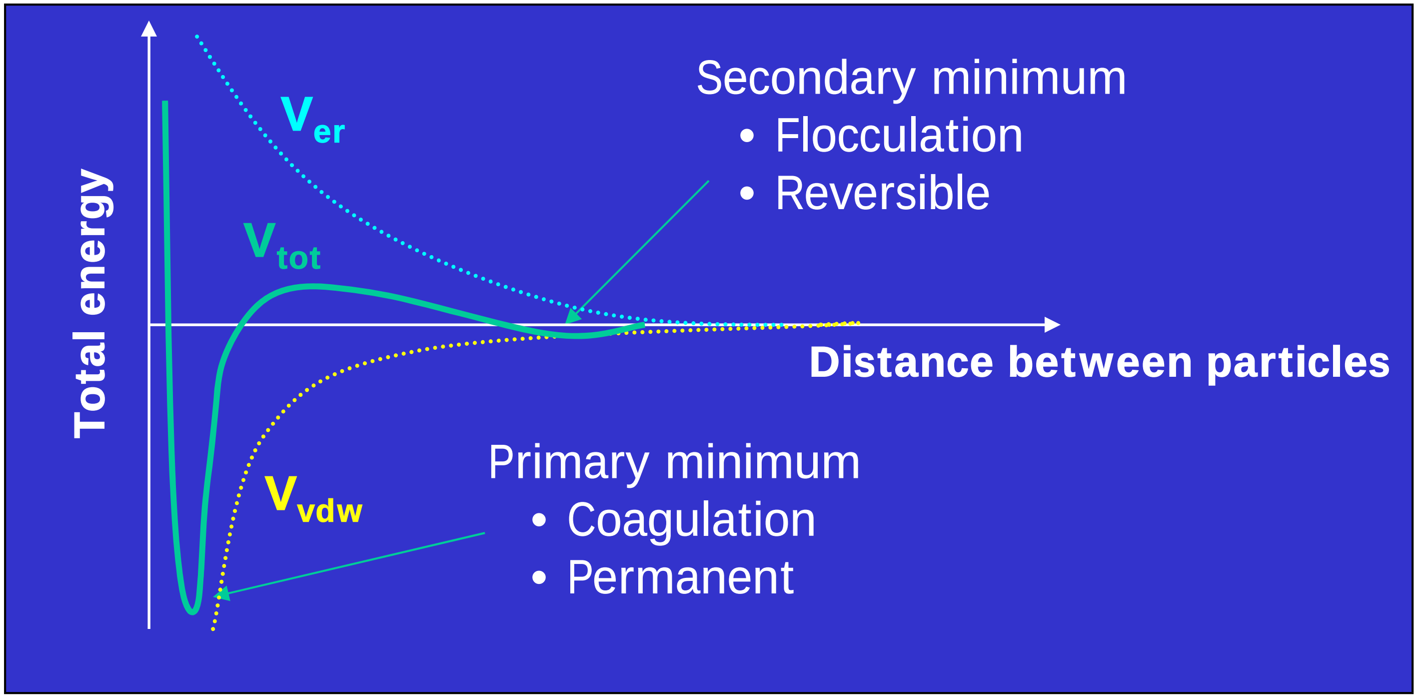
Electrostatic Stability (DVLO)

- Approaching particles undergo two forces
  - Van der Waals attraction (Vvdw)
  - Electrostatic repulsion (Ver)
- Total energy = balance of two
  - Vtotal = Vvdw + Ver

Steric Stability

- Approaching particles undergo two forces
  - Van der Waals attraction (Vvdw)
  - Forces from adsorbed polymers (Vster)
- Total energy = balance of two
  - Vtotal = Vvdw + Vster

Total Interaction Energy Curve: DVLO

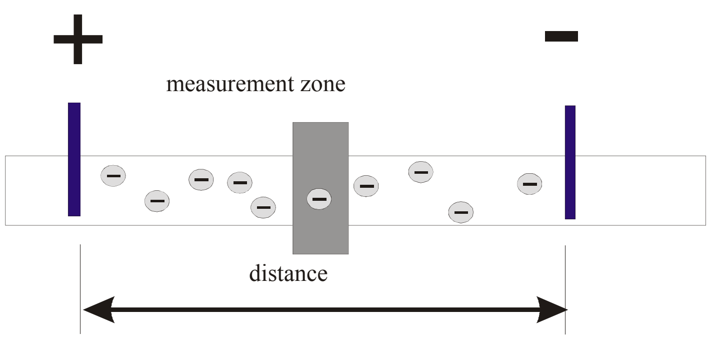


Important parameters:

- 1/K Debye Length, double layer thickness: depends on concentration
- a particle size
- ζ surface charge
- A Hamaker constant, nature of particle

Zeta Potential: 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



Zeta Potential Measurement

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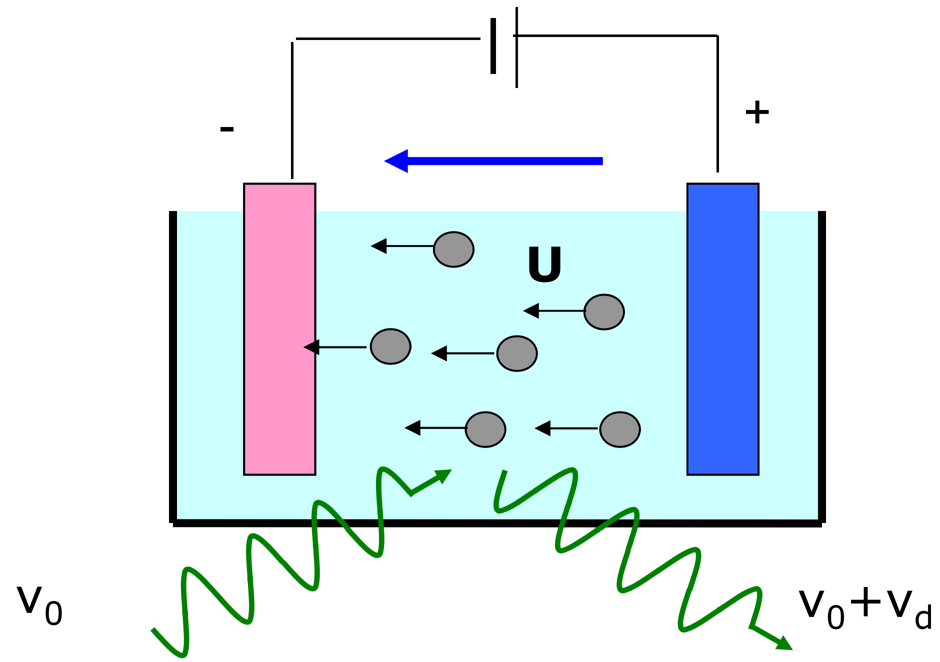

Particle motion causes Doppler shift
Frequency ⟶ mobility
Mobility ⟶ zeta potential

Mobility

$$U = \frac{\lambda \Delta v_d}{2En\sin(\theta/2)}$$

Zeta potential

$$\zeta = \frac{3U \cdot \eta}{2\varepsilon \cdot f(ka)}$$

Measurement Results

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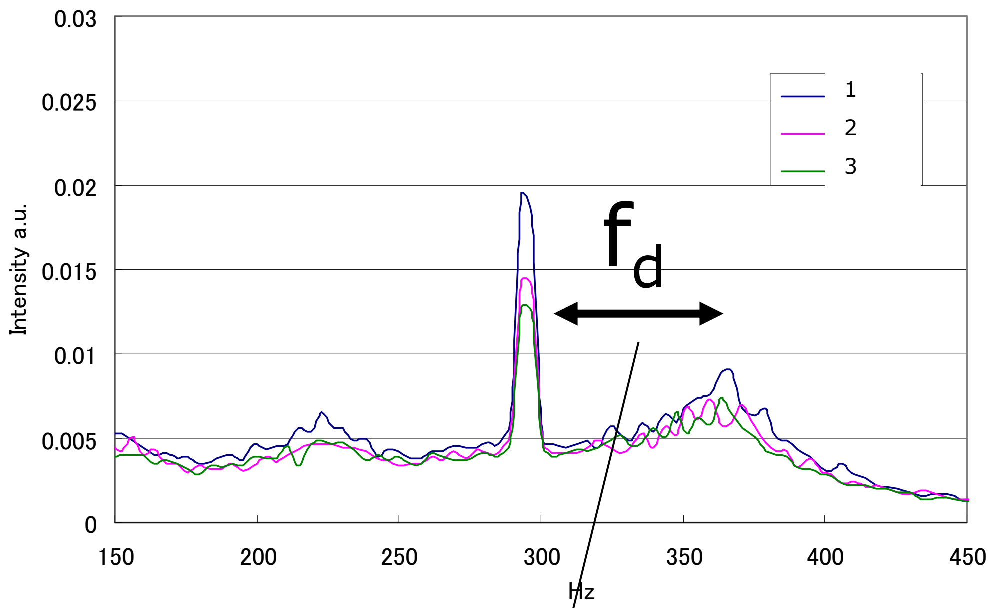
- Polystyrene Polymer Micro spheres: 500nm (100ppm)

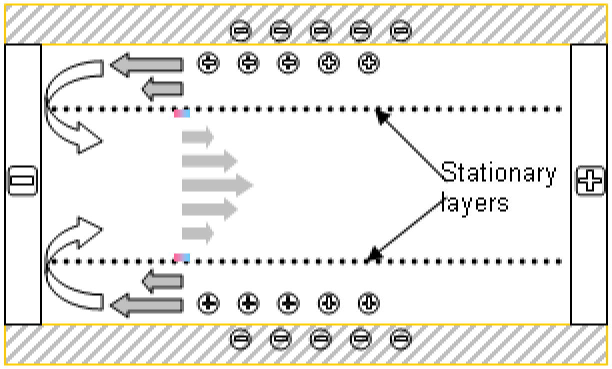


Average value of zeta potential from three times measurements

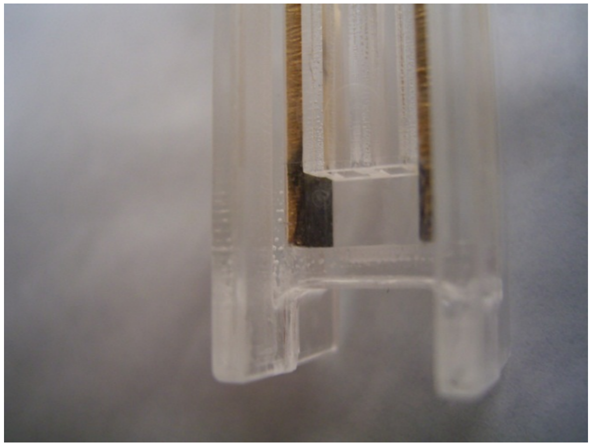
SZ-100	Other
-41.1 mV	-39.5 mV

Measurement Details

- 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

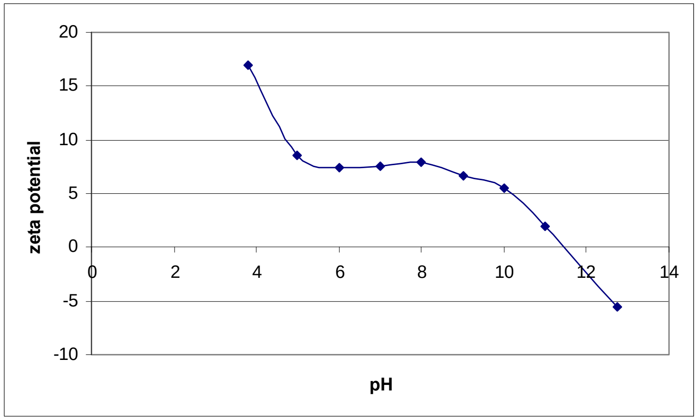


Zeta Potential Cells

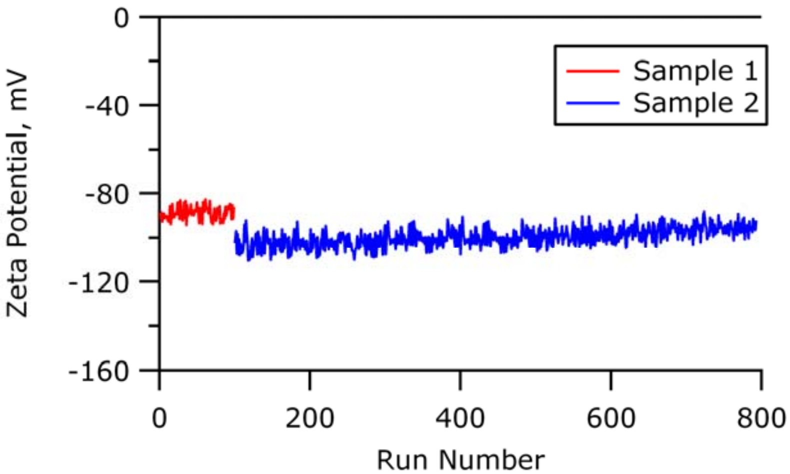


Gold coated electrodes (ruined)

Carbon coated electrodes



IEP 3.4 nm protein



800 measurements with one cell

Thin vs. Thick Double Layer

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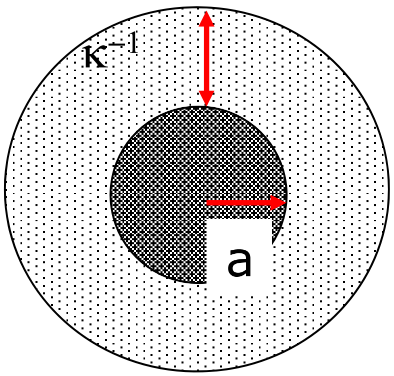
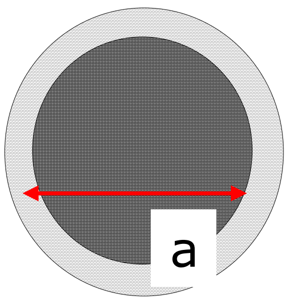
$$\zeta = \frac{3U \cdot \eta}{2\varepsilon \cdot f(ka)}$$

Debye length = κ^{-1} EDL thickness



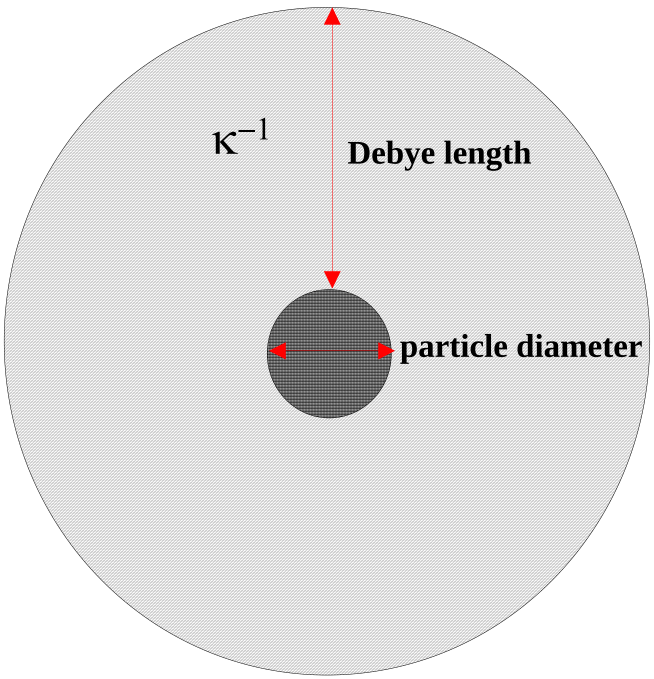
Huckel
$\kappa a = 1$

THIN DOUBLE LAYER



Smoluchowski
$\kappa a >> 1$

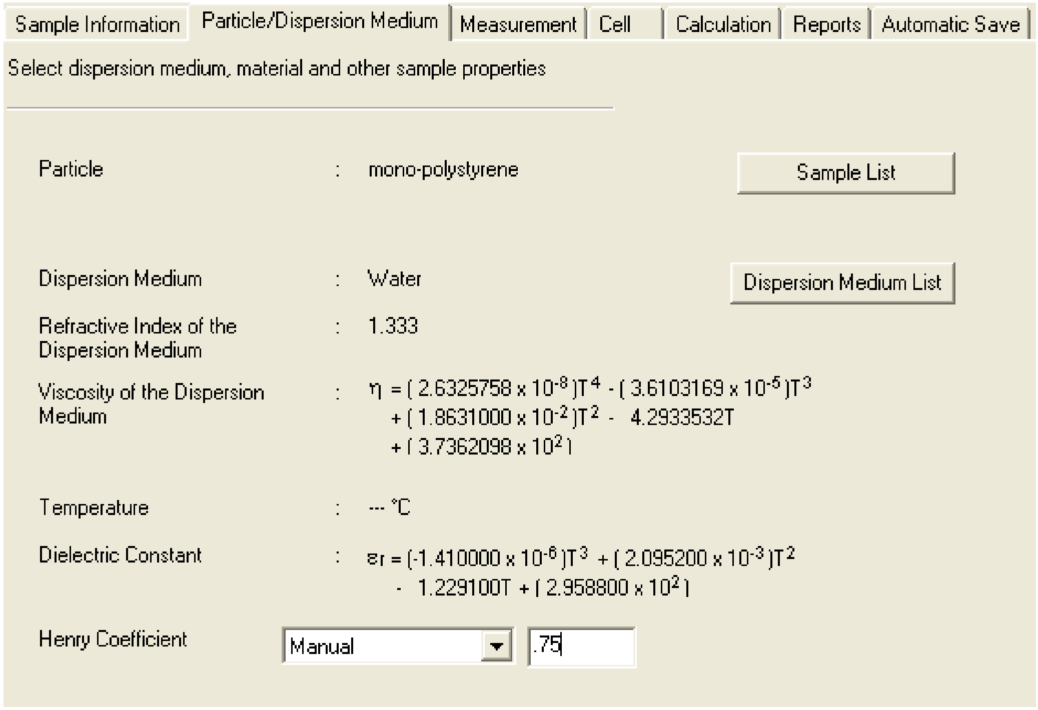
THICK DOUBLE LAYER



$\kappa a << 1$

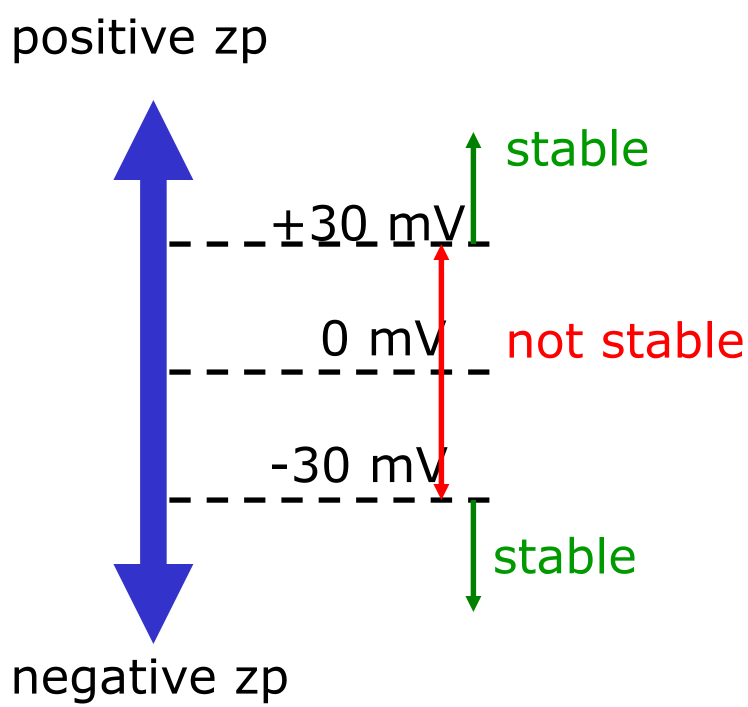
SZ-100 Software

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



Zeta Potential Predicts Stability

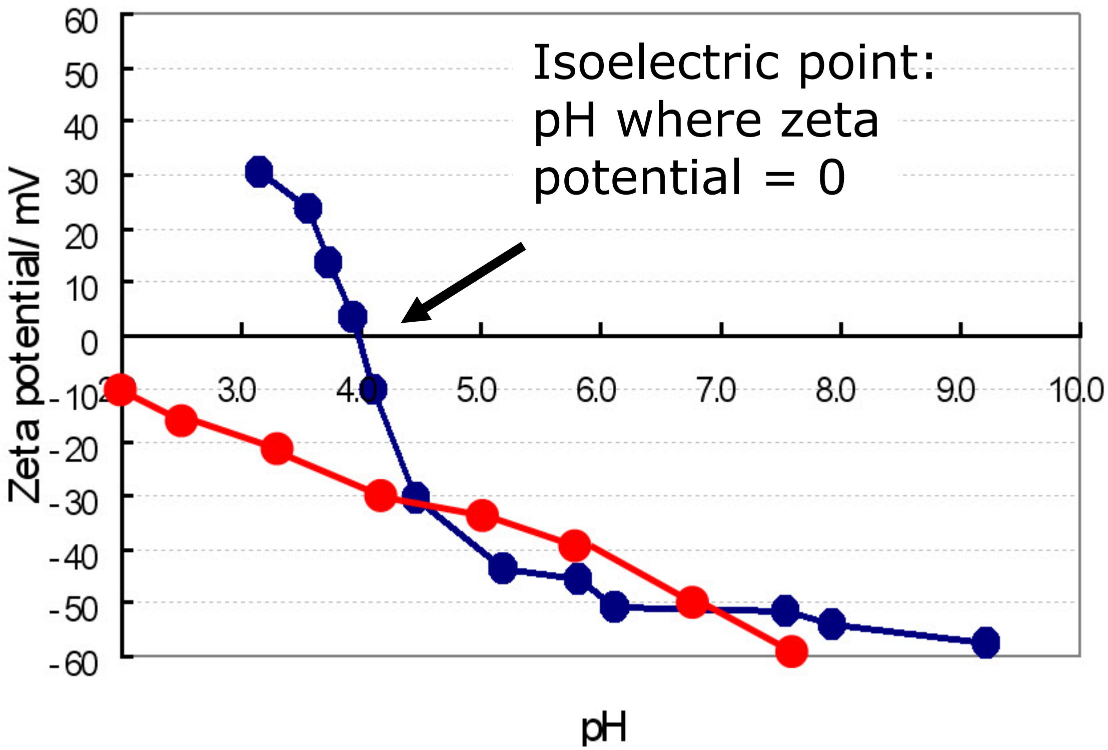
Different guidelines



Sample Dependency

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

Zeta Potential: Emulsion Isoelectric Point (IEP)



Automate IEP studies with auto titrator

Emulsion IEP Study: Stability

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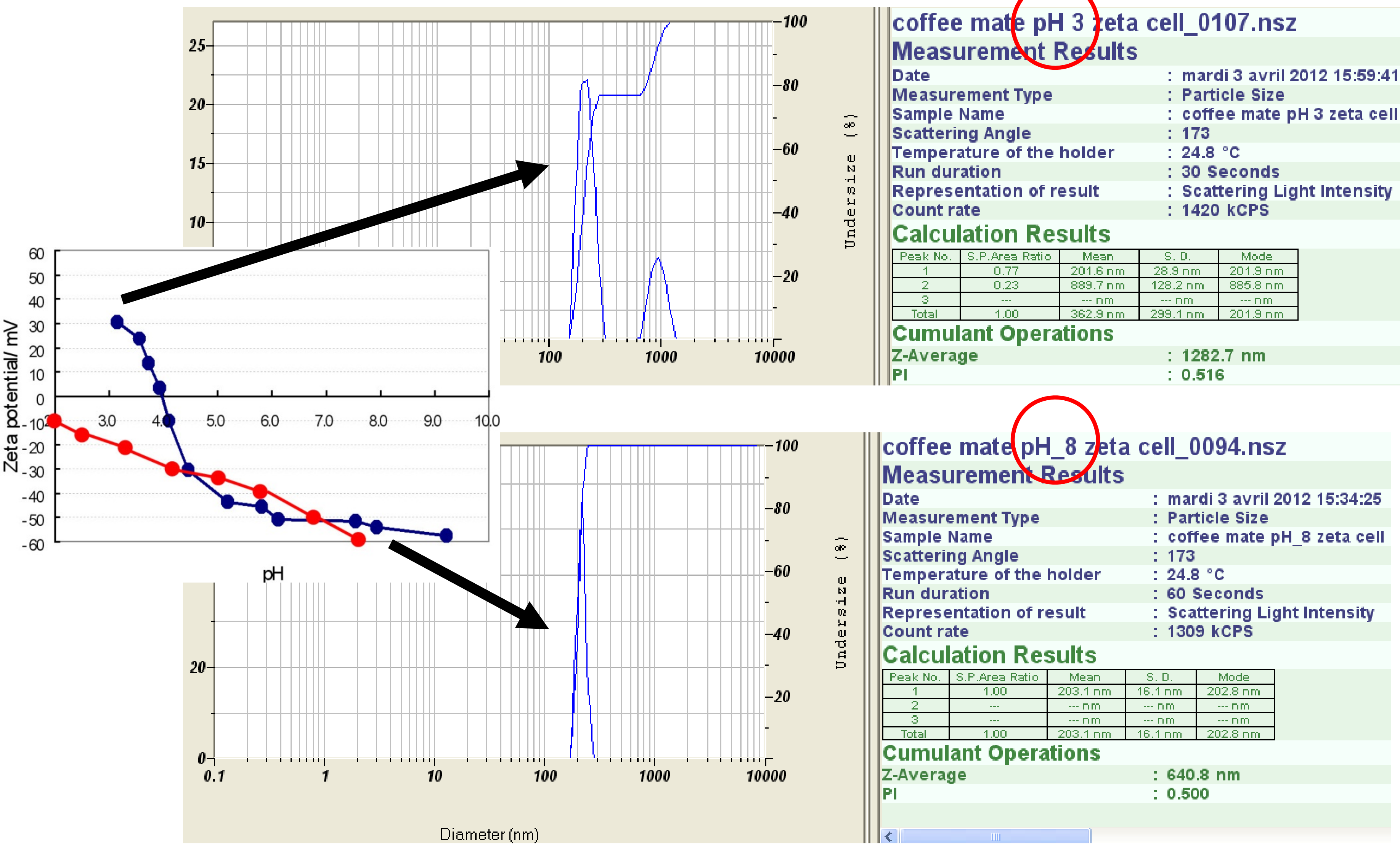
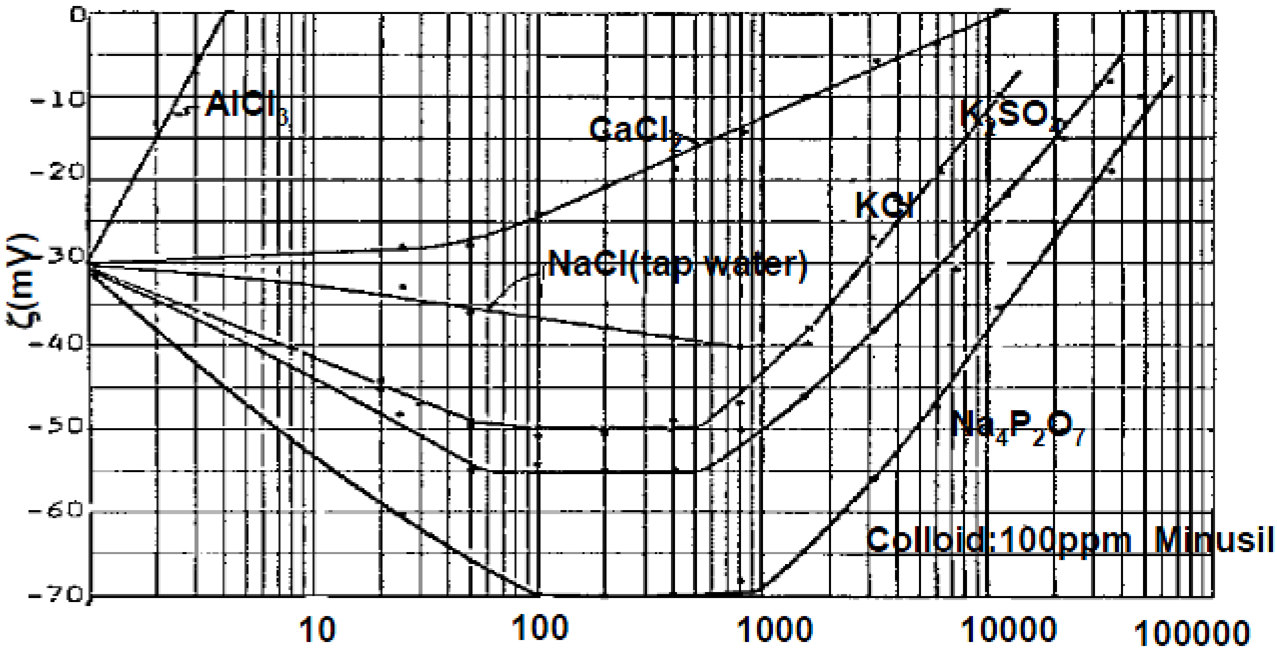


IEP of Some Materials

- Another use of IEP is to characterize the surface of complex particles
- TiO2 coated with alumina will have the IEP of alumina

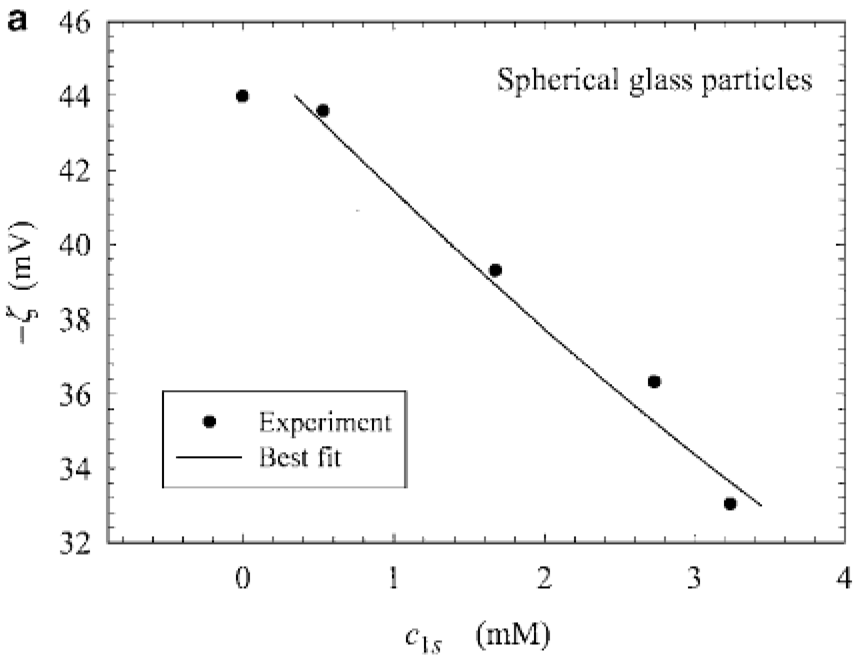
alpha aluminium oxide Al2O3	8-9
alpha iron (III) oxide (hematite) Fe_2O_3	8.4-8.5
antimony(V) oxide Sb_2O_5	<0.4 to 1.9
cerium(IV) oxide (ceria) CeO_2	6.7-8.6
chromium(III) oxide (chromia) Cr_2O_3	6.2-8.1
copper(II) oxide CuO	9.5
delta-MnO2 1.5, beta-MnO2	7.3[5]
gamma aluminium oxide Al2O3	7-8
gamma iron (III) oxide (maghemite) Fe_2O_3	3.3-6.7
iron (II, III) oxide (magnetite) Fe_3O_4	6.5-6.8
lanthanum(III) oxide La2O3	10
lead(II) oxide PbO	10.7-11.6
magnesium oxide (magnesia) MgO	9.8-12.7
manganese(IV) oxide MnO2	4-5
nickel(II) oxide NiO	9.9-11.3
silicon carbide (alpha) SiC	2-3.5
silicon dioxide (silica) SiO_2	1.7-3.5
silicon nitride Si3N4	6-7
silicon nitride Si_3N_4	9
tantalum(V) oxide, Ta_2O_5	2.7-3.0
thallium(I) oxide Tl_2O:	8
tin(IV) oxide SnO_2	4-5.5
titanium(IV) oxide (rutile or anatase) TiO_2	3.9-8.2
tungsten(VI) oxide WO_3	0.2-0.5
vanadium(V) oxide (vanadia) V_2O_5	1 to 2
yttrium(III) oxide (yttria) Y_2O_3	7.2-8.9
zinc oxide ZnO	8.7-10.3
zirconium(IV) oxide (zirconia) ZrO_2	4-11

Salt Concentration Effect

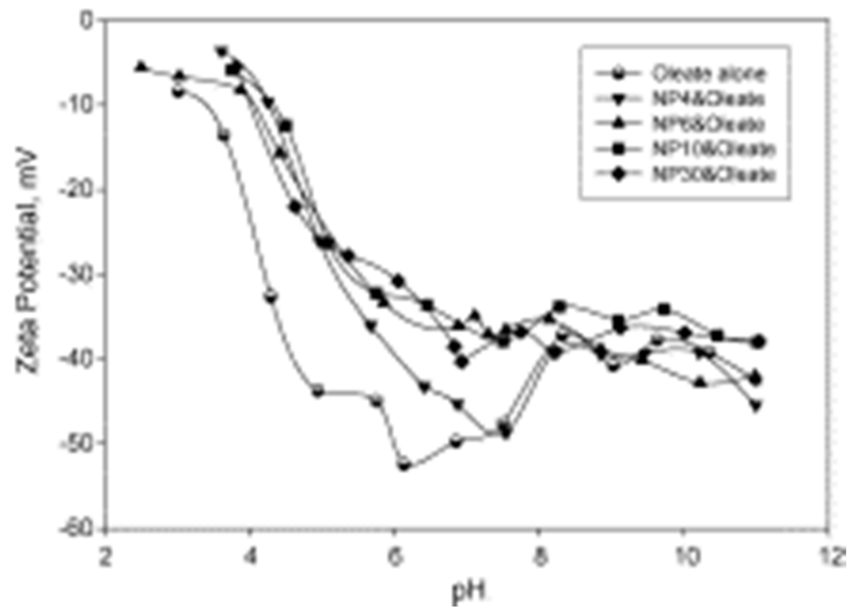


The effect of electrolytes (ppm) on ζ-potential of a colloidal dispersion

Surfactant Concentration Effects



Surfactant concentration vs. ζ

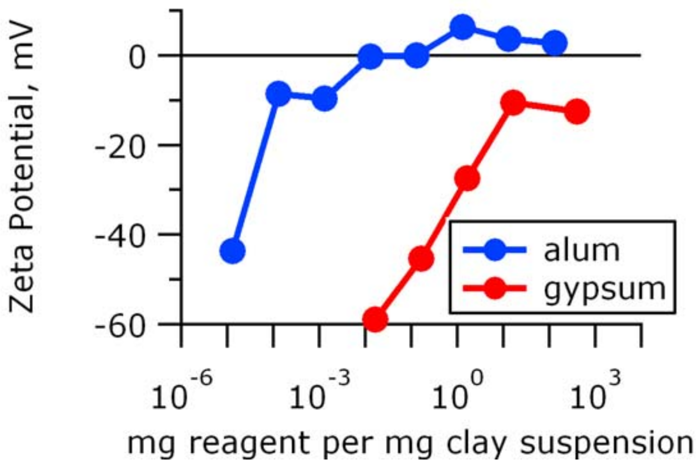


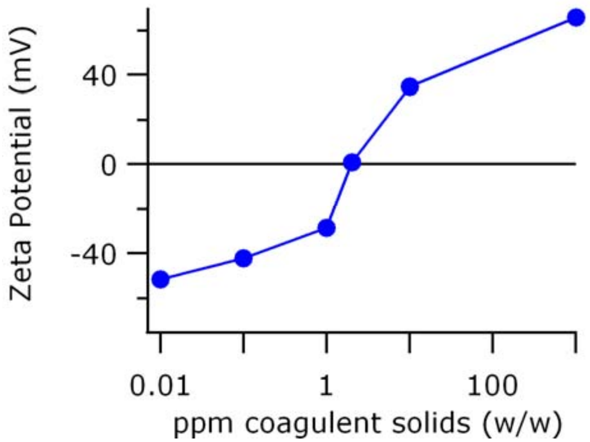
pH, surfactant concentration v

Alter the surface chemistry – alter the zeta potential

De-stabilization

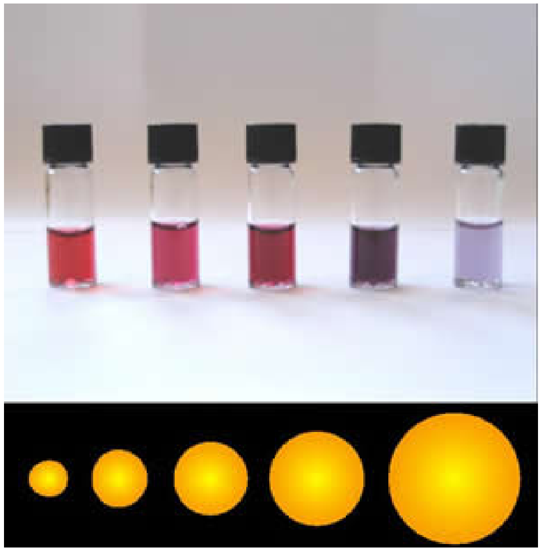
- Can also use zeta potential to study how to cause instability
- Example: water treatment
- Add chemicals to IEP
- Particles flocculate
- Easier to filter

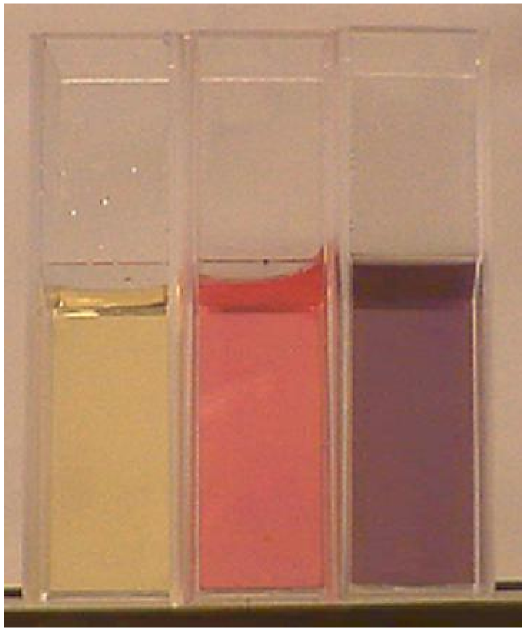




Applications: Colloidal Gold

- Stable base particle
- Used in drug delivery
- Attach proteins, DNA, etc. to surface





Colloidal Gold: Drug Delivery

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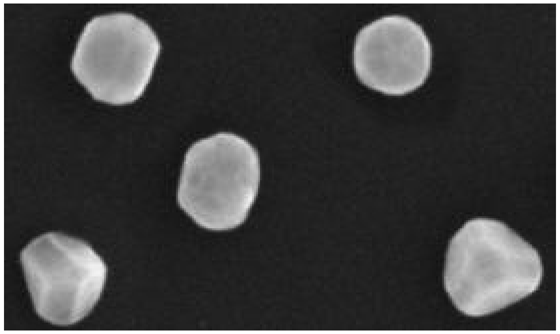
Particle size and zeta potential for colloidal gold base particles (average size 51 nm prior to modification) after immobilizing a prodrug activating enzyme onto the surface at different concentrations.

		Molar ratio of enzyme to gold colloid				
		90:1	180:1	270:1	360:1	450:1
His-NfnB-gold colloid	Size (nm)	53.5	57.5	82.6	69.7	75.4
	Zeta-potential (mV)	-43	-31.7	-30.7	-33.3	-30.4
Cys-NfnB-gold colloid	Size (nm)	56.3	59.8	61.1	69.8	69.7
	Zeta-potential (mV)	-23.4	-25.3	-26.0	-27.7	-34.2

Data generated on SZ-100

Colloidal Gold Modified with a Genetically Engineered Nitroreductase: Toward a Novel Enzyme Delivery System for Cancer Prodrug Therapy
Vanessa V. Gwenin, Chris D. Gwenin, and Maher Kalaji
Langmuir, **2011**, *27* (23), pp 14300–14307

NIST Colloidal Gold



NIST Certificates

Technique	Size nm
Atomic Force Microscopy	8.5 ± 0.3
Scanning Electron Microscopy	9.9 ± 0.1
Transmission Electron Microscopy	8.9 ± 0.1
Differential Mobility Analysis	11.3 ± 0.1
Dynamic Light Scattering	13.5 ± 0.1
Small-Angle X-ray Scattering	9.1 ± 1.8

Technique	Size nm
Atomic Force Microscopy	24.9 ± 1.1
Scanning Electron Microscopy	26.9 ± 0.1
Transmission Electron Microscopy	27.6 ± 2.1
Differential Mobility Analysis	28.4 ± 1.1
Dynamic Light Scattering	
173º scattering angle	28.6 ± 0.9
90º scattering angle	26.5 ± 3.6
Small-Angle X-ray Scattering	24.9 ± 1.2

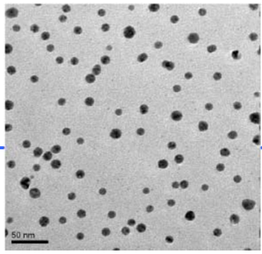
Technique	Size nm
Atomic Force Microscopy	55.4 ± 0.3
Scanning Electron Microscopy	54.9 ± 0.4
Transmission Electron Microscopy	56.0 ± 0.5
Differential Mobility Analysis	56.3 ± 1.5
Dynamic Light Scattering	
173º scattering angle	56.6 ± 1.4
90º scattering angle	55.3 ± 8.3
Small-Angle X-ray Scattering	53.2 ± 5.3

SZ-100 Results

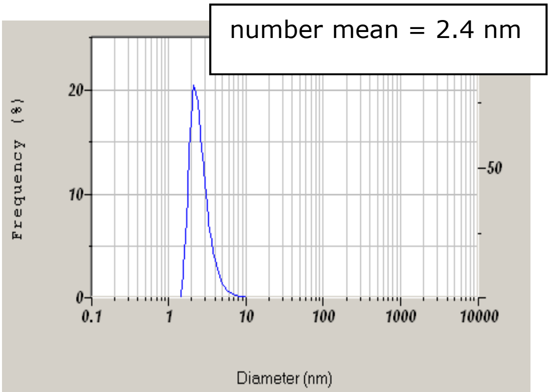
8011		
HORIBA	**Average**	**St dev**
Sample 1	13.4 nm	1,8
Sample 2	12.6nm	1,9
ASTM	**Z ave**	**st dev**
Combined	15.8 nm	4,2

8012		
HORIBA	**Average**	**St dev**
Sample 1	31.5nm	3,9
Sample 2	32.4 nm	5,9
ASTM	**Z ave**	**st dev**
Combined	31.2 nm	3,6

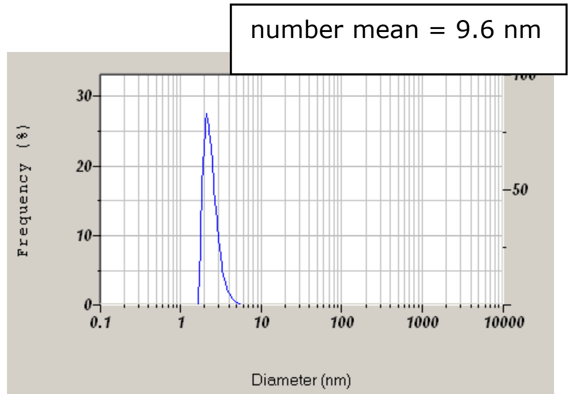
8013		
HORIBA	**Average**	**St dev**
Sample 1	57.6 nm	3,5
Sample 2	58.4 nm	3,9
ASTM	**Z ave**	**st dev**
Combined	59.8 nm	5,0



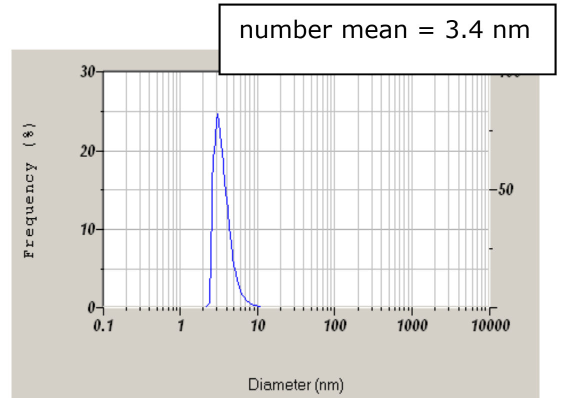
Other Colloidal Metals



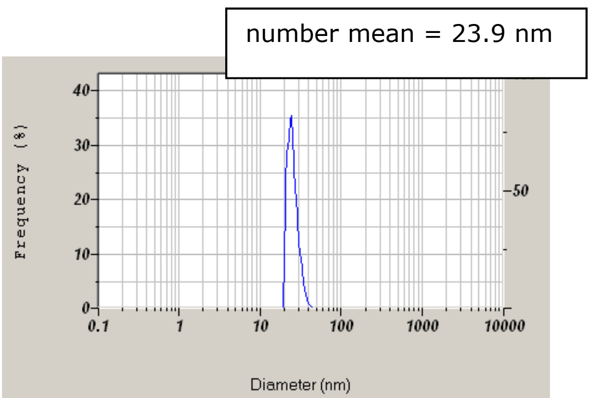
Colloidal silver



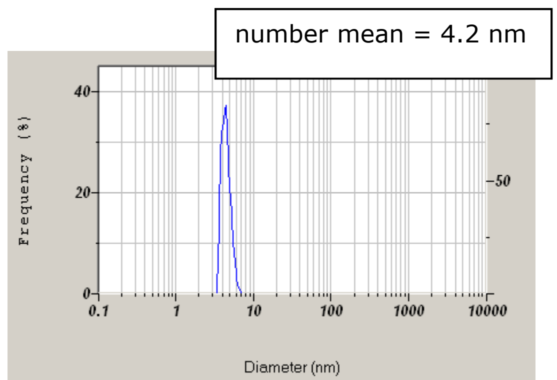
copper



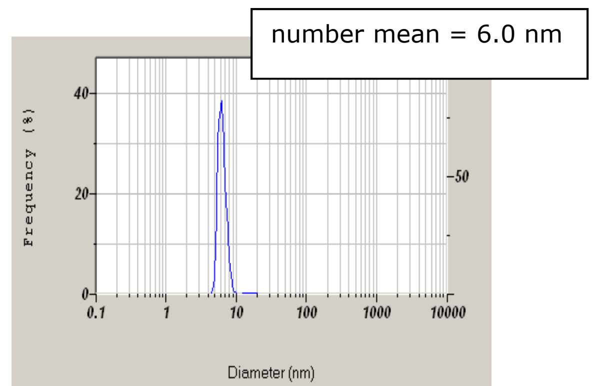
platinum



palladium



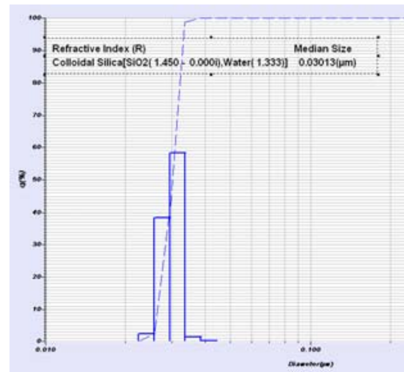
nickel



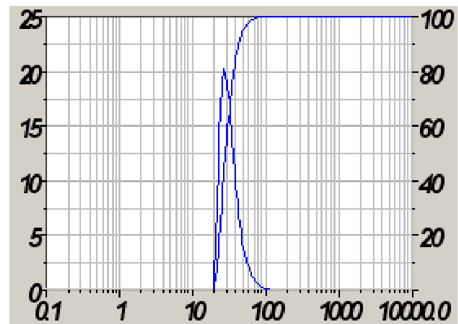
germanium

Colloidal Silica

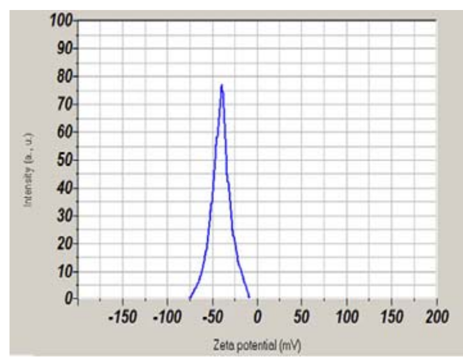
- Possible reference material for both size and zeta potential
- Ludox TM size analyzed on both SZ-100 and LA-950
- Ludox zeta potential can be used to verify zeta potential
- IRMM has issued silica colloidal reference materials ERM-FD100 (20 nm) & ERM-FD304 (40 nm) w/zeta values



S.P.Area	:	2.0183E+6(cm²/cm³)
Mean Size	:	0.02990(μm)
Variance	:	5.0313E-6(μm²)
Median Size	:	0.03013(μm)
Mode Size	:	0.0302(μm)
Skewness	:	-0.2901



	Results
Z ave. (nm)	40.4



	Result
Mobility (μm・cm/V・s)	-3.02
Zeta Potential (mV)	-31.8

New* ISO Standards

- ISO/CD 13099-1 Methods for zeta potential determination — part 1: General Principle
- ISO/CD 13099-2 Methods for zeta potential determination — part 2: Optical Methods
- ISO/NWI 13099-3 Methods for zeta potential determination — part 3: Acoustic Methods

ISO Guidelines: 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

HORIBA

ISO Guidelines: Verification

- No accepted standards, each vendor supplies reference samples
- Measure three times, mean value within 10% of published electrophoretic mobility value
- Repeatability; CV <10%
- Note: expect most customers to use zeta potential values
- If system is within 12%, don't lose sleep

Summary

- Particle size, zeta potential, chemistry all related for colloidal suspensions
- Use zeta potential as a predictive tool for stability
- Alter surface chemistry, does zeta potential improve?
  - pH, salt, surfactant, etc.
- IEP useful for both stability and surface definition

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Resources: www.horiba.com/particle

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View application notes, webinars, etc.

Thank-you

For More Details

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Thank-you

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Thank you

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谢谢

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Gracias

Grazie

Σας ευχαριστούμε

धन्यवाद

Tacka dig

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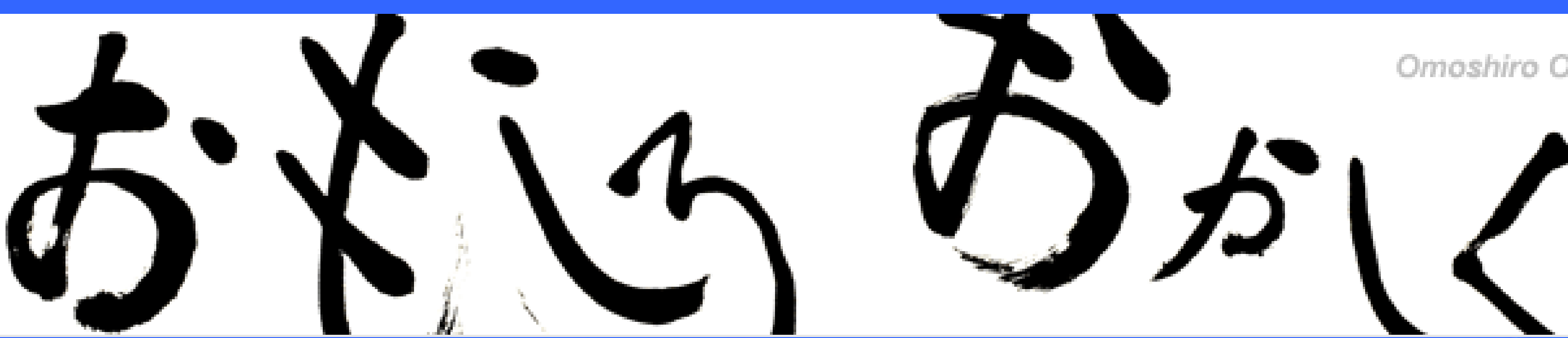
Danke

Merci

Obrigado

감사합니다

Большое спасибо



Omoshiro Okashiku