Particle Characterization using Acoustics and Electro Acoustics

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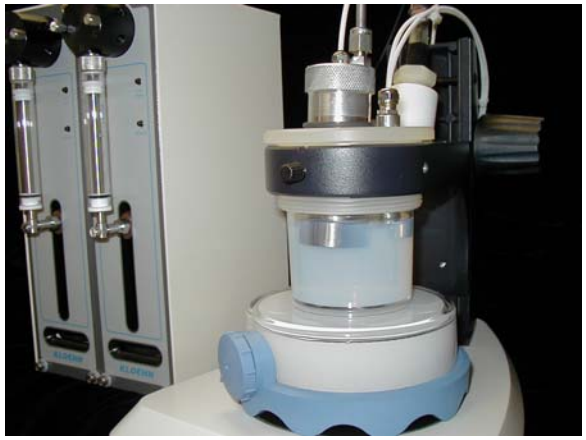
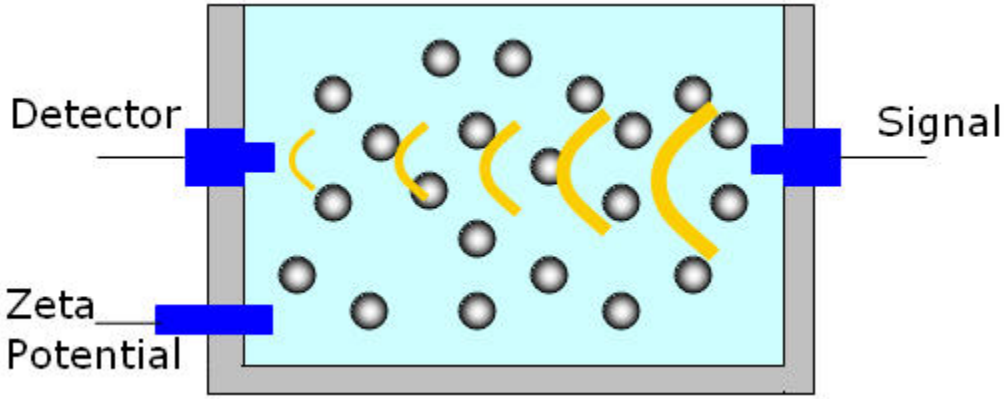
Outline

- Introduce concepts of colloidal stability
- Acoustic theory/modeling
- Electro acoustic theory
- Hardware configurations
- Applications





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Colloids

A **colloid** is a type of mechanical mixture where one substance is dispersed evenly throughout another. Because of this dispersal, some colloids have the appearance of solutions. A colloidal system consists of two separate phases: a **dispersed phase** (or **internal phase**) and a **continuous phase** (or **dispersion medium**). A colloidal system may be solid, liquid, or gaseous.
Size range 1 nm – 1 micron.

		Dispersed Medium (particles)		
		Gas	Liquid	Solid
Continuous Medium (solvent)	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. — An entity phase dispersed to such a degree that the surface forces become an important factor in determining its properties.

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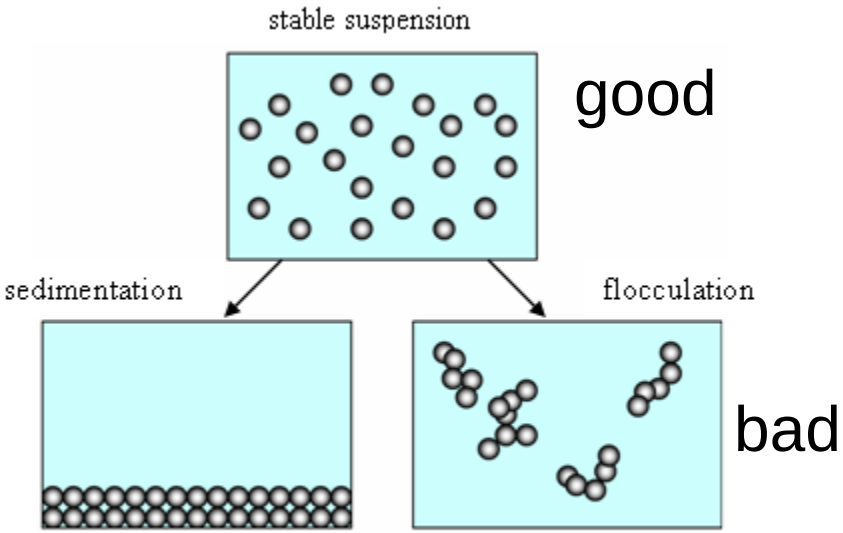
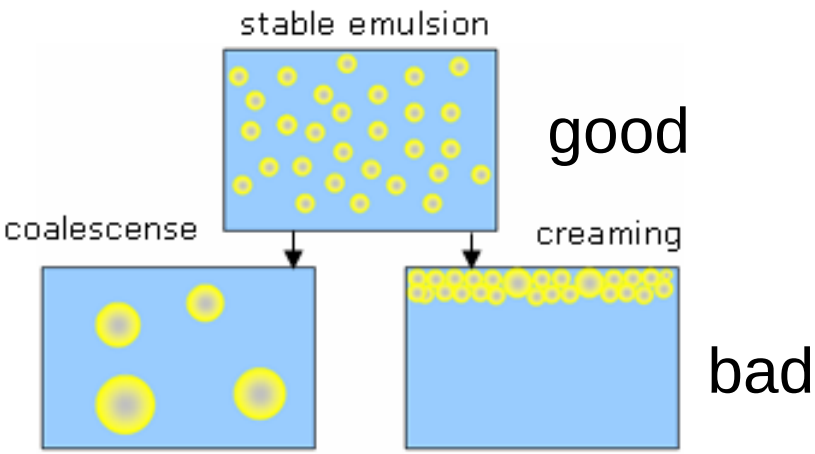
Stability

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





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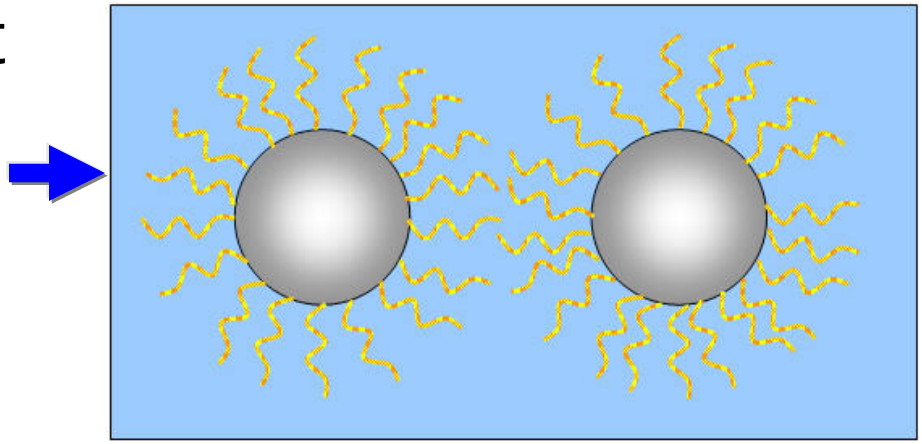
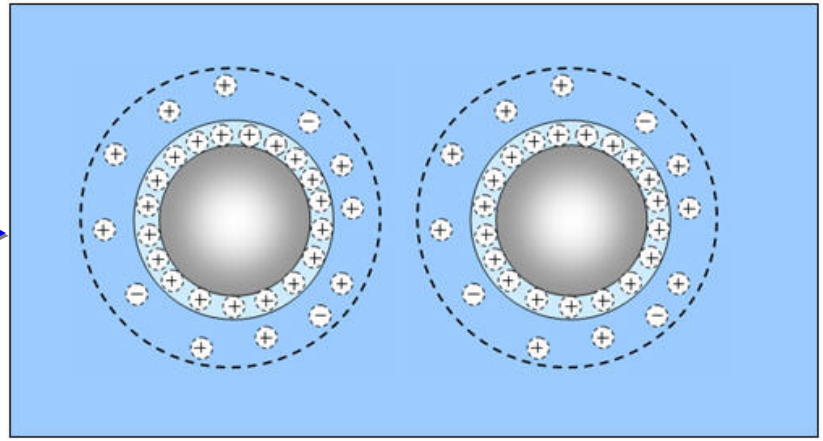
Stabilization

- 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





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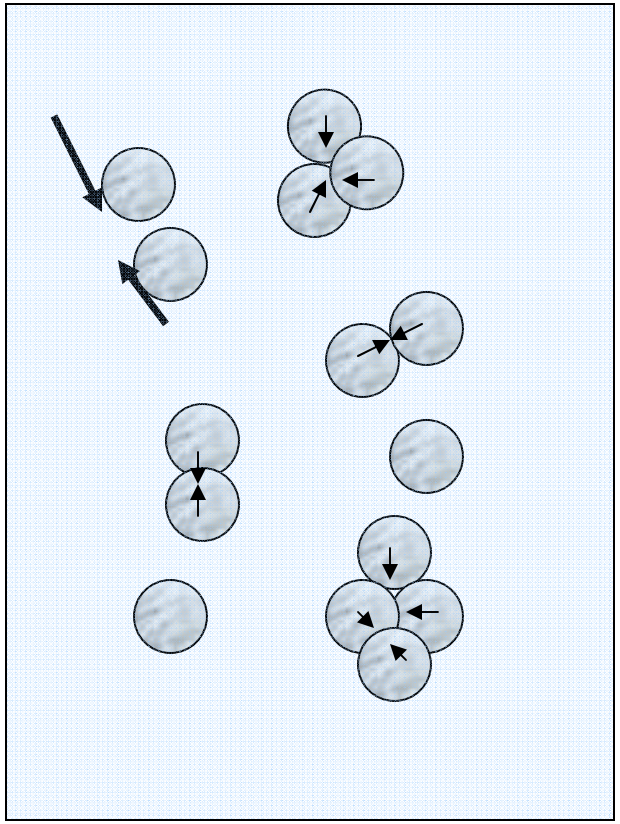
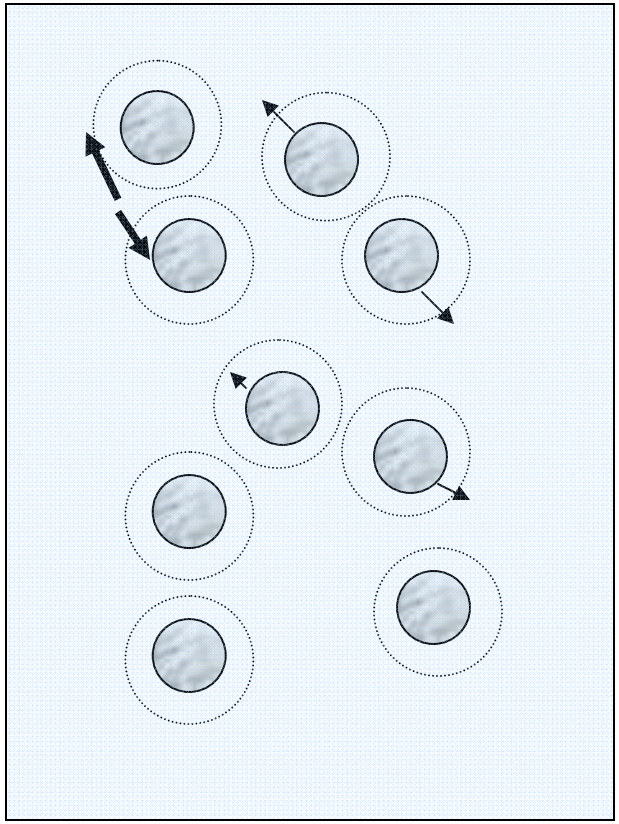
Electrostatic Stabilization

No charge =
collide & aggregate



Charged particles
repel each other



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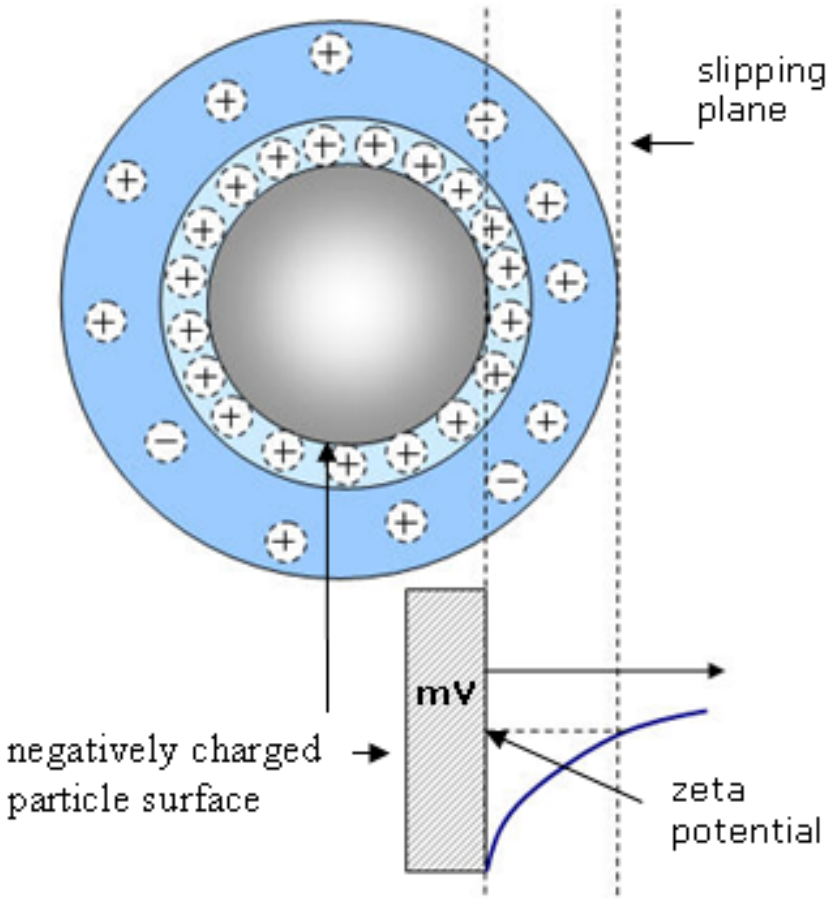
Zeta Potential

- 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



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Zeta Potential & Stability*

Stability	Average Zeta Potential (mV)
Extreme to very good stability	–100 to –60 mv
Reasonable stability	–60 to –40 mv
Moderate stability	–40 to –30 mv
Threshold of light dispersion	–30 to –15 mv
Threshold of agglomeration	–15 to –10 mv
Strong agglomeration & precipitation	–5 to +5 mv

*Stability of Solution-Zeta Potential from "A Control of Colloidal Stability" by Thomas Riddick

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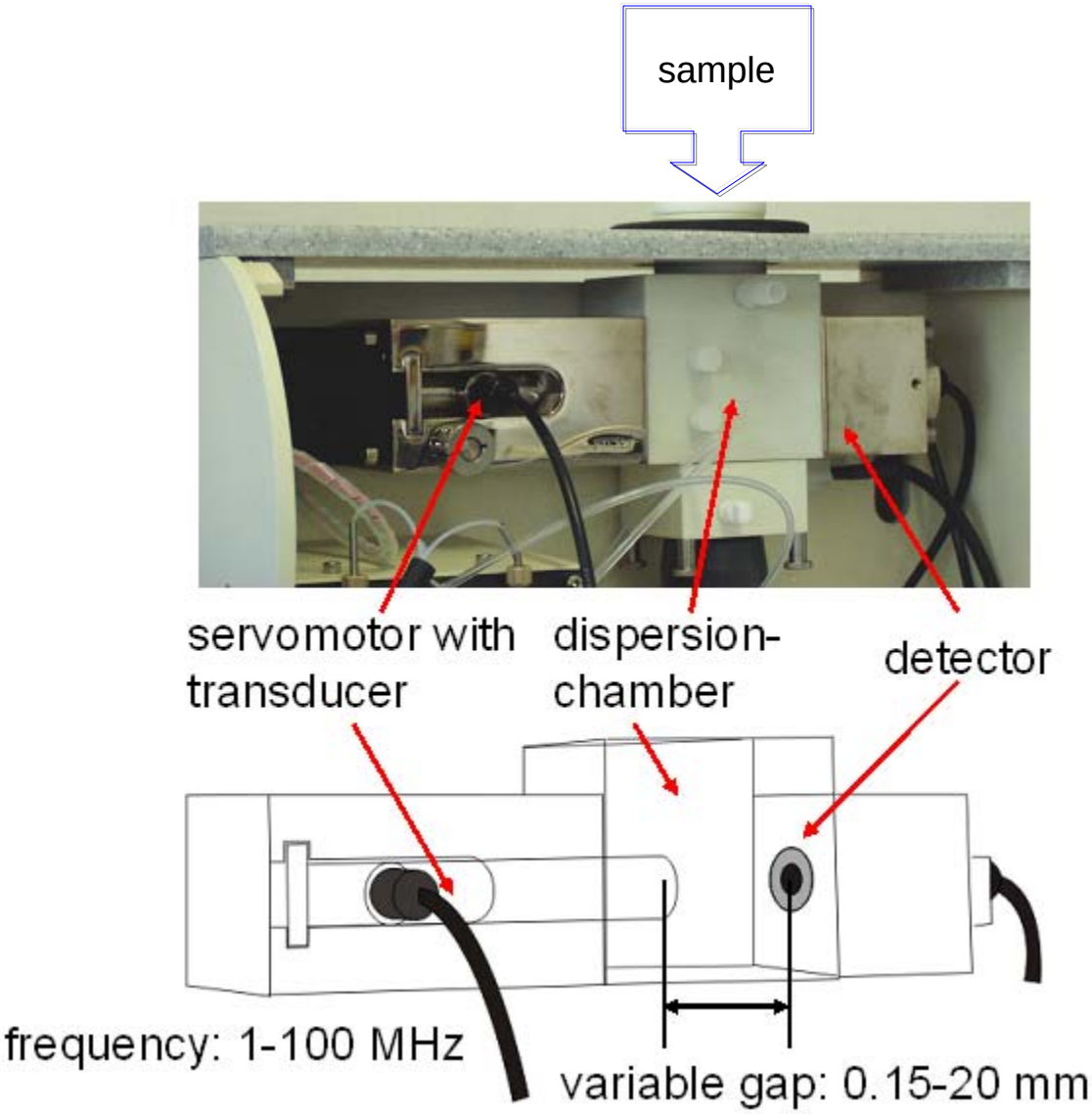
Size Measurement Hardware



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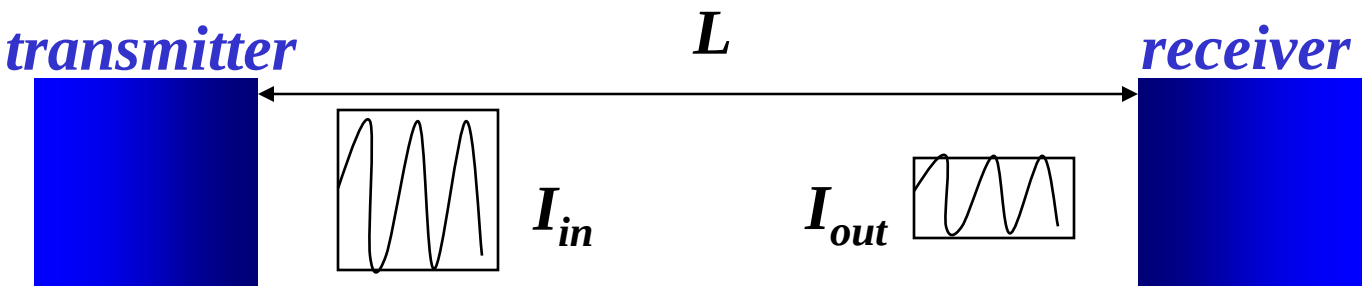
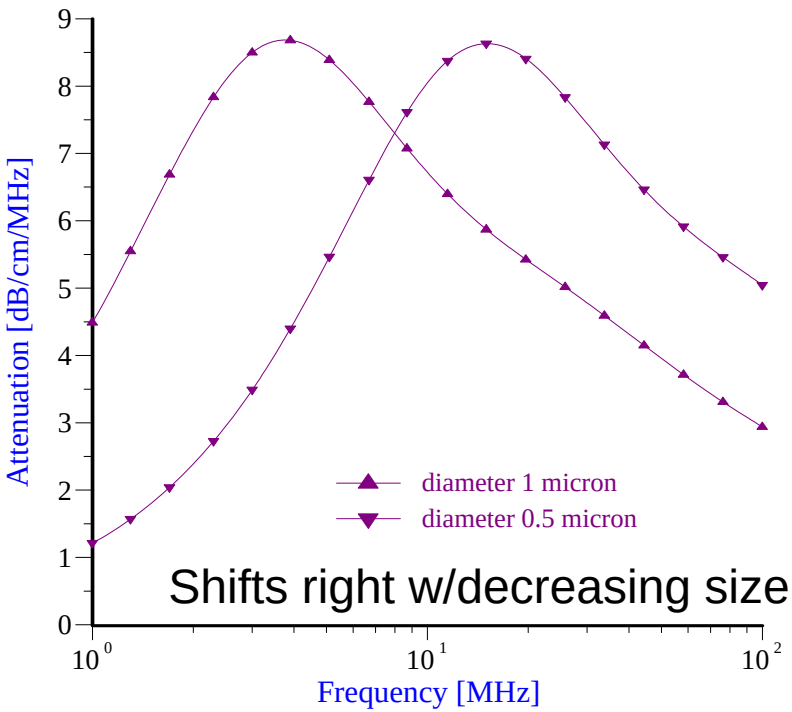
Acoustic Attenuation





Attenuation [dB/cm/MHz]

$$\alpha = \frac{10}{f[MHz]L[cm]} \log \frac{I_{in}}{I_{out}}$$

Sound speed [cm/sec]

$$V = \frac{L[cm]}{t[\sec]}$$

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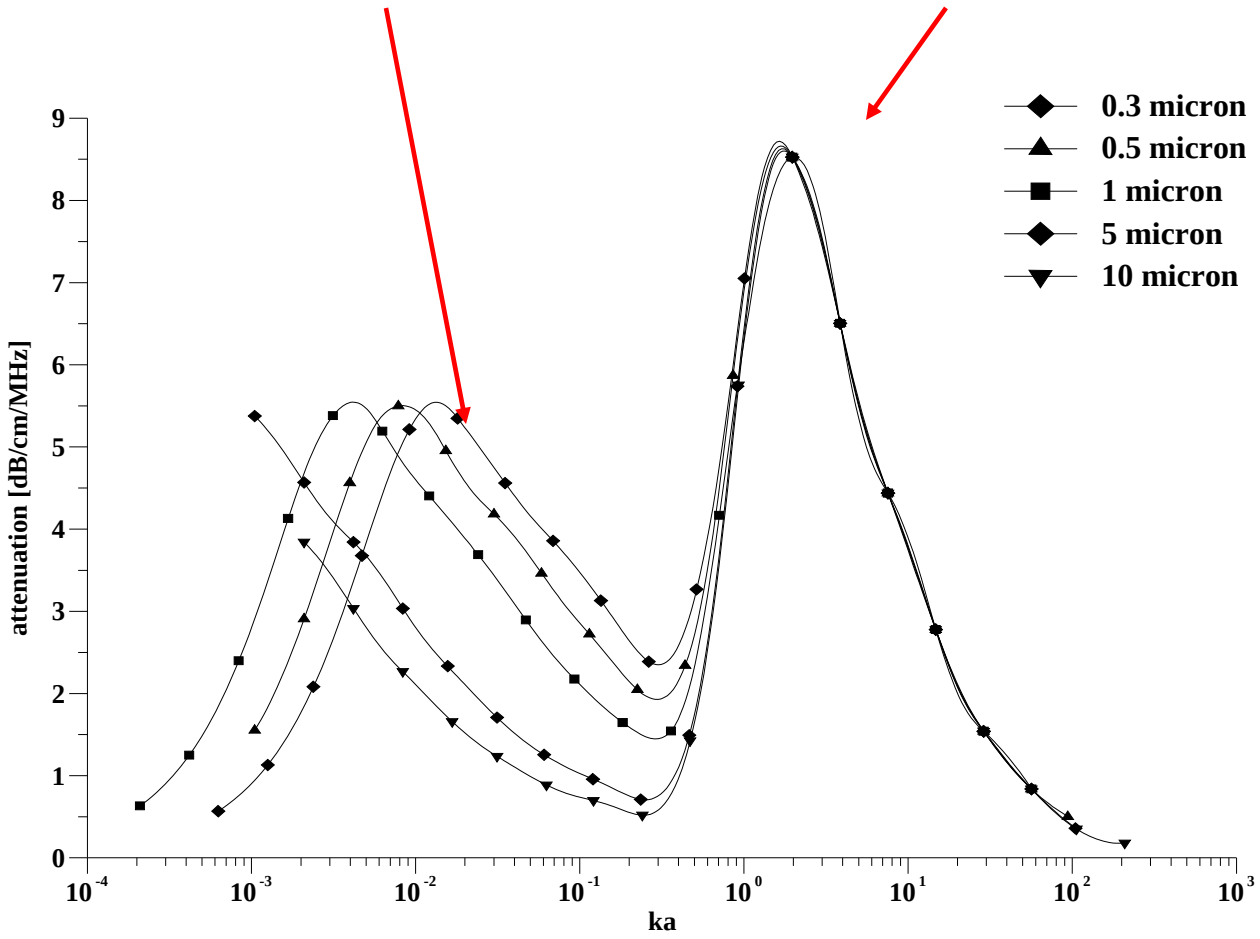
Acoustic Attenuation

Adsorption – conversion to heat

Scattering - energy redirection



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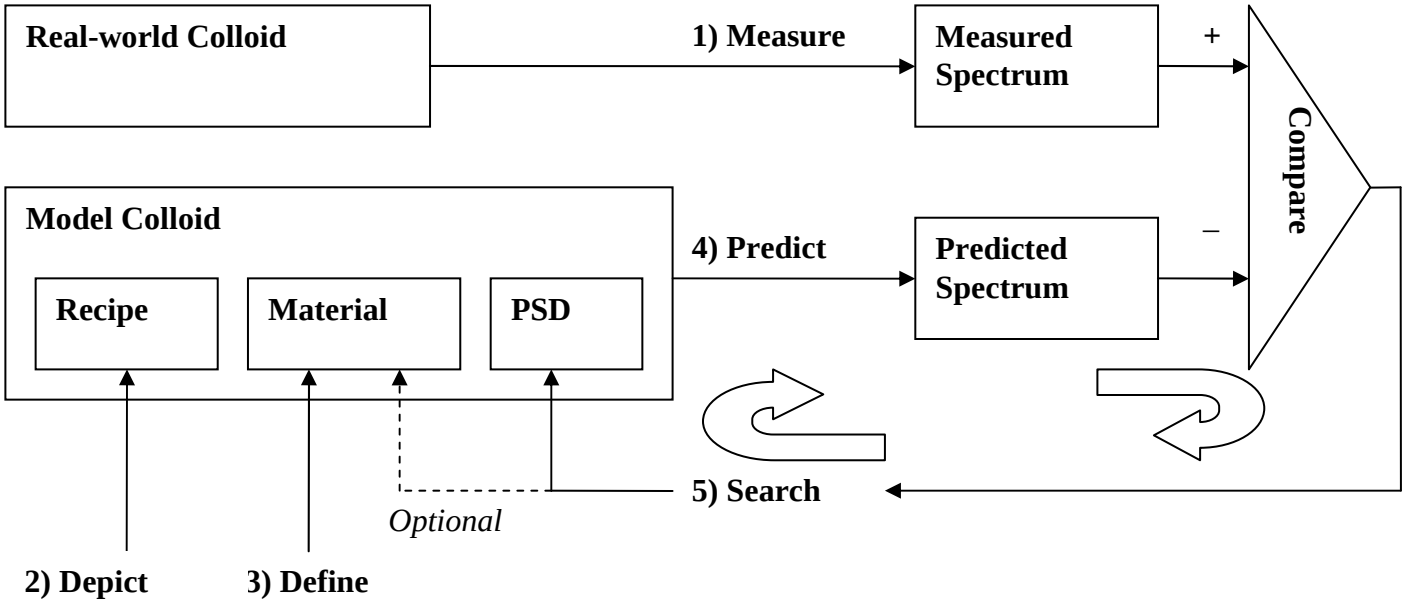
Particle Size Measurement



1. **Measure -** the attenuation spectrum over a wide range of ultrasound frequencies
2. **Depict -** as a *model* colloid making assumptions & defining a recipe w/ name & amount of disperse phase and the suspending media.
3. **Define -** the *relevant physical properties* of these named materials
4. **Predict -** *the sound attenuation spectrum* considering all loss mechanisms for any size distribution and properties
5. **Search -** for particle size distribution that provides the best match between the predicted attenuation spectrum for the model colloid and the measured.

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Loss Mechanisms

- Intrinsic: results from the energy dissipated in the flexing of its molecular structure as the sound wave passes through the material
- Viscous: sound wave causes a relative motion between the particle and the surrounding fluid and some of the energy in the sound wave is converted to heat by virtue of the viscous drag
- Scatter: When the size of the particle becomes comparable to the wavelength of the sound wave, we experience a significant contribution from scattering

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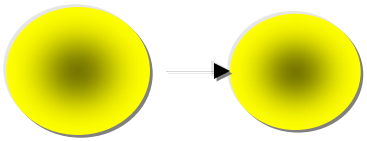
Loss Mechanisms

- Thermal: additional energy loss if the thermal properties of the particles differ from the thermal properties of the medium



Droplet is more easily compressed than H2O as sound wave passes by. Increases temp, heat flows from particle to H2O

- Structural: example; particles in polymer, the polymer establishes links between particles. As particles move polymer linkages are periodically stretched and relaxed causing some additional energy dissipation in the linkages.

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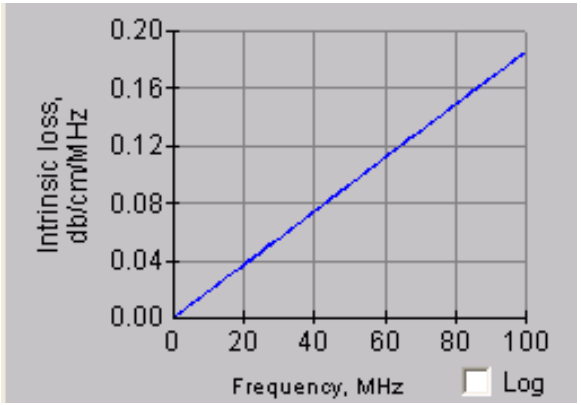
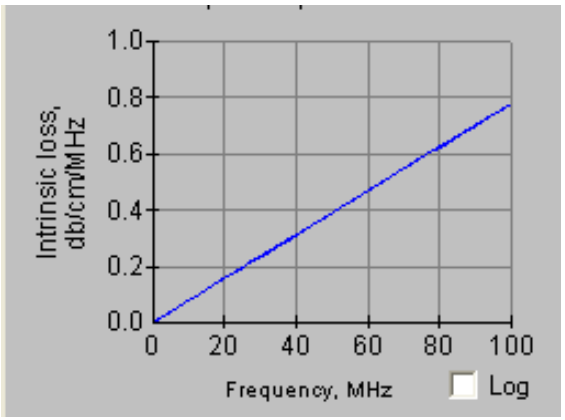
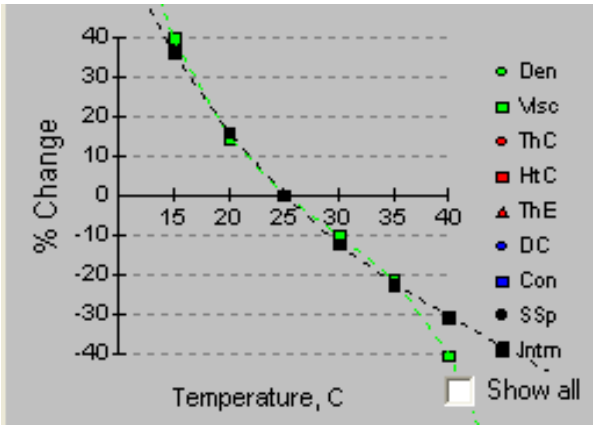
Intrinsic Attenuation



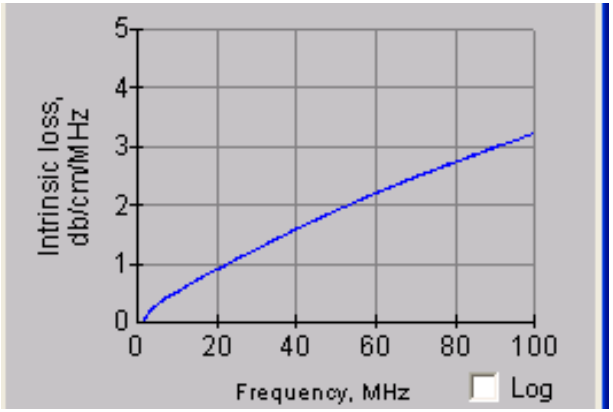
Intrinsic loss of water at 25C



Intrinsic loss of methanol at 25C



Relative change in intrinsic loss for water vs. temperature



Intrinsic loss of corn oil

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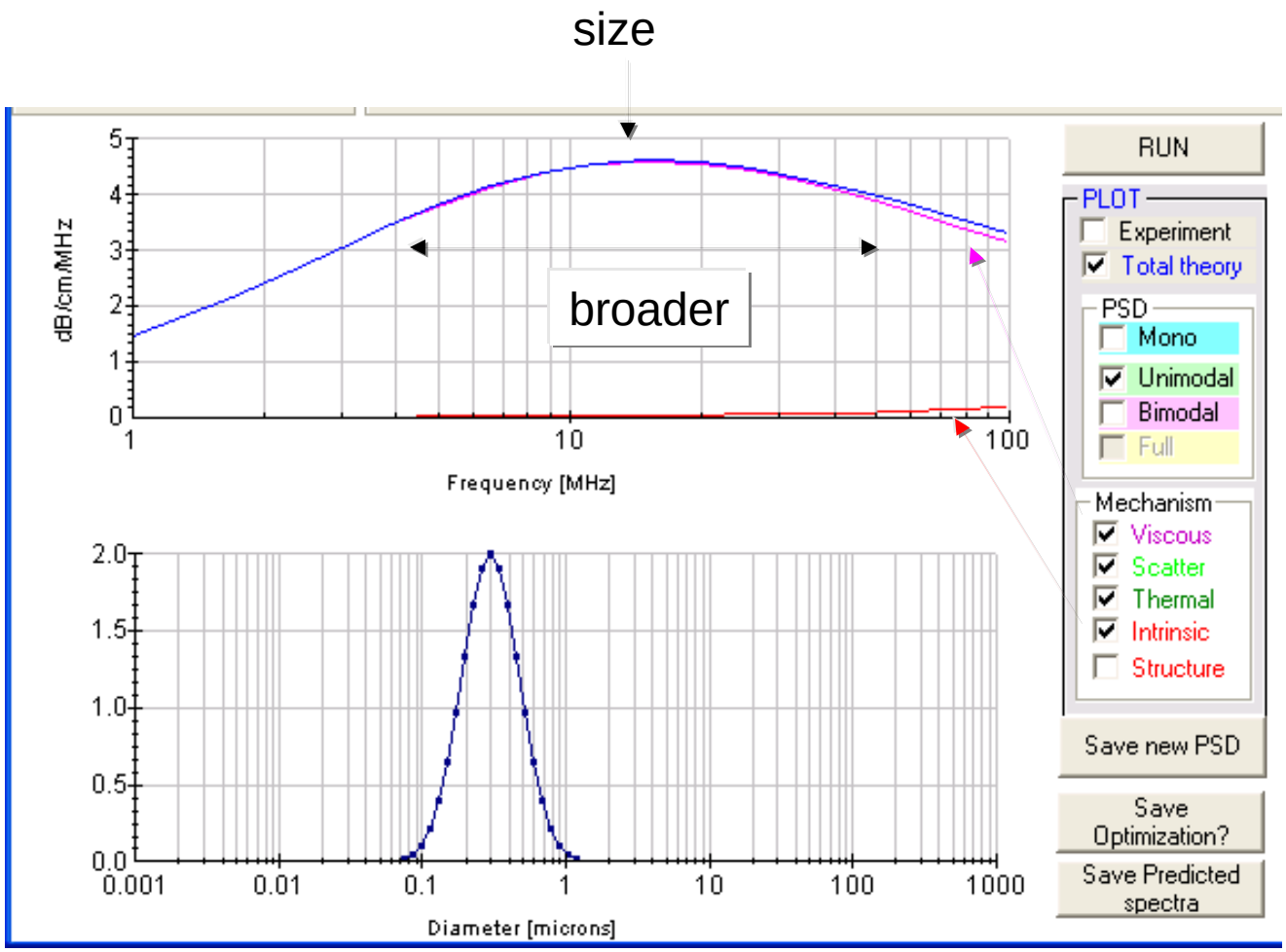
Viscous loss: 0.3 μm Alumina



0.3 micron 5 vol% alumina dispersion in water

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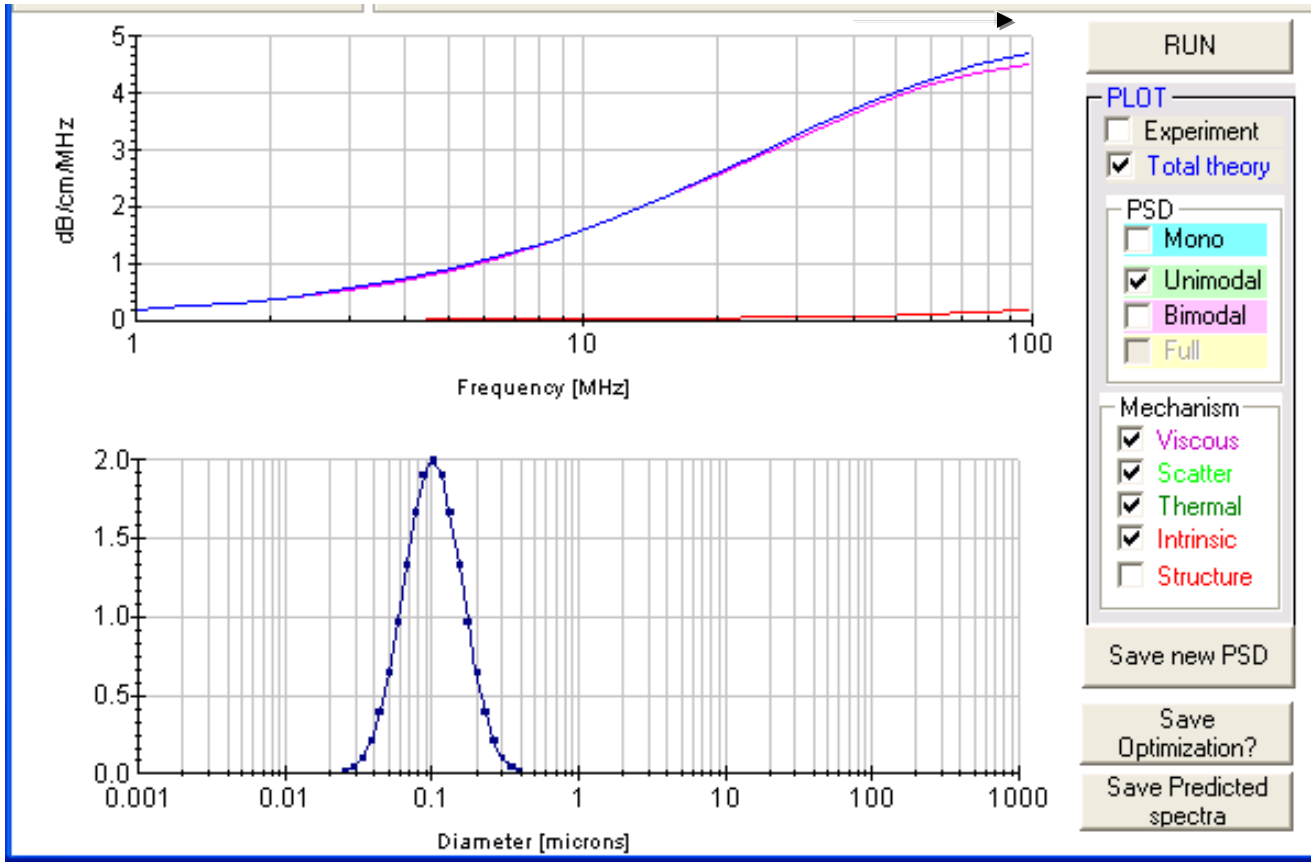
Viscous loss: 0.1 mm Alumina

Shift in frequency changes with the square of particle size

shift



0.1 micron 5 vol% alumina dispersion in water

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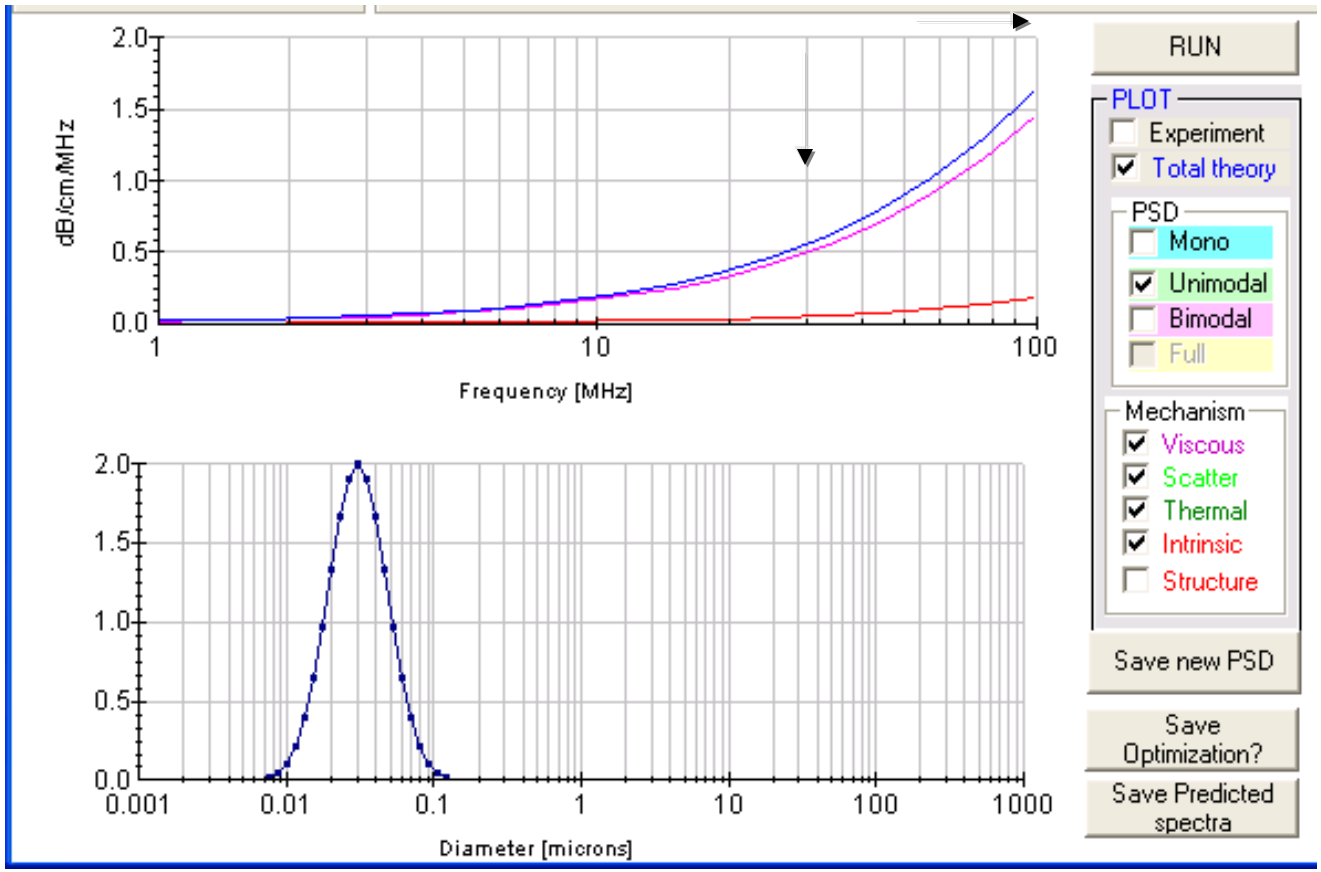
Viscous loss: 0.03 μm Alumina

off scale



0.03 micron 5 vol% alumina dispersion in water

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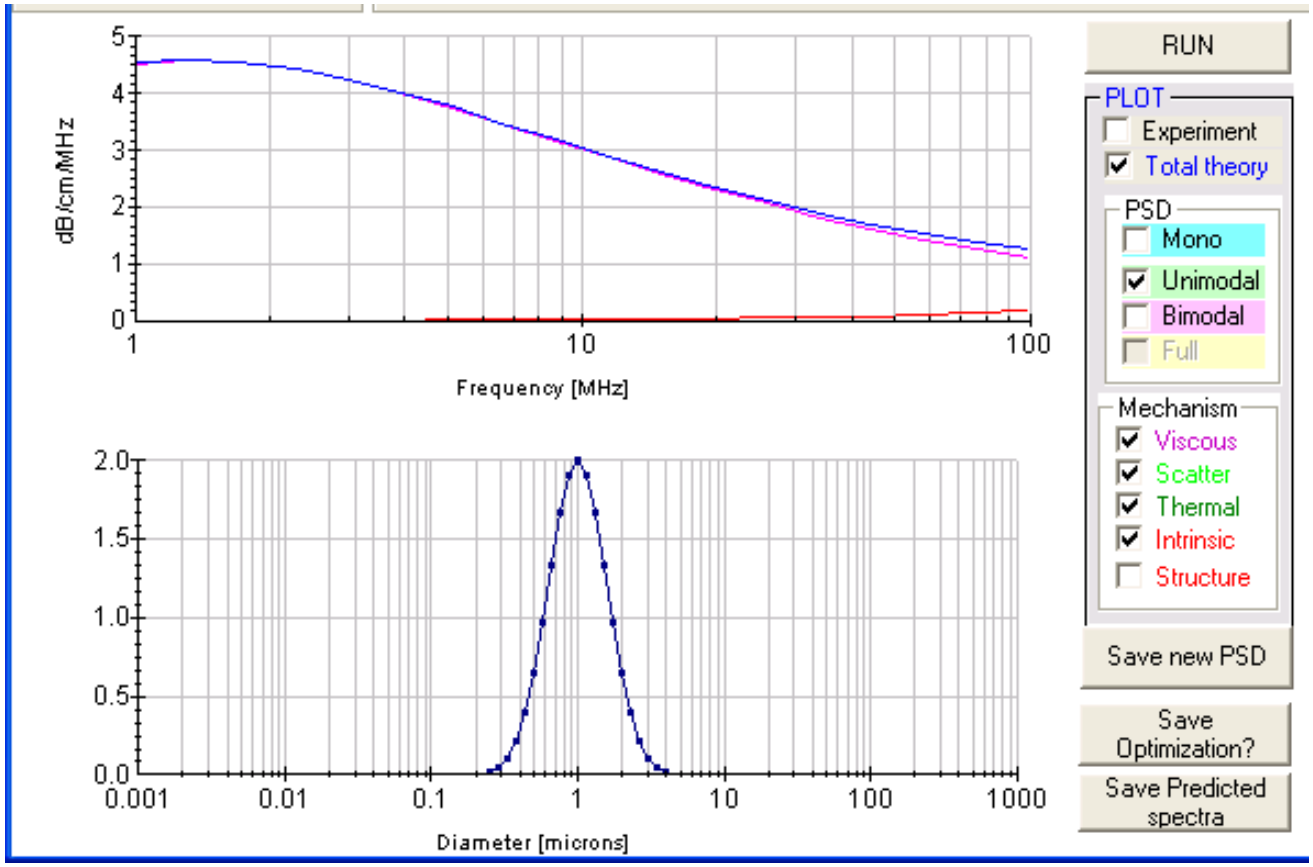
Viscous loss: 1.0 μm Alumina

Shifts to lower frequencies



1.0 micron 5 vol% alumina dispersion in water

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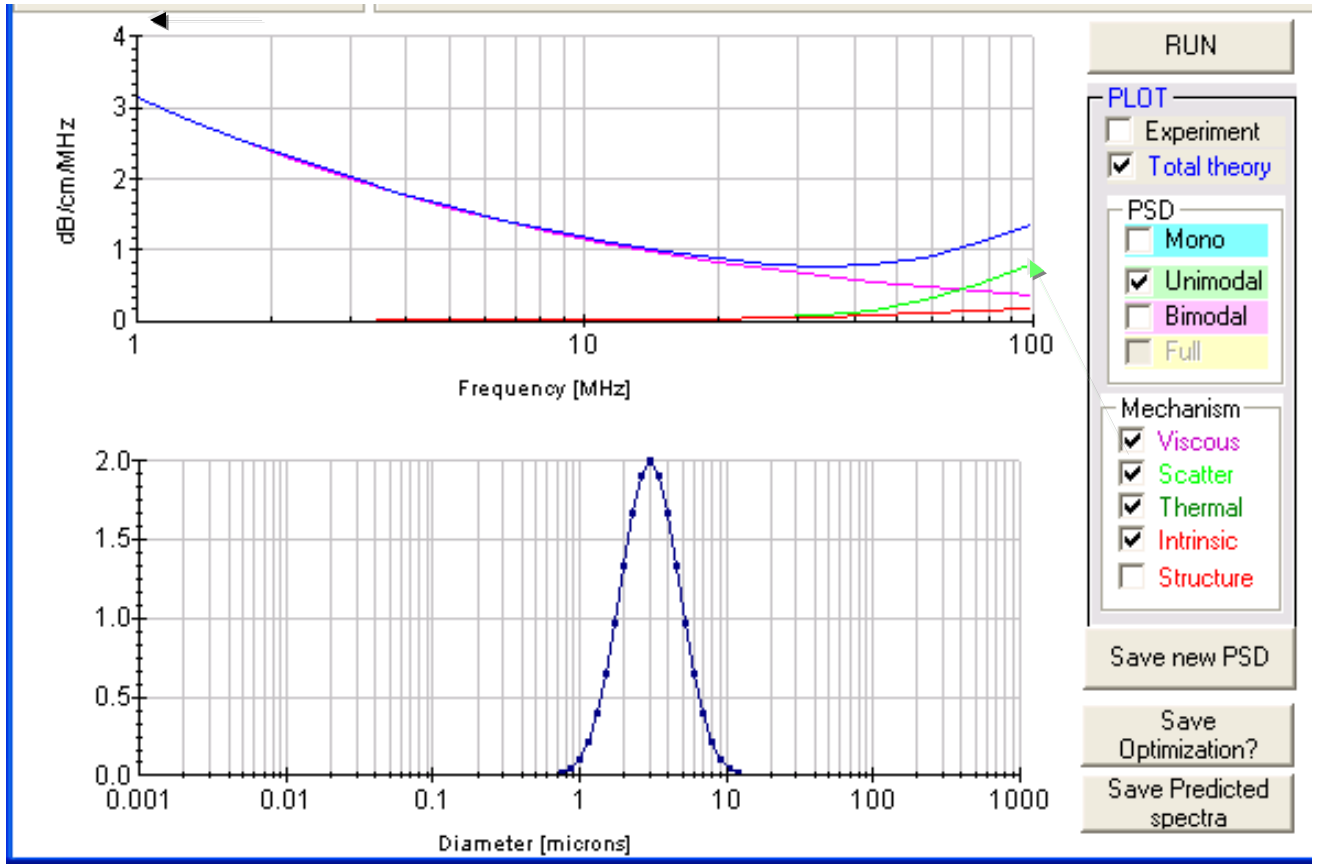
Viscous loss: 3.0 μm Alumina

Off scale, scattering appears



3.0 micron 5 vol% alumina dispersion in water

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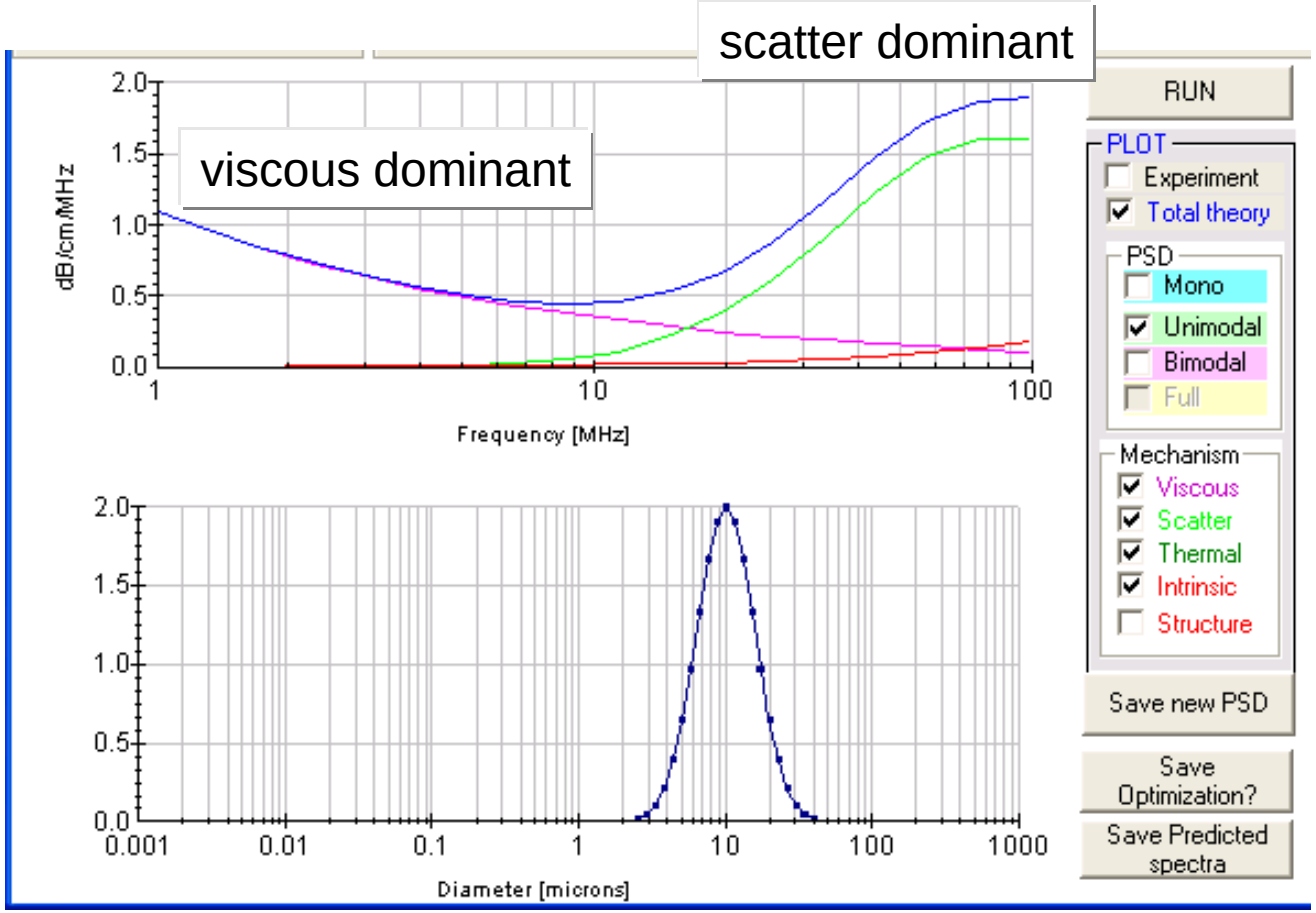
Scatter loss: 10 μm Alumina

Viscous, scattering & intrinsic must all play role, must be understood



10 micron 5 vol% alumina dispersion in water

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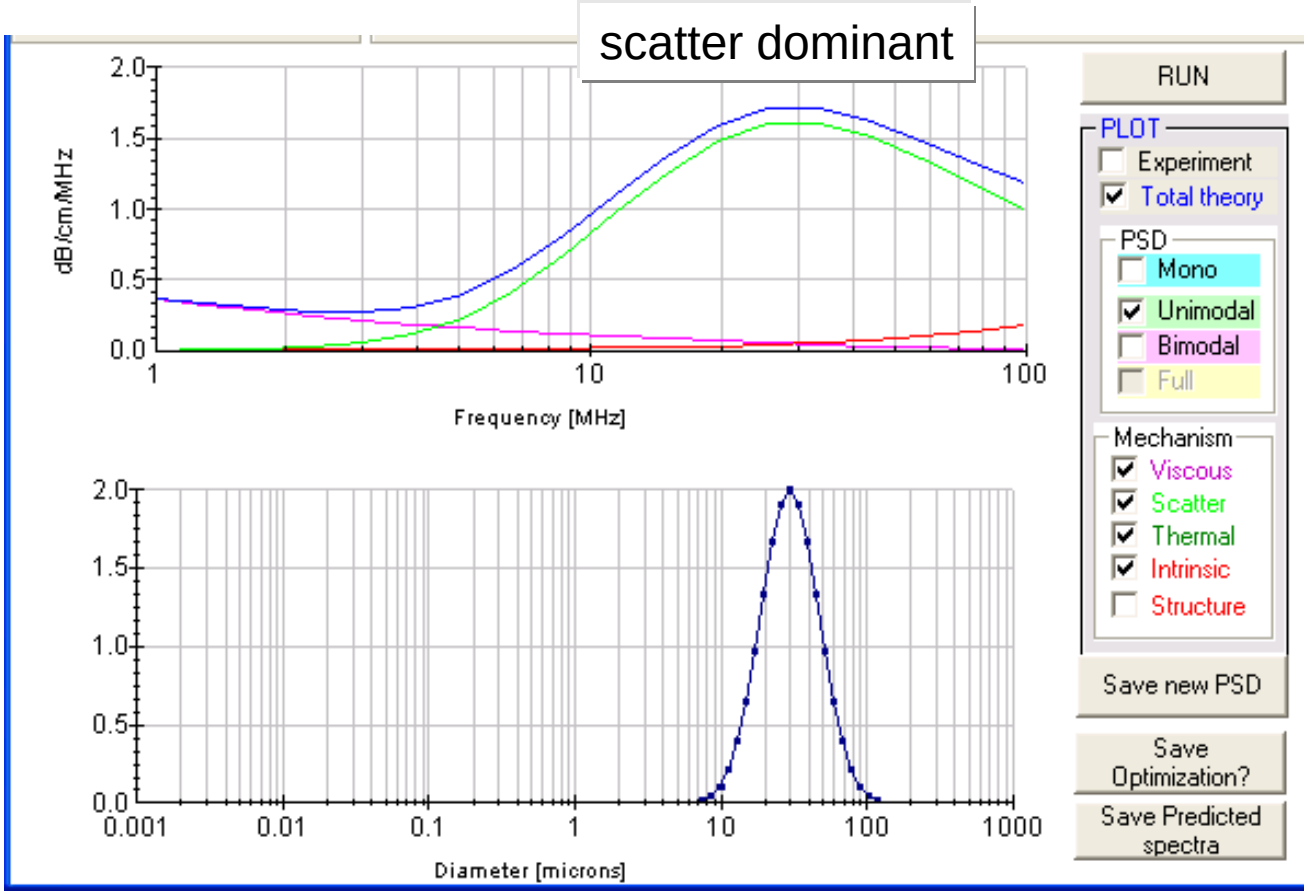
Scatter loss: 30 μm Alumina



30 micron 5 vol% alumina dispersion in water

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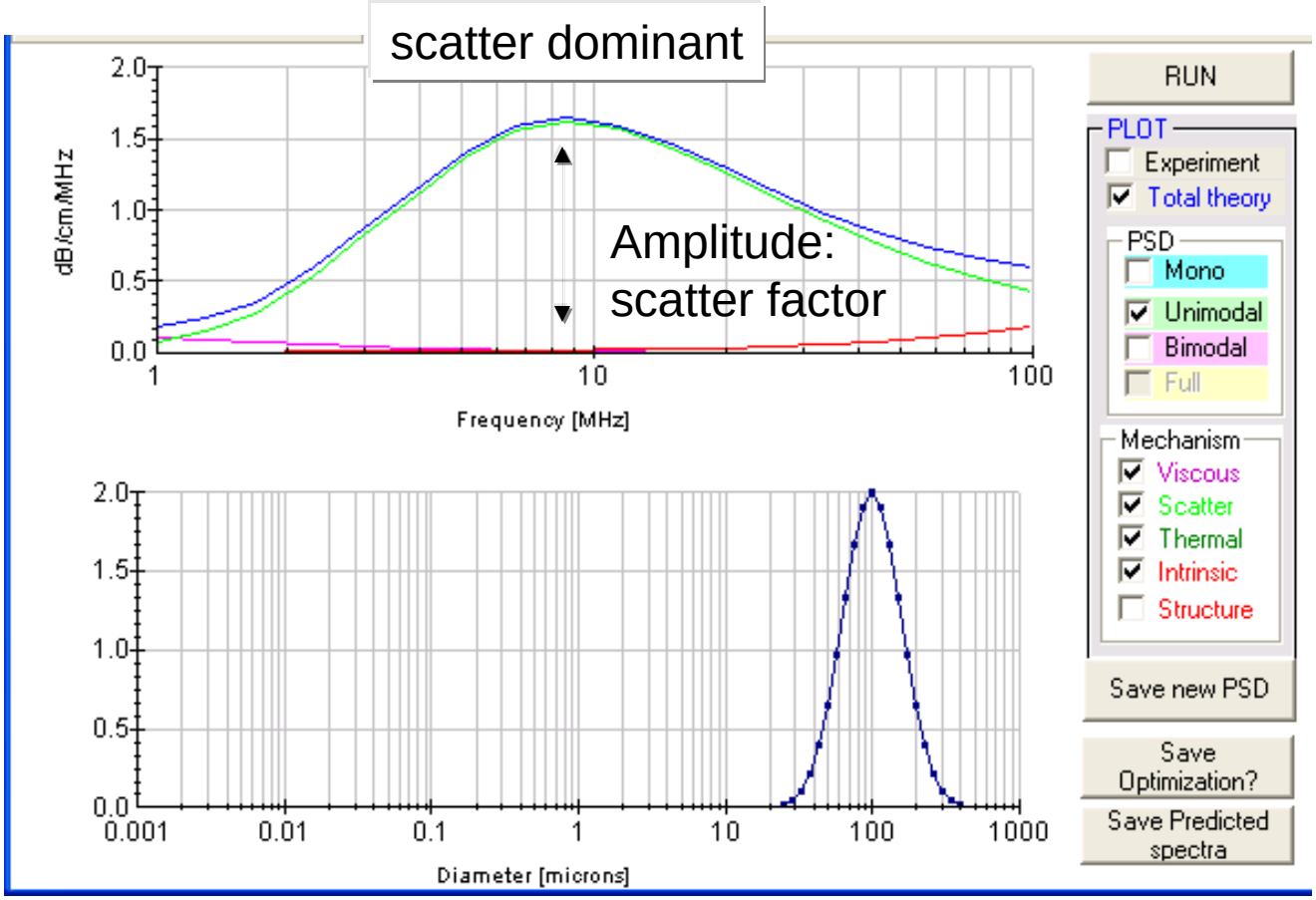
Scatter loss: 100 μm Alumina



100 micron 5 vol% alumina dispersion in water

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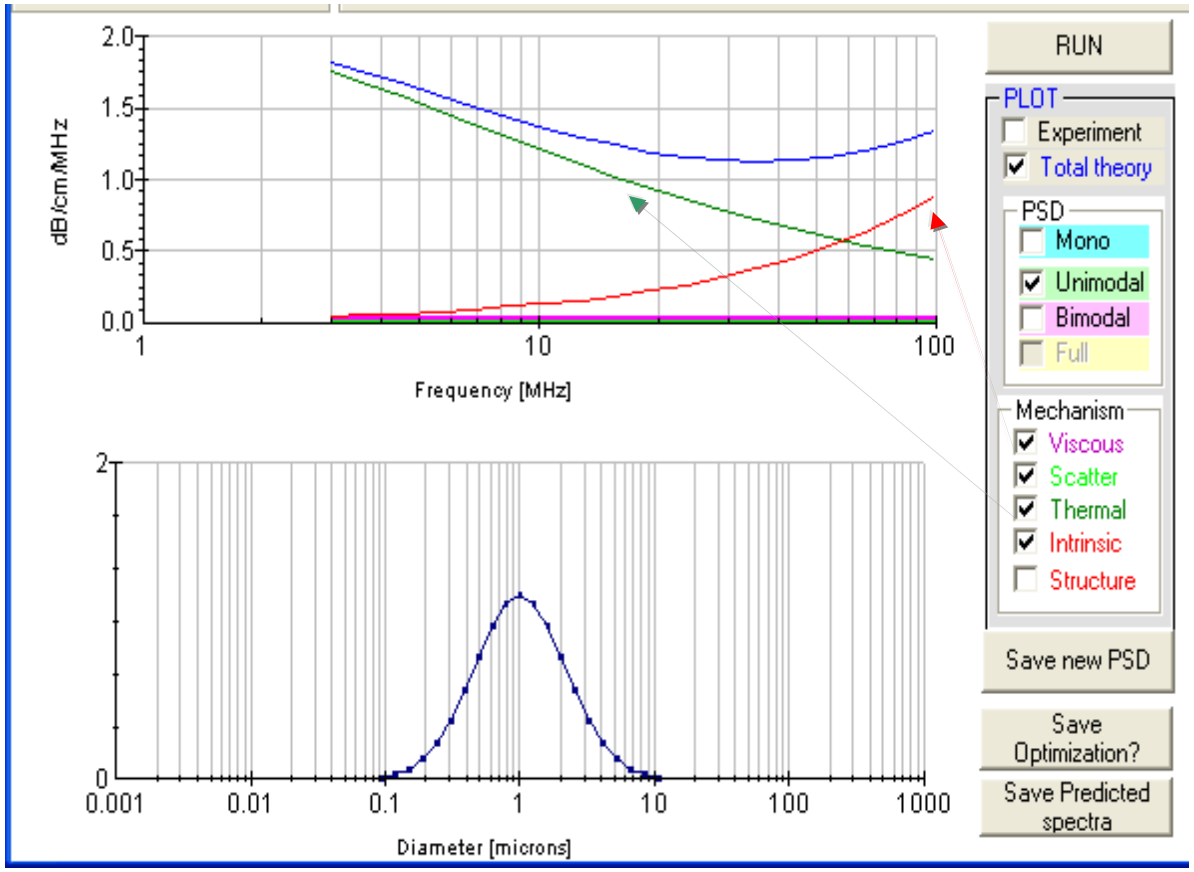
Thermal loss: 1.0 μm Droplet



1.0 micron droplets in 20 wt% corn oil in water emulsion

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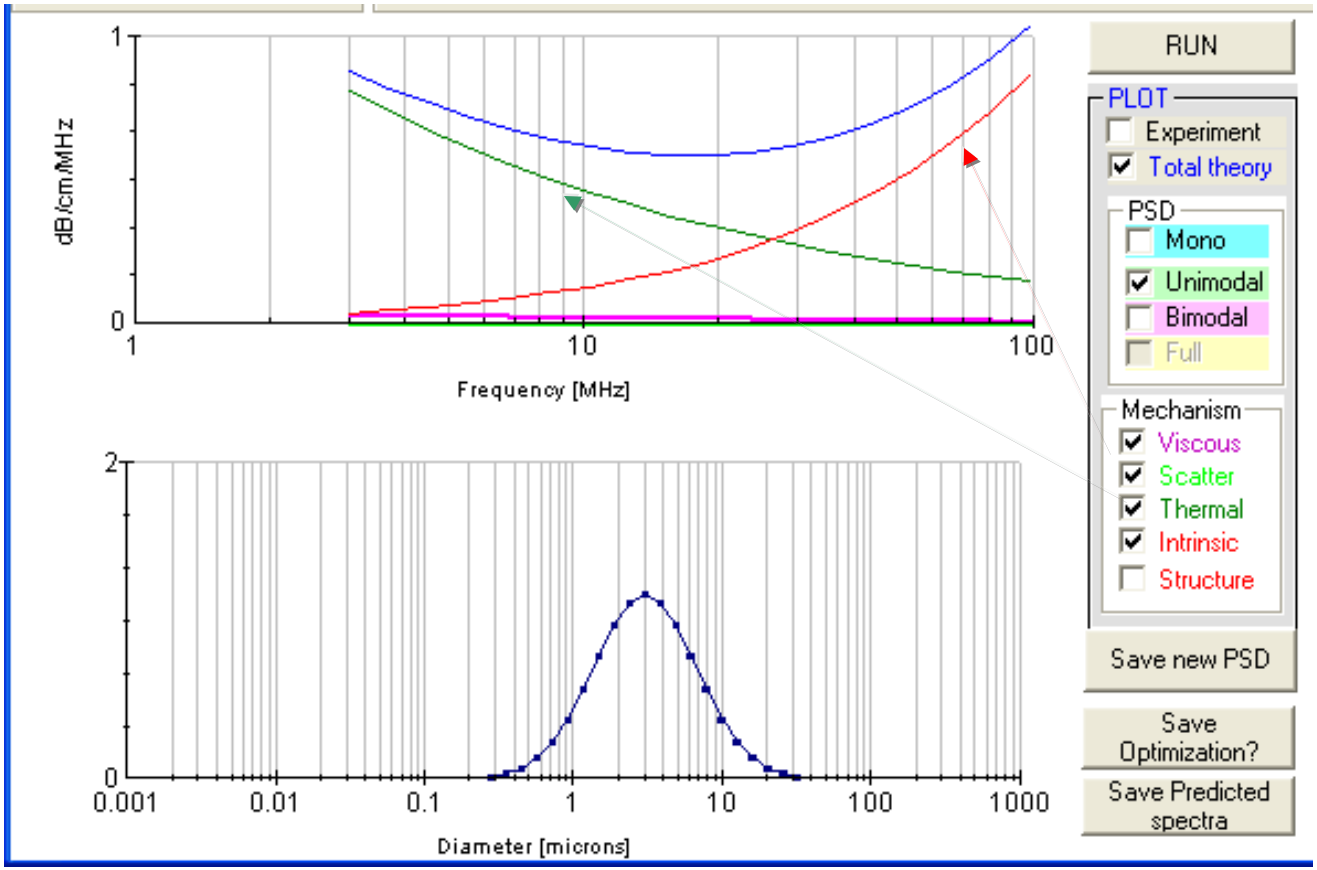
Thermal loss: 3.0 μm Droplet



3.0 micron droplets in 20 wt% corn oil in water emulsion

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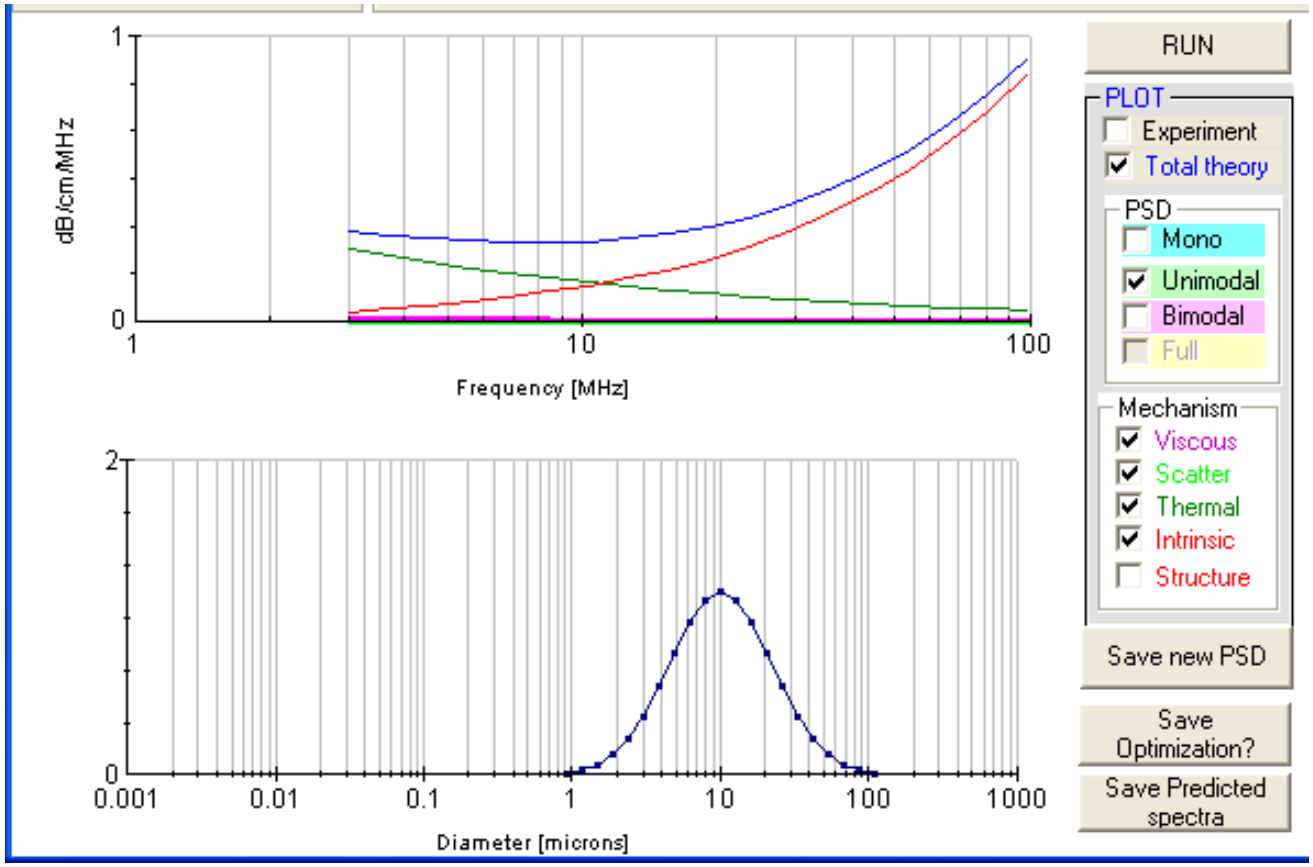
Thermal loss: 10 μm Droplet

Scattering more dominant



10 micron droplets in 20 wt% corn oil in water emulsion

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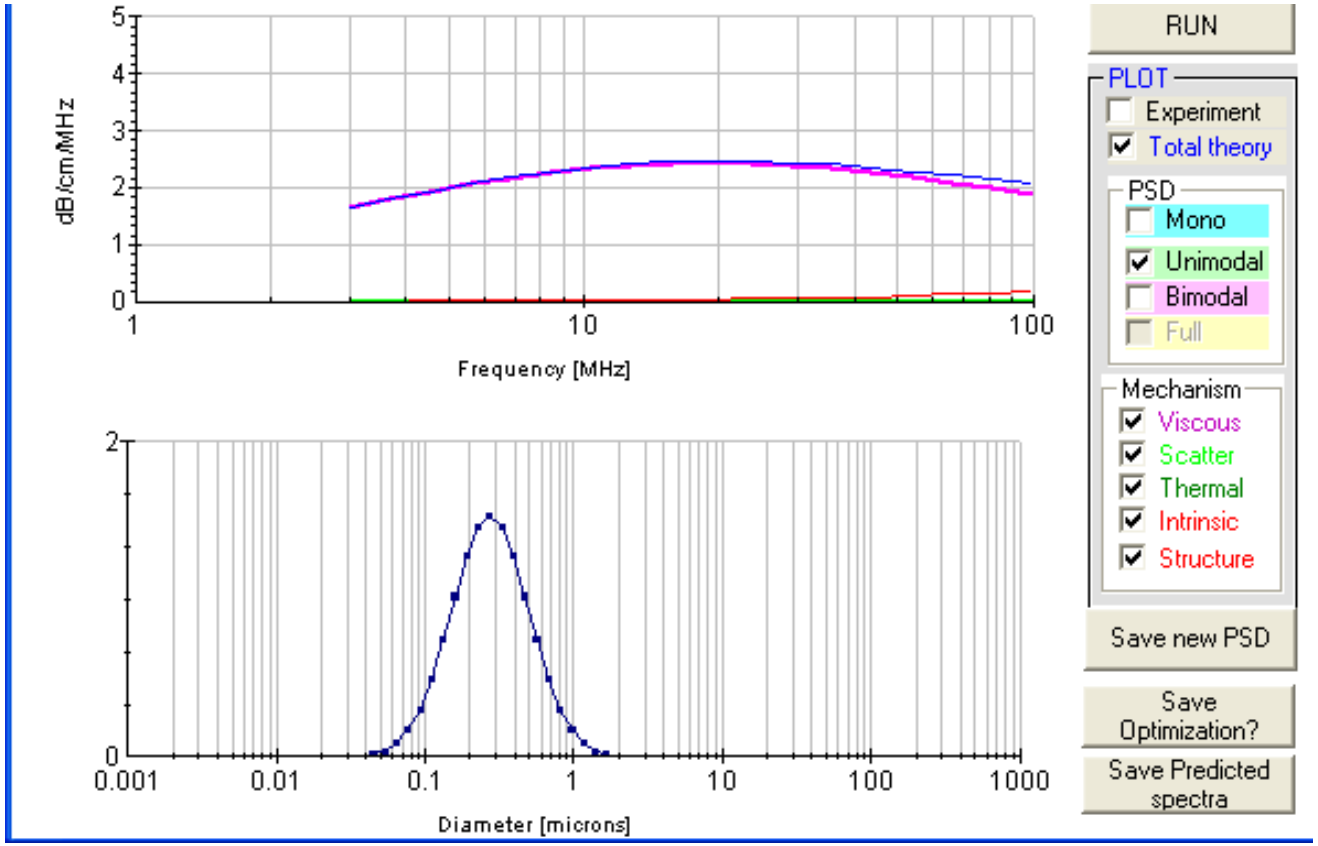
Structural loss: no Links



0.3 micron particles without any structural links between particles

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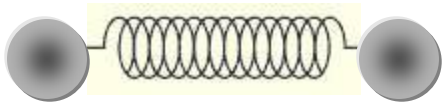
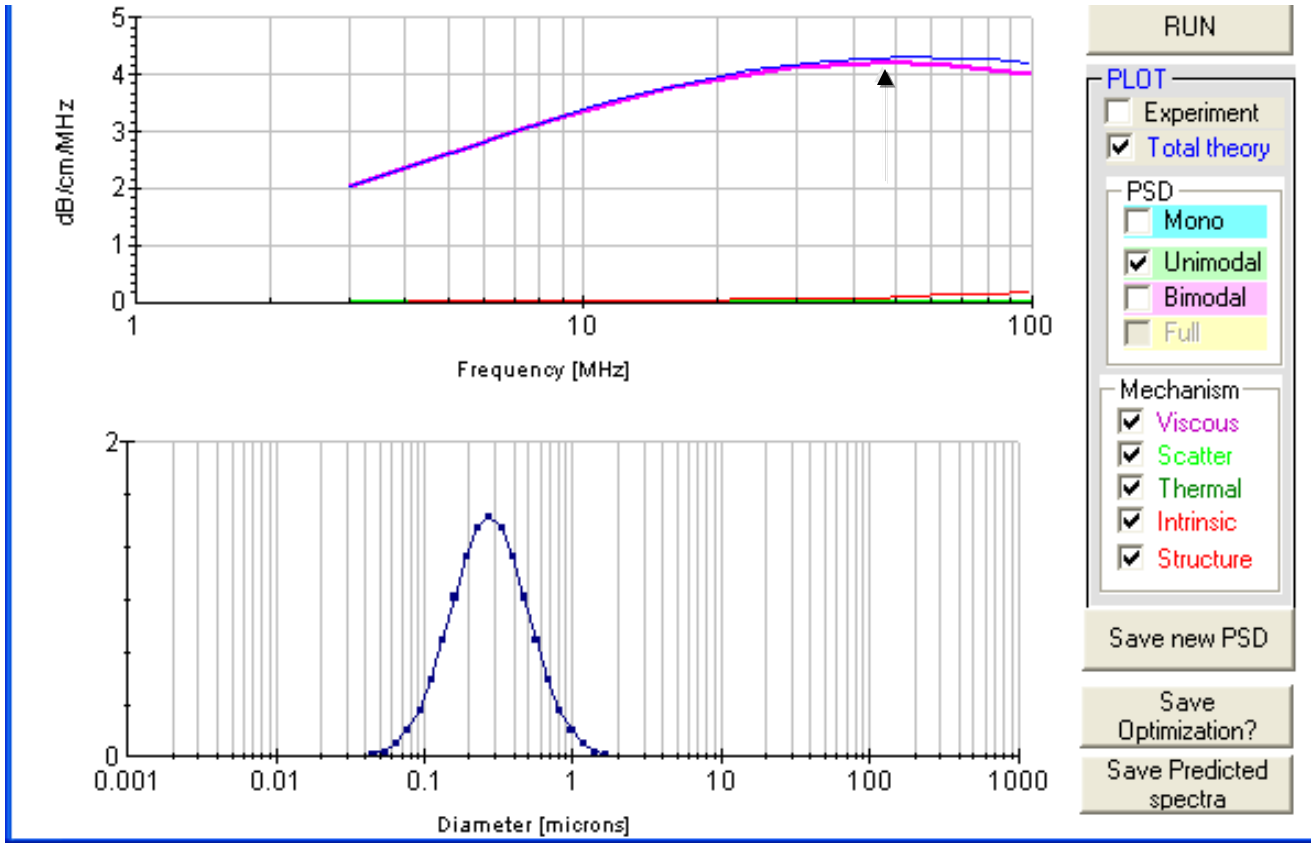
Structural loss: with Links





0.3 micron particles with structural links between particles

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Relevant Properties for Loss Mechanisms

Loss Mechanism >	Intrinsic	Viscous	Scatter	Thermal
Relevant property				
For Particle				
Density		Relevant		
Micro viscosity		Relevant		
Porosity/Fractal No		Relevant		
Thermal conductivity				Relevant
Heat capacity				Relevant
Thermal expansion				Relevant
Sound speed	Relevant			
Scatter factor			Relevant	
Intrinsic	Relevant			
For Media				
Density		Relevant		
Micro viscosity		Relevant		
Porosity/Fractal No				
Thermal conductivity				Relevant
Heat capacity				Relevant
Thermal expansion				Relevant
Sound speed	Relevant			
Scatter factor				
Intrinsic	Relevant			

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What do I Need to Know?

- Must know concentration wt% (>1-2%)
- What is the dispersed & continuous phase
- Relevant properties for loss mechanisms
- Many particles & liquids in software library
- Solid, sub micron particles need density
- Large solid particles determine scatter factor
- Emulsions, “soft particles” some thermal properties

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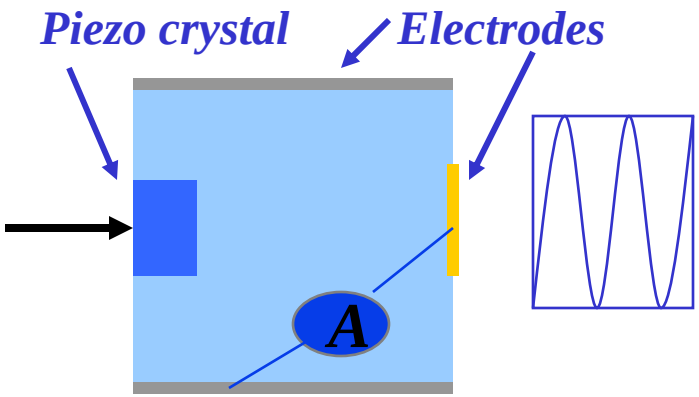
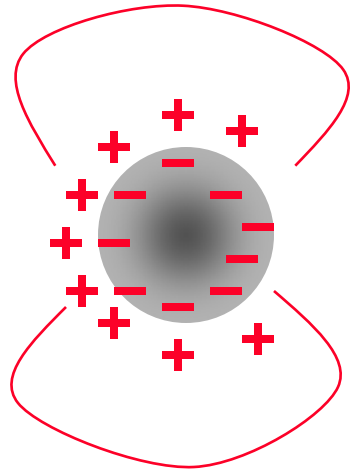
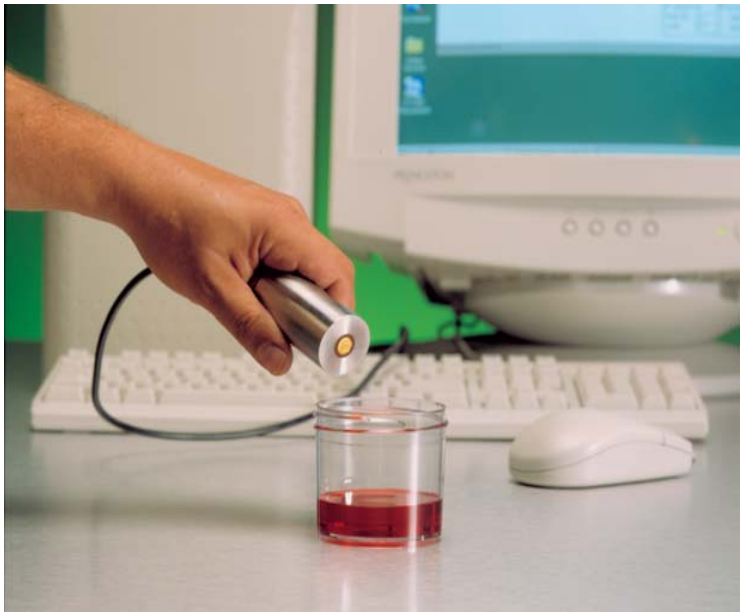
Electroacoustics – Zeta Potential





Zeta Potential Probe



Colloid Vibration Current

$$CVI = C\frac{\rho_p - \rho_m}{\rho_m}\varphi\mu_d\nabla P$$

Dynamic Mobility

$$\mu_d = \frac{\varepsilon_m \varepsilon_o \varsigma}{\eta}\frac{(\rho_p - \rho_s)\rho_m K_s}{(\rho_p - \rho_m)\rho_s K_m}$$

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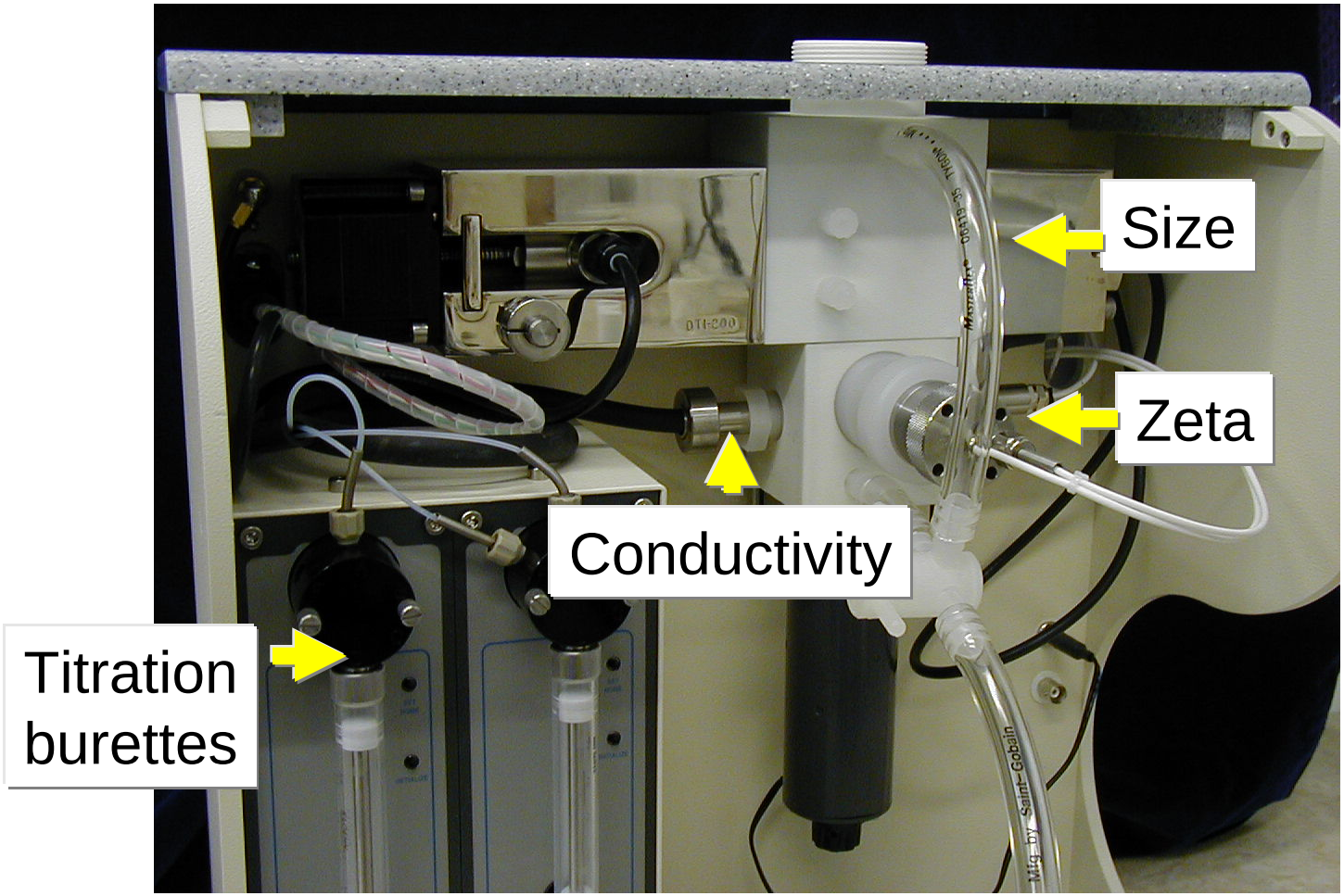
Hardware Configurations



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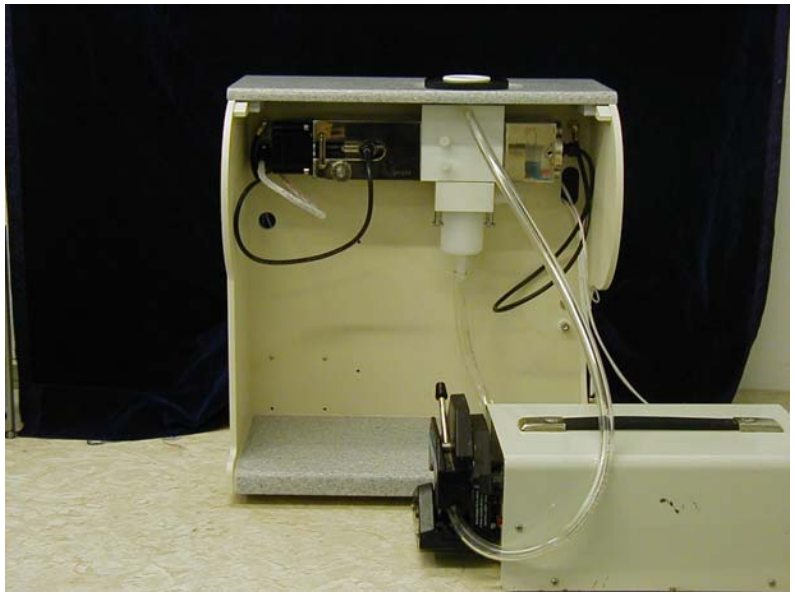
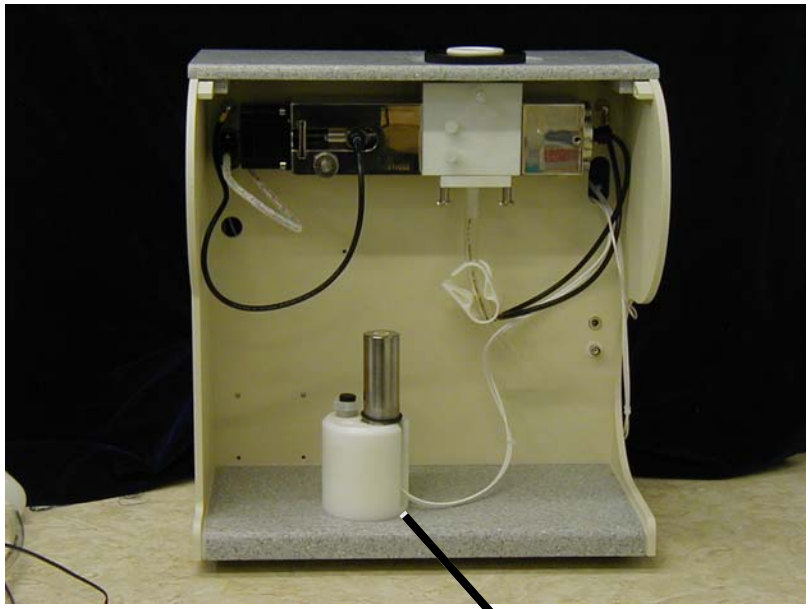
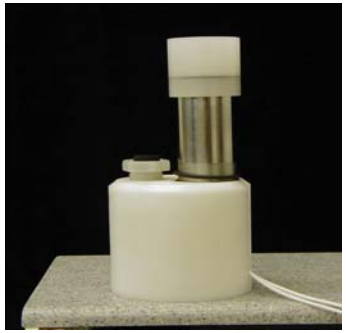
Hardware Configurations



External peristaltic pump



Separate size
& zeta potential



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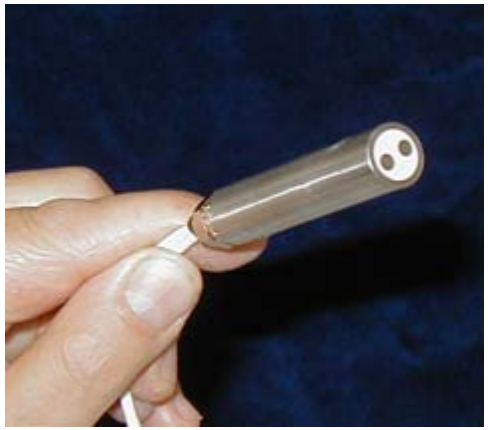
Additional Sensors

- Temperature
- Conductivity
- Dielectric permittivity
- pH



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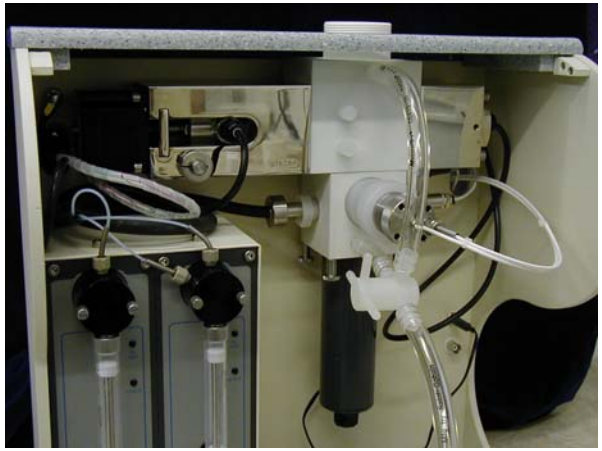
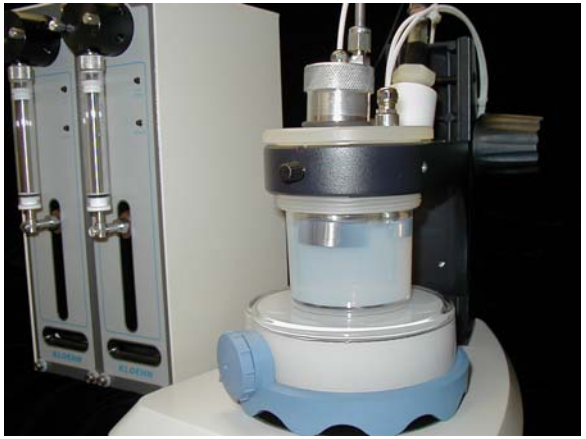
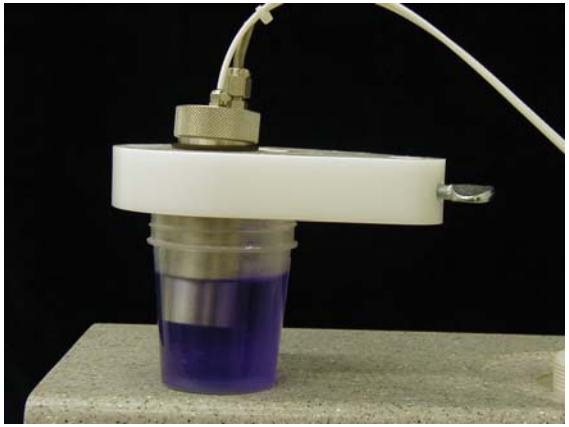
pH vs. Zeta Potential Titrations

- Configure hardware: zeta potential probe can be in acoustic size chamber or simply placed in a beaker with the pH probe







- Fill chemical bottle 1 w/ 1N HCl & chemical bottle 2 w/ 1 N KOH
- Define material
- Double click on “Titration”, Under “Type” select pH ramp, define titration
- Click on “CVI – for zeta potential” and “Run”

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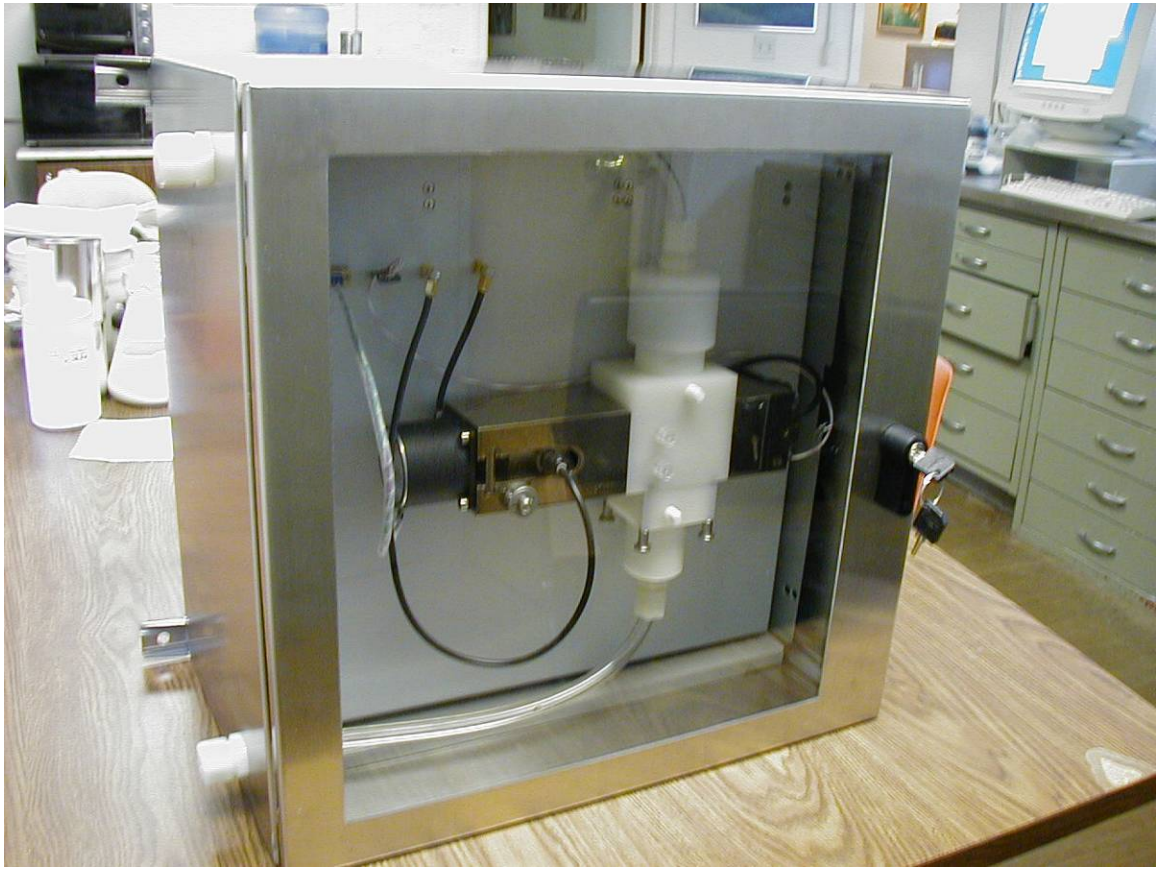
Flow Through



Do basic lab characterizations first

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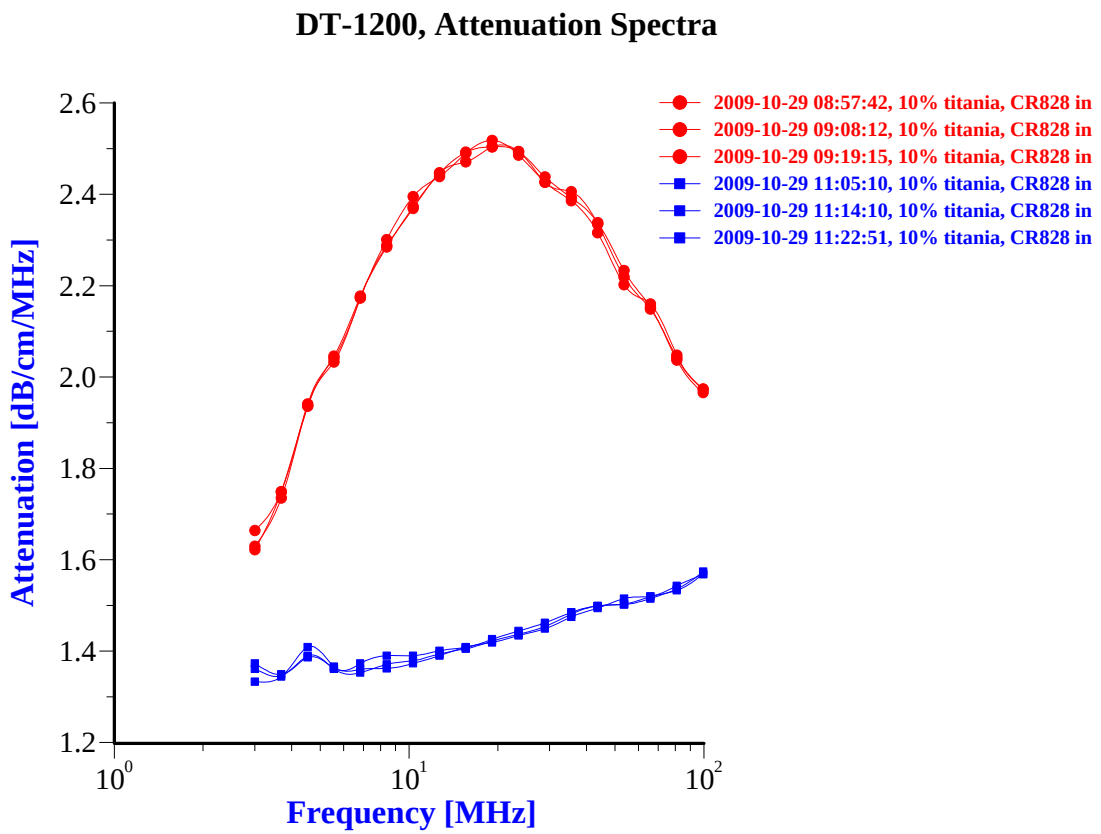
Titania in Water pH = 4, 10



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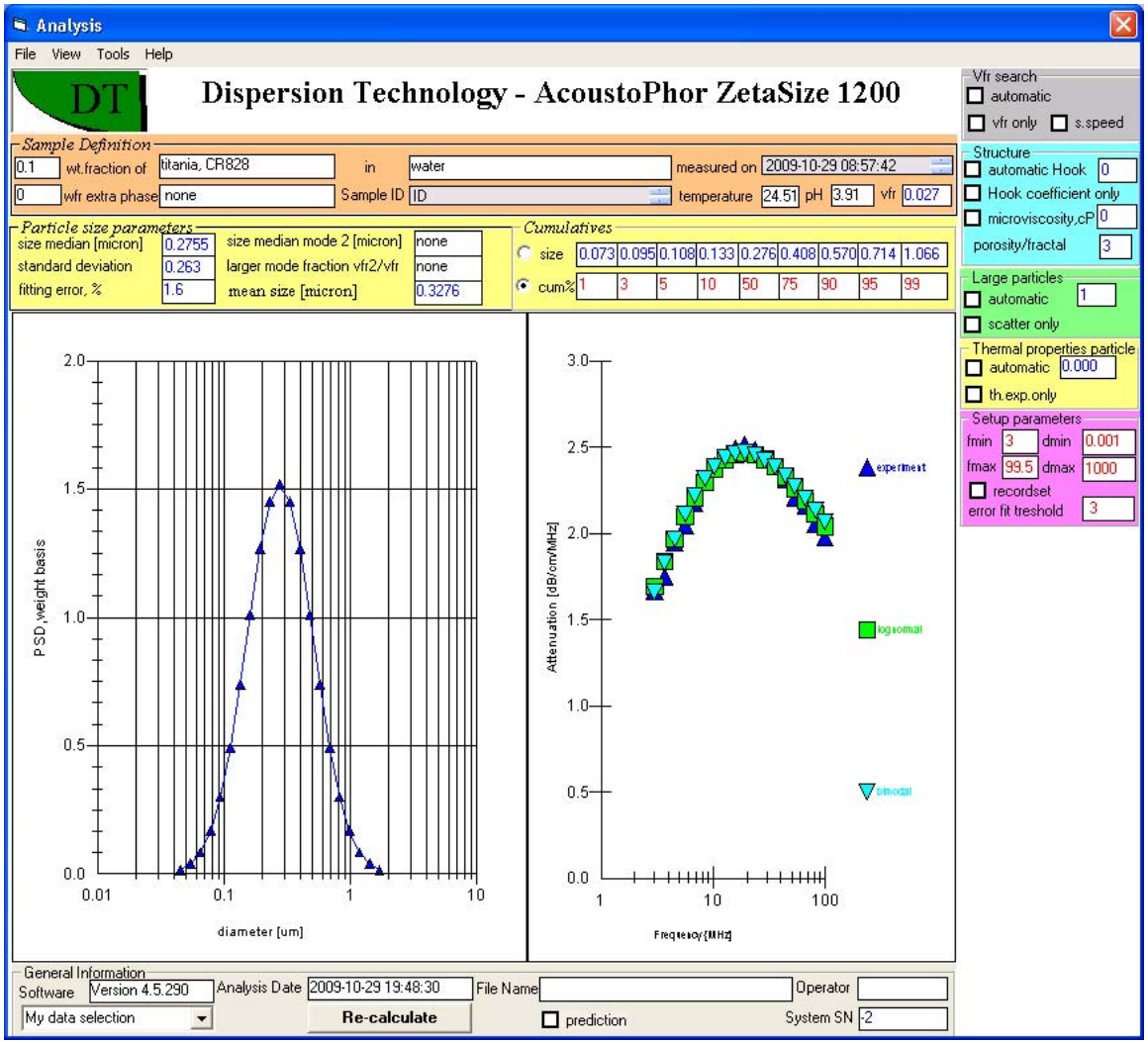
Titania, pH = 4



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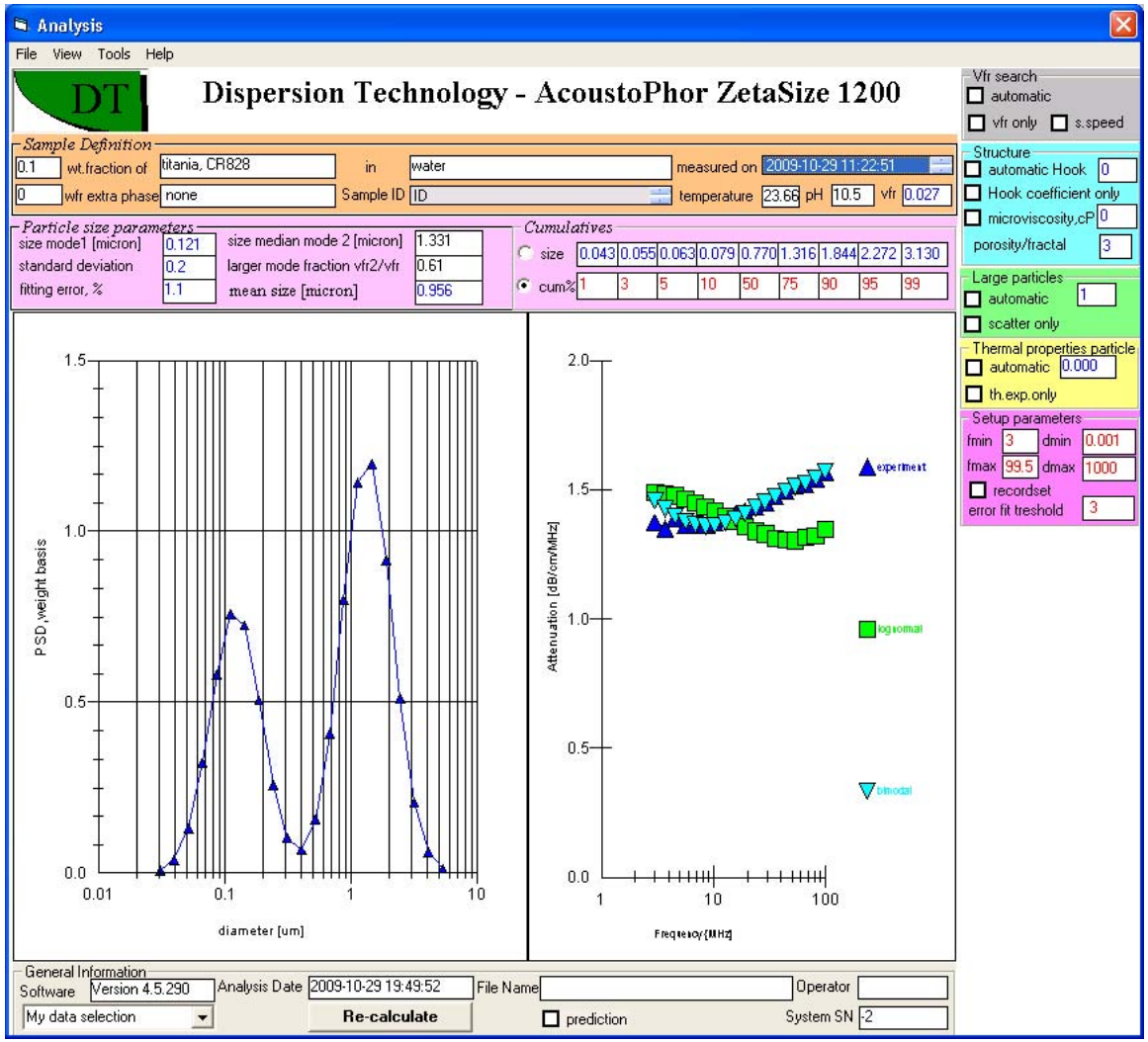
Titania, pH = 10



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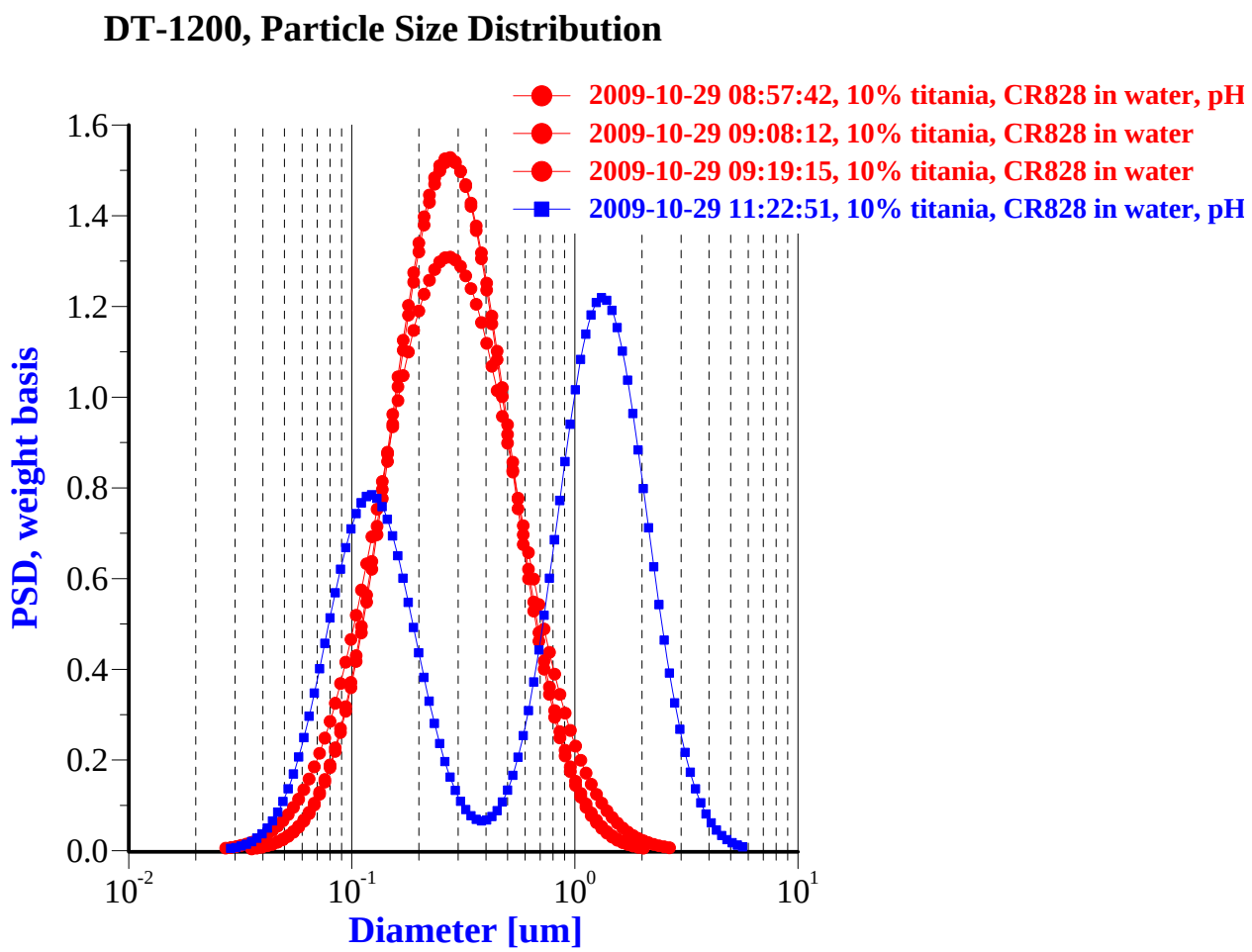
Titania in Water pH = 4, 10



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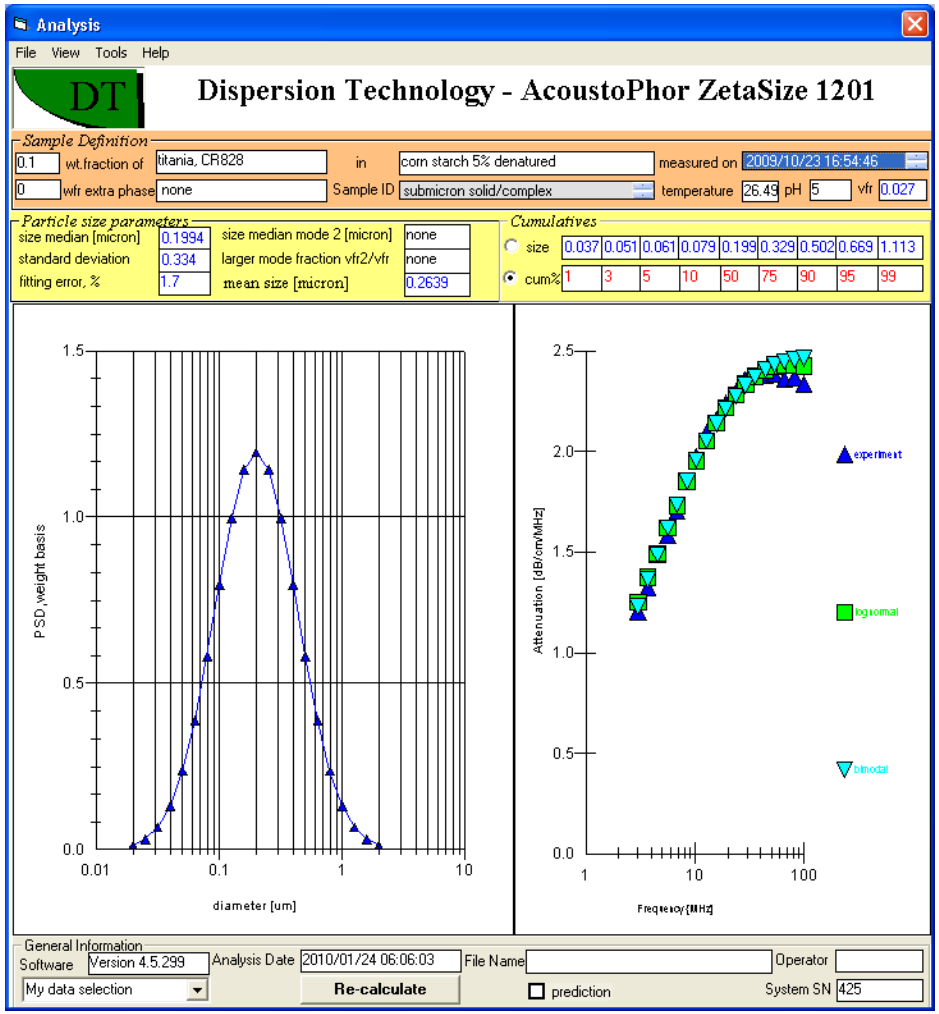
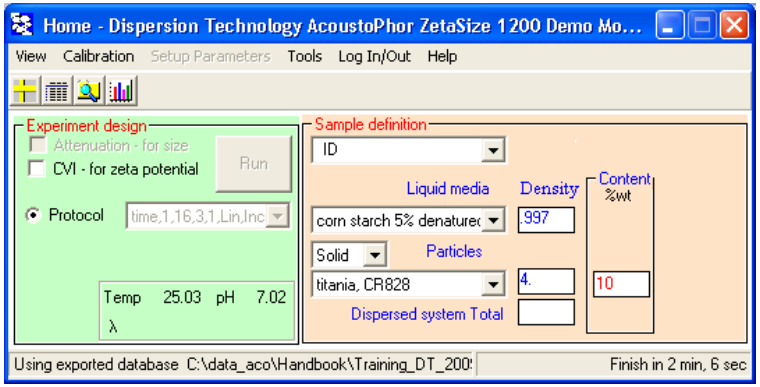
Titania, pH = 3, in Corn Starch



First measure
Intrinsic attenuation
Of corn starch



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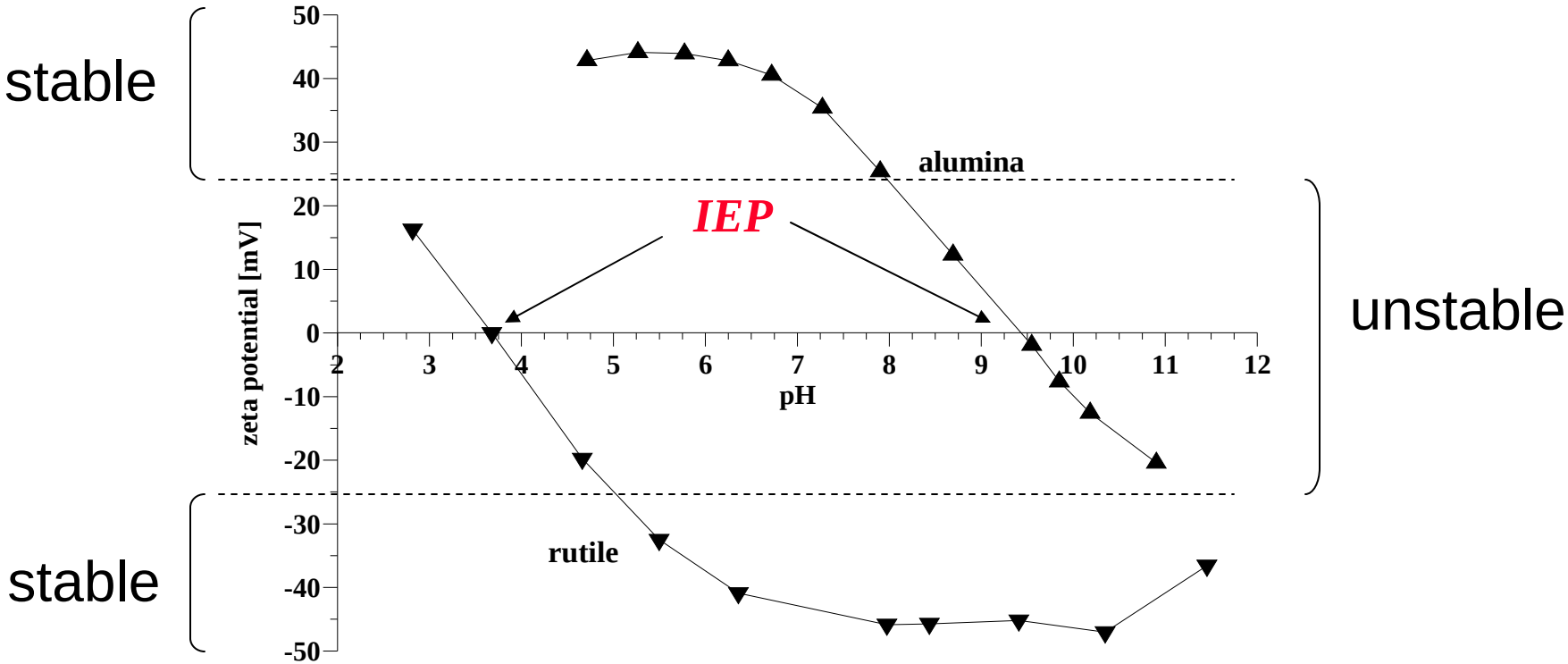
pH Titration of Rutile 7%vl & Alumina 4%vl

Many application notes available on web site www.horibalab.com

Colloidal Stability



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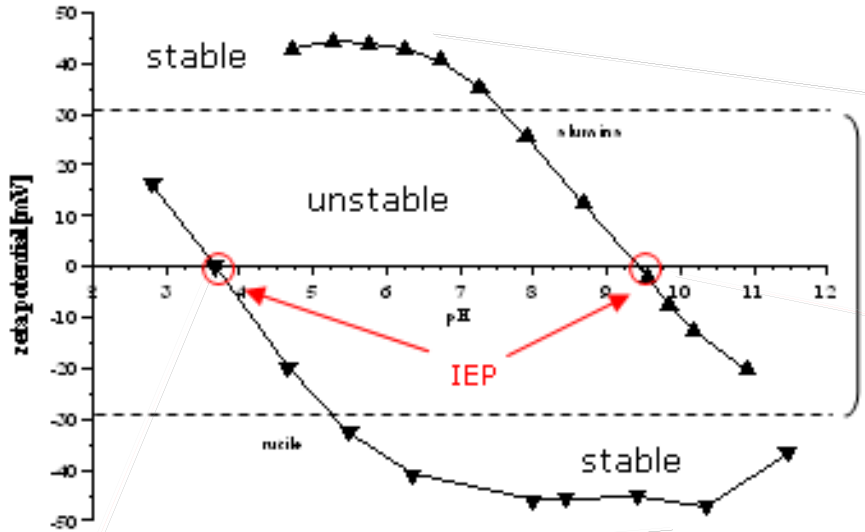
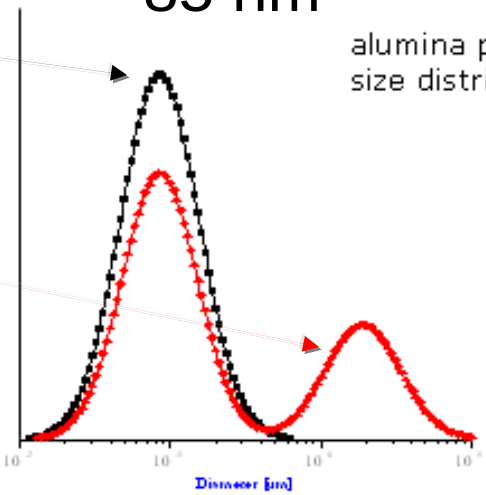
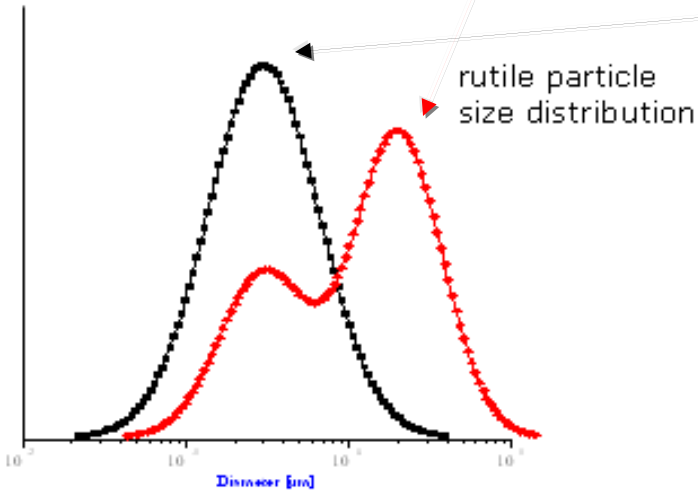
pH Titration of Rutile 7%vl & Alumina 4%vl



85 nm



300 nm



PSD unstable @ IEP
aggregates form

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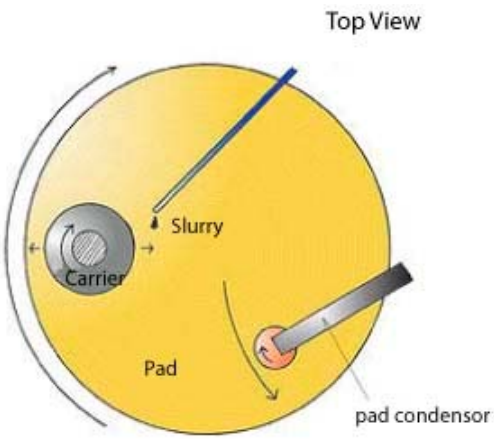
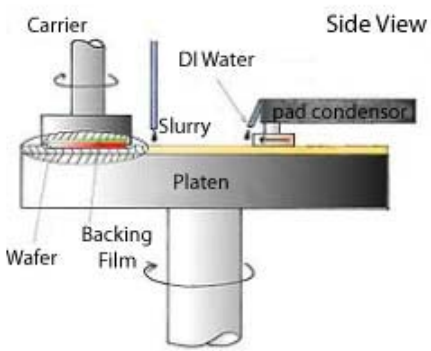
CMP

Chemical Mechanical Polishing fluid





	Manufacturer Size Specification	Acoustics Size Determination
Ludox-TM	22 nm (area basis)	30 nm (weight basis)
Geltech 0.5	0.5 micron	0.65 micron
Geltech 1.5	1.5 micron	1.72 micron
Cabot SS12	N/A	63 nm
Cabot SS25	N/A	62 nm

Particle Characterization Analyzer

Applications Note

DT-Series
AN165
CMP Slurries

CMP SLURRY MEASUREMENT USING ACOUSTIC SPECTROSCOPY

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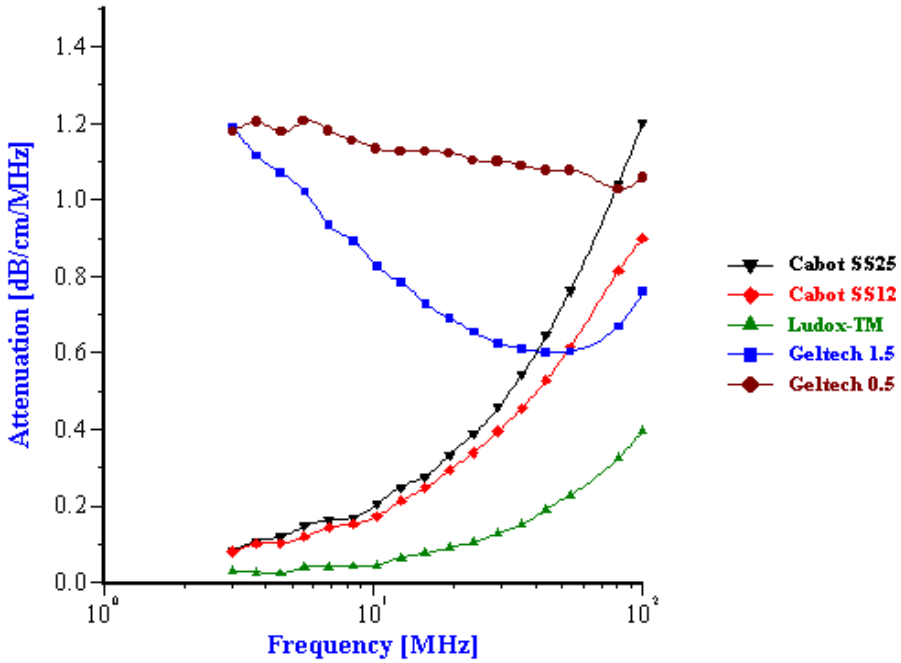
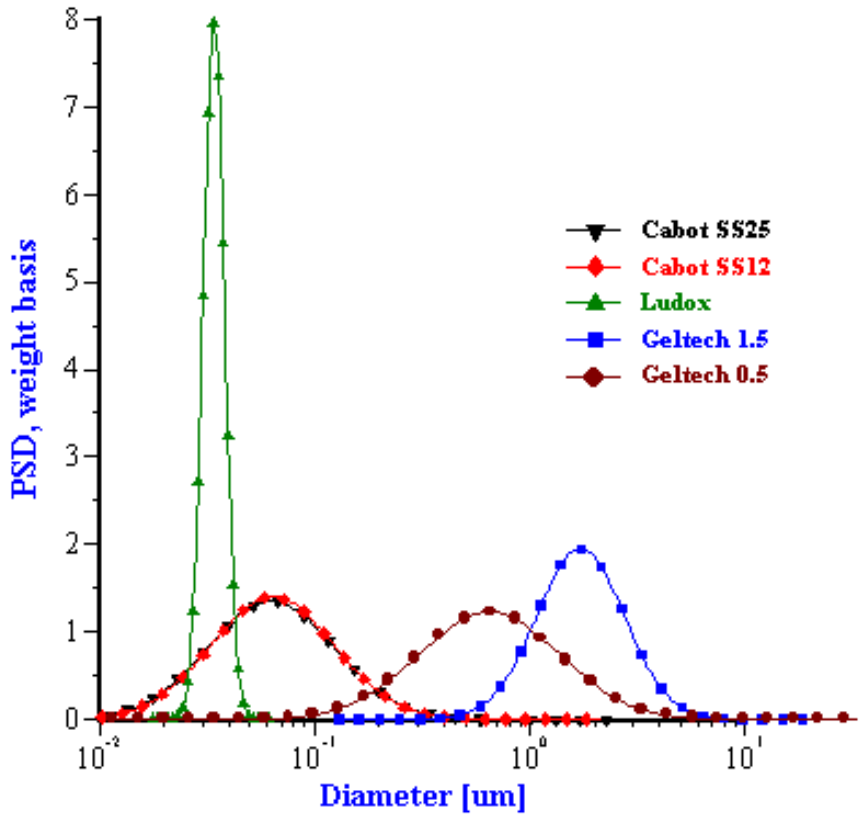
CMP Size Data



Raw Data



Particle Size Distribution

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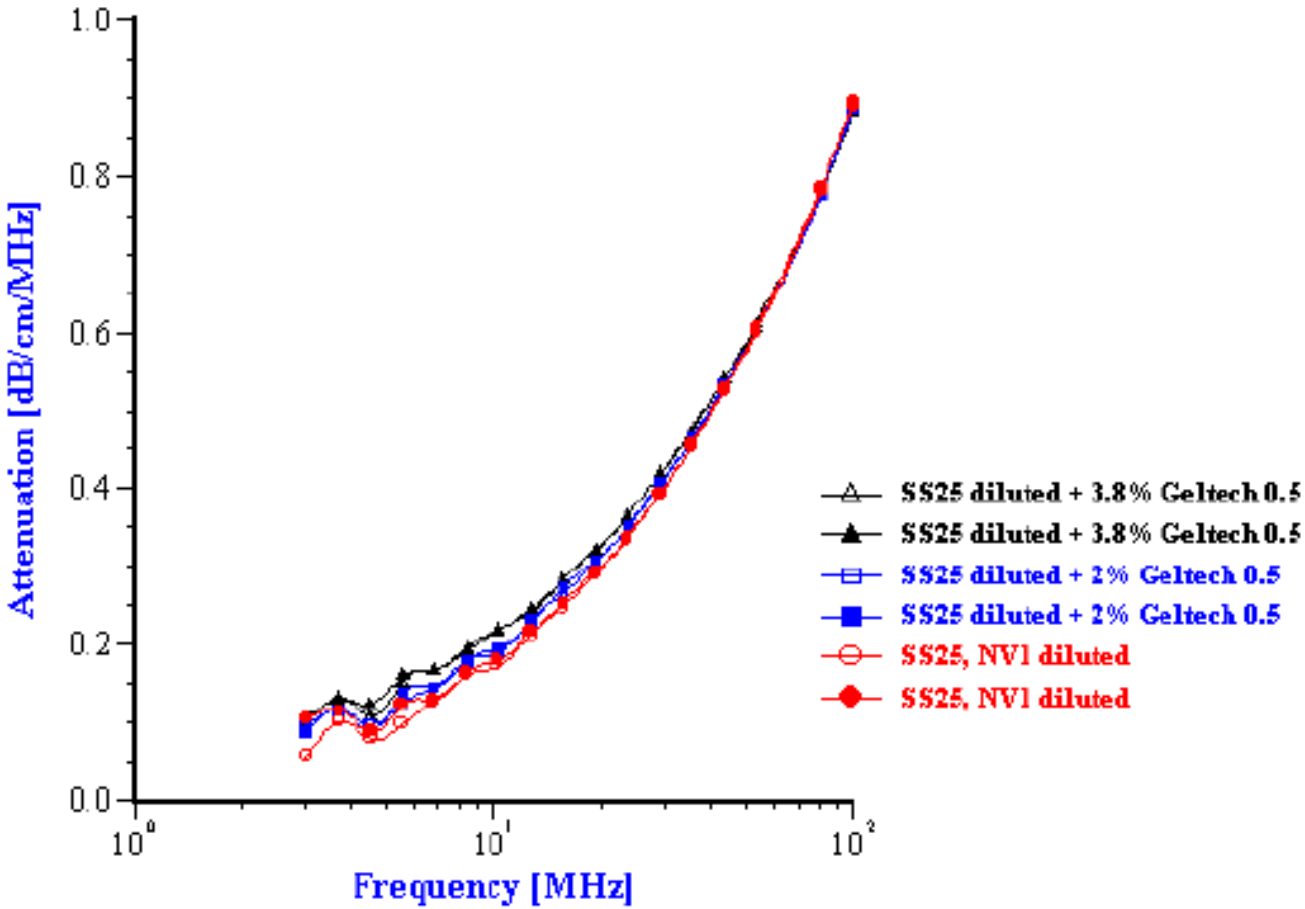
CMP Addition Test: Raw Data



SS25 with various additions of silica Geltech 0.5

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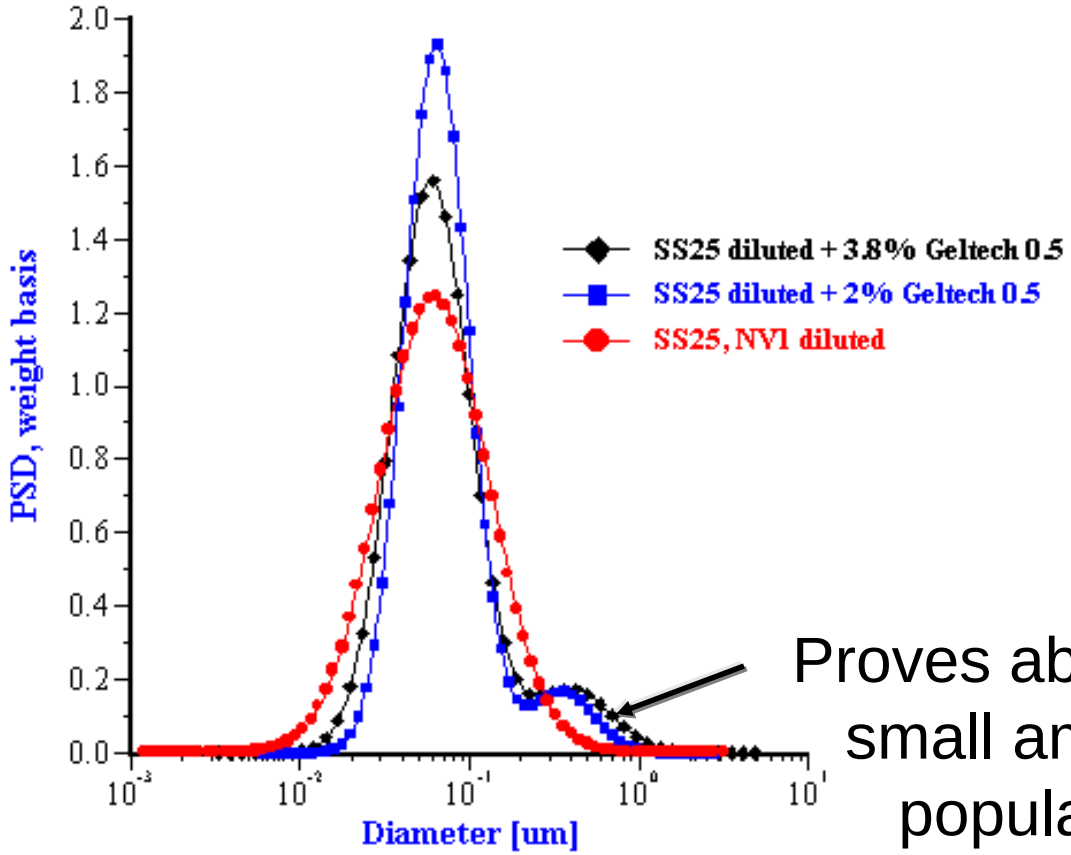
CMP Addition Test: Size Results



Proves ability to detect small amounts of second population

10/18/98 13:40:24 Graph1

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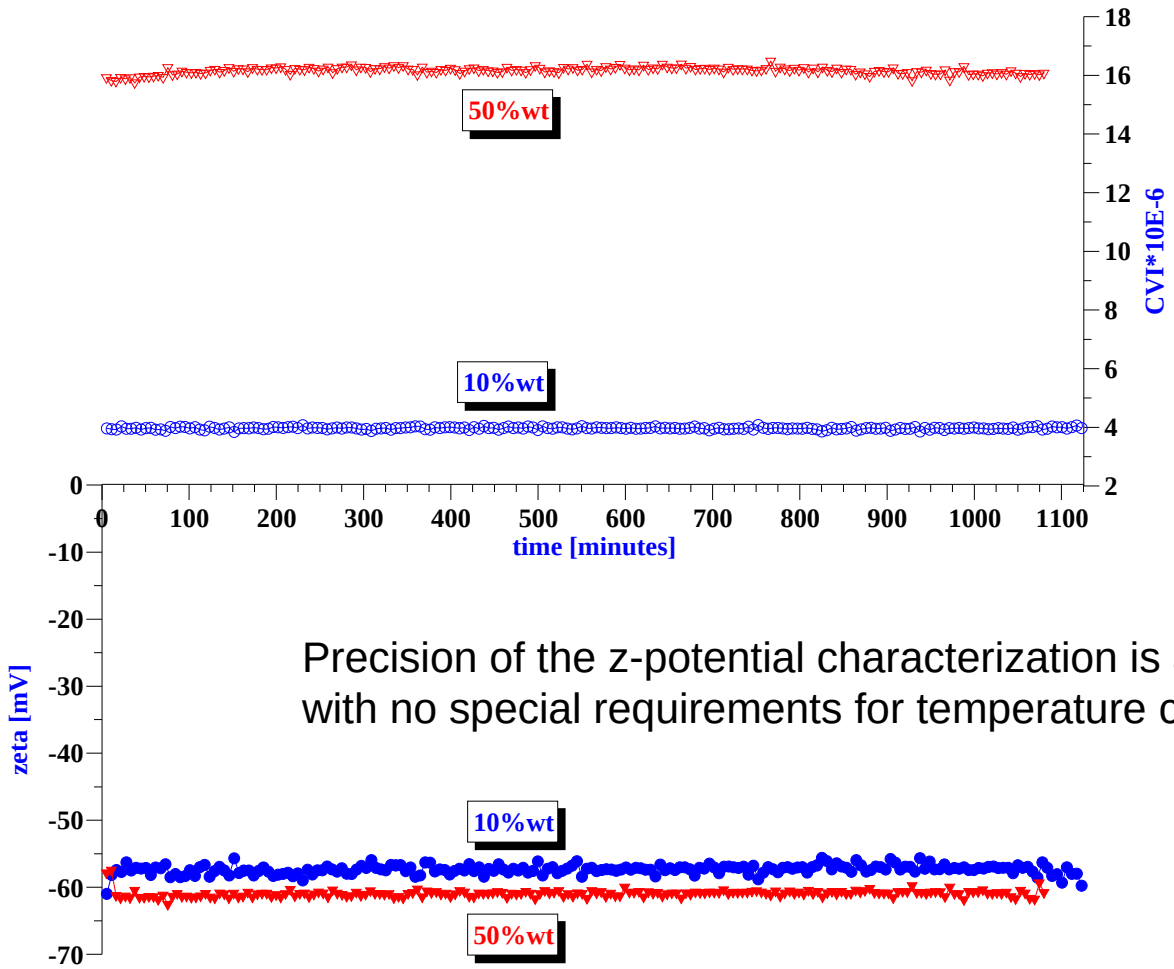
CVI & z-potential for silica CMP

200 continuous measurements



Precision of the z-potential characterization is about 0.2 mV with no special requirements for temperature control.

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Nanoparticles: Zinc Oxide

		DT Series
	Particle Characterization Analyzer	AN171
	Applications Note	Nano-particles using Acoustics

MONITORING NANO-PARTICLES IN THE PRESENCE OF LARGE PARTICLES USING ACOUSTICS

POWDER Name, Manufacturer	Median size, microns	Cum % of nano-particles <100 nm
Zinc oxide, 99.5+% by Acros Organics	0.273±0.01	11.0±1.4
Zinc oxide, reagent ACS by Acros Organics	0.430±0.02	7.0±0.5
Z50-500 USP powder packaged by Fisher Scientific	0.561±0.017	2.7±0.39
Z52-500 USP powder packaged by Fisher Scientific	0.660±0.037	1.9±0.4
S80249 by Fisher Scientific	0.398 ± 0.001	6.1±0.2
Zinc oxide ACS reagent grade by MO Biomedicals, LLC	0.349±0.017	8.2±2.1
Zinc oxide Polystormor by Mallinckrodt Chemicals	0.223±0.009	19.6±1.8
Zinc oxide Nanopowder by American Elements	0.631±0.1	4.7±2.5

Base

Dopant

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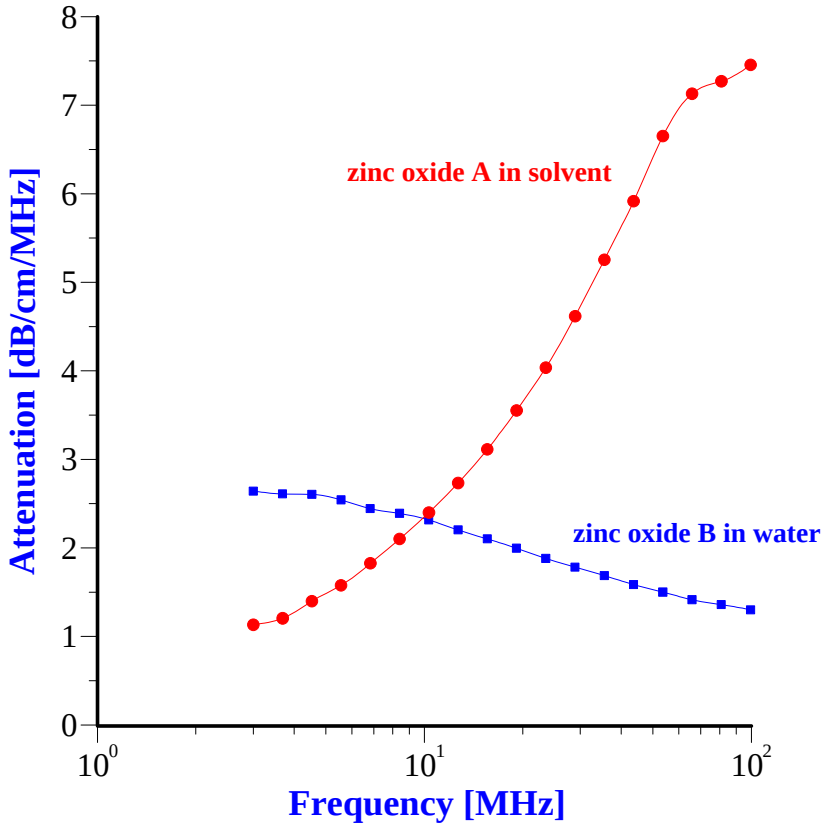
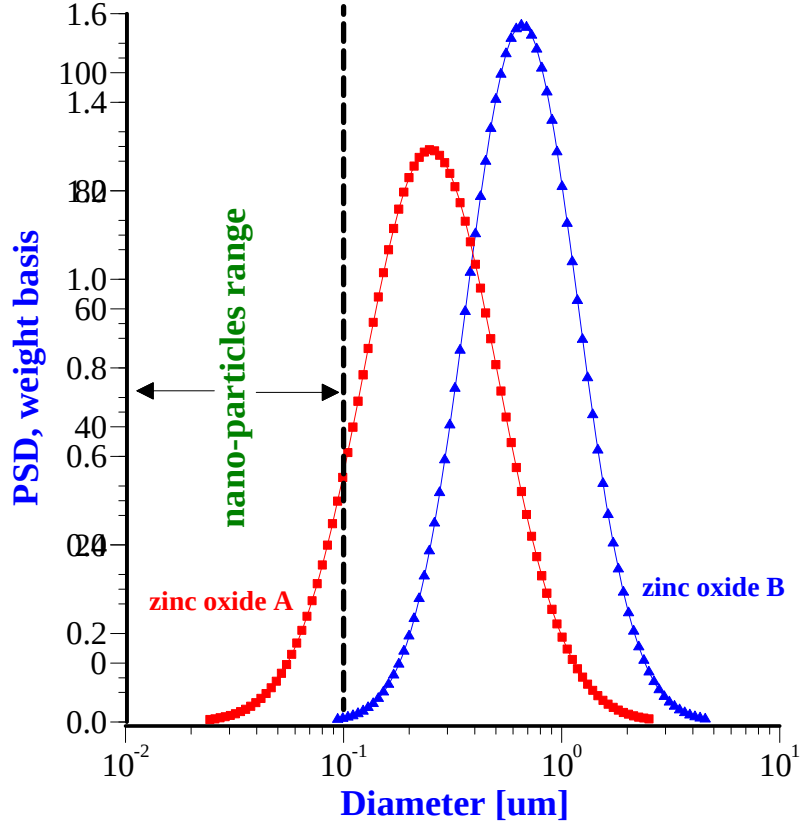
Nanoparticles: Zinc Oxide

< 100nm





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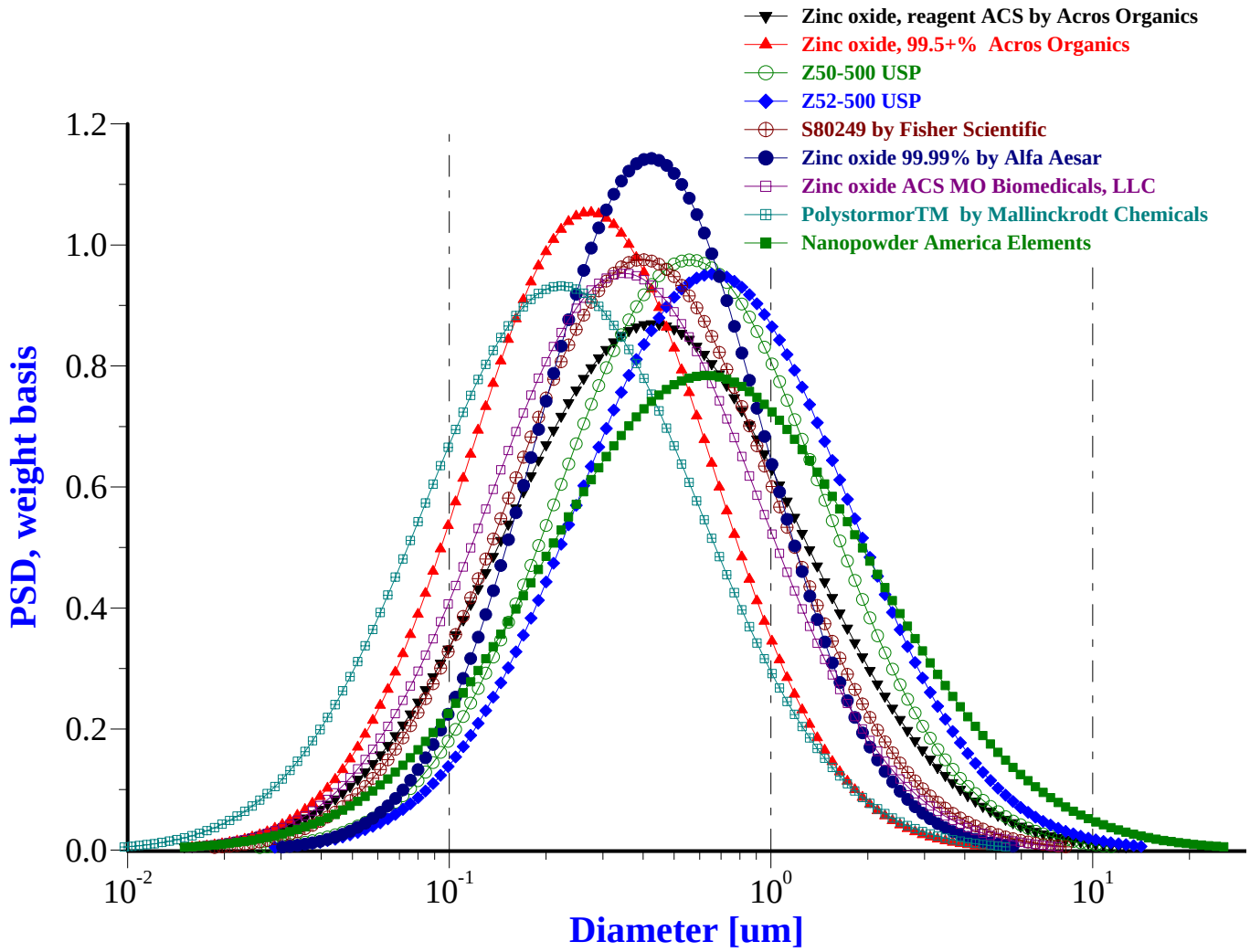
Nanoparticles



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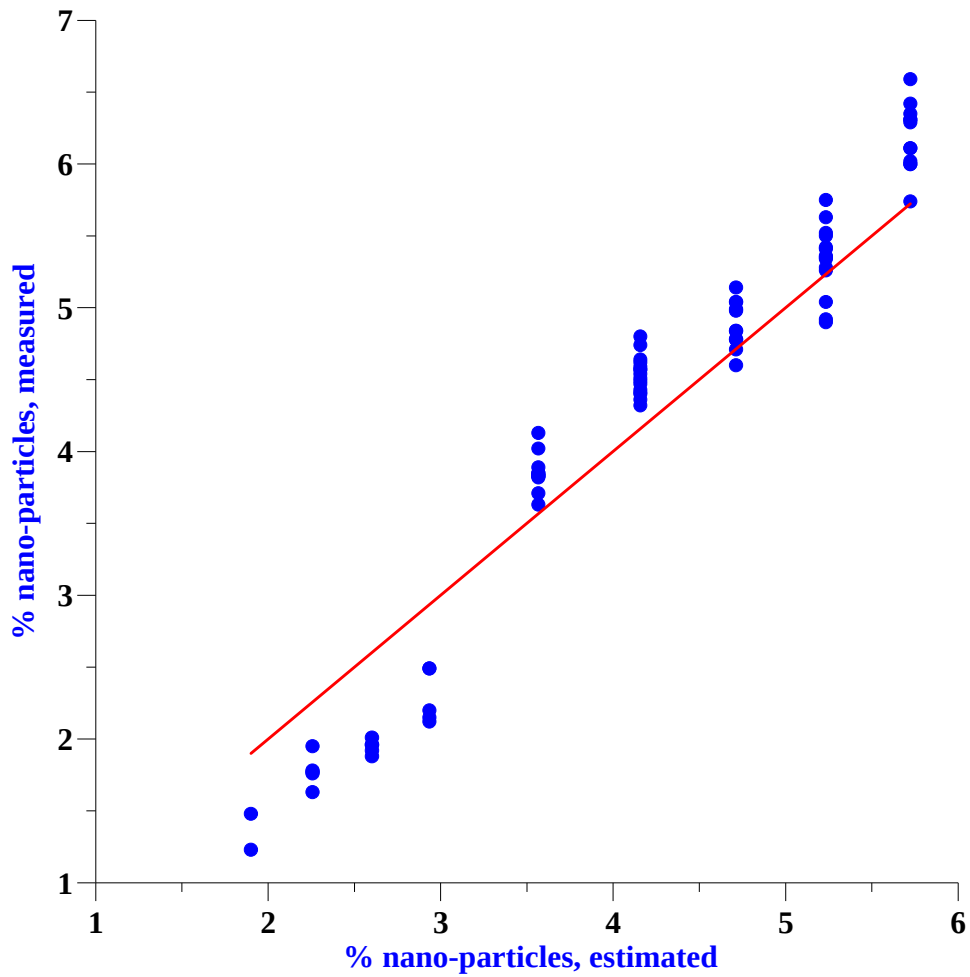
Nanoparticles Detection



Add 223 nm ZnO (dope) to 660 nm ZnO (base)

Plot estimated (x) vs. measured (y) % nanoparticles (<100nm)

Observed deviation ~ 1%

Conclusion: acoustics can detect small amount of nanoparticles, even as smaller second population

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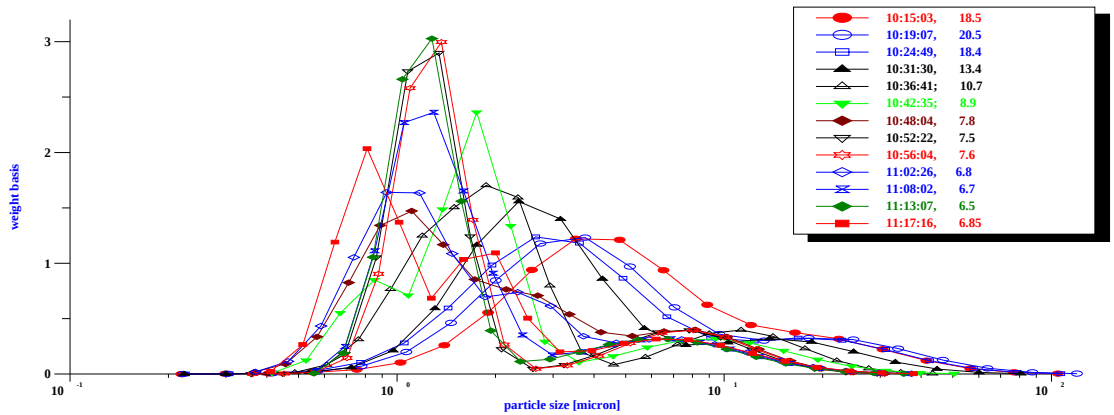
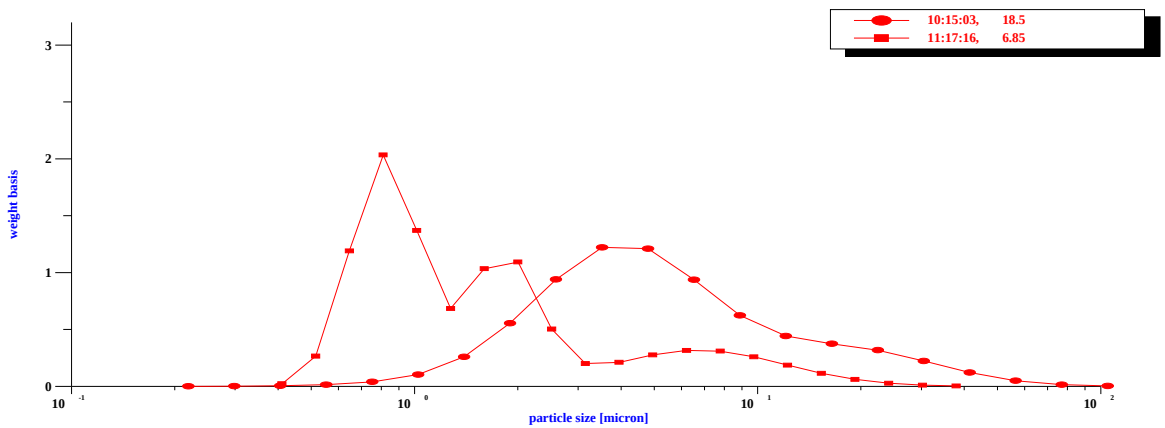
Milling: Simple QC Measurement



20 wt% Alumina

Starting size >20 microns



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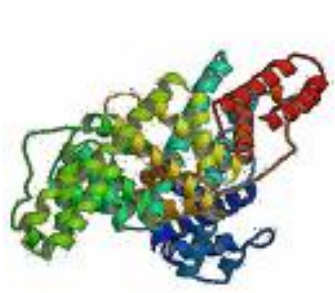
Zeta Potential of Proteins

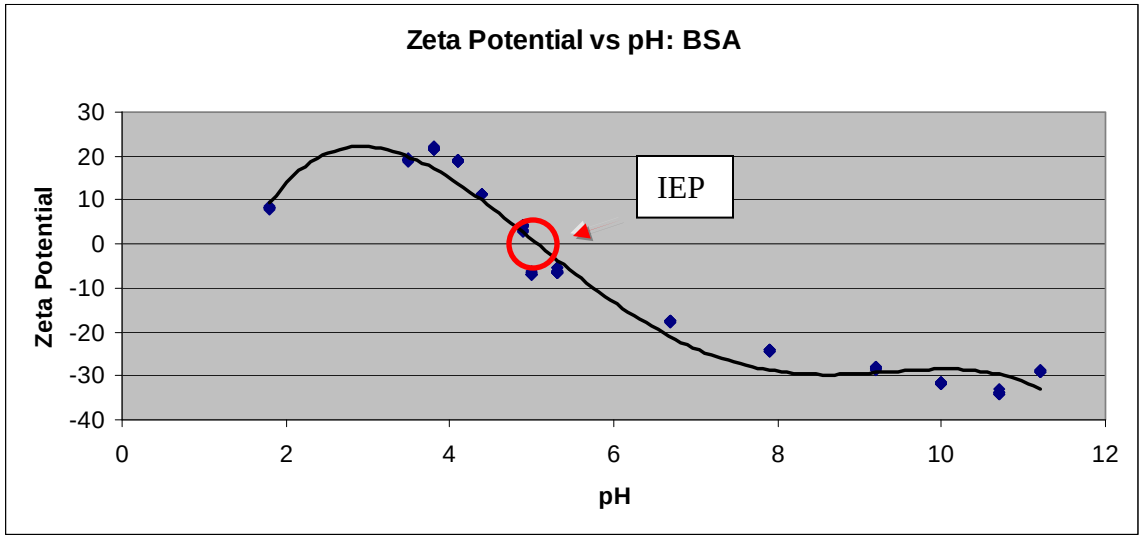
HORIBA

Particle Characterization Analyzer	DT-Series
Applications Note	AN184
	Zeta Potential of BSA

Zeta Potential of Bovine Serum Albumin (BSA) Protein



pH	CVI	Zeta	STD
1.8	157,701	8.2	0.17
3.5	365,881	19.1	0.24
3.8	415,370	21.6	0.26
4.1	363,881	19	0.08
4.4	218,582	11.4	0.07
4.9	72,347	3.8	0.62
5.3	104,411	-5.4	0.06
6.7	329,171	-17.6	0.11
7.9	453,600	-24.2	0.15
9.2	526,892	-28.2	0.15
10	593,132	-31.7	0.29
10.7	634,293	-33.9	0.4
11.2	541,855	-28.9	0.2



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Conclusions

- Particle size without dilution for concentrated (> 1wt %) dispersions
- Zeta potential without dilution for concentrated (> 1wt %) dispersions
- Automatic titration of pH, surfactant conc., etc.
- Micro rheology
- Colloids, nanoparticles, emulsions, dispersion stability

Thank-you

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