

*14 October 2015 – KIT – Karlsruhe (Germany)*

*BELBAR Training Course:*

*“Swelling clays: From compacted bentonite to clay colloids in the context of nuclear waste disposal”*

# **Dynamic Light Scattering - Photon Correlation Spectrometry (PCS): Colloid Size Measurements**

**T. Missana (CIEMAT)**

# Colloids

The word colloid comes from the greek κολλα (glue). The chemist Thomas Graham started investigating colloids in 1860.

*“For some the word **colloid** evokes the imagination of things which are poorly defined with regard to their shape, their chemical composition and their physical properties, and which are unsteady concerning their chemical behavior, i.e., **things which are mysterious and not controllable**”.*

*Hedges, 1931*

1  $\mu$ m

# What does “colloid” mean (at least for us) ?

A colloid is a (organic/inorganic) particle with a size between 1 nm and 1  $\mu\text{m}$  suspended in a fluid.

Better «Colloidal System»: micro heterogeneous system with two phases:

- (1) phase with microscopic size («particles», from 1 nm to 1  $\mu\text{m}$ )
- (2) continuous phase (dispersant).

Smectite Clay



## Environmental studies + NPs



Silica



Clays



Humic Acids



Alumina



iron oxides



bacteria

# Importance of Colloid Size

Particle size is one of the most important factors to understand the properties of colloidal systems. It is strictly related to the chemistry of the system and surface charge.

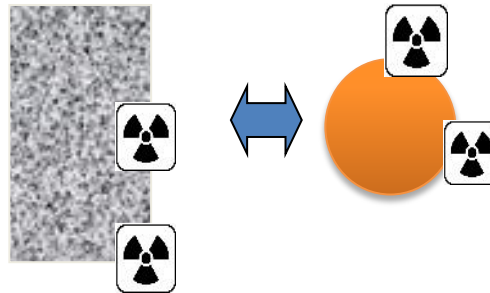
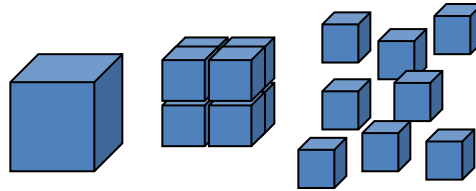
Small particles: Increase in  
surface area



Increase in reactivity  
(adsorption)



Contaminant  
transport



Inmobile phase

Mobile Colloidal Phase

They can move  
faster than water

In transport: Brownian motion, sedimentation, filtration (pores o fractures), etc..

# Examples of mechanisms associated with size (extreme)

$$V_s = \frac{2}{9} \frac{r^2 g (\rho_P - \rho_F)}{\eta}$$

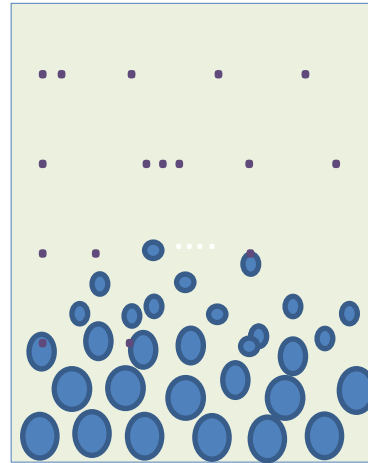
Settling Velocity

$k_b$  = Boltzmann constant  
 $T$  = temperature  
 $r$  = particle radius,  
 $\eta$  = liquid viscosity:  $\rho$  = density

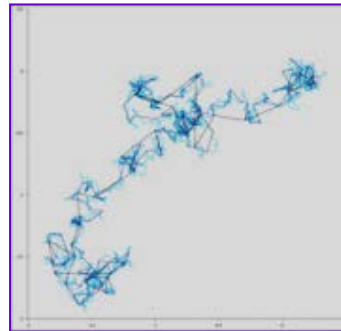
$$D = \frac{k_b T}{6\pi\eta r}$$

Brownian Motion -  
Stokes-Einstein equation

$g$   
↓

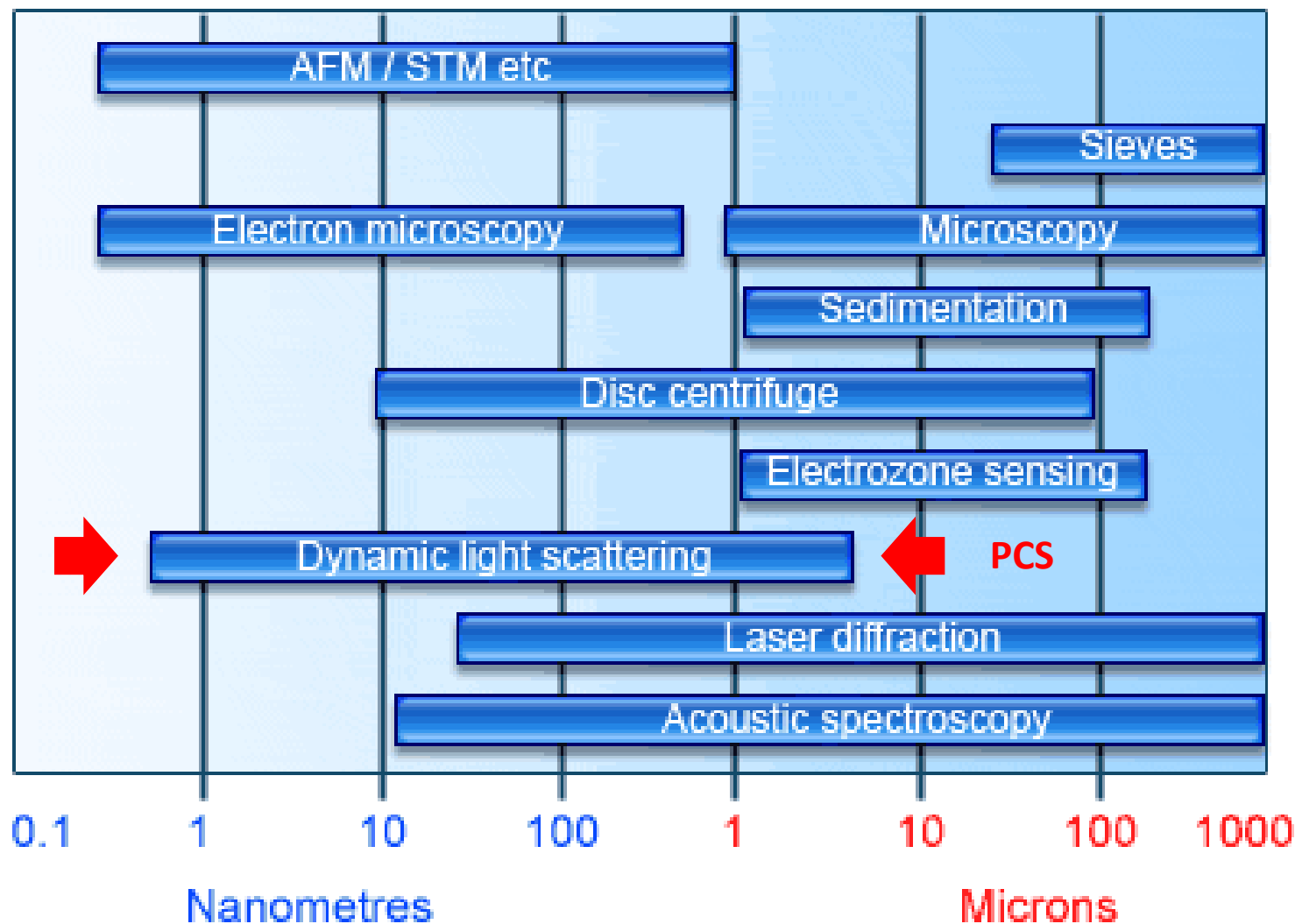


- **Sedimentation** (gravity effect) depends on particle size.
- The smallest (colloids) are able to remain suspended in solution, the biggest deposit and “disappear” from solution.



- **BM** : first observed in 1828 by Robert Brown (pollen in fluid). Diffusive motion to the thermal agitation of the fluid.
- The movement of the particles is random (unless a gradient exist).
- Drives other processes (collisions, attachment, filtration, ...)

# Technique selection for colloid analyses



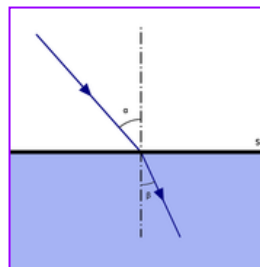
Direct and  
indirect  
methods

Advantages/  
Drawbacks

# Colloids and light

Optical properties very important for development of colloid characterisation technics.

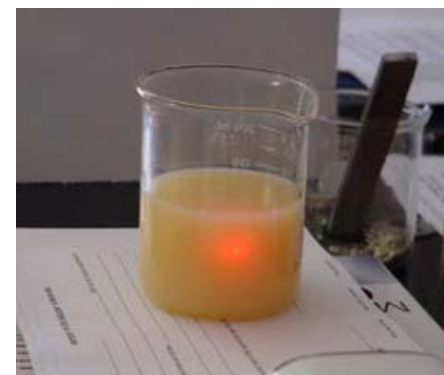
A true solution does not affect light propagation. Only a change of velocity can be observed  $v=c/n$  with  $n$  = refraction index.



¿ What does occur with suspended particles are present?

Dispersion of light will occur (scattering), i.e. the emission of light in all the directions (leading to decrease of light intensity at beam direction). The size of colloid is enough to interact with light, they become centres of emission.

Able to distinguish true solutions from colloids ?





## *(Just mentioning)* Light scattering theories

- **1. Rayleigh scattering** elastic scattering of light by particles smaller than the wavelength of the radiation.

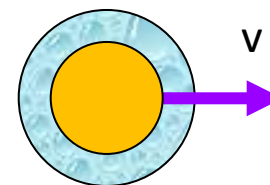
$$I = I_0 \frac{(1 + \cos^2 \theta)}{2R^2} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 - 1}{n^2 + 2} \right)^2 \left[ \left( \frac{d}{2} \right)^6 \right]$$

- **2. Mie theory:** scattering by particles similar to, or larger than, the wavelength of light.



# How does PCS work ?

- It is based on the property of colloids of dispersing light
- It allows an --indirect measurement-- of colloid (hydrodynamic) size.



Hydrodynamic size

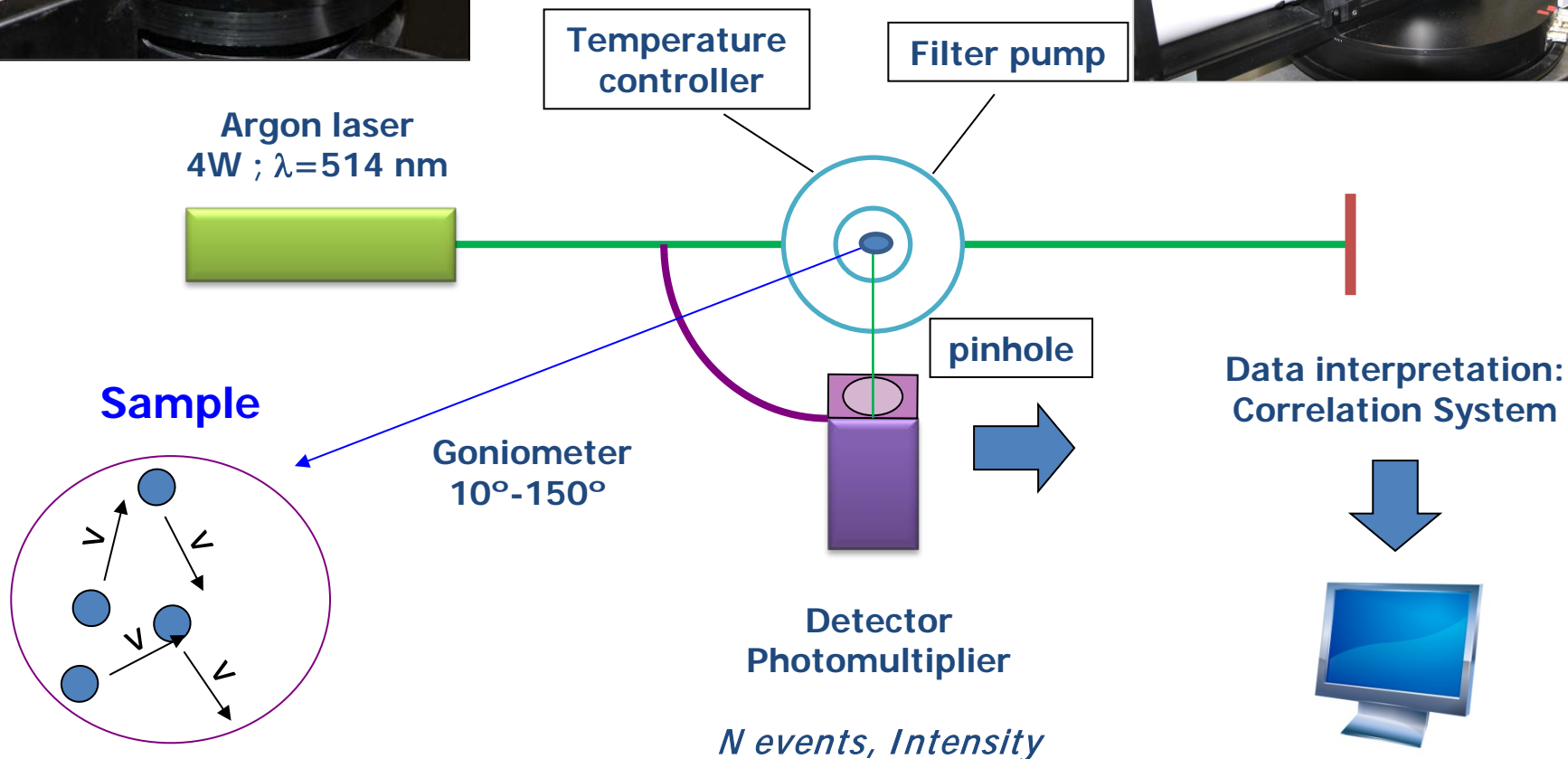
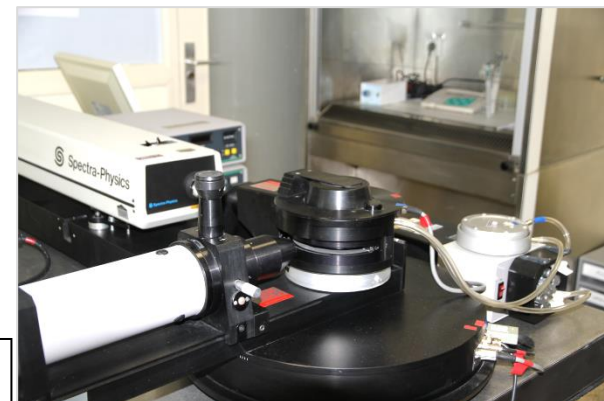
- Colloids are subject to Brownian Motion: if  $D$  is measured,  $r$  can be obtained.
- Small particles moves faster
- Large particle move slower

$$\longleftrightarrow D = \frac{k_b T}{6\pi\eta r}$$

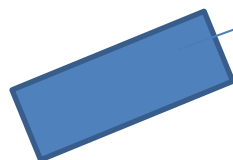
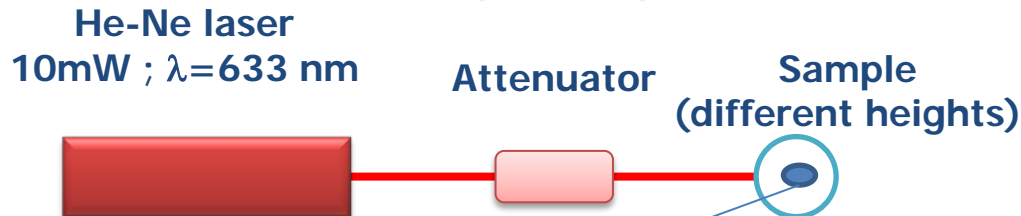
The basic idea is to measure the distribution of velocities of the moving particles, considering the intensity ( $I$ ) fluctuations of the scattered light.



# Schematic of PCS Malvern 4700



# Schematic of PCS NanoS Malvern (Rad.lab)



Data interpretation:  
Correlation System



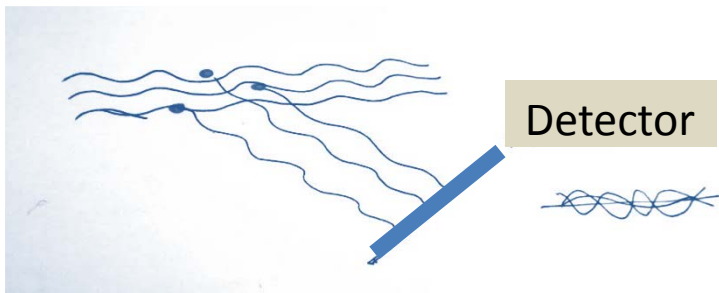
173° (Backscattering)



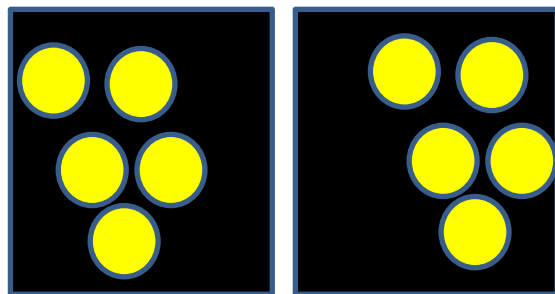
- Less travel within the sample; Minimum effect of multiple scattering (180) --- High concentrated samples
- Larger (contaminating) particles mainly scatter in the fwd direction.



# PCS: Correlation methods



- The light scattered from the sample is collected by the **detector/ photomultiplier**. The photons are counted by the correlator during a “sample time”. Due to particle movement light intensity is subject to **fluctuations**.
- The fastest particles (smallest) have shorter fluctuation times. For the largest the opposite is true.

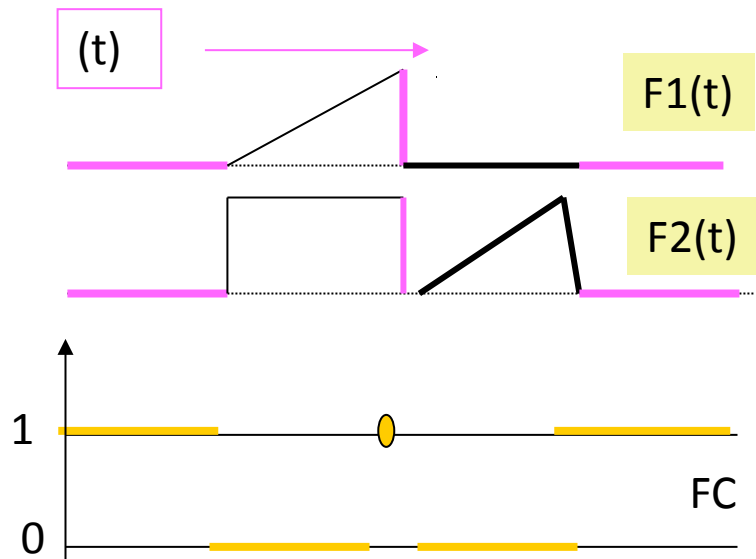


→  
 $T+t$



The rate of these light fluctuations is used to determine the size distribution of the particles, by correlation (and statistical) methods.

# Correlation Functions



- A correlation function (FC ( $F1(t)$ ,  $F2(t)$ )) indicates if two functions have common properties within a certain period of time.
- It indicates the “degree” of similarity –
- $0 < FC < 1$  : perfect correlation = 1 / no correlation 0.

- In our case, a digital correlator analyse the fluctuations in different channels, corresponding to different times  $t$ ,  $t+\tau$ ,  $t+2\tau$ ,  $t+3\tau$ , ...
- Information stored and compared with the following: autocorrelation)

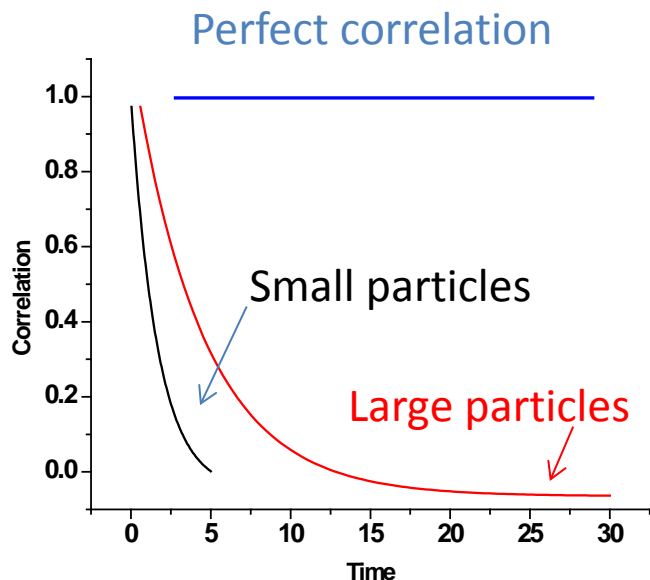
- If  $\tau$  is short ( $t$  near 0) the changes registered are limited as the particles cannot have moved a lot. This in a statistical term, the position of the particles will be highly correlated (1)
- Contrarily, at long times ( $t=\infty$ ), the position of the particles will not be correlated at all (0).



# Correlation functions



If can be shown that in the case of monodispersed spherical particles the autocorrelation function (G) is exponential.



$$G(t) = \langle I(t)I(t + \tau) \rangle = \exp(-t \cdot \Gamma)$$

$$\Gamma = D \cdot q^2$$

$$q = \frac{4\pi \cdot n}{\lambda_0} \sin\left(\frac{\theta}{2}\right)$$

$$r = \frac{kTq}{6\pi\eta\Gamma}$$

Experimental conditions  
and Stokes – Einstein  
equation

From the fit of the correlation function the size distribution (by intensity) can be obtained.

# Size distributions (Cumulant method)

- Cumulant method is commonly used (for monodisperse, spherical particles) to obtain size parameters from the correlation function.
- The method give the **mean size** and the **polydispersity index (PDI) of the particles**. Intensity PSD, not mass or number mean.
- Other methodologies available.

In the cumulant method, the Ln of correlation function is fitted to a (second order) polinomial.

$$\ln(G) = a + bt + ct^2 + Dt^3 + \dots$$

**a** = related with signal noise  
**b** = second cumulant or Z-average diffusion coefficient (conversion to size knowing dispersant viscosity and instrumental conditions)

$\frac{2C}{B^2}$  = Poly (distribution of the particles from 0 to 1)



# Size distributions (Cumulant method)

Cumulant method, which gives the mean size and the polydispersity index.

In the correlator: 
$$G(\tau) = \langle N \rangle^2 \left( 1 + b \exp\left(\frac{-\tau}{t_c}\right) \right)$$

$N$  = photons/time

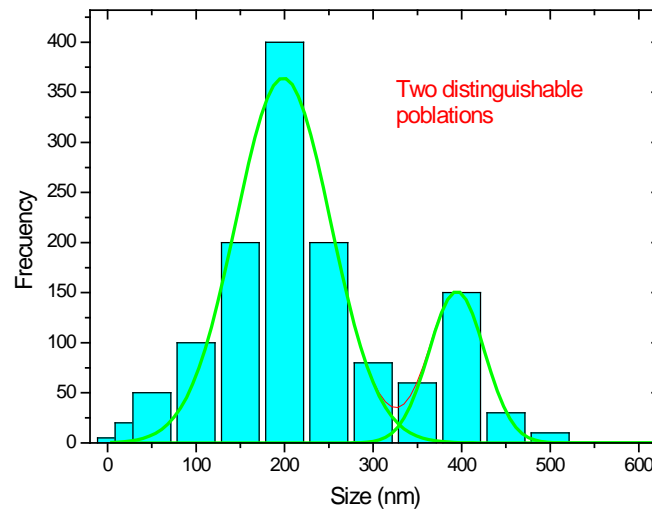
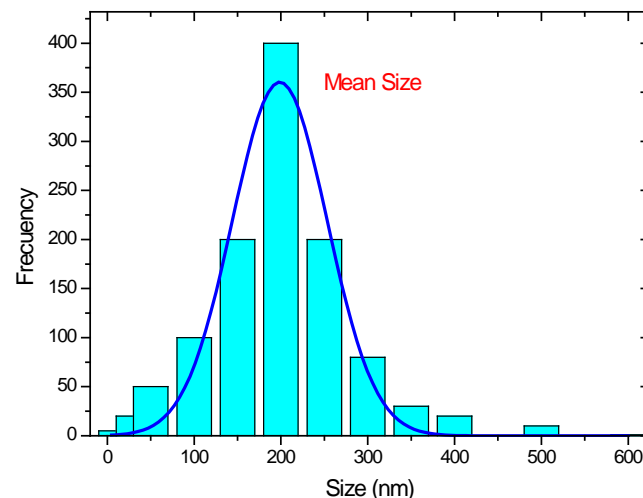
$\tau_c = 1/\Gamma$  = decay time (D, q)

$\tau$  = sample time

For a suspension with particle of different size the previous equation does not longer applies, therefore it has to be generalised:

$$G(\tau) = \langle N \rangle^2 \left( 1 + b |g(\tau)|^2 \right)$$

In the cumulant analysis the correlation function  $g(\tau)$  is analysed by fitting a second order polynomial.

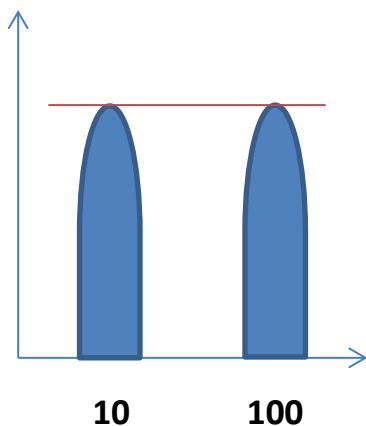


# Intensity, volume, number

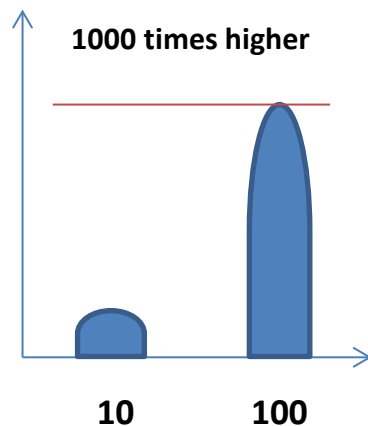
Measurements give Intensity based Particle Size Distribution (PSD). Others may be calculated (Mie theory). Attention must be paid when data are compared.

Main differences supposing to have a sample with the same number of particles of two sizes (10 nm and 100 nm).

Number based PSD



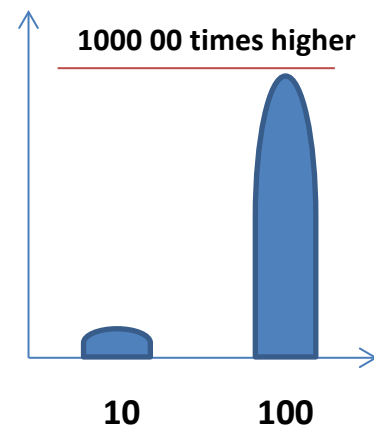
Volume based PSD



$$V = \frac{4}{3}\pi r^3$$

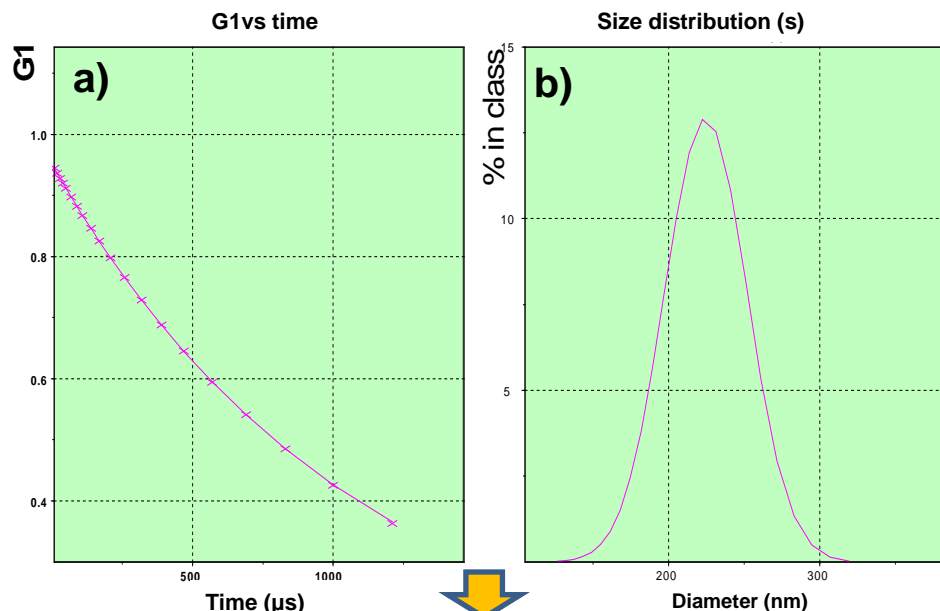


Intensity based PSD



$$I \propto r^6$$

# Size Distribution of latex particles (standard)



c)

Run	KCps	ZAve	Poly
1	680.7	242.9	0.064
2	671.8	238.4	0.080
3	699.8	242.8	0.028
4	684.6	243.7	0.022
5	714.5	243.7	0.063
6	726.0	240.3	0.026
7	723.5	240.3	0.009
8	753.8	238.6	0.082
9	721.8	240.4	0.028
10	721.2	244.5	0.029
Average	709.8	241.6	0.043
+/-	25.2	2.2	0.026

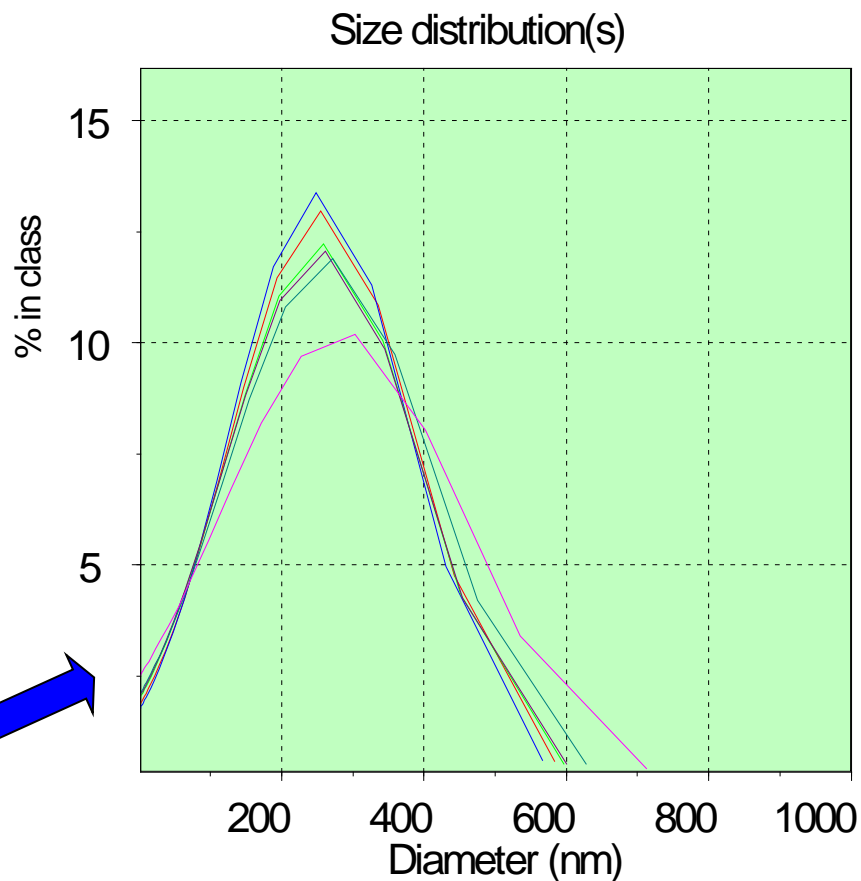
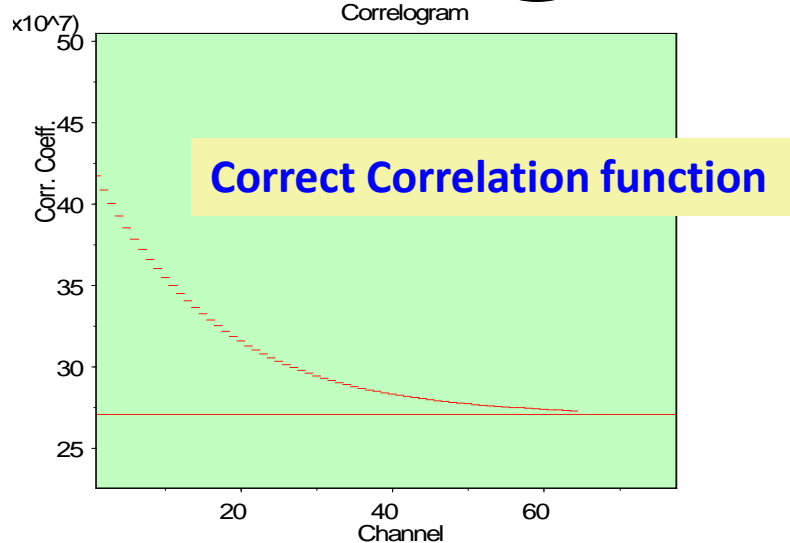
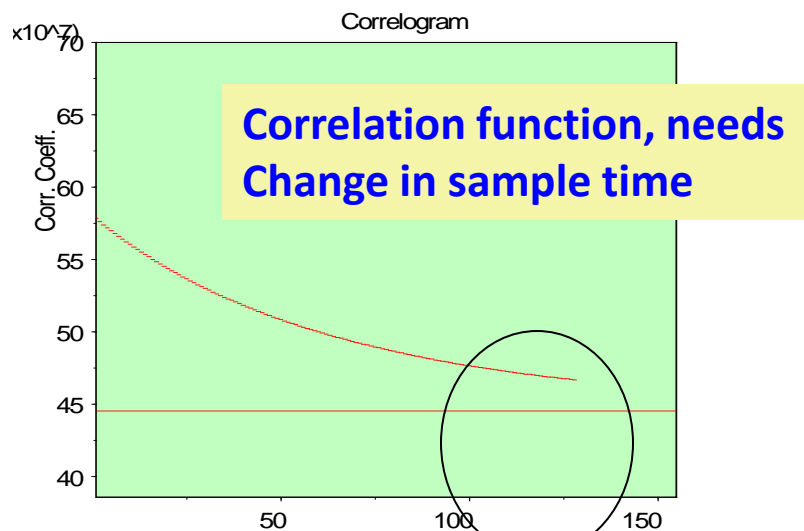
**Polyestirene latex 240 nm**

a) Correlation function (G1);  
b) Size distribution  
c) Results over ten measurements

**Zave = 241.6±2.2**

**PDI = 0.043**

# Size distribution of clay colloids in $\text{NaClO}_4$ ( $5\text{E-}04 \text{ M}$ )



Z-size average:  $263 \pm 11 \text{ nm}$

PDI = 0.3

# Advantages

- This is a versatile technique which allows measuring easily particles with a size between 1 nm to 3  $\mu\text{m}$  (approx.);
- No previous treatment of the sample, suspension directly measured;
- Very good statistic (it can be improved adjusting measurement time, sample concentration, angle, etc). The analysis account for a large number of events.
- Different types of suspensions can be used (particles and fluid);
- Studies as a function of different physico-chemical parameters (pH, I, temperature...);
- Kinetic studies of colloid stability (time-resolved dynamic light-scattering);

# “Drawbacks”

- Important parameter (ej: “*sample time*”) depends on the sample (colloid size, often unknown). Some of the newer instruments are “black box”;
- Correlation methodology is not “intuitive”;
- Data interpretation need the knowledge of refraction index, absorbance etc.;
- Luminescent, fluorescent or highly absorptive samples are not well measurable;
- In polydisperse samples the signal of the large particles “hides” the signal of the small one (intensity is measured). Mean size may appear larger than the real one. Previous sample treatment needed;
- Sensitivity depends on colloid type. Bentonite clay around 1 ppm, the error on size measurement increases drastically, as the measurement is near the detection limit. Concentration maybe still measured.

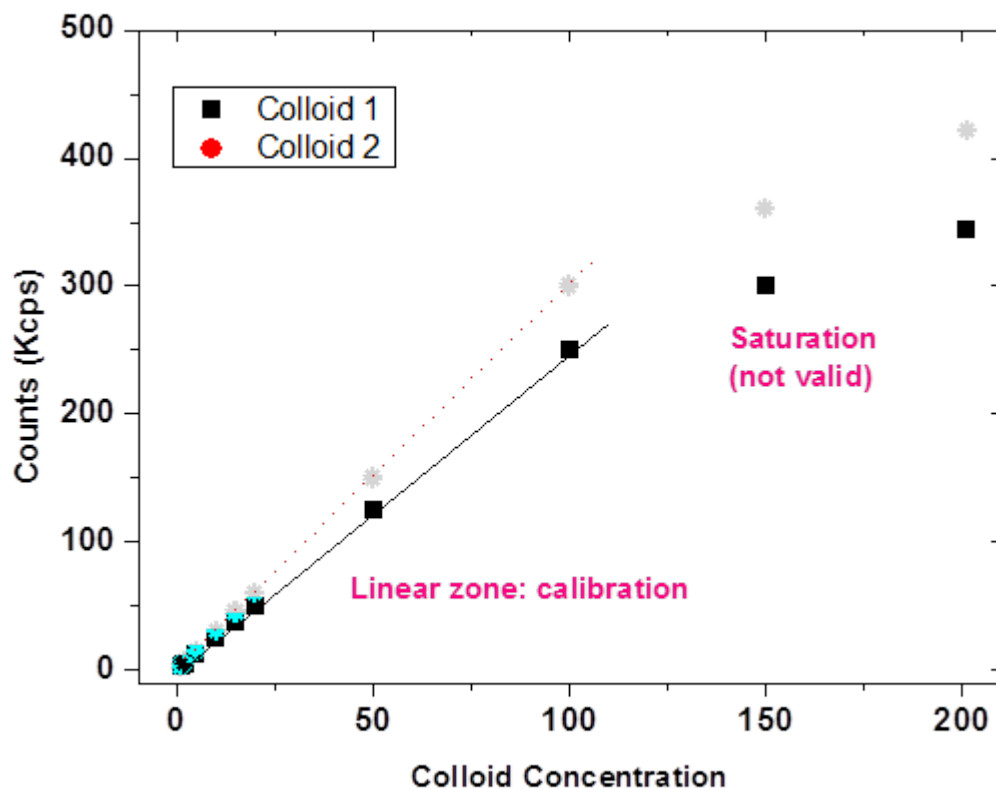
## Take care...

- Cuvette cleanliness;
- Background measurement as reference in the selected experimental conditions (attenuation, height, ... );
- Use standards. Polydispersity of latex ( $<0.1$ ) otherwise bad alignment or other problems may be present.
- Sample concentration: not too low (low scattered light, highly imprecise measurements); not too high (multiple scattering or particle interactions). Concentration to be used depends also on the particle size, as the count-rate (consider enough scattering but also enough particle/volume);
- Comparing PSD data (intensity, volume, number): transformation can be made if the properties of colloids are known.
- Performing “calibration curves” for each colloids very useful for optimizing conditions; perform tests under “comparable” conditions.



# Colloid concentration determination

Photons detected by the photomultiplier (under appropriate conditions) are proportional to colloid concentration. Experimental methodology to obtain results in “mass” starting from Intensity measurements.



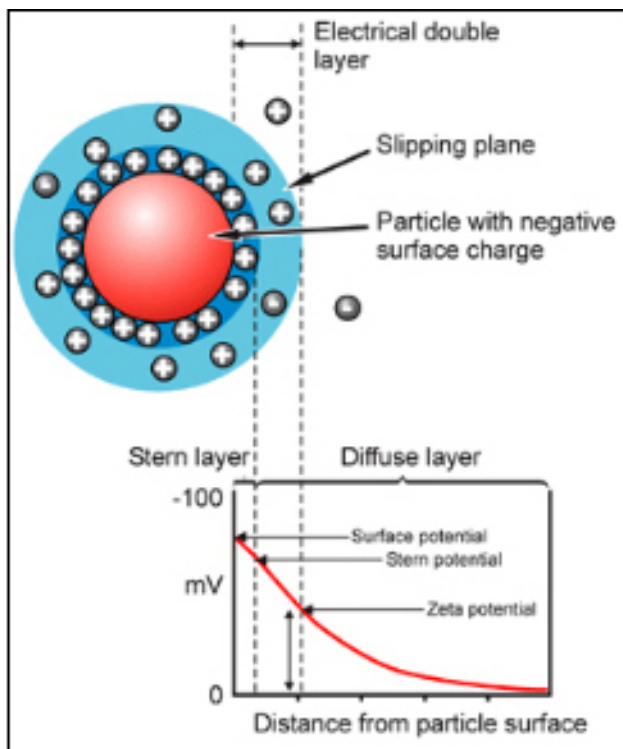
Calibration curves needed, because the response is different for different types of colloids.

The approximation has to be used in the linear zone. Saturation of detector, dead.time.

Cannot be used for samples whose nature is unknown.

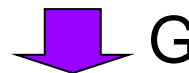
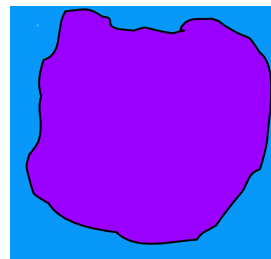
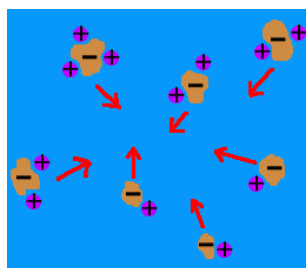
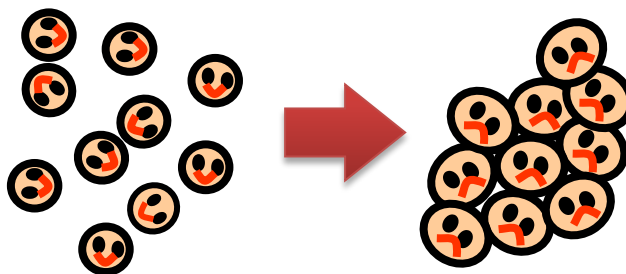
# Colloid stability studies

Electrical double-layer, surface charge and colloid size.



Electrostatic repulsion due to a the potential barrier.

After colloid collision a probability that attachment occur exist (depending on the potential).  $W$  = stability ratio ( $n$  collisions /  $n$  attachments).

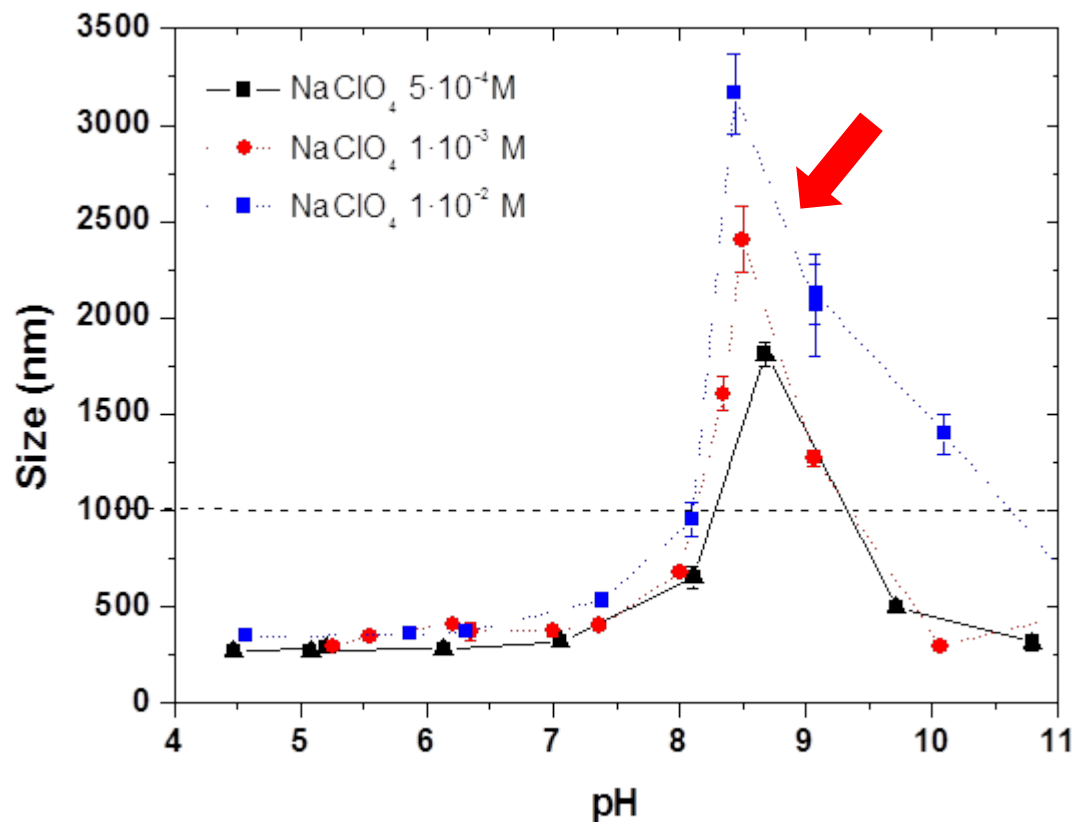


COAGULATION  
PROCESS

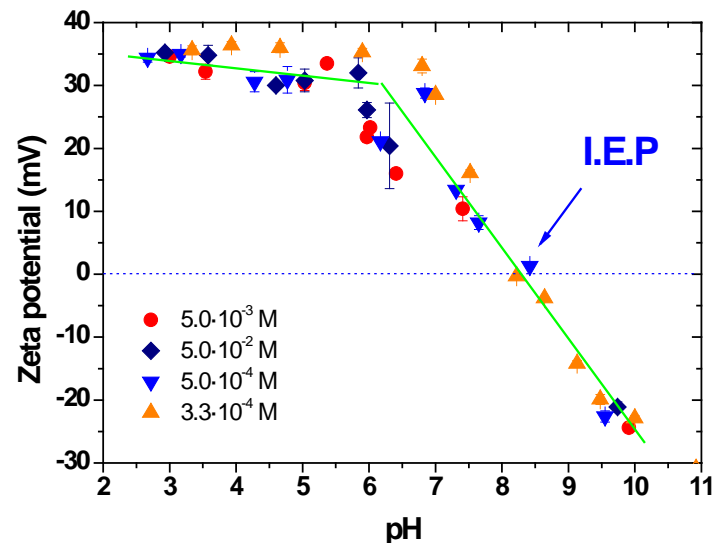
MEAN SIZE  
INCREASES

Sedimentation

# Point of zero charge determination.

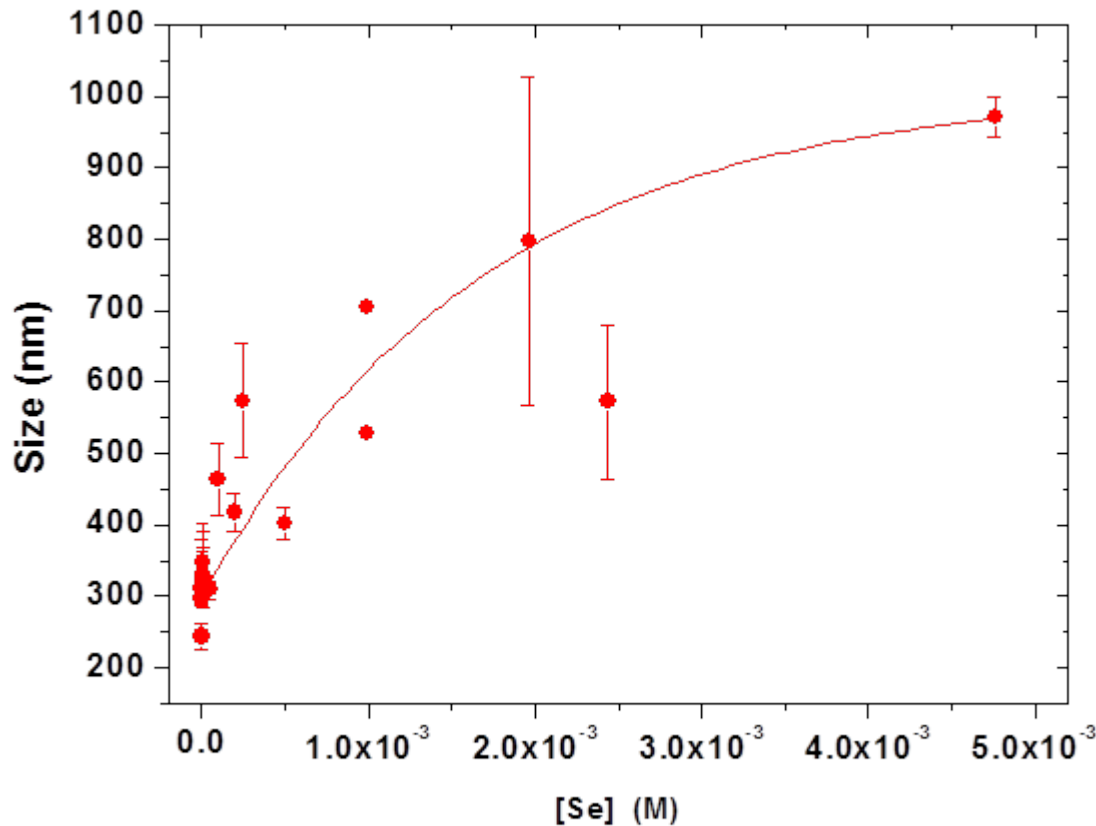


Size of the alumina NPs as a function of pH



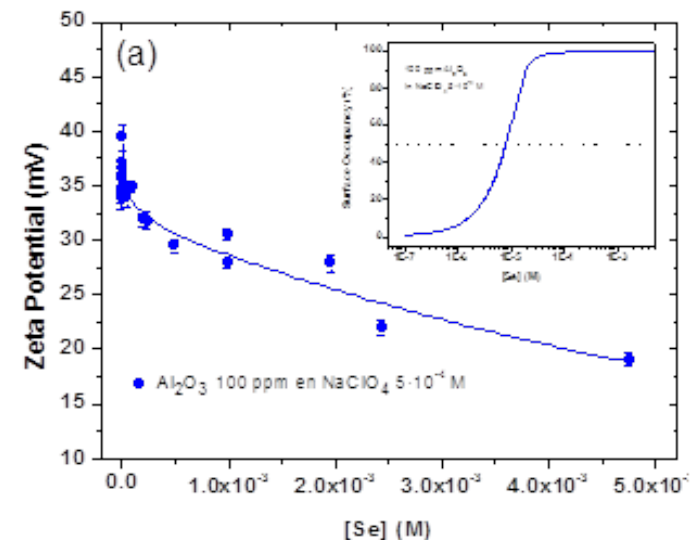
$\zeta$ -potential of the alumina NPs. IEP at pH 8.5

# Effects of specific interactions (sorption) on colloid stability



Size of the alumina NPs as a function of Se content

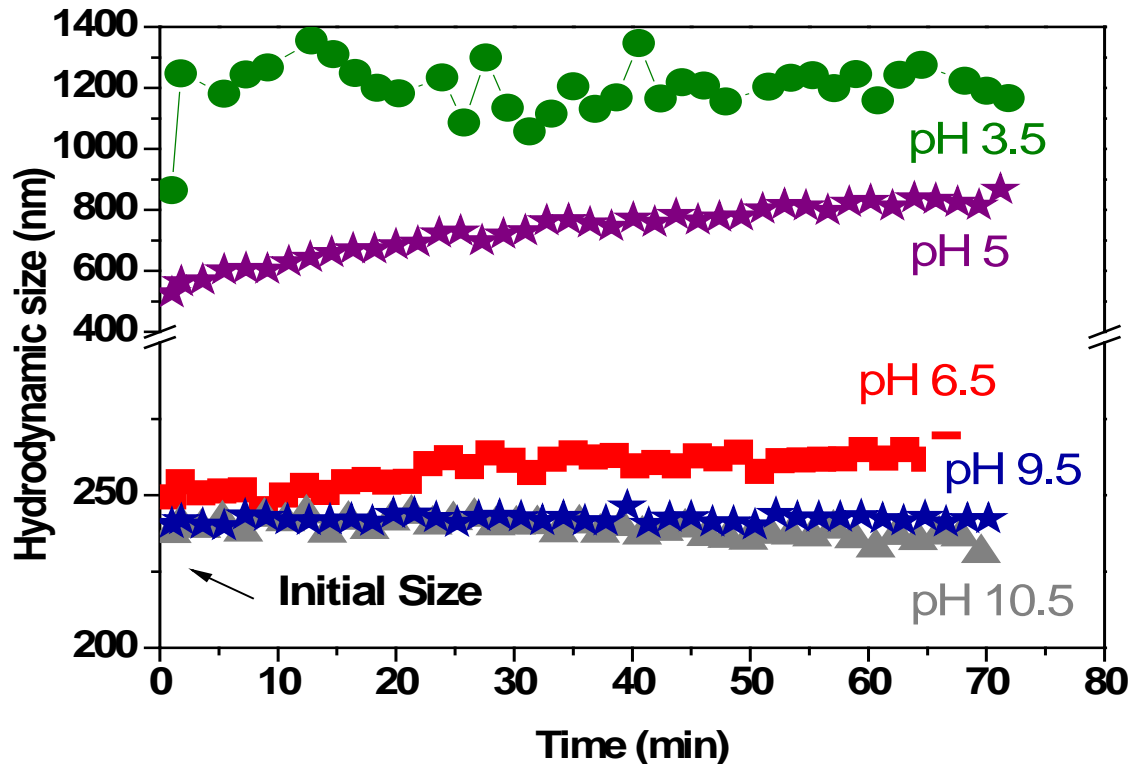
Alumina stability at pH 4.5 adding a sorbing anion (Se)



$\zeta$ -potential of the alumina increasing Se content.

# Kinetic of colloid aggregation

## (Time-resolved light – scattering)



Smectite clay colloid aggregation as a function of pH.

Fast aggregation under acidic conditions;

Stability under alkaline conditions.

**Thanks for your attention !!**