Our innovative solutions for **nanoparticle size** measurements

VASCO™ γ series

Batch

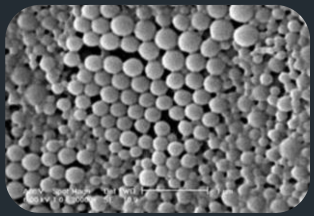
Opaque & concentrated media

VASCO™ FLEX

In-situ

"bring the measurement to your sample"

Nano-Materials & Nanoparticles : a new era in science and industry



- Promise of major technologic, economic and societal impacts
- NPs and NMs already in the field : cosmetics, batteries, paints, inks, food, medicines, advanced coatings, aerospace, etc….. And it is just the beginning!

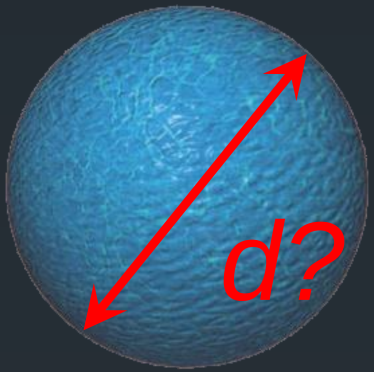
    

- Booming demand for advanced materials and application requires to scale up production installation (incoming material control, process control, quality control)

➢ **New monitoring tools required to migrate NPs from R&D labs to pilot plant and mass production!**

Sometimes size matters… In particular for NPs!

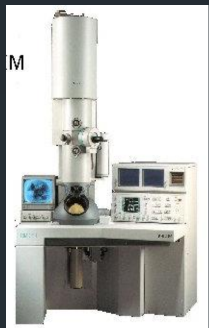
- Related to the specific surface of the particles
- Ability to penetrate membranes or interact with surface
- Aggregation and stability of suspensions
- Functionalization and self assembly capabilities
- Optical, mechanical and electrical properties
- Etc.

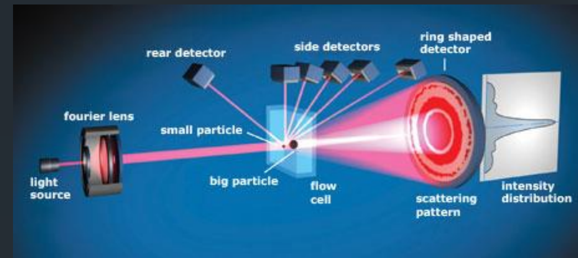


Many mature characterization techniques for particle size:

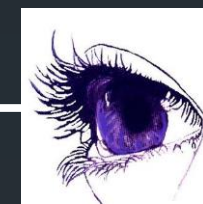
- Electronic Microscopy: TEM,
- Electrozone Coulter counter
- Mass sensing: Differential Centrifugal Sedimentation, resonant mass detection
- Optical : Particle tracking, Laser Diffraction, Dynamic Light Scattering (DLS)

DLS vs. other techniques





Laser Diffraction
(Static light scattering)



0 | 1 nm | 100 nm | 1 µm | 1 mm

SAXS, TEM

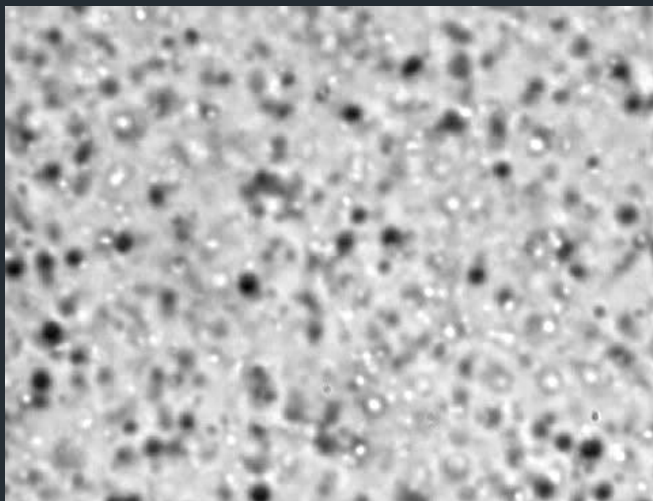
Classical Optical microscopy

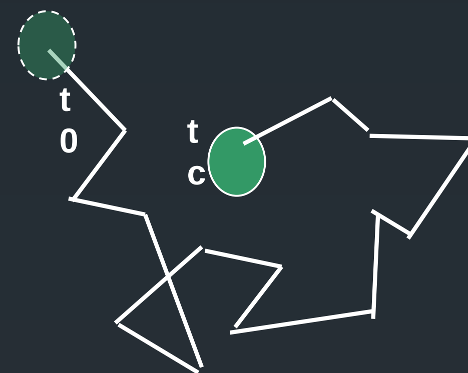
DLS: 1 nm to 10 µm

DLS : 4 decades of size range!!!

DLS uses Brownian motion as a signature of particle size

Brownian motion= Random “walk”





Diffusion coefficient time

$$< X^2(t) > \sim 2\, D\, t$$

L. BACHELIER (1901)

Viscosity *Boltzmann* *Temperature*

NPs:
hard spheres without interactions

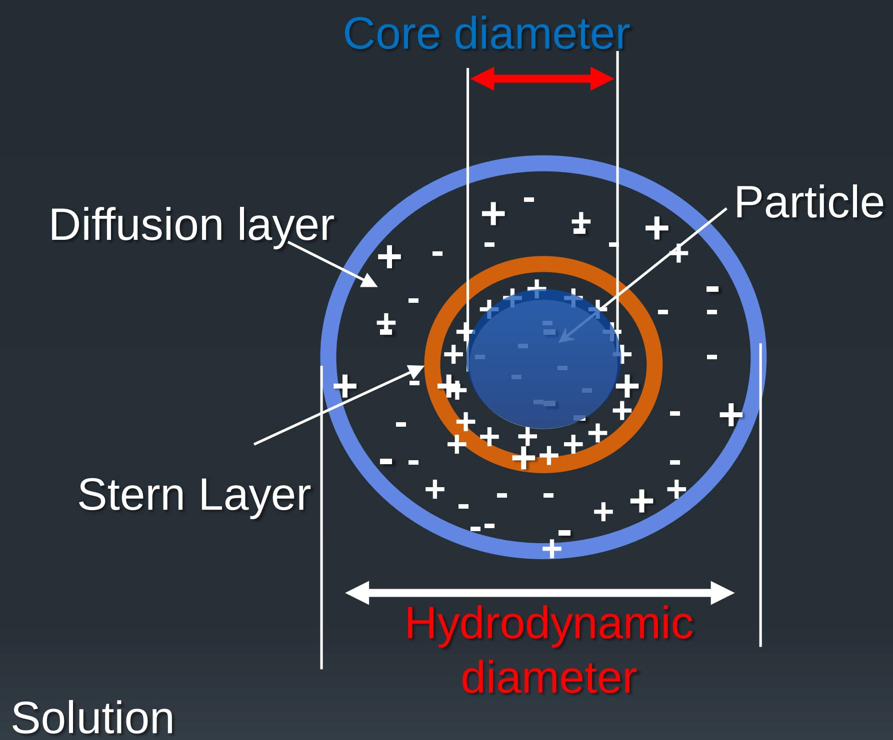
$$D = \frac{KT}{3\pi\eta\, \phi_H}$$

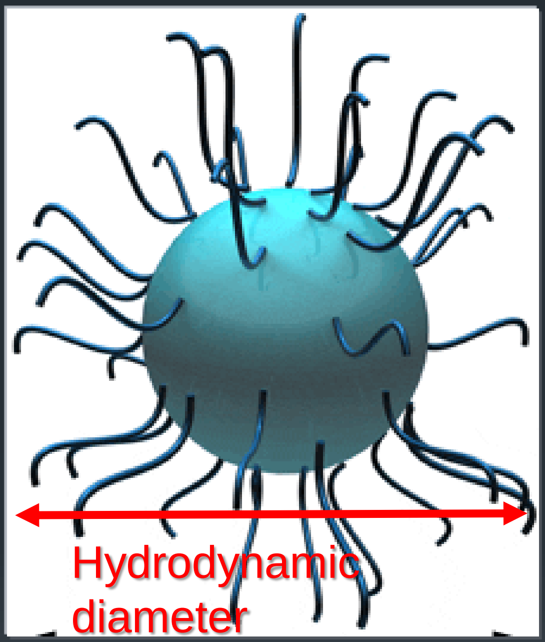
$$\phi_H = \frac{KT}{3\pi\eta D}$$

EINSTEIN (1905)

Meaning of hydrodynamic diameter $\emptyset_H$

Hydrodynamic diameter = diameter of the particle **+** double layer thickness

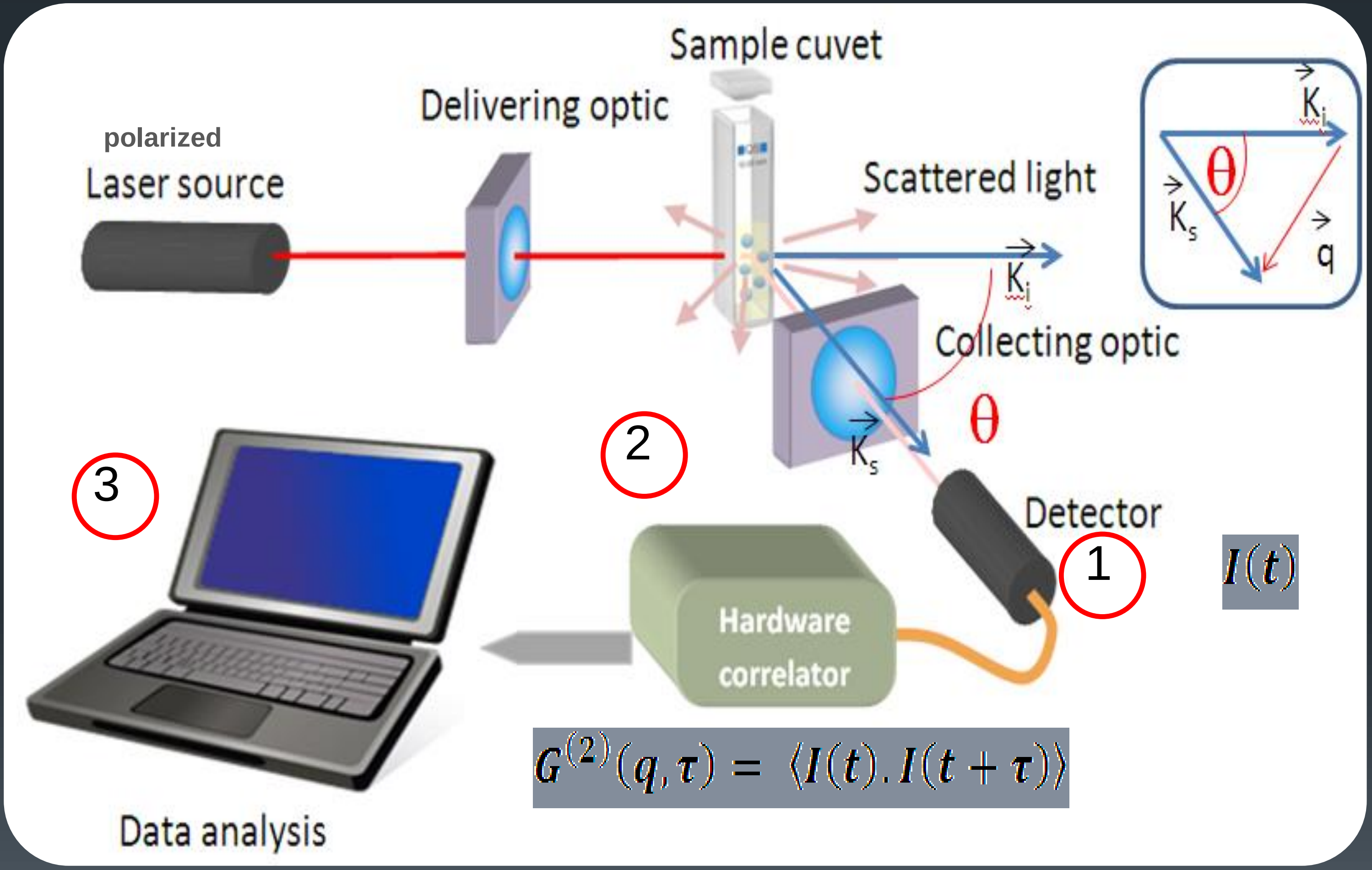




Hydrodynamic diameter is usually > Core diameter (TEM/SAXS) Value by several nm!

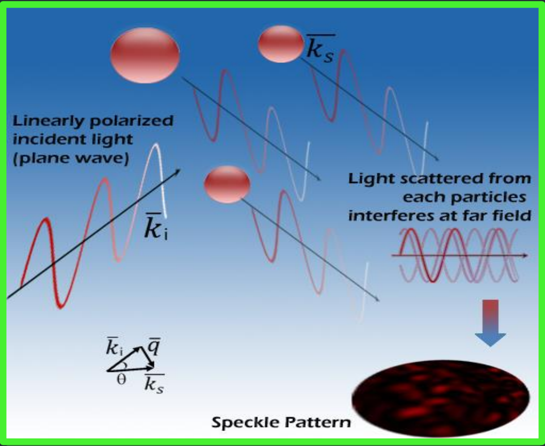
DLS measurement principle:

- Measure light scattering fluctuation to probe the Brownian motion



Intensity measurement and correlogram

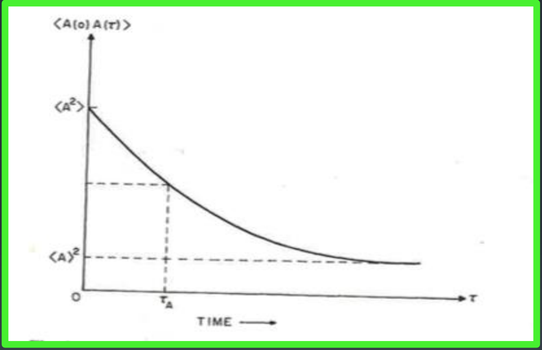
Considering coherent electromagnetic waves scattered and measured at a specific angle (scattering vector $\mathbf{q}=\mathbf{k}_i-\mathbf{k}_s$) :



Detected field and Intensity :

EM field: $E_{tot\_detect}(\omega t)=\Sigma E_i \exp(i(\mathbf{q}.\mathbf{r}-\omega t))$

Intensity: $I(t)= E_{tot}(t) \times E_{tot}{}^*(t)$



Autocorrelation :

Field : $g^{(1)}(\tau) = \dfrac{<E^*(t)E(t+\tau)>}{<E^2(t)>}$

Intensity : $G^{(2)}(\tau) = \dfrac{<I(t)\,.\,I(t+\tau)>}{<I^2(t)>}$

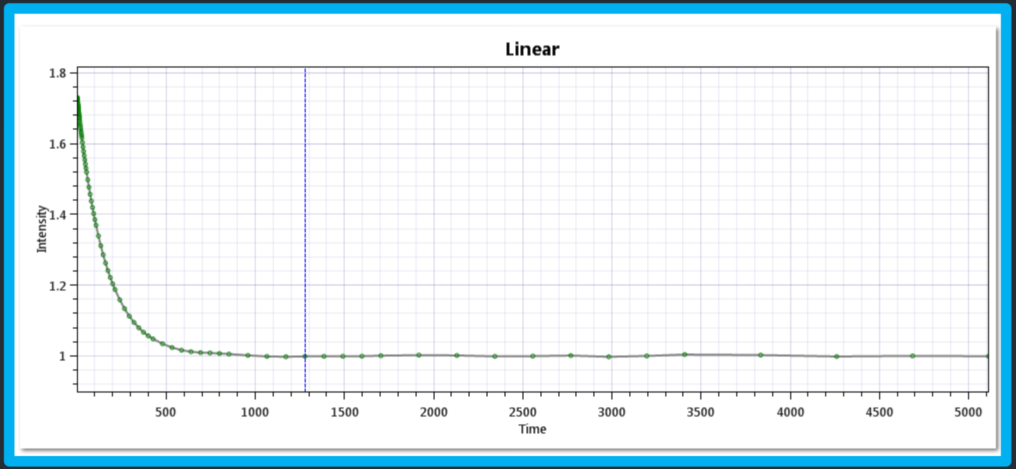
This leads : $G^{(2)}(\tau) = A + \beta \exp(-2q^2 \mathbf{D} \tau)$

with $q=\dfrac{4\pi n_0}{\lambda}\sin(\theta/2)$

Correlogram representation: Linear vs Logarithmic

Cordouan: linear correlator

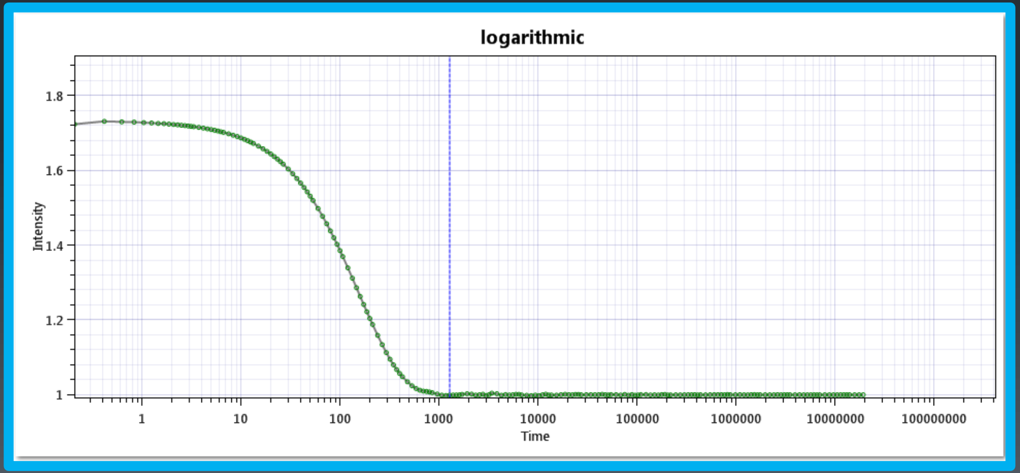
Normalized Amplitude
Linear



Linear time scale

Competitors: Multi-tau correlator

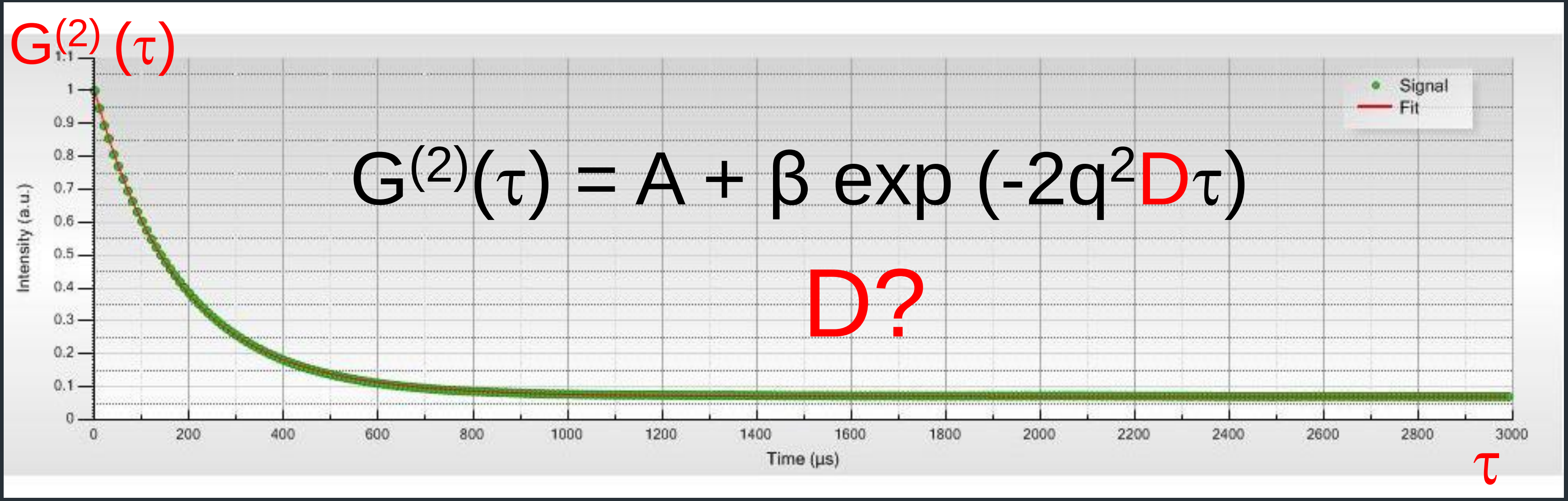
Normalized Amplitude
Linear



Logarithmic time scale

Correlogram treatment

Inversion problem : How to find the best exponential curve fitting the experimental curve?

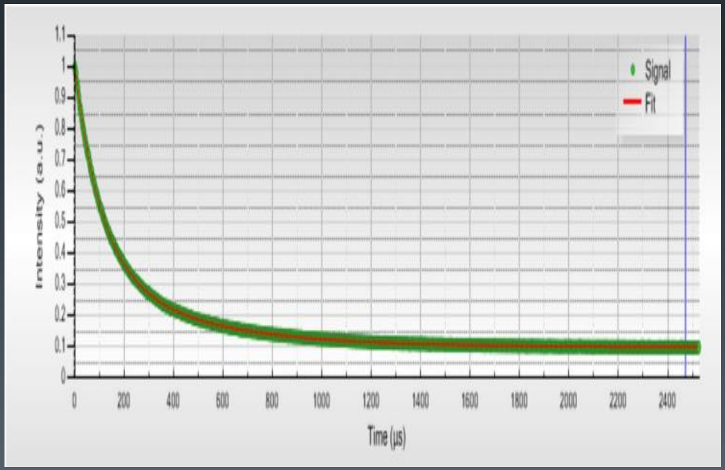


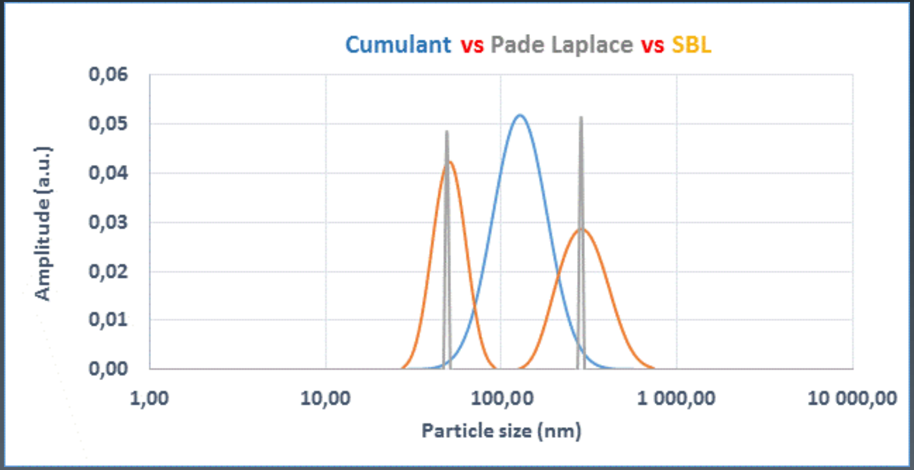
Fit leads to D, and D to the diameter of NPs $\emptyset_H$.

D → $$\emptyset_H = \frac{KT}{3\pi\eta D}$$

Inversion algorithms for monomodal and polymodal analysis

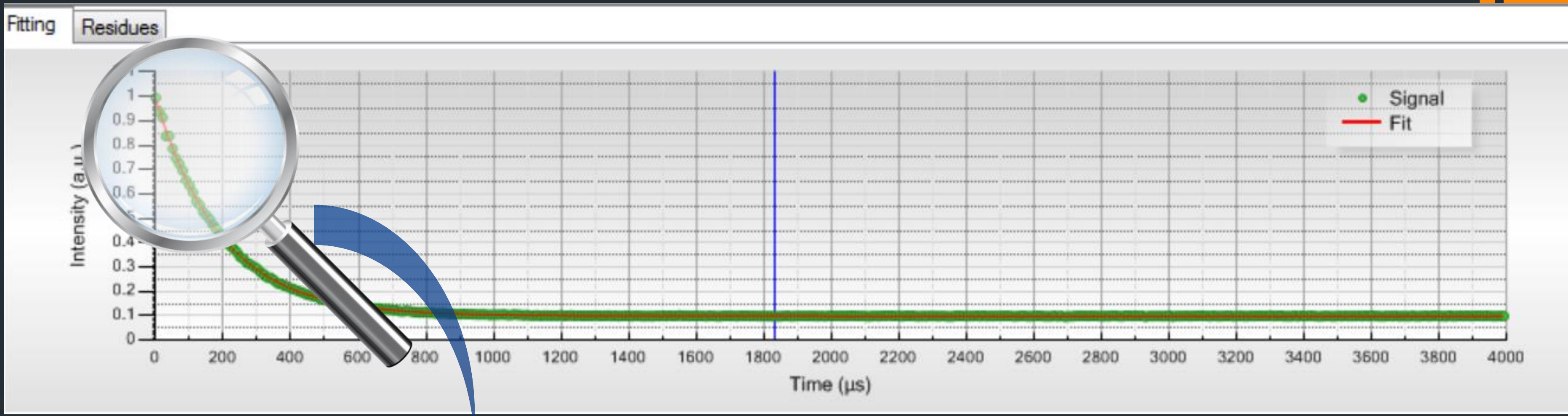
Algorithm	Number of populations	Distribution	Model
Cumulants	1 continuous	Yes	Assuming a Gaussian distribution around a specific size ($Z_{average}$)
Pade Laplace	Multi (up to 3) discrete	No	Using Laplace transform of the decay
SBL	Multi continuous	Yes	Using a computing method based of Probabilities



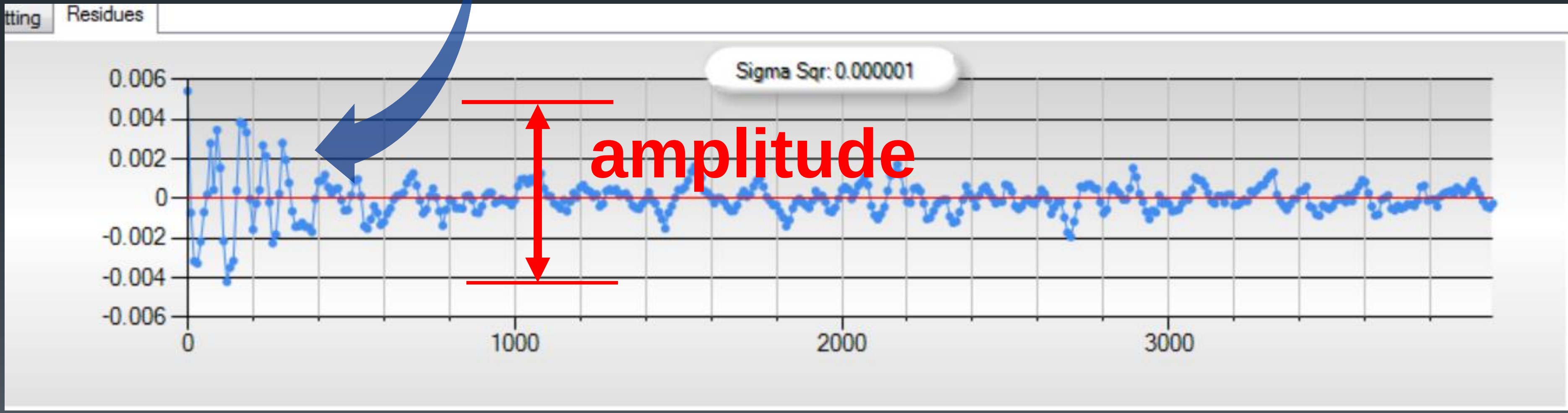


The key point of the results : the FIT and the Residues

FIT= mathematical solution given by the algorithms (red curve)

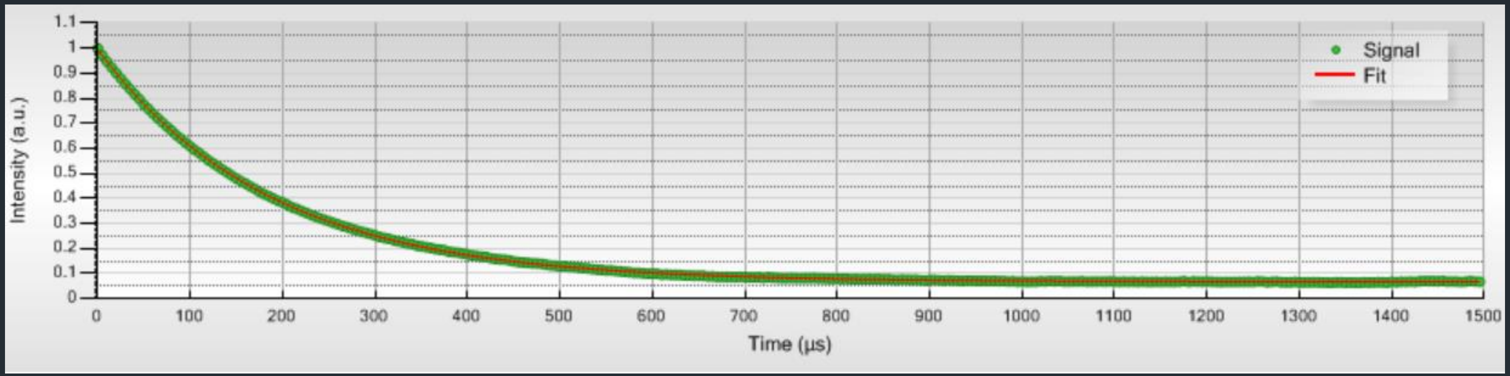


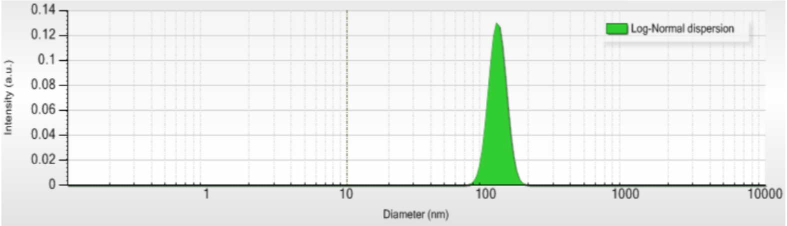
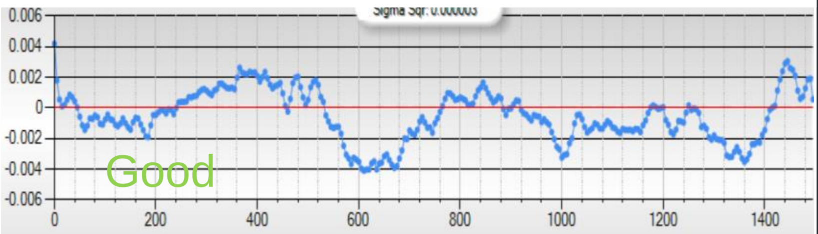
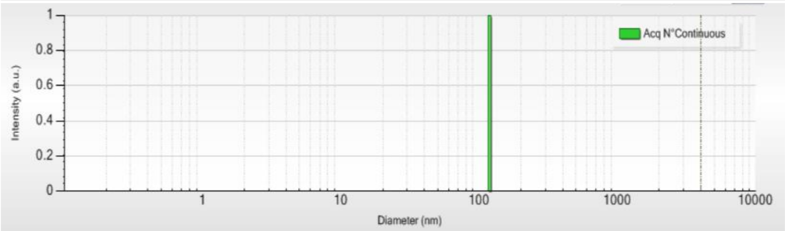
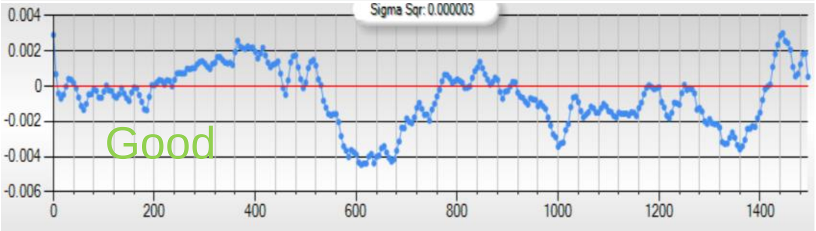
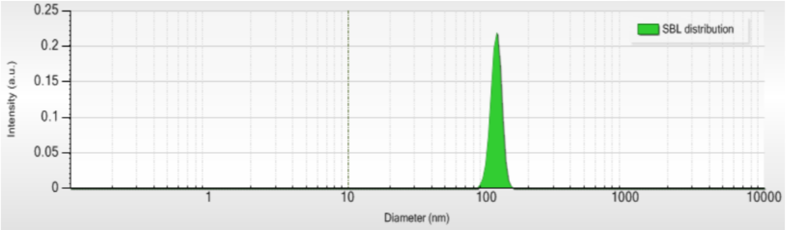
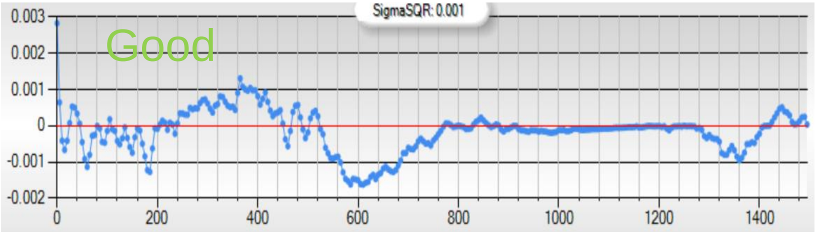
Residues = difference between Fit and measured correlogram



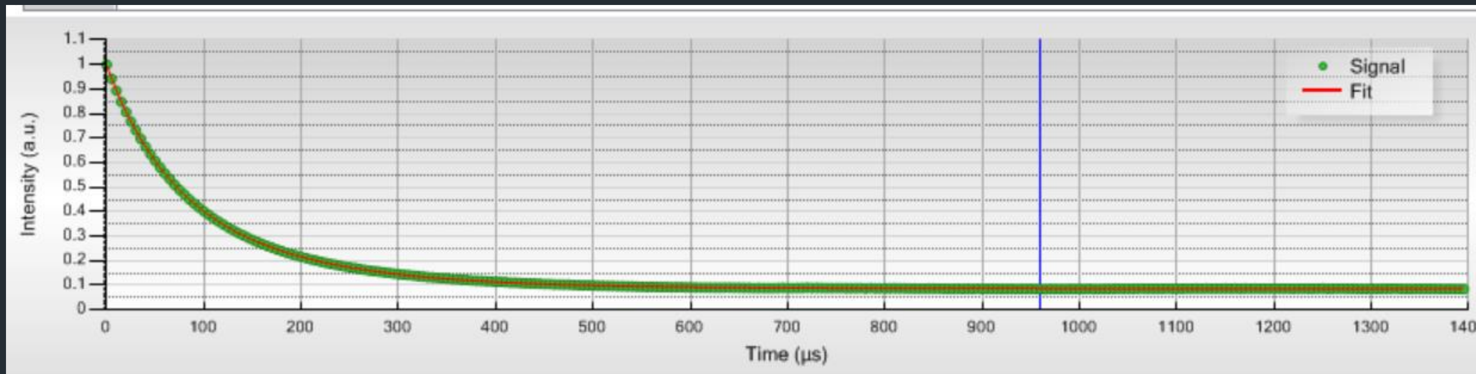
A good fit = Low amplitude (<0,01) and statistically distributed residues

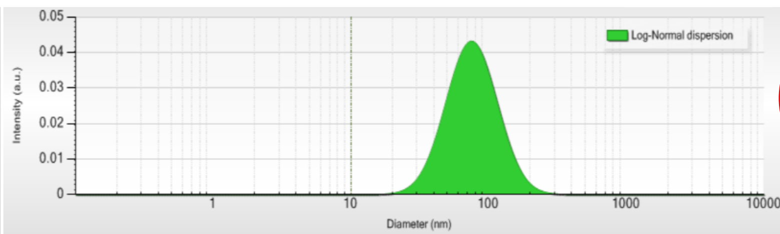
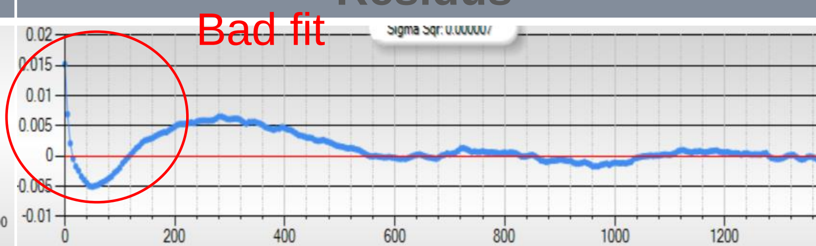
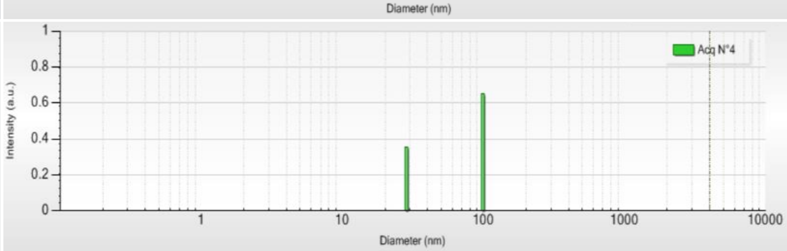
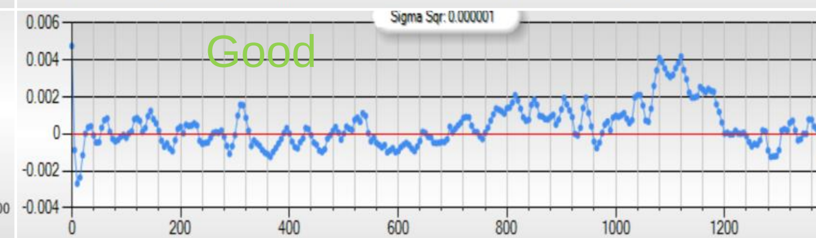
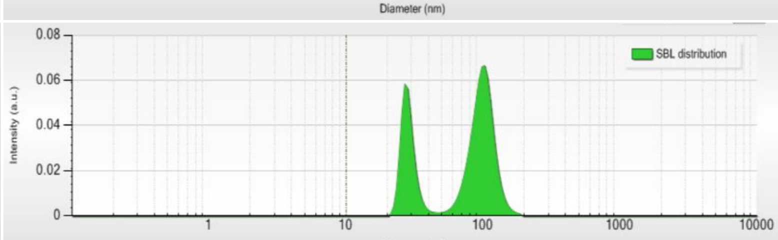
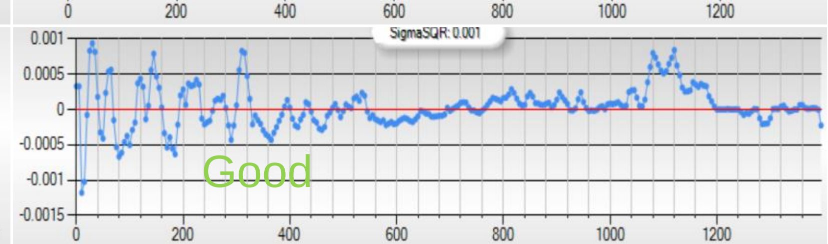
Monomodal sample (one population) 100 nm Latex NPs



Algorithm	Size	Residus
Cumulants		 Good
Pade Laplace		 Good
SBL		 Good

Bi-modal sample (two populations) 30 nm +100 nm Latex NPs mixture

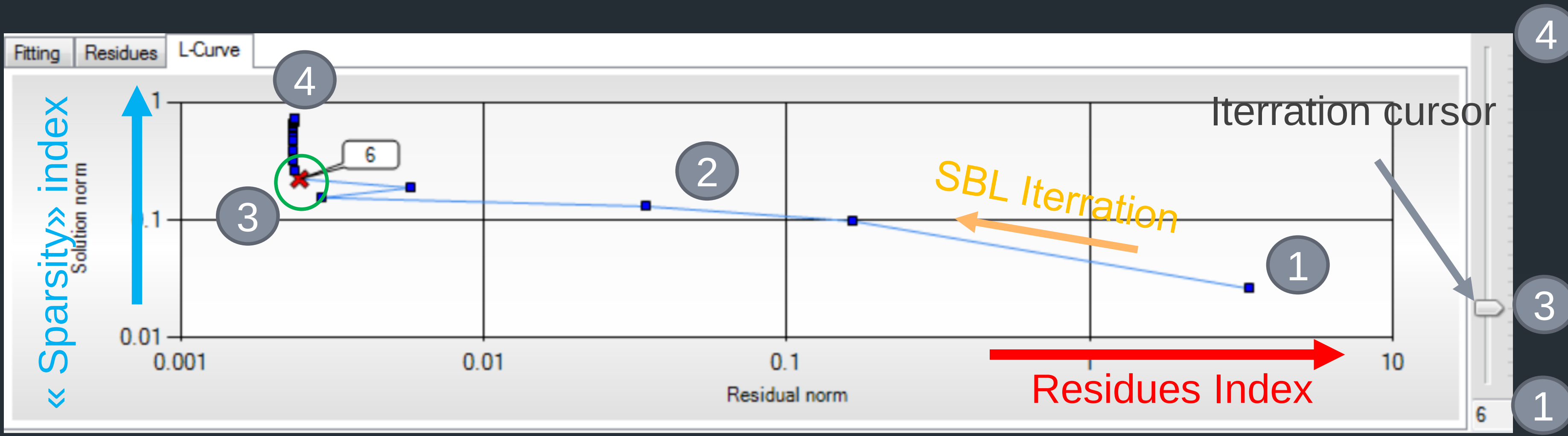


Algorithm	Size	Residus
Cumulants		
Pade Laplace		
SBL		

SBL: What is the meaning of the L Curve?

SBL is based on a iterrative algorithm for particle size distribution calculation

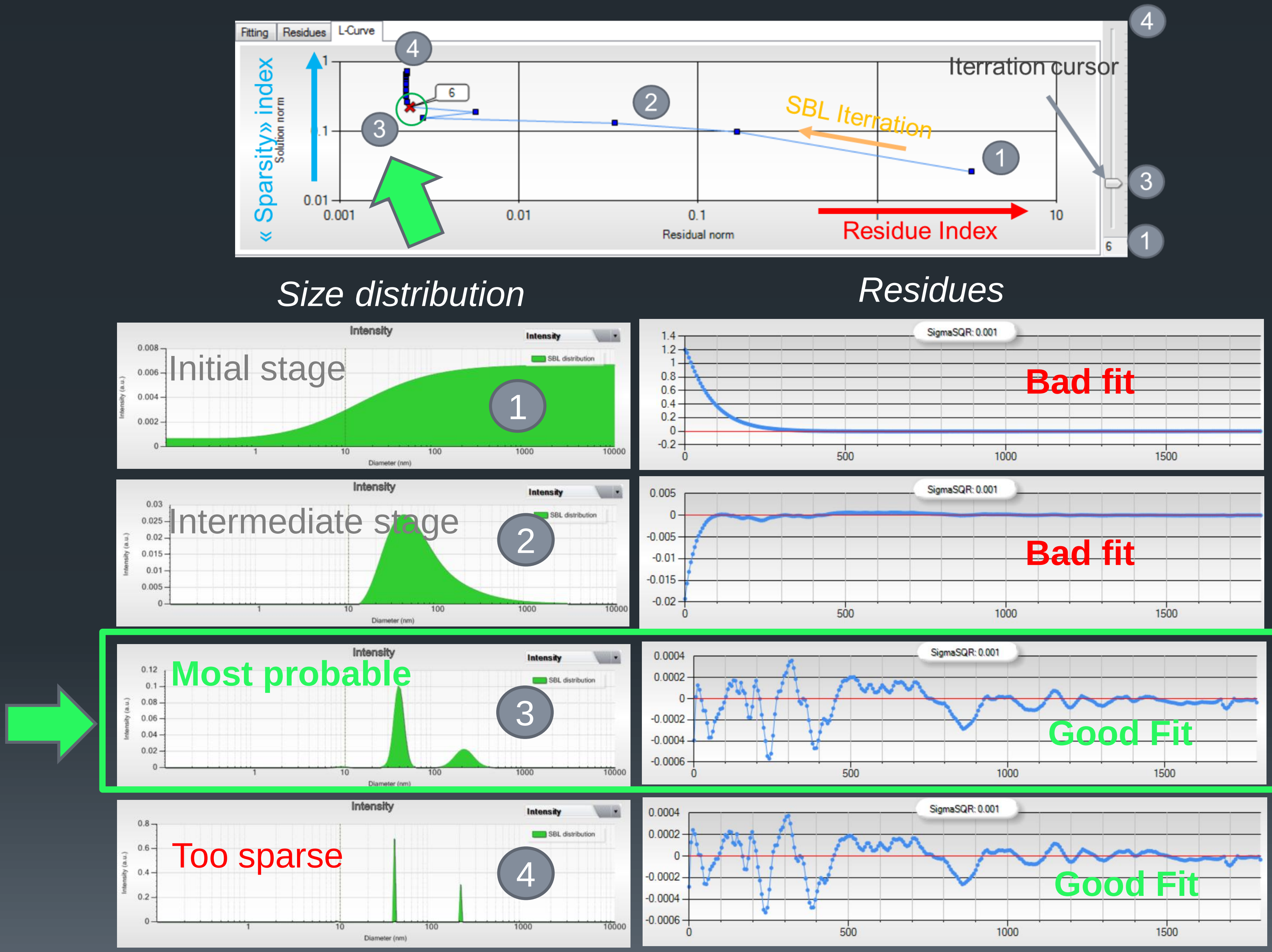
The L curve is a graphic representation of SBL successive iterrations according to two figures of Merit: **Residues index (X axis)** and Sparsity index (Y axis)



1. SBL Initial iterration state
2. Intermediate iterration state
3. Most probable solution
4. Final iterration state

The most probable size distribution= lowest Sparsity and Residues indexes

SBL: how to read and tune the L Curve?



Light Scattering: some useful rules of thumb (1):

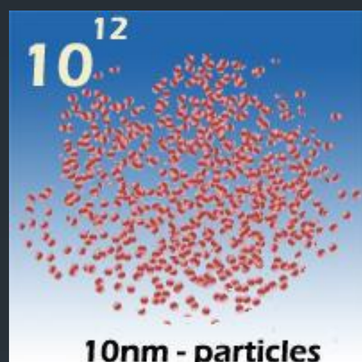
MIE/ Rayleigh Theory

$$I_{Scatt} \sim K \cdot I_0 \left(\frac{(n^2-1)}{(n^2+2)}\right)^2 \cdot \frac{\phi_H^{6}}{\lambda^{4}}$$

Particle refractive index

Laser Wavelength

Rule of thumb #1: light intensity scattered by 1nm spherical particles is 10^6 (one million!) times lower than for 10 nm particles, and 10^{12} time lower than for 100 nm ones respectively



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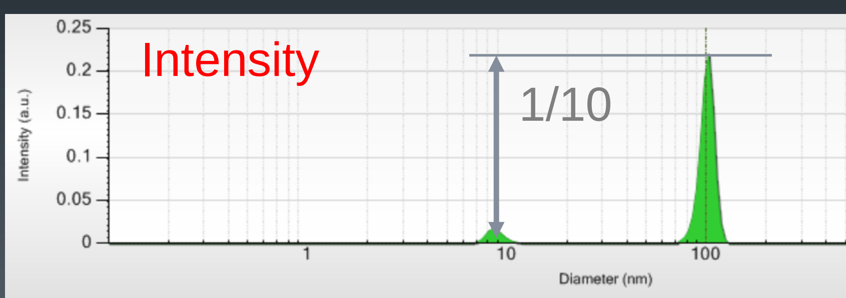
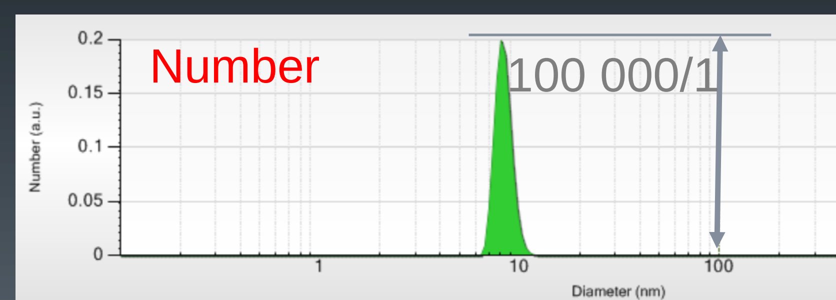


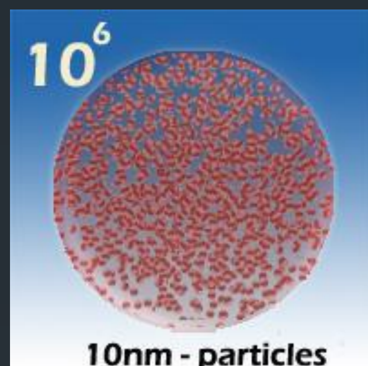


Rule of thumb #2: the scattering efficiency (cross section) of the particles is 2.3 times higher for a laser wavelength @532 nm than that of a laser @656 nm

Light Scattering: some useful rules of thumb (2):

$$\text{Volume} = \frac{\pi}{6}\, \emptyset_H^{\,3}$$

Rule of thumb #3: the volume occupied by one 1µm – sphere is the same as one occupied by 10^6 spheres with a 10nm diameter



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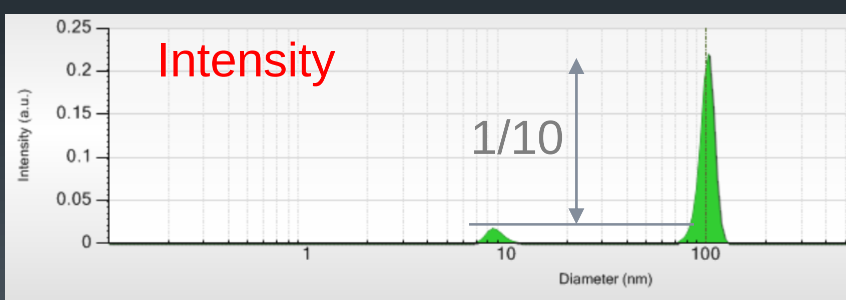
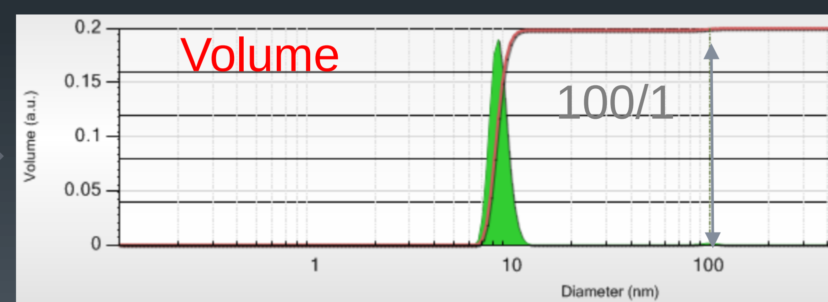




Particle Size and size distribution: some definitions

Cumulants analysis

$$\boldsymbol{Z_{avg}} = \frac{k_B T q^2}{3\pi\bar{\Gamma}}:$$

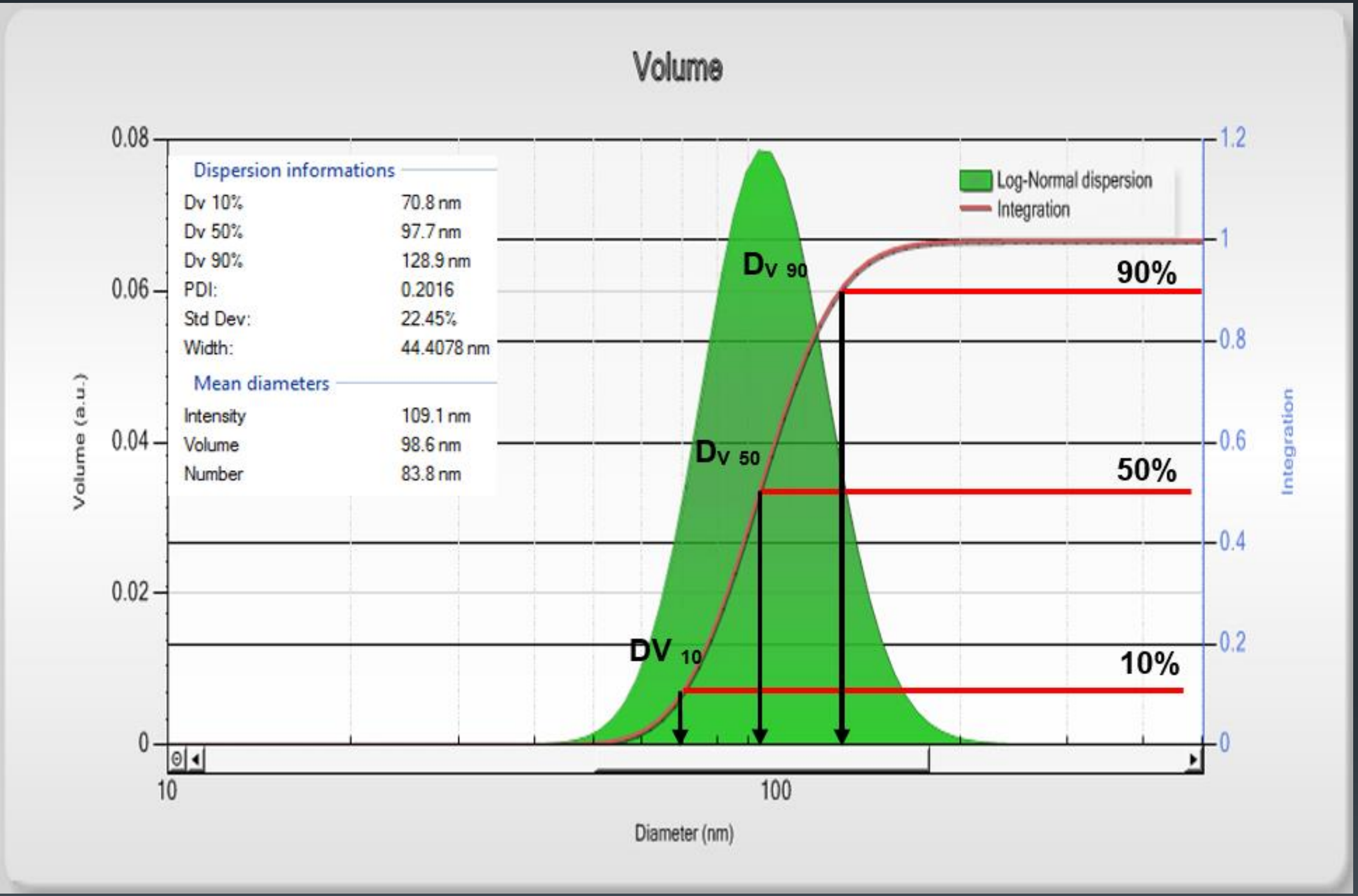
$\bar{\Gamma}$ is the average decay rate according to relations:

$$\bar{\Gamma} = \int_0^{\infty} G(\Gamma)\Gamma d\Gamma$$

Z-average can be expressed as the intensity weighted based harmonic mean size

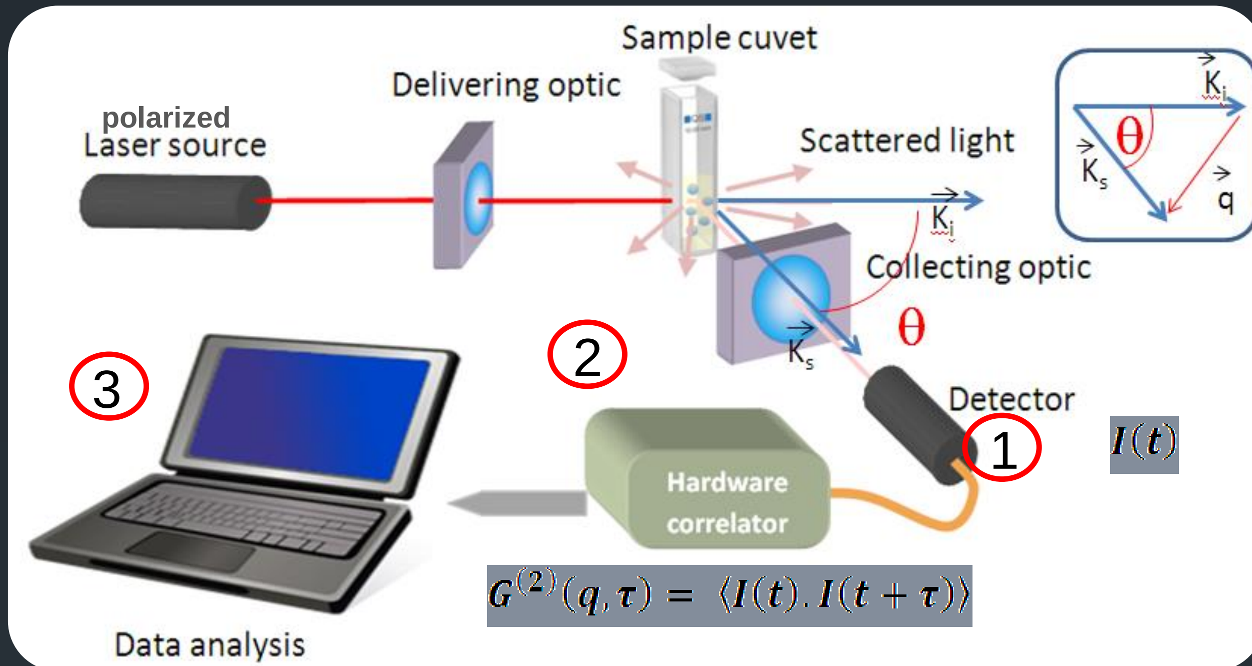
$$\textit{Distribution width} = Z_{avg} * \sqrt{PDI}$$

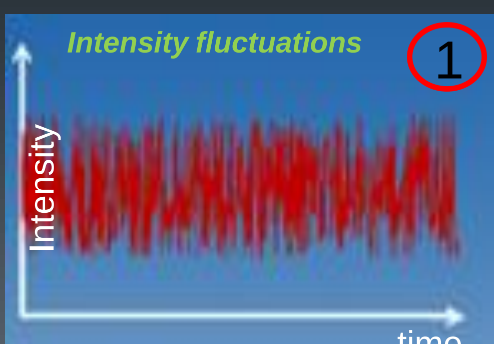
Particle Size and size distribution: some definitions

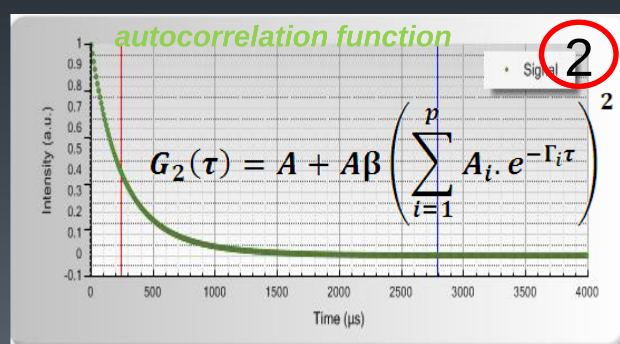


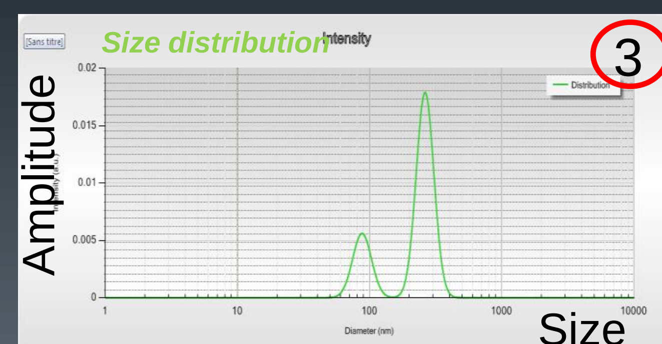
DLS measurement principle: 3 steps process

- Measure light scattering fluctuation to probe the Brownian motion









Our Solutions for Nano-particles size characterization

VASCO™ $^{\gamma}$ series

Batch

Opaque & concentrated media

VASCO™ FLEX

In-situ

"bring the measurement to your sample"

- Based on Dynamic Light Scattering (DLS)
- Measurement in dark and/or concentrated suspension
- Size range : from 1nm up to 10µm
- Proprietary inversion algorithm for efficient size distribution analysis
- Technology transfer from French Petroleum Institute

ifp Energies nouvelles

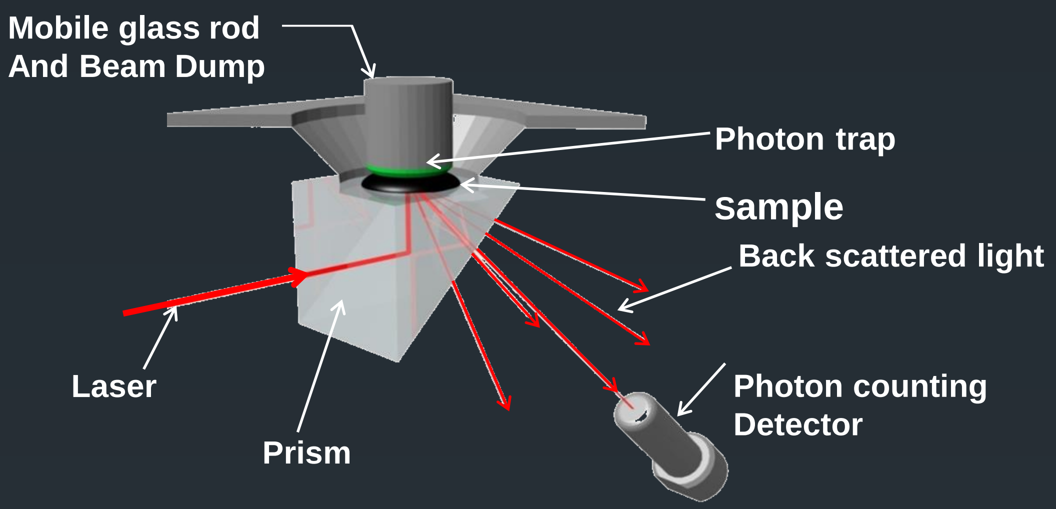
VASCO™ γ 2 and 3 serie

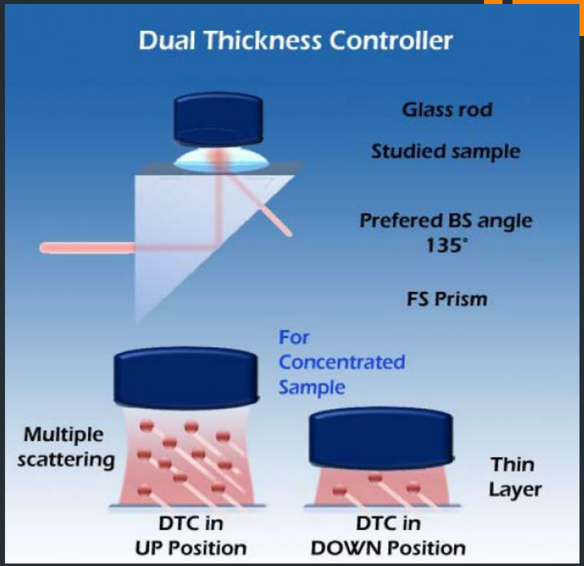
Batch Measurements

Opaque & concentrated media

Vasco particle size analyzer: a unique sample Cell design

The thin layer analysis mode





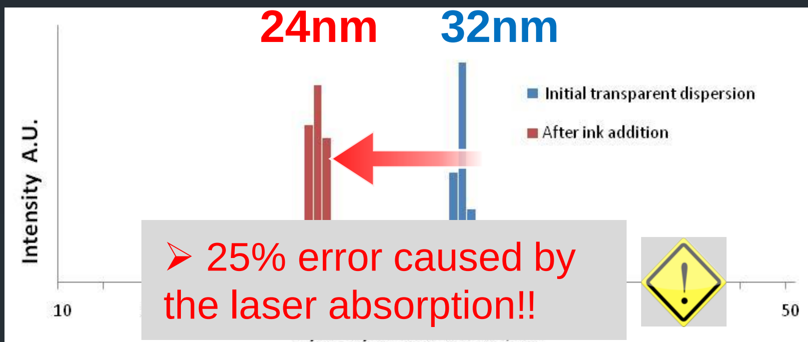
- Innovation in the sample cell configuration: Dual Thickness Control (DTC- patented)
- Thin layer analysis: prevents the sample from local heating and multiple-scattering.
- Backscattering detection (135°): low multiple scattering, better contrast for small particles
- Higher detection efficiency in opaque media.
- Solvent-proof cell measurement without consumables
- Proprietary inversion algorithm allowing efficient size distribution analysis
- Technology transfer from the French Institute of Petroleum

Common DLS artefacts and DTC benefits:

- Measurement of dark /opaque media

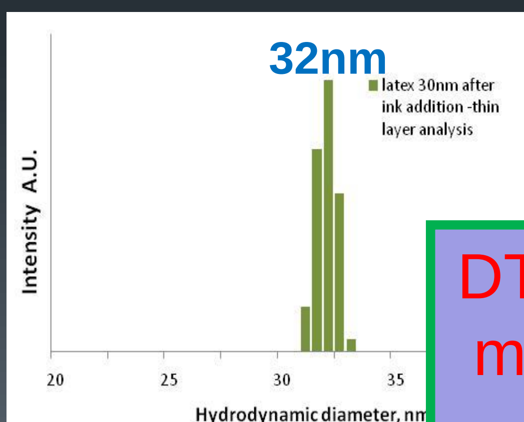
*A standard polystyrene latex (Ø=**30nm** by TEM) is mixed with black soluble ink (10wt%).*

Without DTC



- 25% error caused by the laser absorption!!

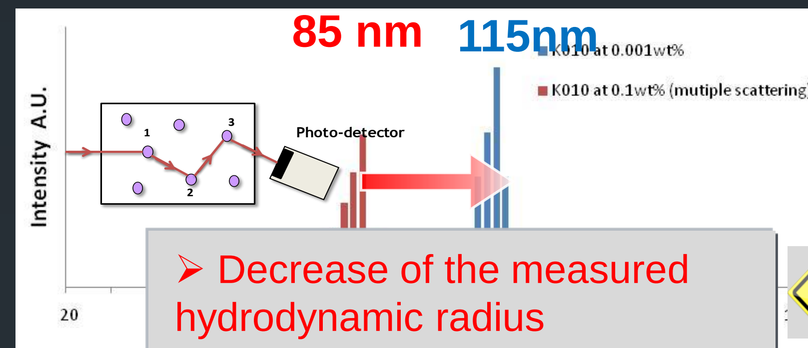
With DTC



- Measurement of concentrated samples

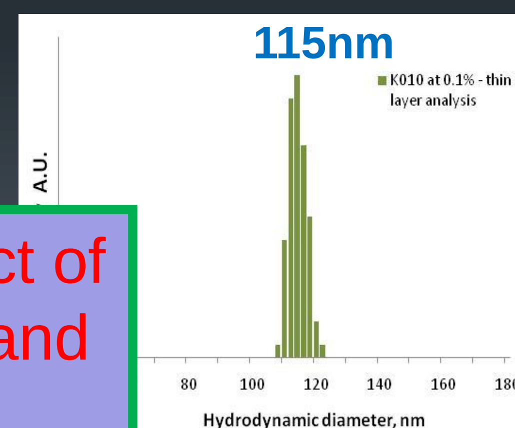
*A standard polystyrene latex (Ø=**100nm** by TEM) measured at 0.1 wt%*

Without DTC



- Decrease of the measured hydrodynamic radius

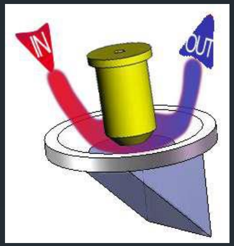
With DTC



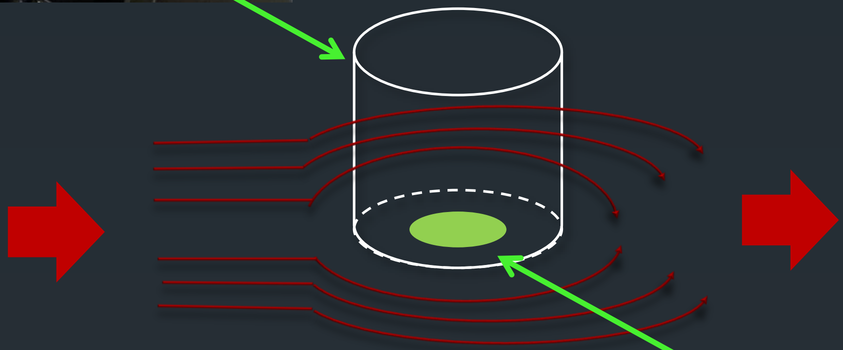
DTC reduces impact of multiple scattering and light absorption

Unique Online measurement capabilities

Dual Thickness Controller

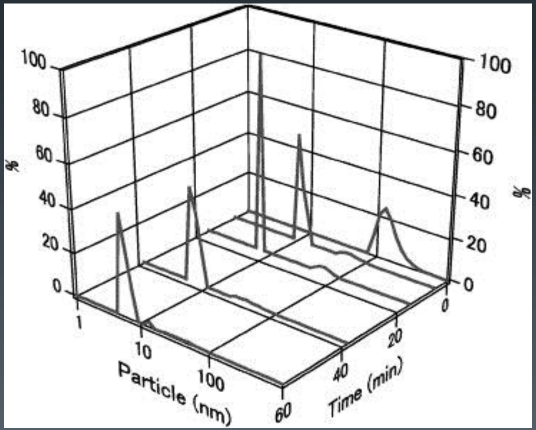


VASCO coupled on line with a peristaltic pump



Sample Volume trapped in the cell

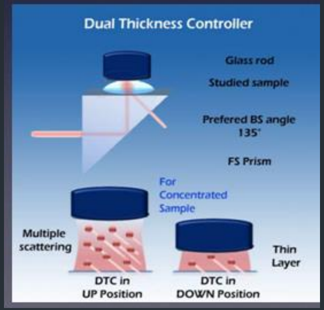
- ON line size kinetics measurement achieved without stop flow thanks to DTC



DLS equipments until today

Disposable cell

Embedded cell



- Mature and standardized method (ISO 13321 (1996) & ISO 22412 (2008)
- Bench top configuration: solutions dedicated to laboratory analysis
- Requires batch sampling: bring the sample to the measurement!
- Need sample preparation: filtering, diluting,
- Time consuming
- Risk of contamination or sample degradation

⇨ **Need for a new approach for process monitoring!**

A change of paradigm:*"bring your measurement to your process!"*

Combination of the power of DLS, the flexibility of Optical fiber design

<u>Features:</u>

- Non invasive
- Small footprint
- Adjustable working distance /scattering angle
- Alignment laser for easy installation
- High accuracy remote temperature sensor
- Easy maintenance
- Ideal for measurements in glass capillaries, or in situ

VASCO FLEX: The power of DLS, the flexibility of Optical fiber design

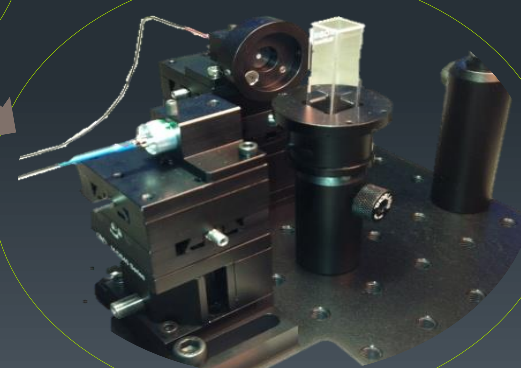
- Unique concept: “*bring your measurement to your process!*”
- The idea: *fit the solution to each application specs*

***In situ* head**

DTC head

Central unit

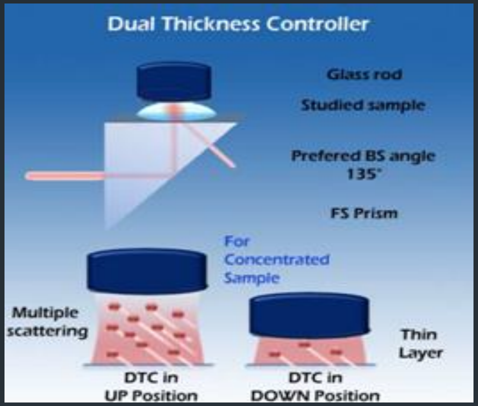
Thermalized head



Custom head

The idea: fit the solution to each application specs

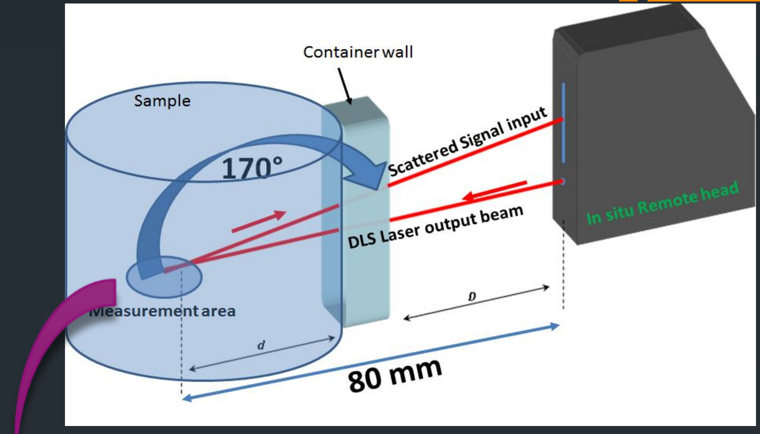
Fiber Remote cell option

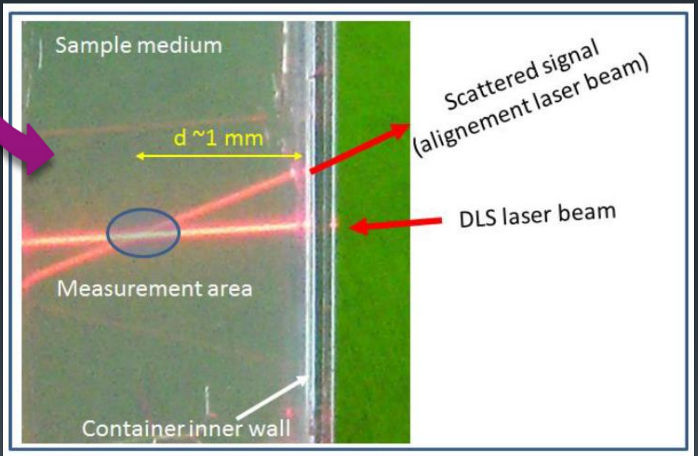


Features:

- Easy to install, easy maintenance
- On-demand fiber length from 1 up to 10 m
- The capabilities of a VASCO with the versatility of a remote cell
- Compact :ability to work in confined environment (glove box)
- Flexibility and upgradability : can easily be detached and replaced by another option
- Dual thin film Thickness Control (patented) for concentrated and or opaque sample.
- No sample heating, no multiple-scattering

In Situ fibre remote head option

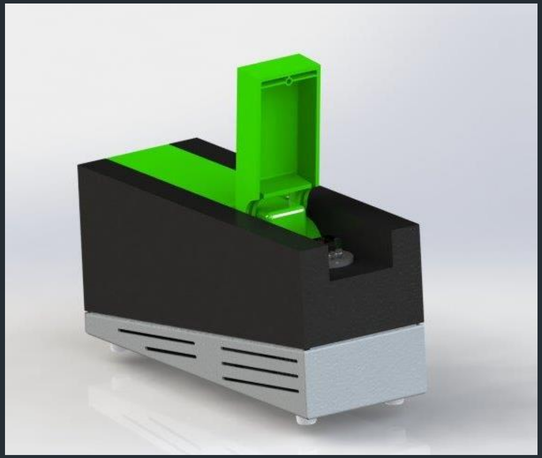




Features:

- Non invasive
- Small footprint
- Adjustable working distance /scattering angle
- Alignment laser for easy installation
- High accuracy remote temperature sensor
- Flexibility and upgradability : easy switch between options
- Easy maintenance
- Ideal for measurements in glass capillaries, or in situ

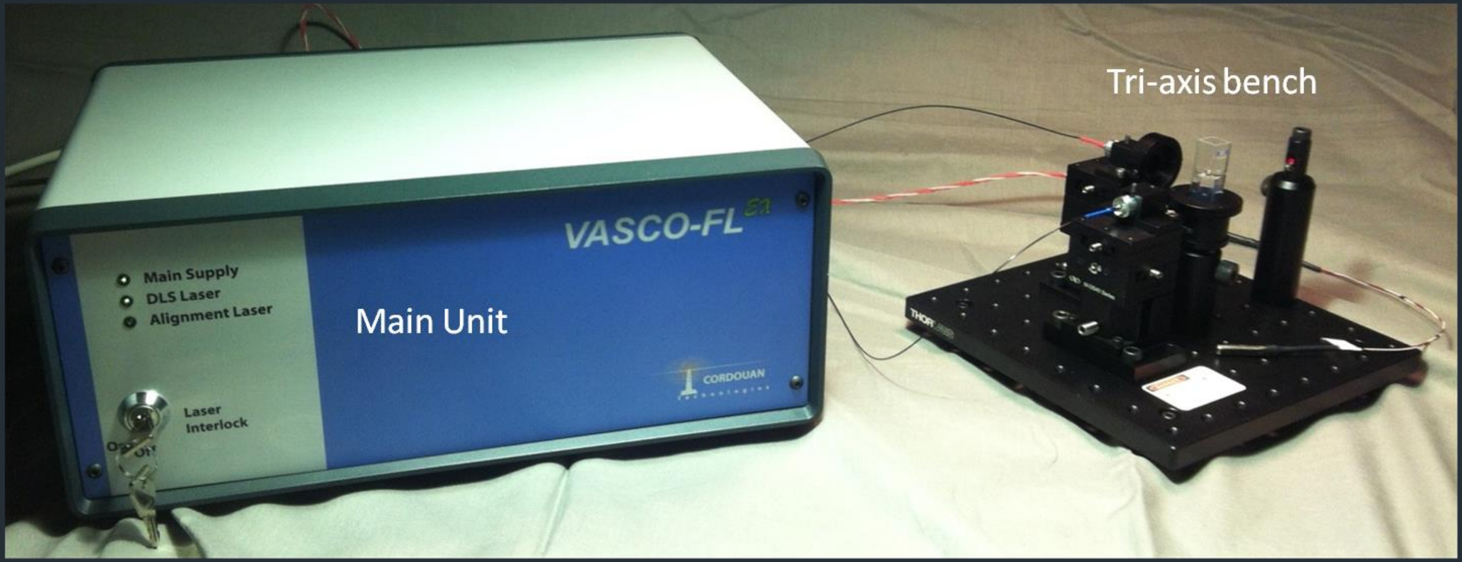
Thermalized head option

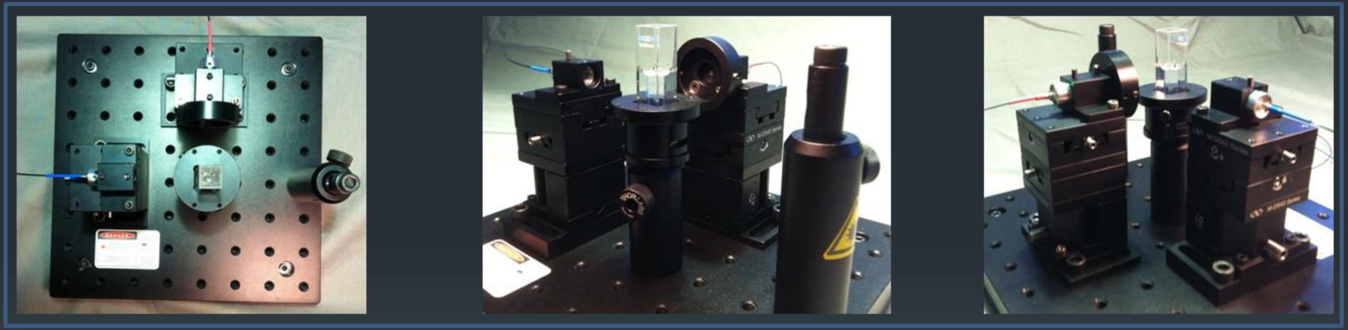


<u>Features:</u>

- Broad temperature range : 5° to 80°C ; +/- 0.005° ;
- Compact : ability to work in confined environment (glove box) ;
- Compatible with standard 10x10 mm² cuvette (disposable or QS)
- No cross contamination, easy sampling ;
- Fluorescence filter option ;
- Cuvettes options : disposable cell, glass cell, micro-cell, flow cell …

Custom setup head option





Features:

- Lab set up for dedicated application
- Compatible with standard 10x10 mm2 cuvette (disposable or QS)
- No cross contamination, easy sampling,
- Fluorescence filter option

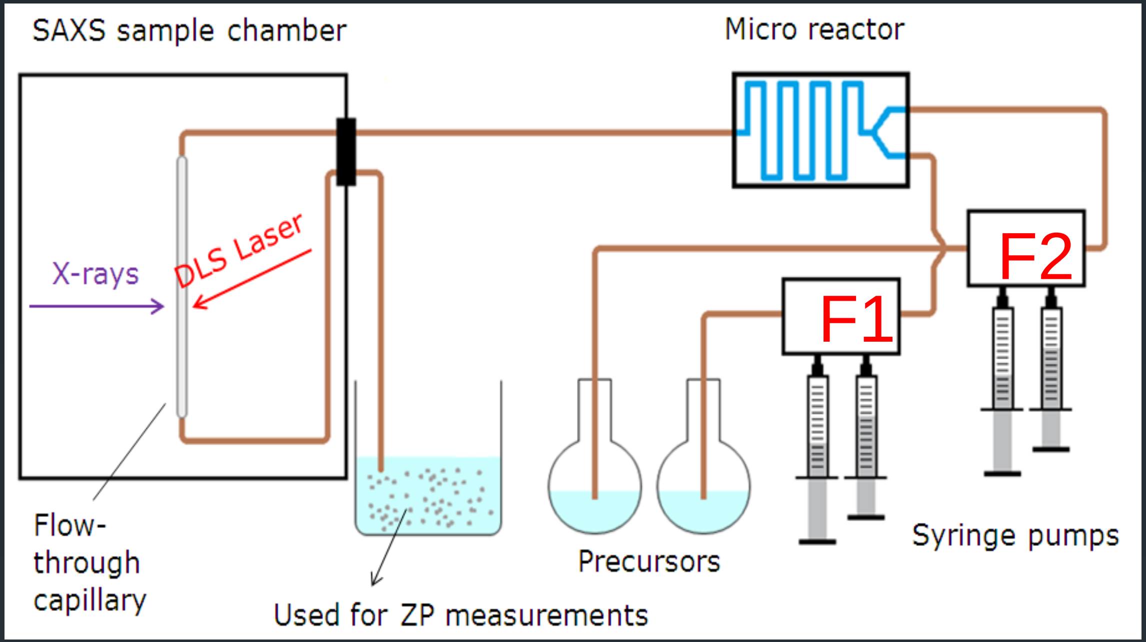
Examples of use of In situ remote head and applications

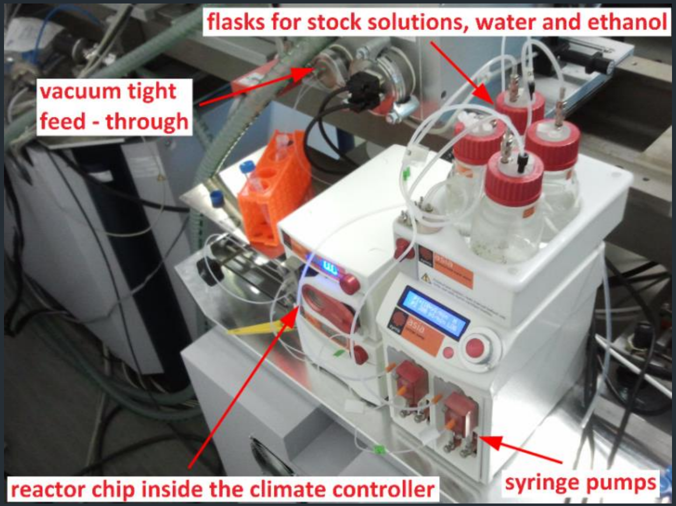
Example 1

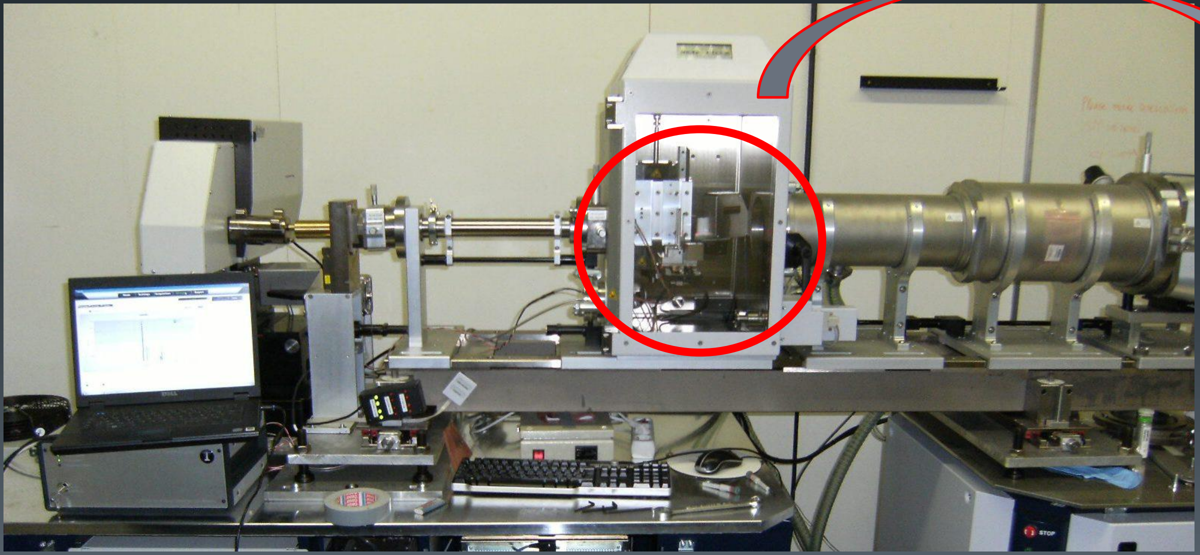
Combined Remote DLS & High flux SAXS for NPs synthesis monitoring

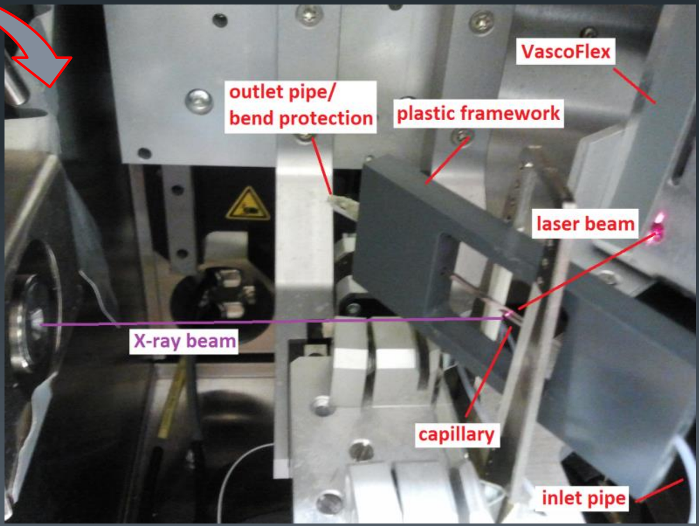
SNOW CONTROL FP7 Project

Combined Remote DLS & High flux SAXS for NPs synthesis monitoring





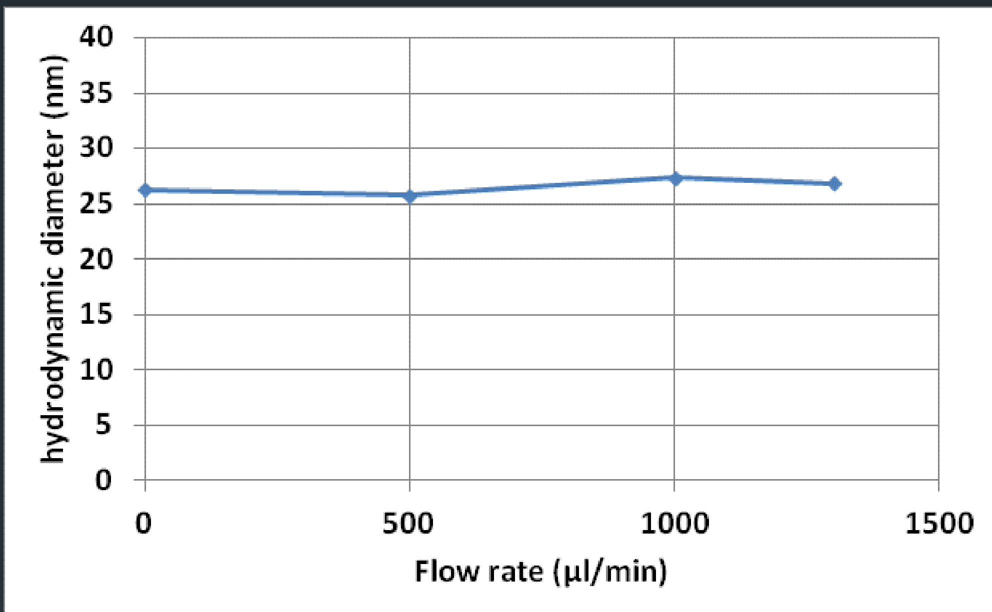




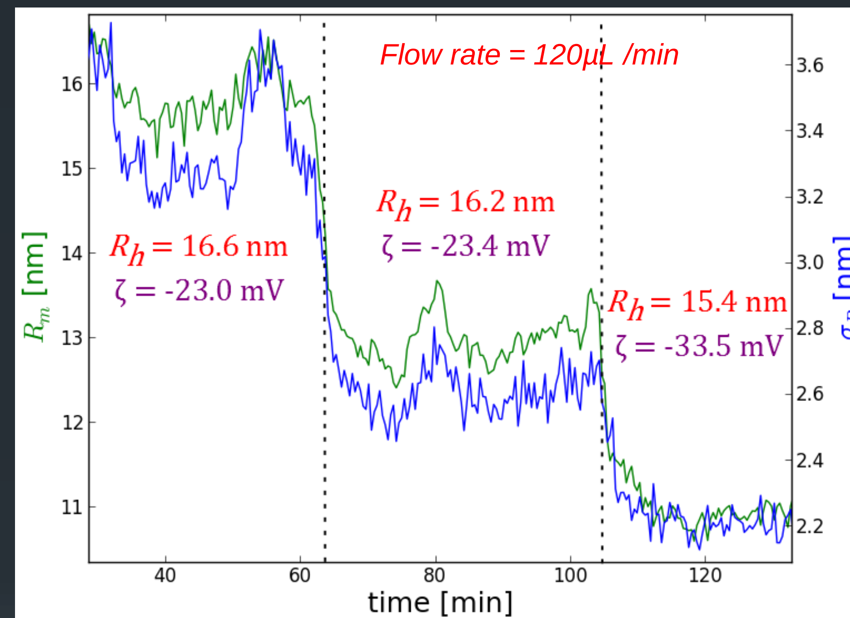
On line SiO2 NPs synthesis monitoring

Hydrolysis –condensation method : TEOS in Ethanol (F1) + NH3 in H2O (F2)

Impact of flow rate (F1+F2)



Impact on precursors mixing ratio (F1/F2)

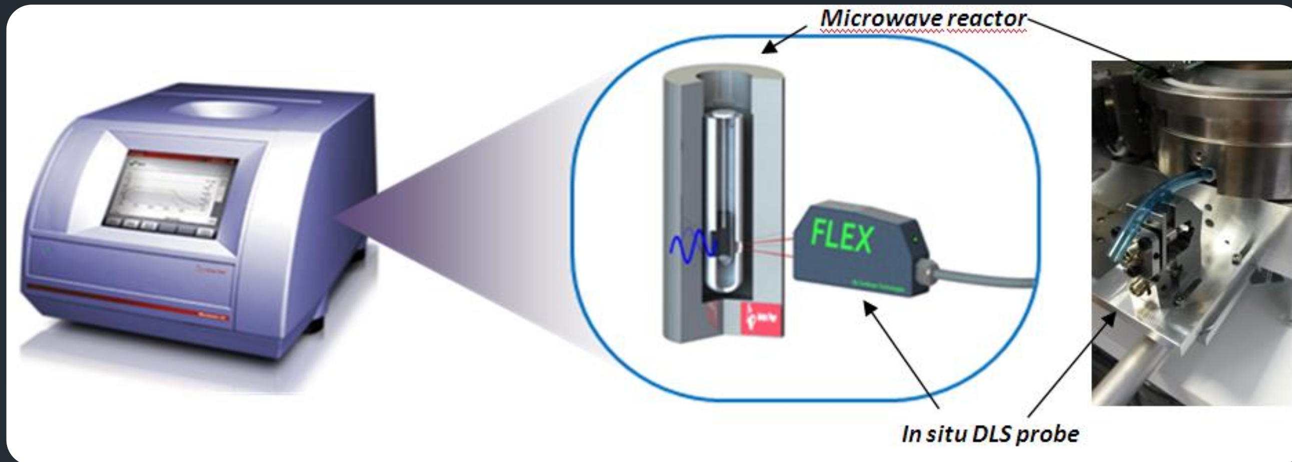


- Consistent results between SAXS and DLS measurements
- Allow to track and tune synthesis process in an accurate way

Example 2

In situ kinetics monitoring
of Microwave assisted NPs synthesis

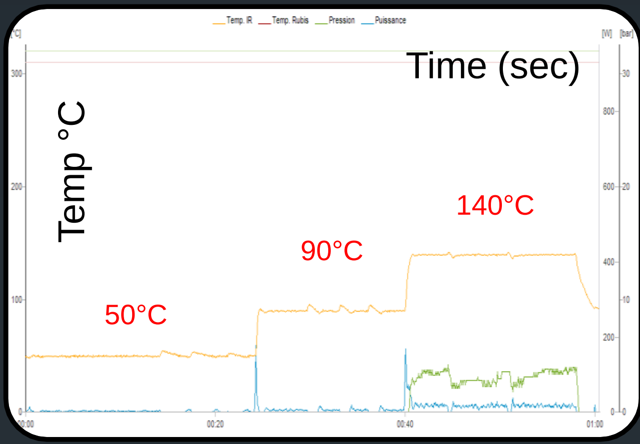
In situ kinetics monitoring of Microwave assisted NPs synthesis

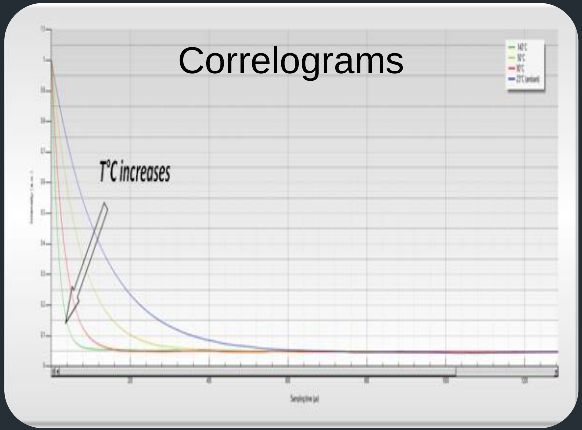


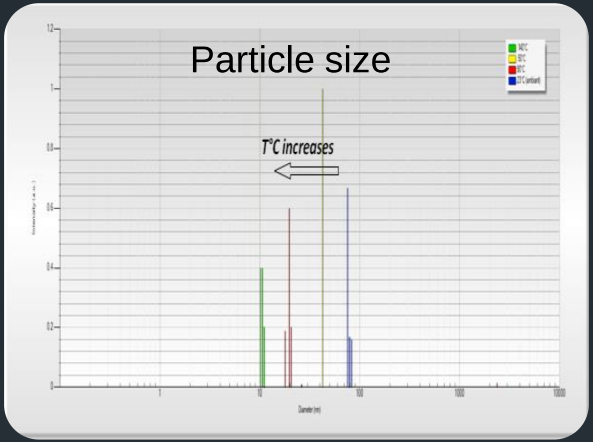
- In situ DLS successfully integrated into a commercial microwave reactor
- Under test and qualification at the College de France-Paris

Real-time & In situ monitoring of Microwave assisted NPs synthesis

Validation tests done on SiO2 slurries







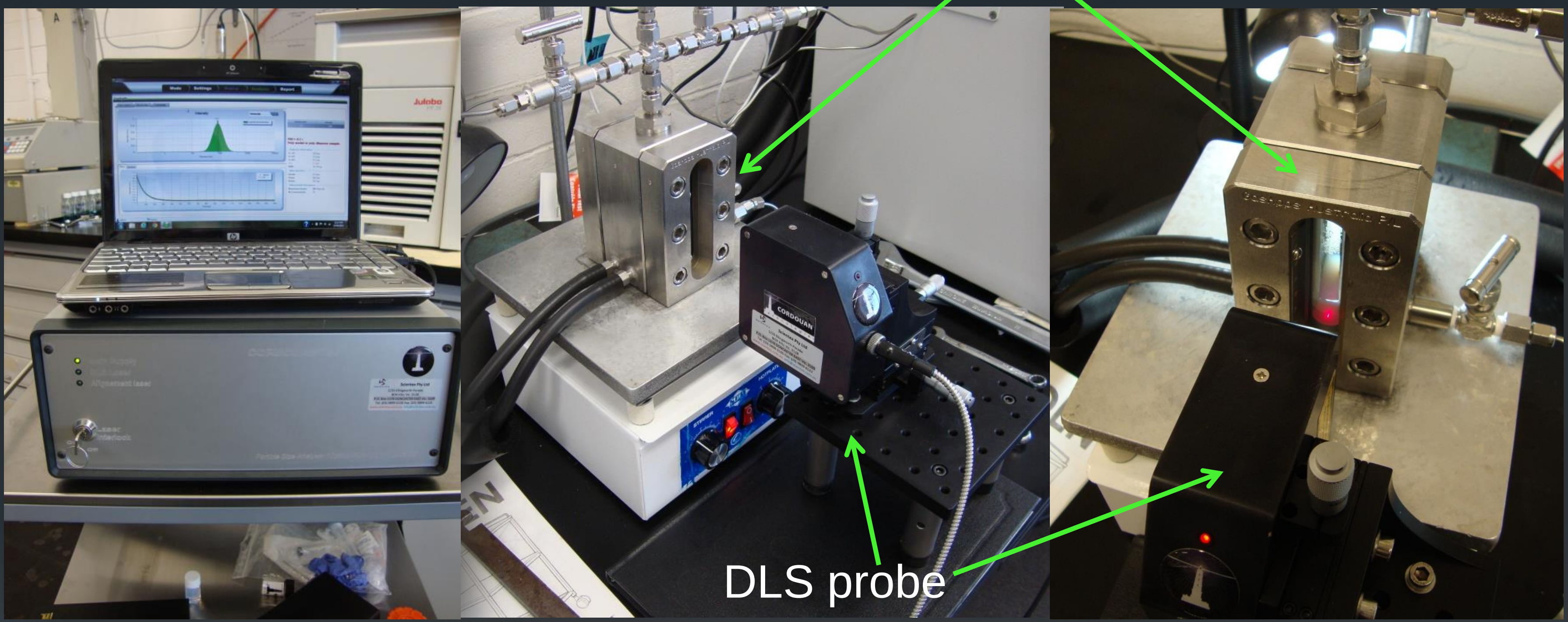
True temperature	Corresponding Viscosity (cP)	Corrected Averaged size (nm)
50°C	0.55	**76**
90°C	0.3	**72**
140°C	0.196*	**68**

- Very consistent an d reproducible results
- 1st demonstration ever done opening up new possibility on NP synthesis monitoring

Example 3

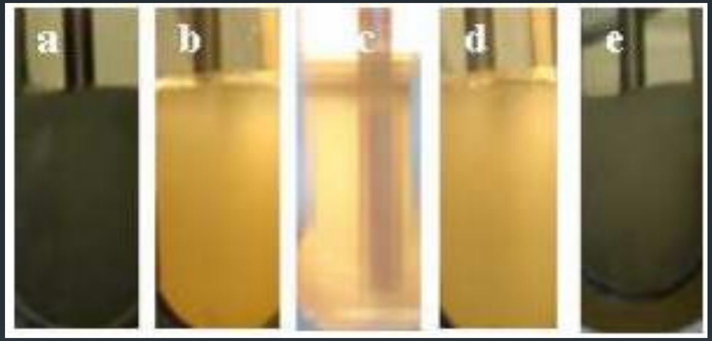
Particle Size Measurement inside supercritical CO_2 synthesis reactor

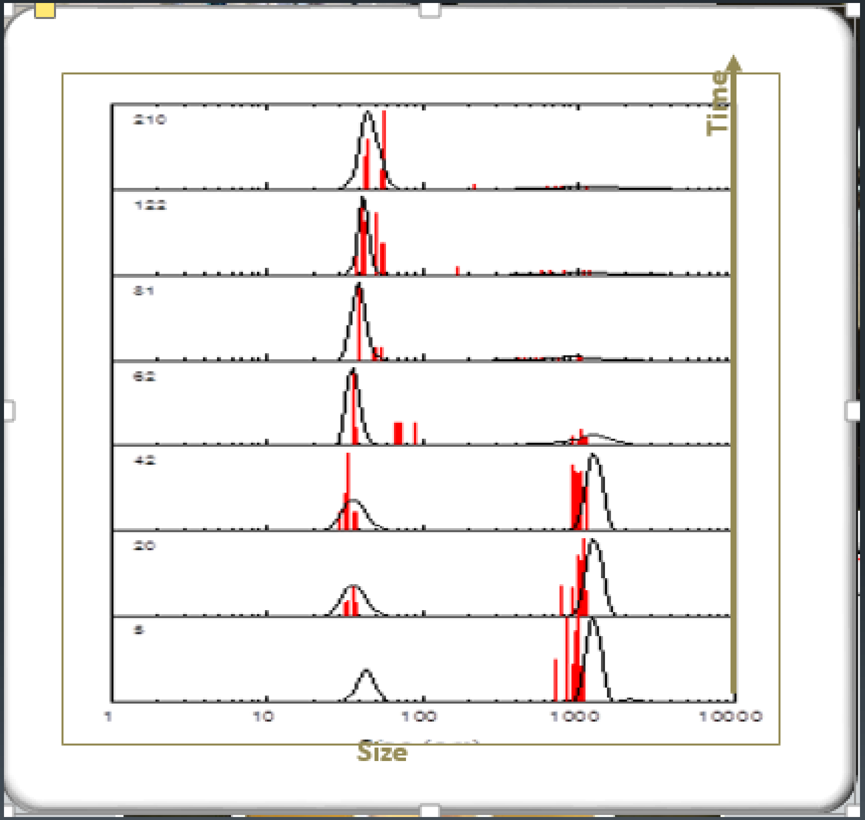
Particle Size Measurement inside supercritical CO_2 synthesis reactor



Particle Size Measurement in supercritical CO_2 synthesis reactor

- 10 wt% styrene rel. to system, 10 wt% Dowfax 8390 (surfactant) rel. to monomer, 8 wt% Hexa Decane rel. to styrene
- Sonicated for 10 min, 65% input intensity
- CO_2 is used to control the size of nano-emulsion droplets





- Use DLS measurements to correlate turbidity variation with particle size
- Implement accurate control of the size of monomer droplets/NP

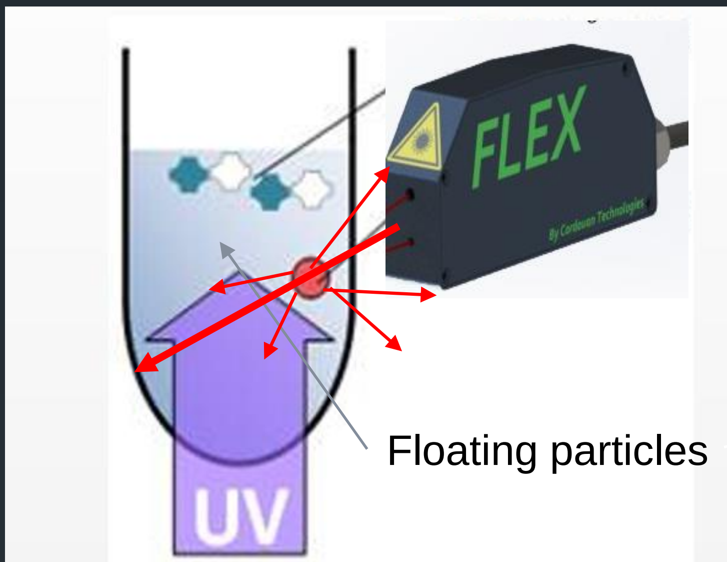
Example 4

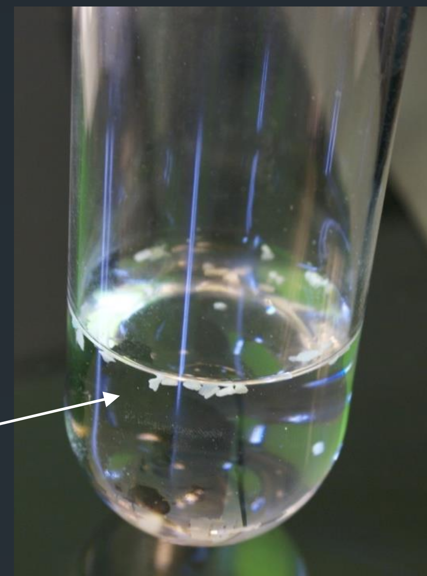
Environmental application: Nano Plastic detection in Ocean water

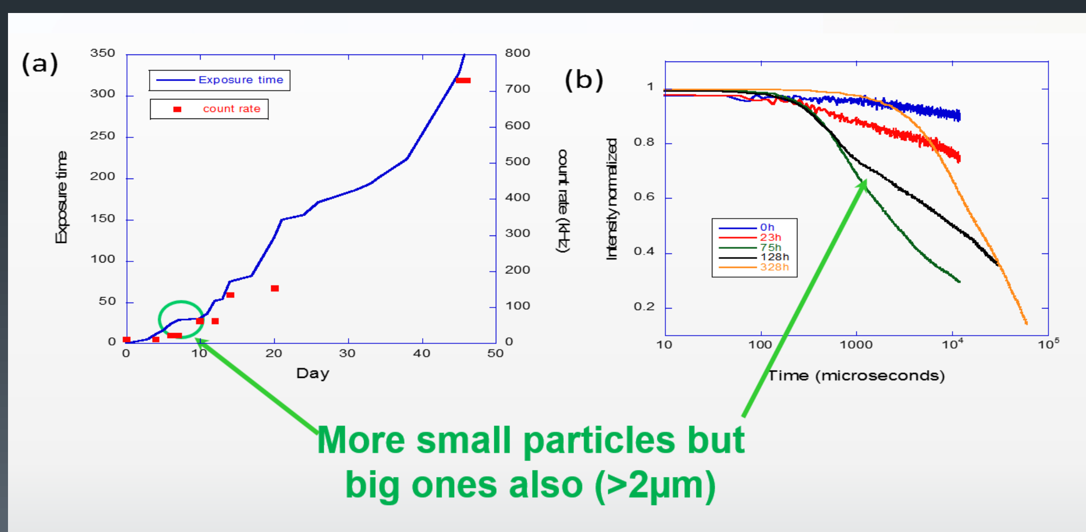
EXPÉDITION 7e CONTINENT

Environmental study : Evidence of Plastic Nps in Ocean

Lab study of Plastic NPs formation under oceanic like UV insolation conditions



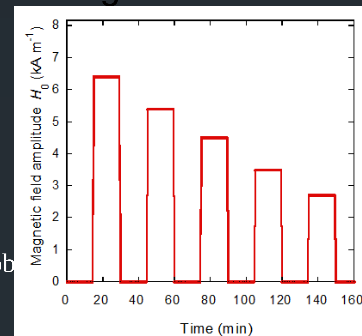


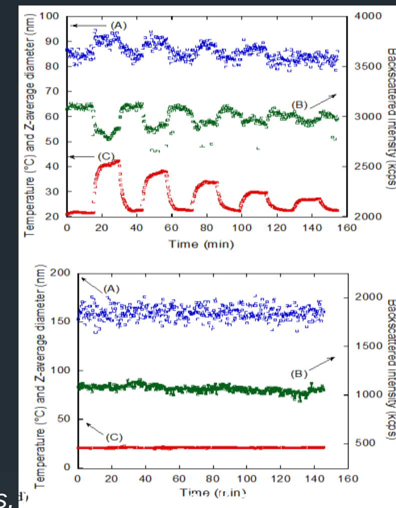


Other examples…

Magnetic Hyperthermia experiment on NPs for Bio-med applications

Magnetic coil





Polymer-grafted iron oxide nanoparticles as thermosensitive MRI contrast agents and magnetic nano-heaters,
Journal of Physics D: Applied Physics

Other examples of coupling

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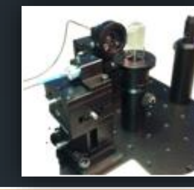
- *Dynamic Light Scattering*, *John Wiley* & Sons, Inc. New York by *Berne*, B.J. and *Pecora*, R. (*1975*)
- Laser Light Scattering: Basic Principles and Practice. Second Edition (Dover Books on Physics) by Benjamin Chu (2007-05-11)
- Particle Characterization: Light Scattering Methods, Kluwer Academic Piblisher; ISBN: 978-0-7923-6300-2, by Xu, Renliang ,

Some publications with VASCO Flex system:

- Polymer-grafted iron oxide nanoparticles as thermosensitive MRI contrast agents and magnetic nano-heaters, Gauvin Hemery & al, , Journal of Physics D: Applied Physics
- Combining SAXS and DLS for simultaneous measurements and time-resolved monitoring of nanoparticle synthesis; A. Schwamberger & al, Nuclear Instruments and Methods in Physics Research B 343 (2015) 116–122
- Structure and Dynamic Properties of Colloidal Asphaltene Aggregates; Joëlle Eyssautier & al; *Langmuir*, 2012, 28 (33), pp 11997–12004 - American Chemical Society
- Investigation on Physical Properties and Morphologies of Microemulsions formed with Sodium Dodecyl Benzenesulfonate, Isobutanol, Brine, and Decane, Using Several Experimental Techniques, Ayako Fukumoto & al, Energy Fuels 2016 to be published- American Chemical Society
- **Marine plastic litters: the unanalyzed nano-fraction,** Julien Gigault & al; The Royal Society of Chemistry, *Env. Sci. Nano*, 2016, **00**, 1-3

VASCO FLEX specifications



	DTC head	« In situ » head	Thermalized Head	Custom head
Measurement principle	Optical Fiber Dynamic Light Scattering (DLS)			
OPTICAL HEADS’ SPECIFICATIONS				
Temperature Monitoring	Yes	Yes + Customer sensor interfacing	Yes	Yes + Customer sensor interfacing
Temperature Range (°C)	15°C - 70°C (option 90°C)	Customer range	5°C - 80°C	Customer range
Min. Sample Volume (µL)	<50µL (cell dependant)			
Sample Cells	Built-in (patented)	In situ	Standard cell*	Custom
Solvent compatibility	Aqueous & Organic solvents	All solvents		
Scattering Angle (°)	135°	170°	170°	Custom
Particle size range	0.5 nm – 10 µm (sample dependant)			
Sample concentration range	10^{-4} % to 40% volume	10^{-5} % to 5~10% volume (sample dependant)		
Head’s weight	3.5 kg	< 0.5 kg	0.5 kg	Custom
Head’s dimensions	110 x 185 x 250 mm (HWD)	50 x 25 x 120 mm (HWD)	100 x 90 x 235 mm (HWD)	Custom
Options & accessories	Online measurement	Thermalized cell (10-70°C)	-	-

Our product portfolio

CORDOUAN Technologies

PARTICLE SIZE ANALYZER by DLS

VASCO

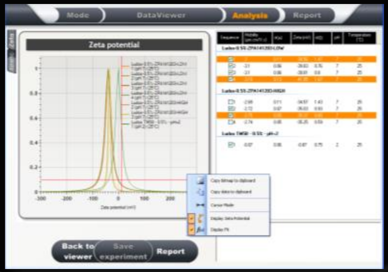
- Patented DTC technology for concentrated / absorbent samples
- Unique algorithms (Pade Laplace & SBL) for a better distribution analysis
- Flex: In–situ measurement / easy coupling to reactors
- Patent pending on new applications
- Synthesis kinetics monitoring

VASCO flex™

ZETA POTENTIAL ANALYZER

WALLIS™

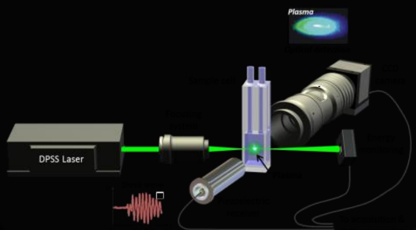
- The best resolution thanks to modern data acquisition & computing
- Unique carbon electrodes



NP TRACES (size & cc.)

MAGELLAN™

- Unique LIBD technology
- Size range: 15 to 1000nm
- Cc ranges :
  $10^3 - 10^{11}$ part/ml *(det. only)*
  $10^6 - 10^{11}$ part/ml *(det. + size)*



ELECTRON MICROSCOPY

LVEM5 (Delong)

- Unique TEM/SEM/STEM benchtop microscope

ELMO™

- Glow discharge for EM grids functionalization

Thank you for your attention

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