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METROLOGY OF NANOPARTICLES WITH SMALL ANGLES X-RAY SCATTERING (SAXS)

FROM SIMPLE CASES

TO NANOPARTICLES COMPLEX MEDIA

O. Taché

Dr. V. Geersten, E . Barruet, Dr. O. Spalla , Dr. A. Thill, Dr F. Testard, S. Doco

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91191 GIF SUR YVETTE CEDEX FRANCE

SAXS PLATFORM AT CEA PARIS-SACLAY

LIONS

O. Spalla, A. Thill, F. Testard, V. Geertsen, D. Carriere, F. Gobeaux, O. Taché

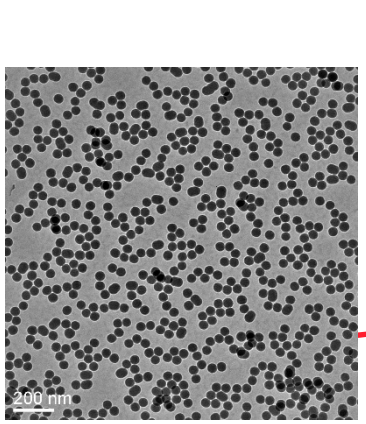
LLB (SANS laboratory) :

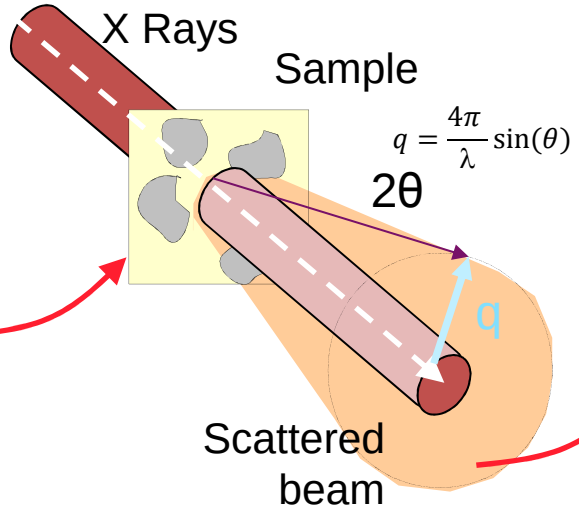
A. Brulet, F. Cousin, J. Jestin, A. Cheneviere

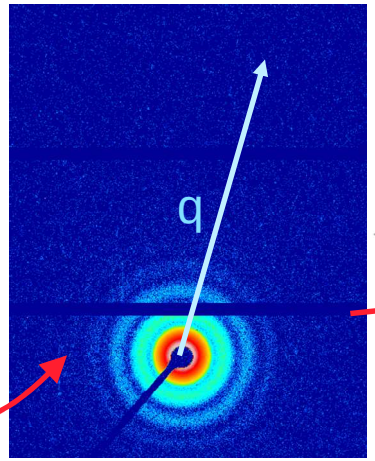
150 m2 dedicated to SAXS:
4 experiments , Preparation workshop chemistry lab
Sample environments
Open source software

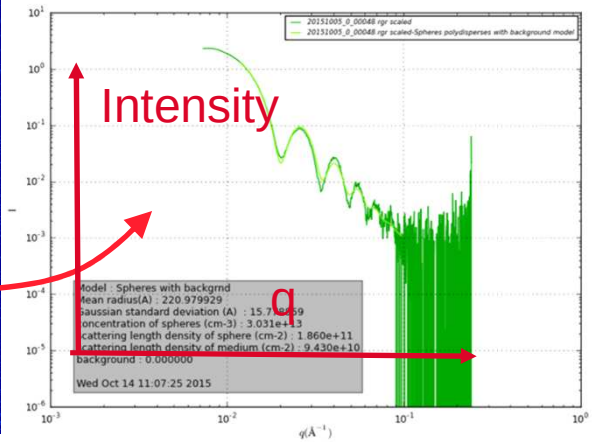
- Home made and commercial setup
- Different configurations, different energies
- Methodology from sample preparation to data treatment (sample thickness, calibration, modelization,…) for size and concentration determination

SMALL ANGLE X-RAYS SCATTERING (SAXS)



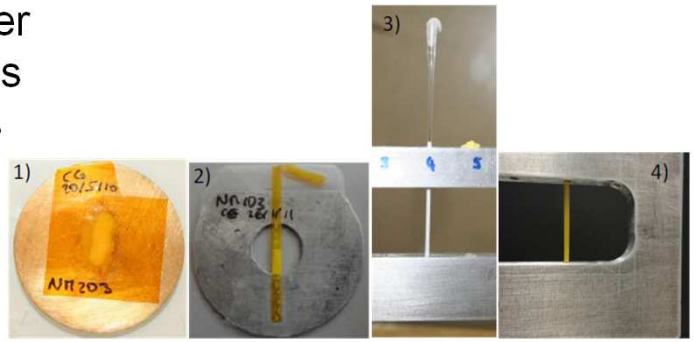


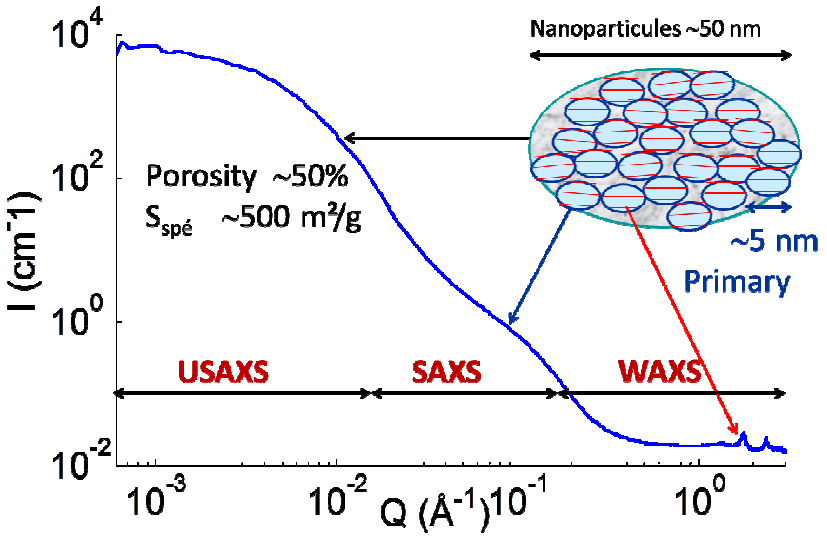




SAXS – Small Angles X-Rays Scattering :

- Quantitative informations on morphology of nanomaterials, size, volume, surface, polydispersity.
- Dispersion state, concentration, agregation
- *in situ* observation without sample modification
  - Powder
  - Liquids
  - Solids





Fleury, B.; Neouze, M.-A.; Guigner, J.-M.; Menguy, N.; Spalla, O.; Gacoin, T.; Carriere, D. Acs Nano **2014**, *8 (3), 2602 2608.*

METROLOGY WITH SAXS

SAXS a well known technic

- 30 synchrotron beamlines
- 5 commercial available laboratory intruments (Brucker, Anton-Paar, Xenocs, Rigaku, Malvern-Pananalytical)
- Guinier A and Fournet G 1955 Small-Angle Scattering of X-Rays (New York: Wiley)
- Tao Li, Andrew J. Senesi, et Byeongdu Lee, « Small Angle X-ray Scattering for Nanoparticle Research », Chemical Reviews 116, no 18 (2016): 11128-80,.

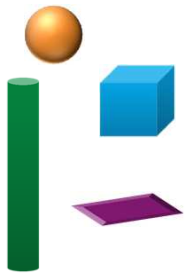
SAXS for Metrology / traceability

- result can be related to a reference through a documented unbroken chain of calibrations
- measurement uncertainty
- comparison of measurements
- original definition of the unit (SI)

Not a direct technic

- SAXS is an ensemble technique (like DLS)
- Scattering sensitive to electron density contrast
- Scattering theory (form factor), traceability!
- The results are AMBIGOUS but representative
- Interparticle interferences are not negligible

SAXS Intensity = Form factor x Structure



- Size
- Concentration
- Composition
- Electron density
- …

TRACEABLE SIZE DETERMINATION

INTERNATIONAL STANDARD **ISO 17867**

First edition 2015-05-01

Particle size analysis — Small-angle X-ray scattering

Analyse granulométrique — Diffusion des rayons X aux petits angles

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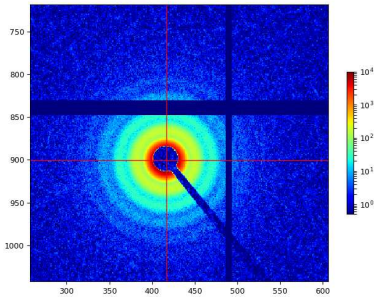
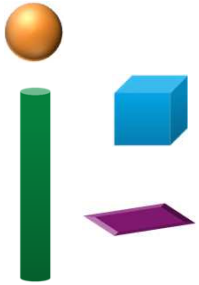
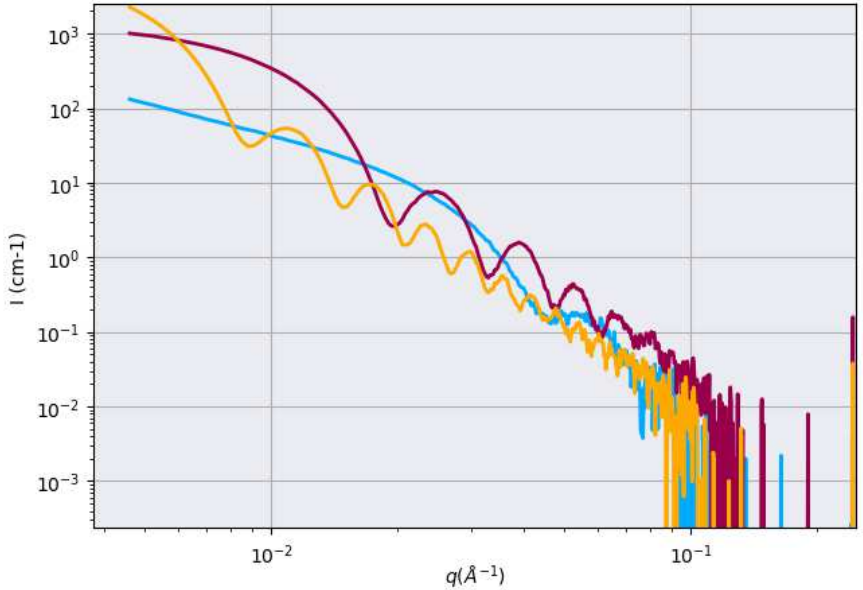




- Size
- Concentration
- Composition
- Electron density
- …

Spheric Silica Nanoparticles

19 nm 44 nm 104 nm



Xeuss instrument 1800s exposure time

TRACEABLE SIZE DETERMINATION

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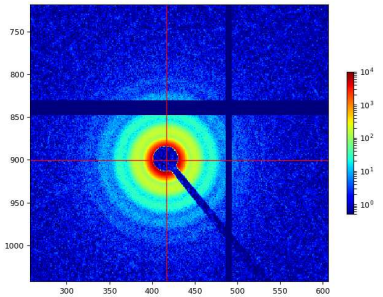

- Size
- Concentration

Spheric Silica Nanoparticles

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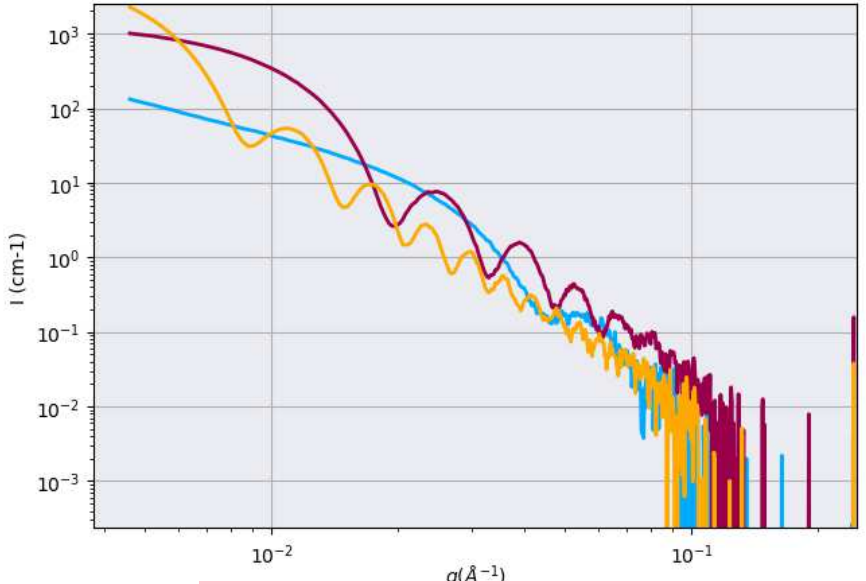
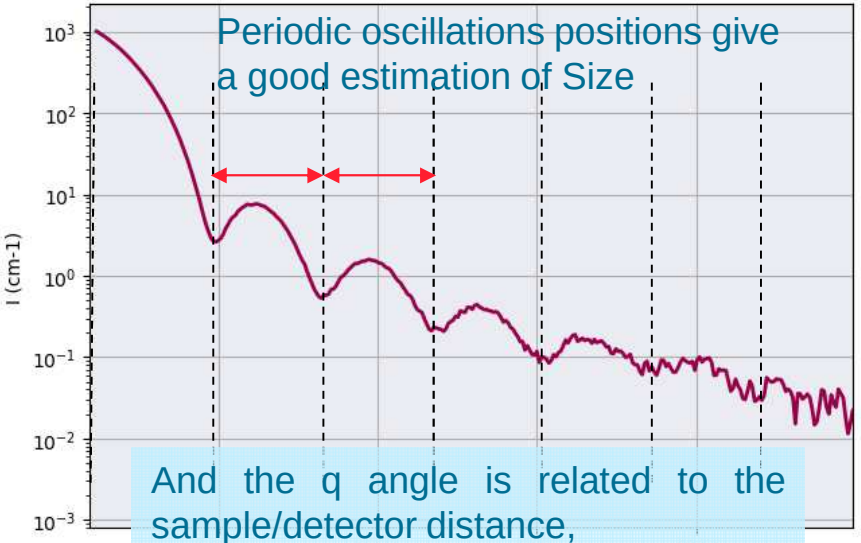




Periodic oscillations positions give a good estimation of Size

And the q angle is related to the sample/detector distance, and directly related to the meter

Metrologically traceable

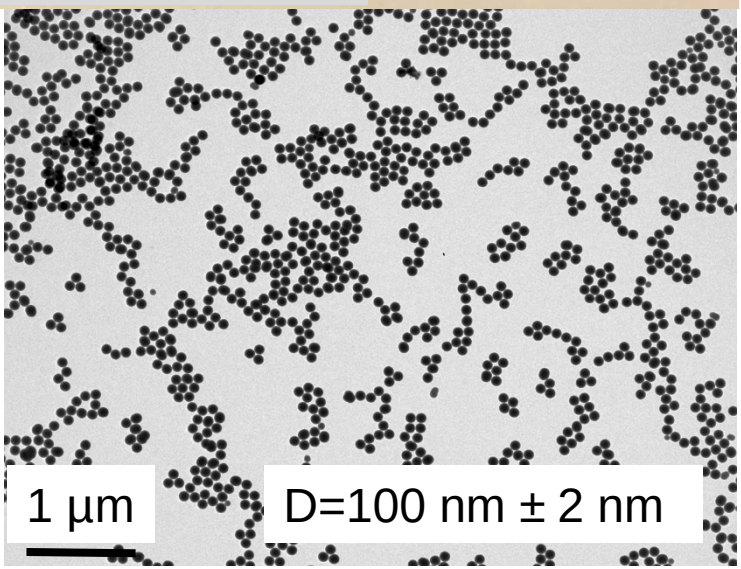
Uncertainty for size is less than 1%

EU INNANOPART PROJECT

Measurement of nanoparticles concentration

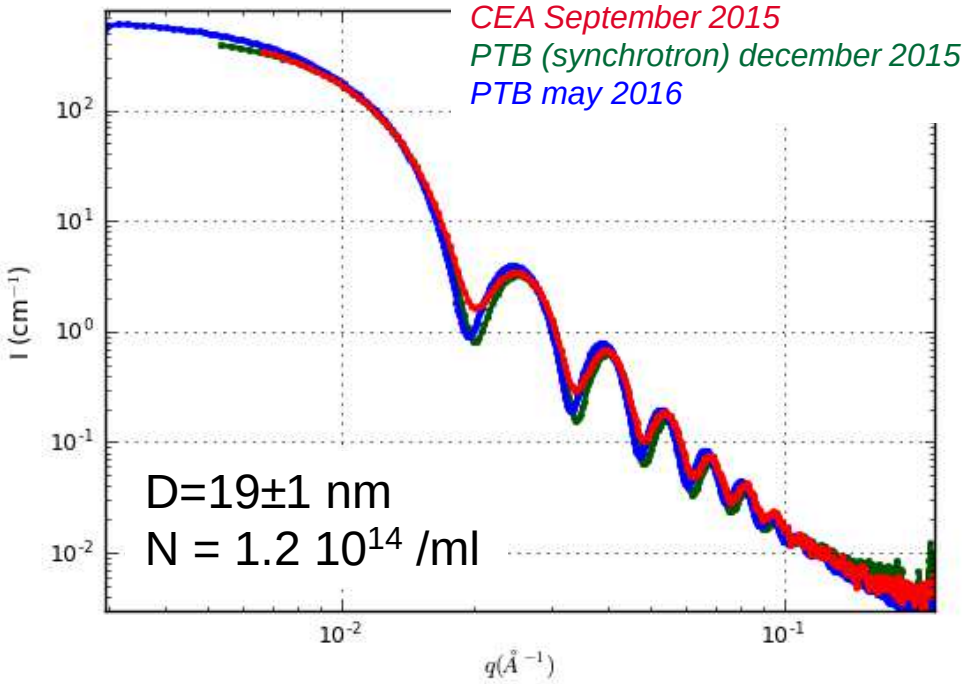
O. Taché, A. Thill, V. Geertsen, E. Barruet, F. Gobeaux

19 nm ± 1 nm
44 nm ± 1.5 nm
100 nm ± 2 nm



D=100 nm ± 2 nm

- Synthesis of Monodisperses Spheric Silica nanoparticles (FWHM/diameter mean < 20%) for 5 different sizes
- Monitoring the stability of samples(concentration, size)

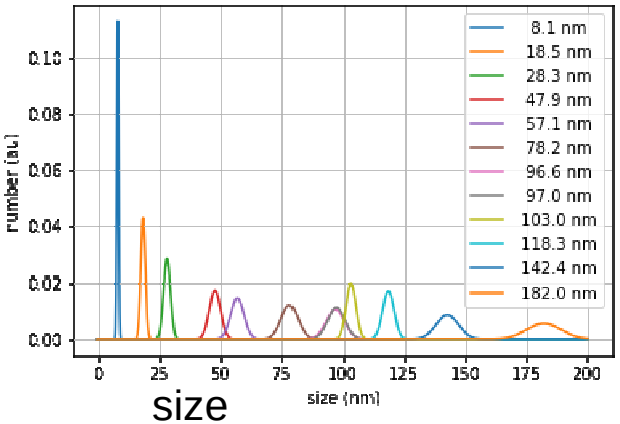


After 30 months of strorage :

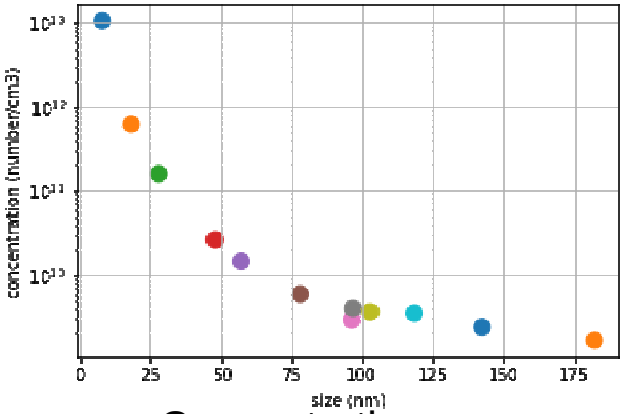
- Size is constant
- Concentration is relatively stable

CONTRIBUTION TO ACCURATE SPHERICAL GOLD NANOPARTICLES SP-ICPMS ANALYSIS

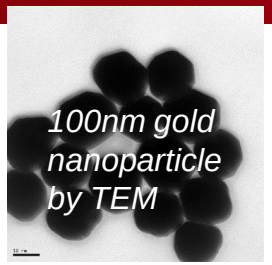
- **Commercials Gold nanoparticles measured by SAXS**



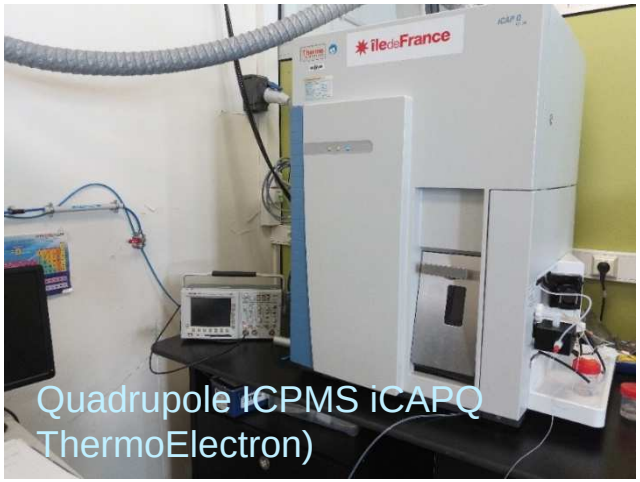
size



Concentration

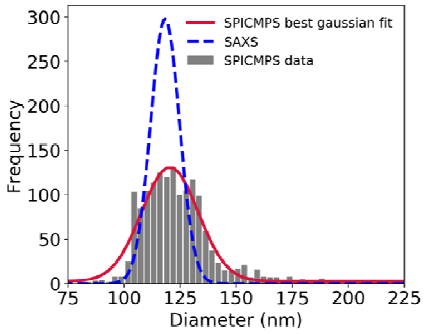


- **SP-ICPMS measurement (V. Geertsen)**



Quadrupole ICPMS iCAPQ ThermoElectron)

Supplier		SAXS			SAXS+ICPMS
Diameter (nm)	[AuNPS] p/mL	d (nm)	sigma (nm)	[AuNPS] p/mL	[AuNPS]b p/mL
30nm	1.80E+11	28.3	4	1.60E+11	1.70E+11
50nm	3.50E+10	53.3	6.5	2.80E+10	3.10E+10
60nm	1.90E+10	57.1	7.7	1.50E+10	1.80E+10
80nm	7.80E+09	78.2	9.4	5.90E+09	7.30E+09
100nm	3.80E+09	96.6	10.6	4.00E+09	4.40E+09
150nm	3.60E+09	142.5	13	2.40E+09	3.10E+09



Histogram (nb/nm)
spICPMS-SAXS comparison

Contribution to Accurate Spherical Gold Nanoparticle Size Determination by SPICPMS: A Comparison with SAXS Anal. Chem. 2018, 90, 9742−9750

MIXTURE OF NANOPARTICLES

Mixture of suspension silica nanoparticles synthetized by CEA

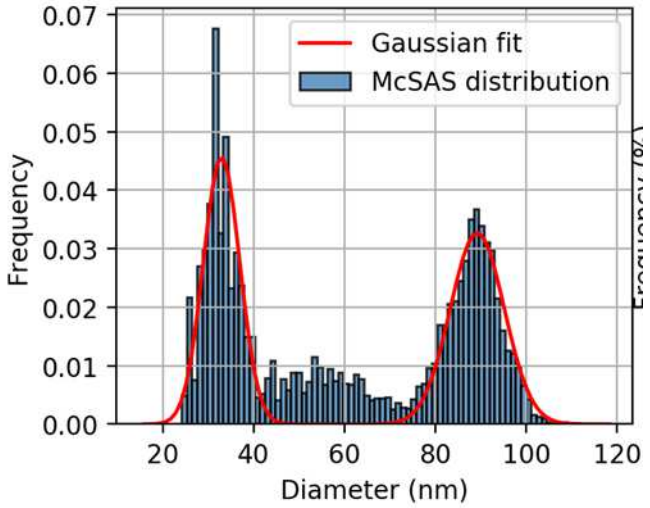
2018 French round robin organized by Club-Nanometrologie

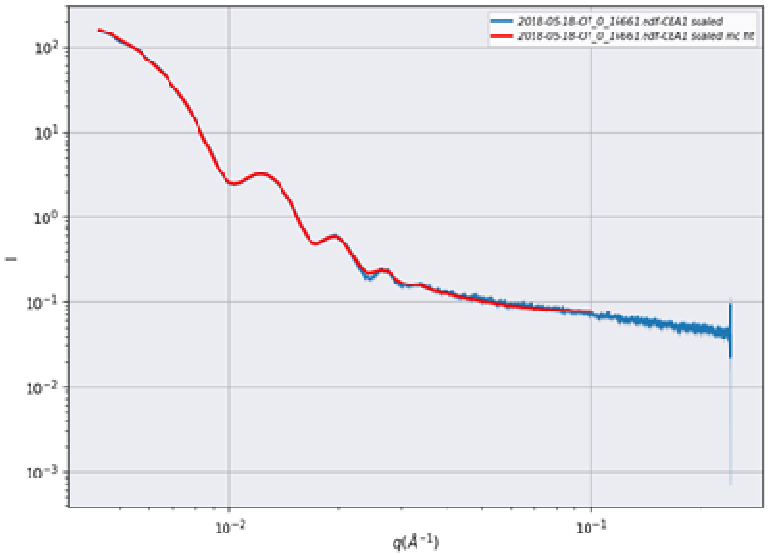
2018-2021 European EMPIR Project npSize

-International intercomparison

-different ratio, forms, polydispersity

The unambiguous correlation of possible health and sustainability risks to nanoparticle size must be enabled by reliable measurement of nanoparticle size, to ensure comparability and compatibility between results measured under different methods.





TRACEABLE SIZE DETERMINATION OTHER PARAMETERS

Size determination uncertainties :

- Xray wavelength
- stable source

- Detector to sample distance

Changing the distance with the same sample for an accurate measuring

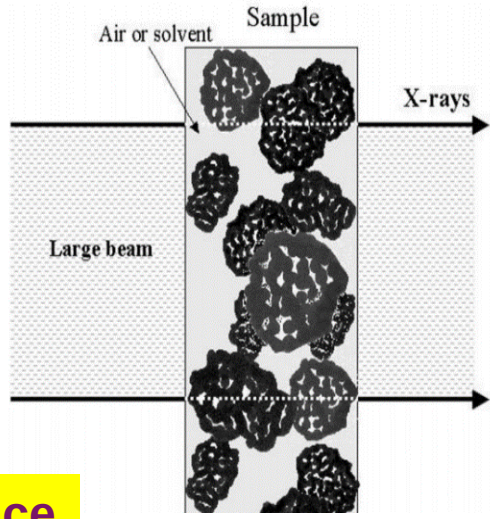
Now possible with laboratory instruments

When the system is too complex, model fitting approach is not relevant

High Polydispersity, Isotropic
matrix or solvent scattering is removed

Signals can be decomposed

N : density
V : volume
Rg : Giration Radius

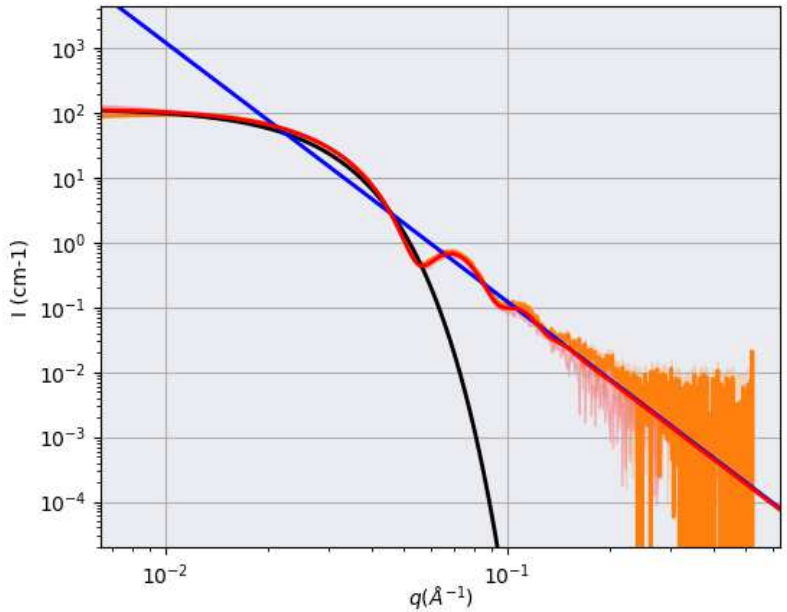


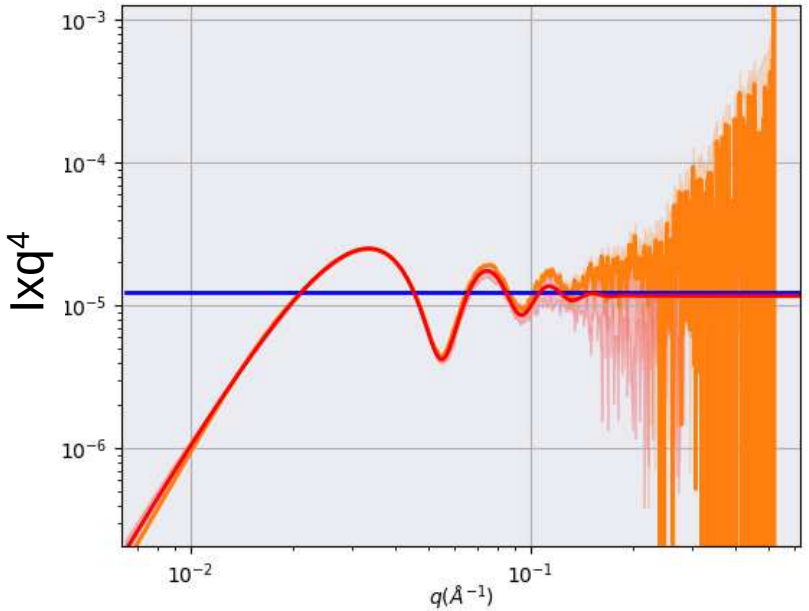
Pores filles by air or solvent

Guinier law $$I_{Guinier}(q) = N(\Delta\rho)^2 V^2 e^{\frac{-q^2 Rg^2}{3}}$$

Porod law $$I_{porod}(q) = 2\pi N(\Delta\rho)^2 S \; q^{-4}$$

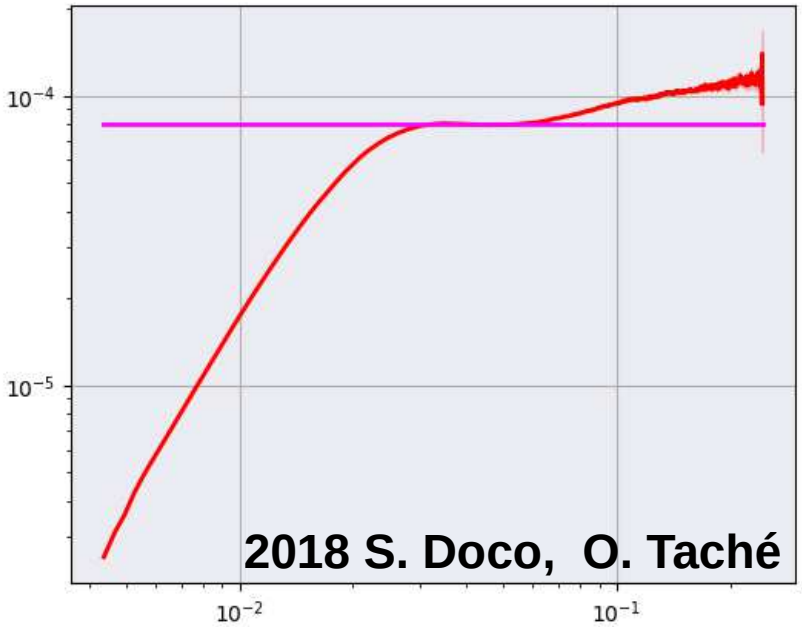
S : **specific surface**



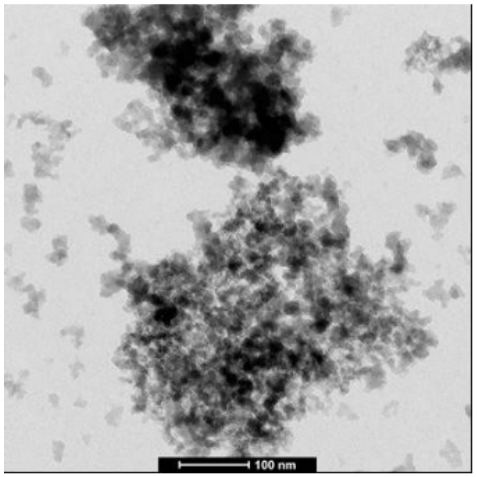


AMORPHOUS REFERENCE SAMPLE

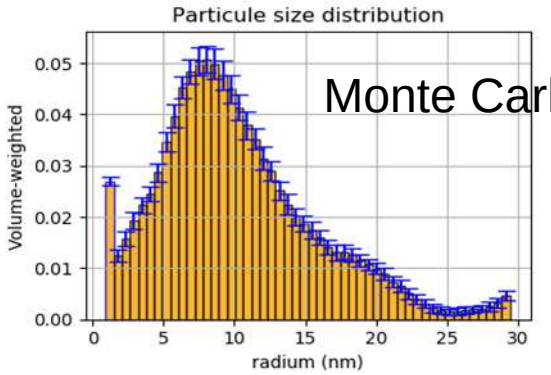
Synthetic Amorphous Silicon Dioxide (NM-200, NM-201, NM-202, NM-203, NM-204): Characterisation and Physico-Chemical Properties
JRC Repository: NM-series of Representative Manufactured Nanomaterials



2013 O. Spalla, C. Guiot



Sample	Type	2013 Diameter (nm)	2018 Diameter (nm)
NM200	SiO2	22	36.7
NM201	SiO2	22	26.6
NM202	SiO2	15	16.6
NM203	SiO2	16	20.1
NM204	SiO2	21	26.1
NM101	TiO2	8	9.2
NM103	TiO2	28	41.4
NM104	TiO2	27	30.2



Monte Carlo estimation

CONCLUSION

Complementary with microscopy

Traceable Size determination of nanoparticles using SAXS has been established:

- ISO standard
- Round robin SAXS Instrument comparison

Determination of concentration nanoparticles using SAXS

- no standard
- No reference samples
- INNANOPART Project
- Comparison with other techniques

Improvement of the methods

- npSize Project
- Intercomparison

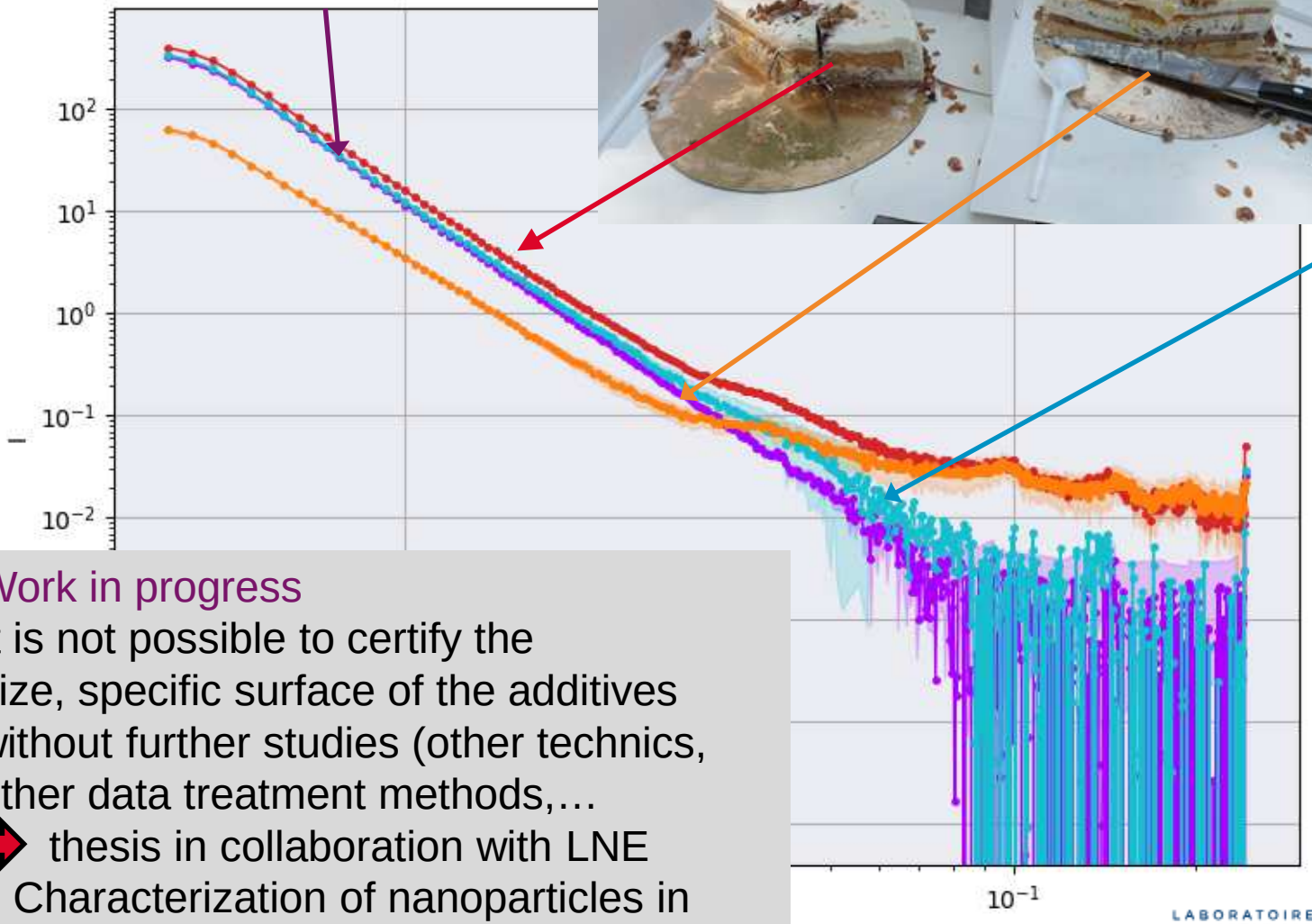
Determination of specific Surface

Application to nanoparticle in complex media

NANOPARTICLES IN FOOD ADDITIVES

STANISLAS DOCO, F. TESTARD, O.TACHÉ

Subtraction
(additives only)



Work in progress

It is not possible to certify the size, specific surface of the additives without further studies (other technics, other data treatment methods,…

⇨ thesis in collaboration with LNE « Characterization of nanoparticles in complex media »