DE LA RECHERCHE À L'INDUSTRIE

cea

nanosciences & innovation

nimbe

www.cea.fr

USING PYFAI ON SAXS LABORATORY INSTRUMENTS. USE CASE : METROLOGY OF NANOPARTICLES

OLIVIER TACHÉ

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

DESIGN CEA

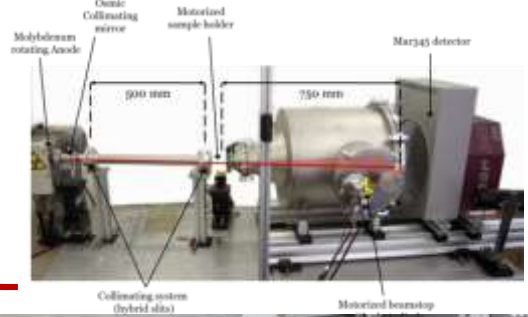
USAXS ultra small angles

q range : 2x10^{-4} to 10^{-1} A^{-1}
High resolution
λ=0.154 nm
E=8keV
1D detector

SAXS high brilliance

q range : 7x10^{-3} to 3.5x10^{-1} A^{-1}
(fixed configuration)
λ=0.154 nm E=8 keV

Flux : 125x 10^{6} ph/s
Kinetic studies



SAXS – WAXS (MOMAC)

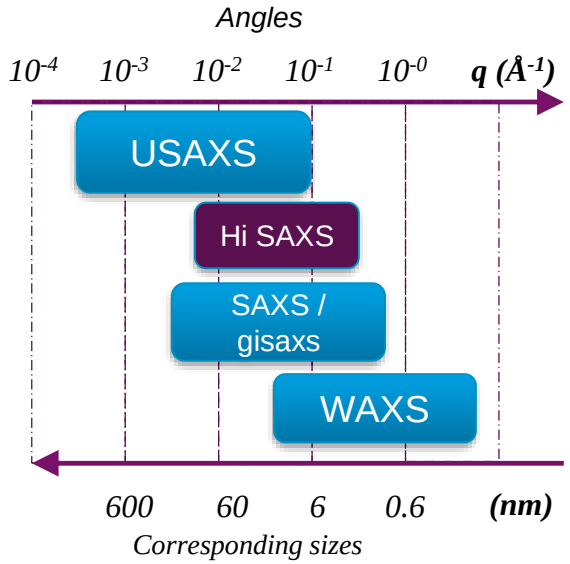
q range : 4x10^{-2} to 4 A^{-1}

λ=0.07 nm **E=17 keV (nanomaterials)**
Flux : 100 x 10^{6} ph/s

SAXS / GISAXS

q range : 3x10^{-3} to 5x10^{-1} A^{-1}
Polyvalent configuration
Sample under vacuum/air
Big size Pilatus1M Detector

Flux : 20 x 10^{6} ph/s



150 m^2 dedicated to SAXS:

- 4 experiments
- Preparation workshop
- Mini 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

METROLOGY OF NANOPARTICLES WITH SAXS

SAXS a well known technic

- 30 synchrotron beamlines
- 5 commercial available laboratory intrur aar, Xenocs, Rigaku, Malvern-Pananalytical)

Guinier A and Fournet G 1955 Small-Angle Scattering of X-Rays (N

Tao Li, Andrew J. Senesi, et Byeongdu Lee, « Small Angle X-ray Sc », Ch 11128-80,.

Taché, O., Rouzière, S., Joly, P., Amara, M., Fleury, B., Thill, A., La ., 2016 *instrument dedicated to nanomaterials »*. Journal of Applied Crystall i.org/1

Pauw, B.R., Kästner, C., Thünemann, A.F., 2017.
« Nanoparticle size distribution quantification: results of a small-ang ry comparison ». Journal of Applied Crystallography 50, 1280–1288. https://doi.org/10.1107/S160057671701610X

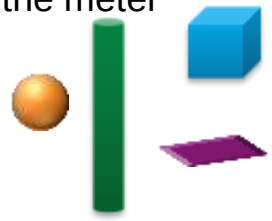
SAXS for Metrology / traceability

Why ? Need of regulation for EU, need of better nanomaterial characterization for industry

- results can be related to a reference through a “documented unbroken chain of calibrations”
- measurement uncertainty
- comparison of measurements to other technics/instruments
- original definition of the unit (SI International System) related to the meter

Not a direct technic / microscopy

- SAXS is an ensemble technique (like DLS)
- No need of sample preparation
- Scattering sensitive to electron density contrast
- Scattering theory (form factor)
- Interparticle interferences are not negligible



- Size
- Concentration
- Composition
- Electron density
- …

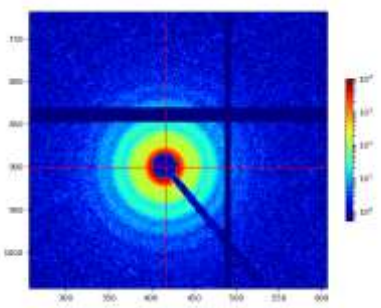
SAXS Intensity = Form factor x Structure

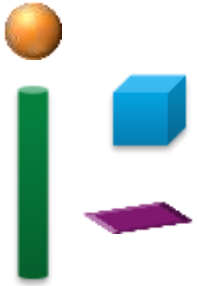
TRACEABLE SIZE DETERMINATION

INTERNATIONAL STANDARD **ISO 17867**

Particle size analysis — Small-angle X-ray scattering

SAXS Intensity = Form factor x Structure

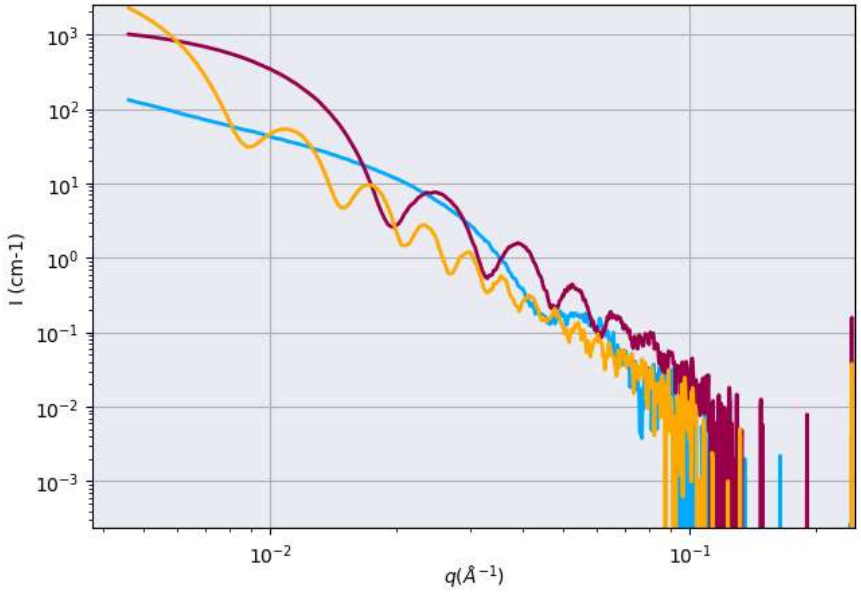




- Size
- Concentration
- Composition
- Electron density
- …

Spheric Silica Nanoparticles

19 nm 44 nm 104 nm



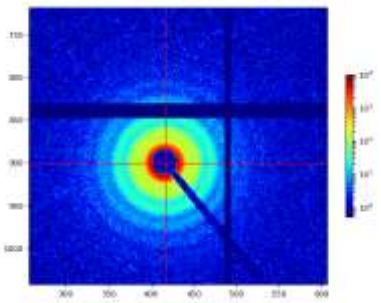
Xeuss instrument 1800s exposure time

TRACEABLE SIZE DETERMINATION

INTERNATIONAL STANDARD **ISO 17867**

Particle size analysis — Small-angle X-ray scattering

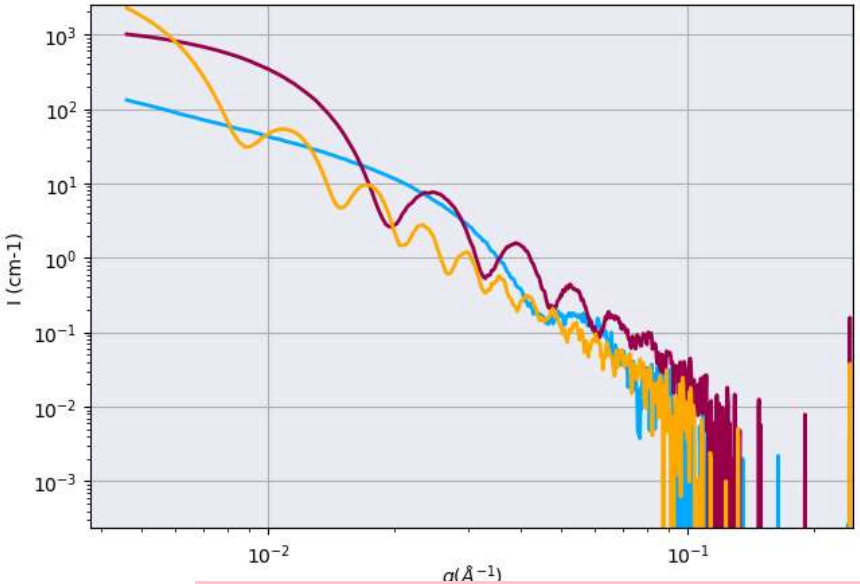
SAXS Intensity = Form factor x Structure

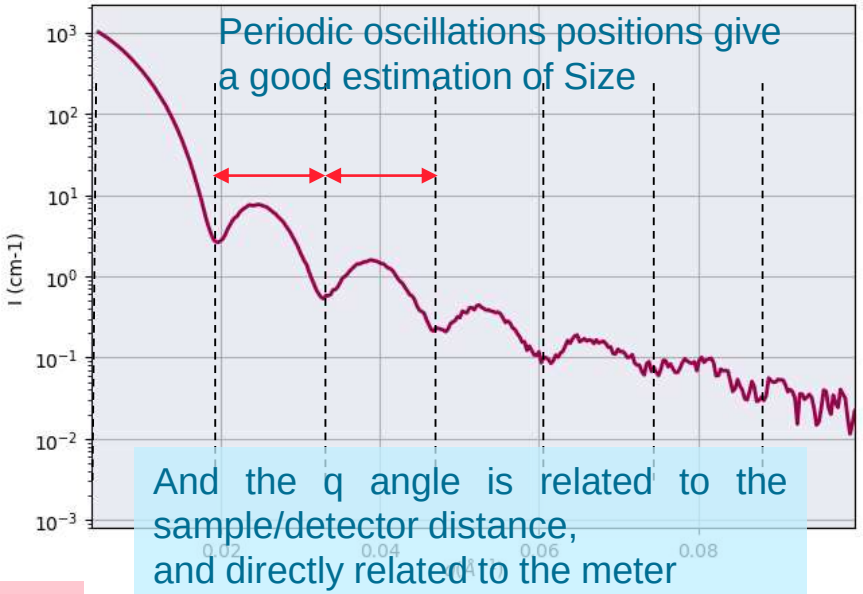


- Size
- Concentration

Spheric Silica Nanoparticles

19 nm 44 nm 104 nm





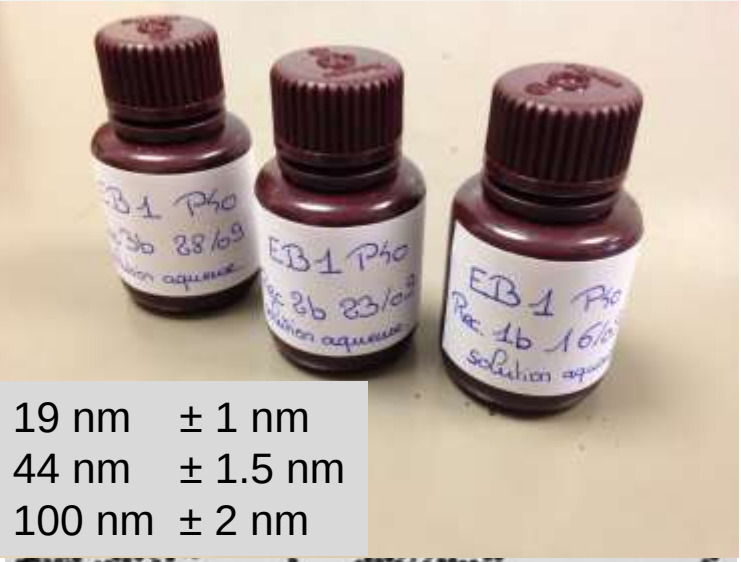
Uncertainty for size is less than 1%

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

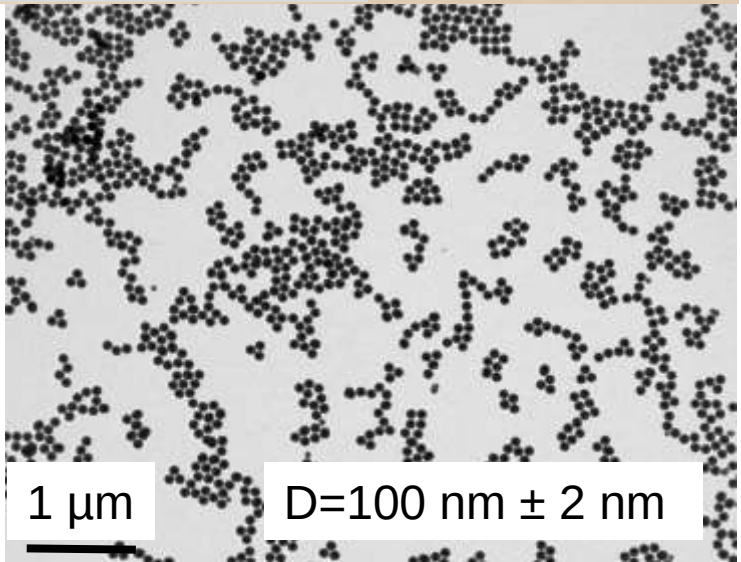
EU INNANOPART PROJECT

Measurement of nanoparticles concentration

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

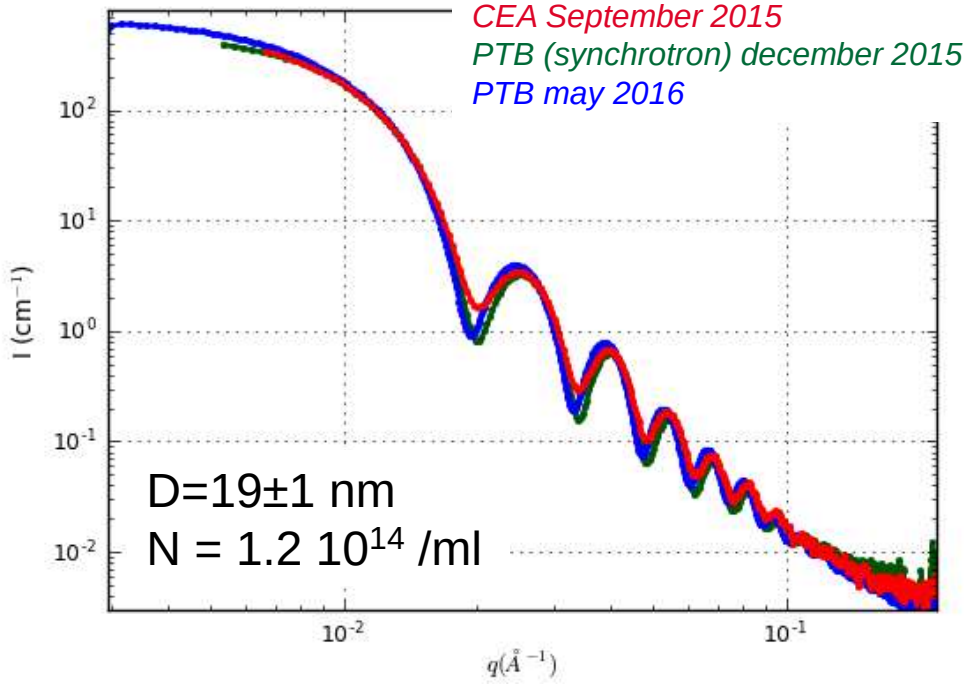


19 nm ± 1 nm
44 nm ± 1.5 nm
100 nm ± 2 nm



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

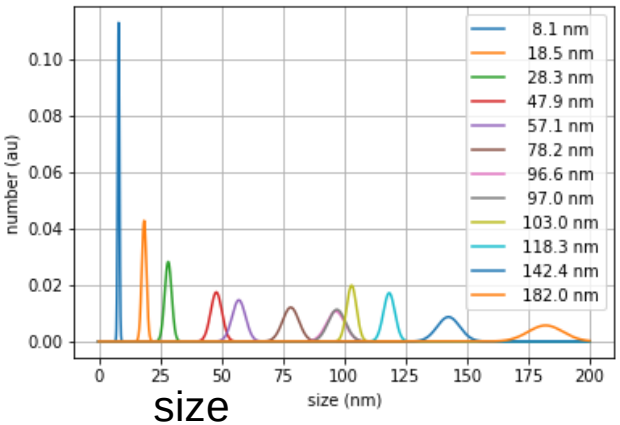
CONTRIBUTION TO ACCURATE SPHERICAL GOLD NANOPARTICLES SP-ICPMS ANALYSIS

nanosciences & innovation

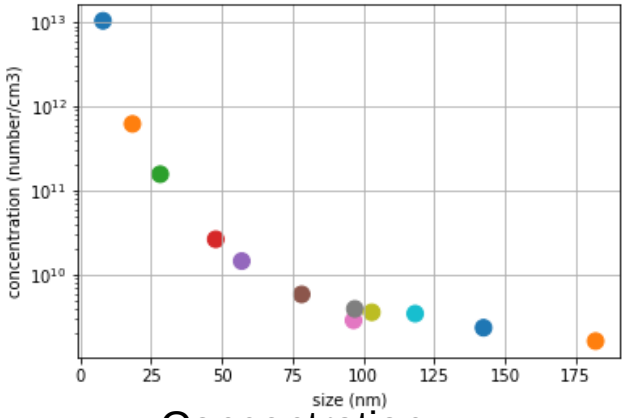
Geertsen V., Barruet E., Gobeaux F., Lacour J.L and Taché O.

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

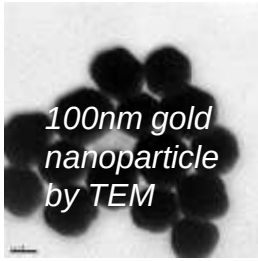
- **Commercials Gold nanoparticles measured by SAXS**



size



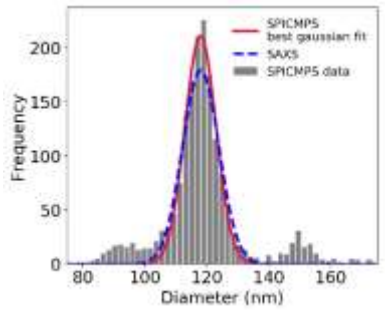
Concentration



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

Single Particle Inductively Coupled Mass Spectrometry (SPICPMS)

- a counting technique
- providing the number of composing atoms of each nanoparticle.
- It is a fast and quantitative technique allowing the measurement of thousands of nanoparticles in a few minutes.
- Assuming nanoparticles shape, it provides number size distribution.



Histogram SAXS spICPMS comparison

SPHERIC SILICA NANOPARTICLES

nanosciences & innovation

nimbe

EMPIR

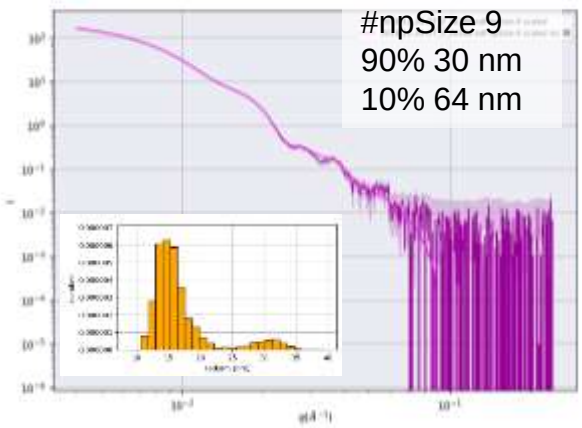
EURAMET

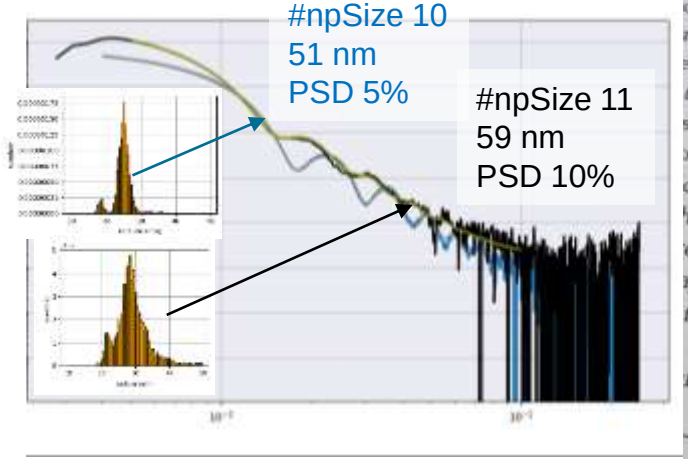
nPSize

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

2018-2021 European EMPIR Project npSize
Improved traceability chain of nanoparticle size measurements

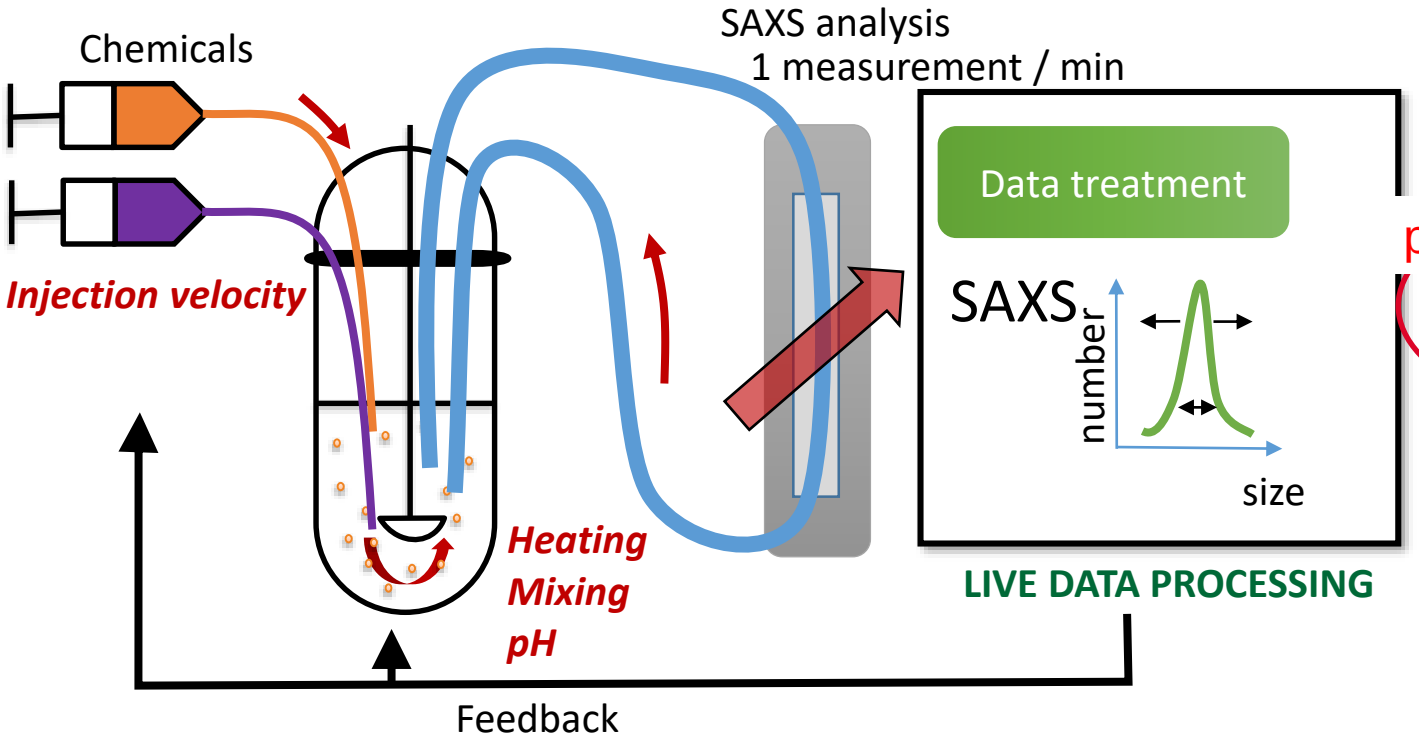
- Nanoparticles as reference material
- International intercomparison / different techniques
- Mixture of spheric silica nanoparticles in suspension synthetized by CEA

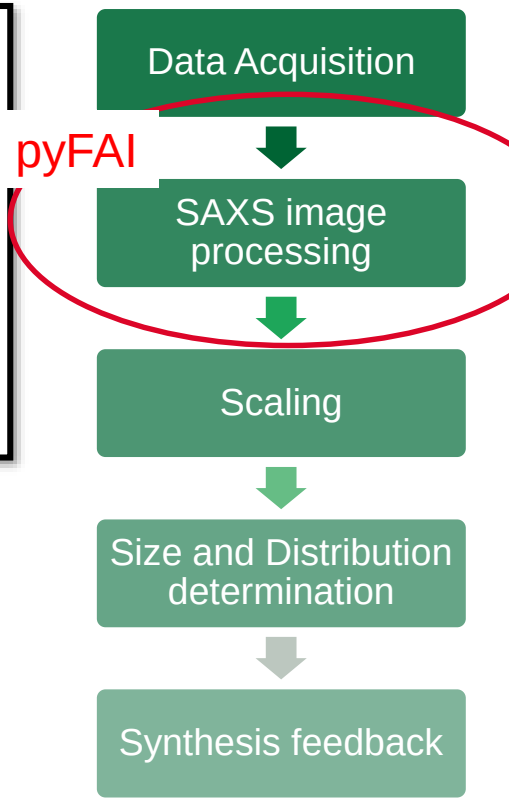




Precise control of nanoparticles size during the synthesis

OPTIMIZED SYNTHESIS OF NANOPARTICULES





Project : kinetics of nanoparticles synthesis

- Kinetic synthesis (1 characterisation/min)
- Control chemical product injection
- Control synthesis
- stop injection

« in demand » nanoparticles with sub-nanometric size diameter, concentration, size distribution

pySAXS, an Open Source Python package and graphic user interface for SAXS data treatment

Series of modules entirely written in Python (2&3) language allowing to process the different operations for the SAXS data treatment.

pySAXS is open source and based on Numpy and SciPy libraries, matplotlib, pyQT5

Initially designed for the SAXS experiments (USAXS, SAXS, WAXS), the package is completely independent from instrument

pySAXS contains libraries with basic functions for manipulating data (merge, subtract, add,…), setting in absolute scale

Uncertainties are carefully propagated at each step of data manipulation

Available on pypi
Continuously in development
Not fully documented

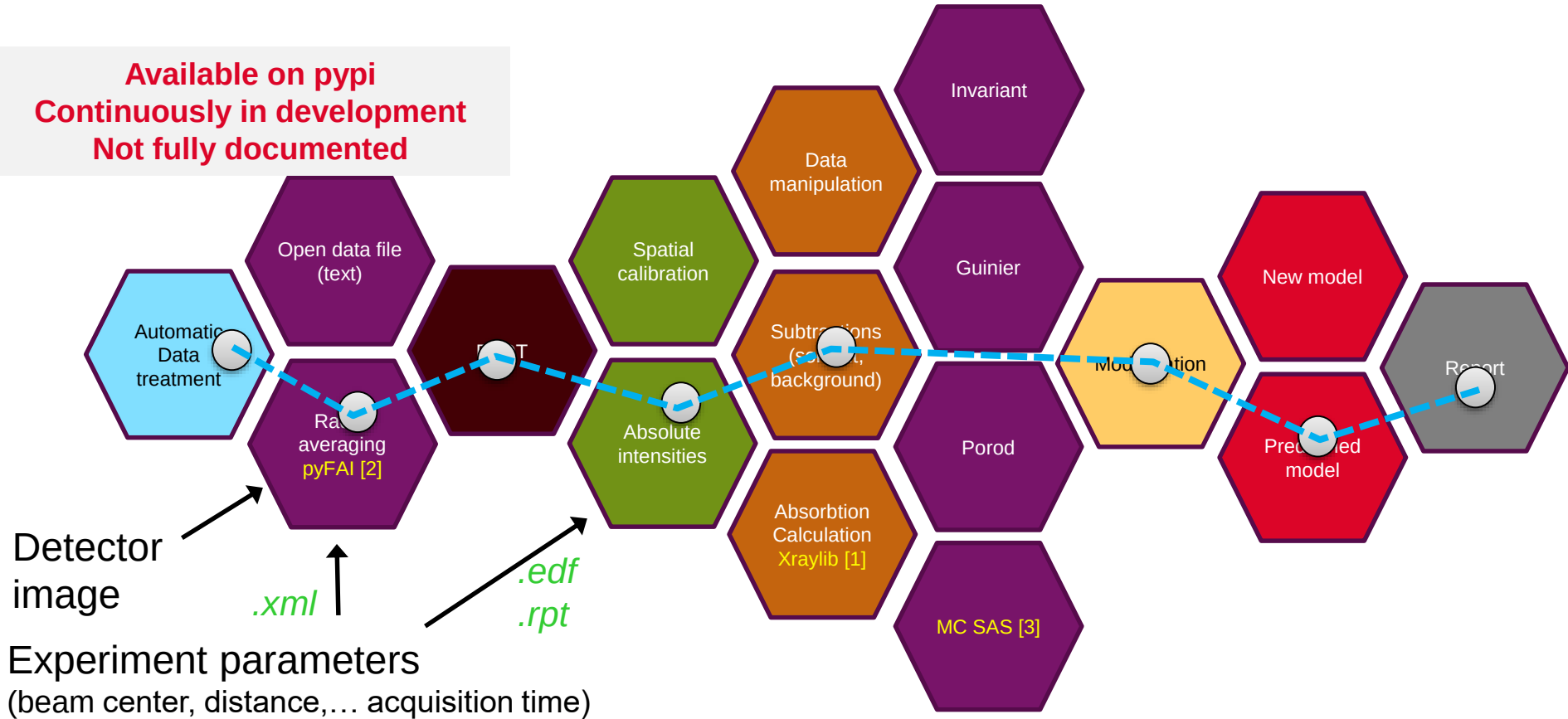


IMAGE MASKS, EXPERIMENT PARAMETERS

pyFAI need :

- Image mask
- Pixel size
- Detector to sample distance
- Beam position,
- …

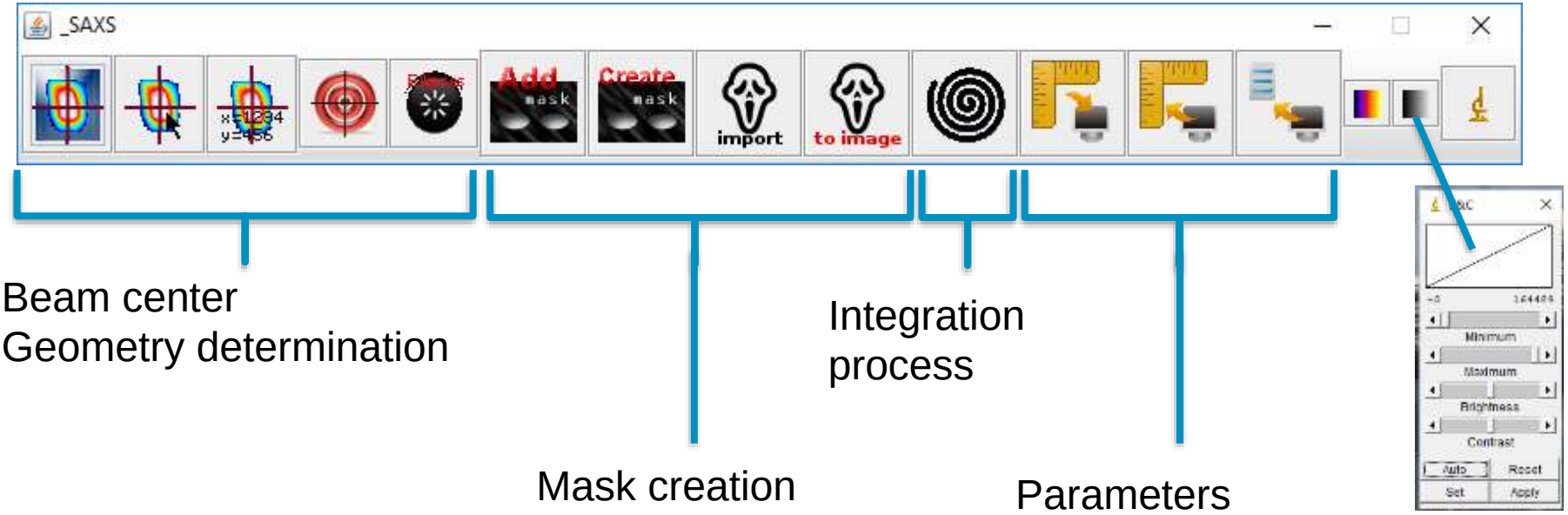
http://rsbweb.nih.gov/ij

ImageJ
Image Processing and Analysis in Java

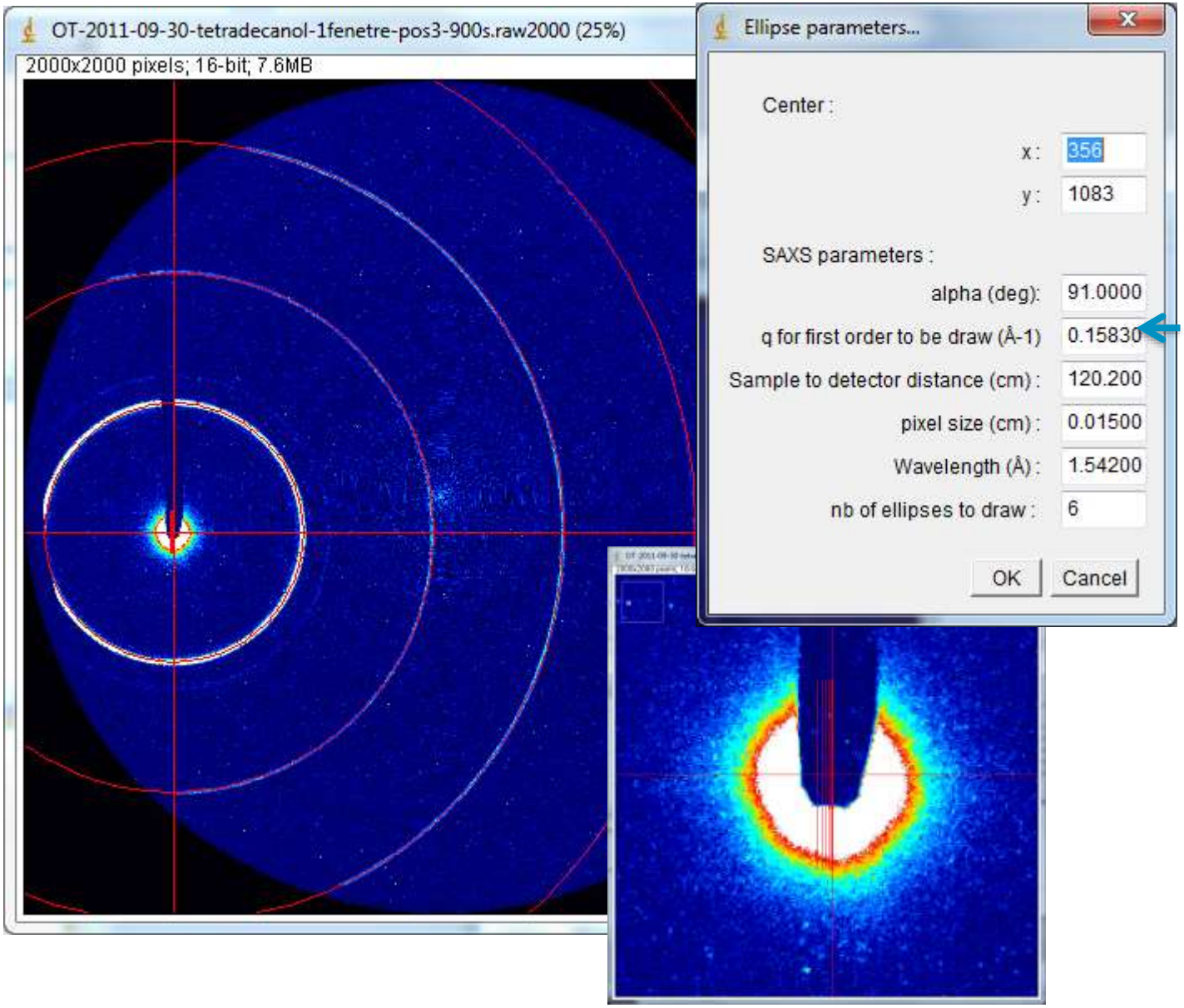
- Open source
- Very large community

Plugins for SAXS :

- Beam center and geometry determination
- Mask creation
- Radial averaging
- tools



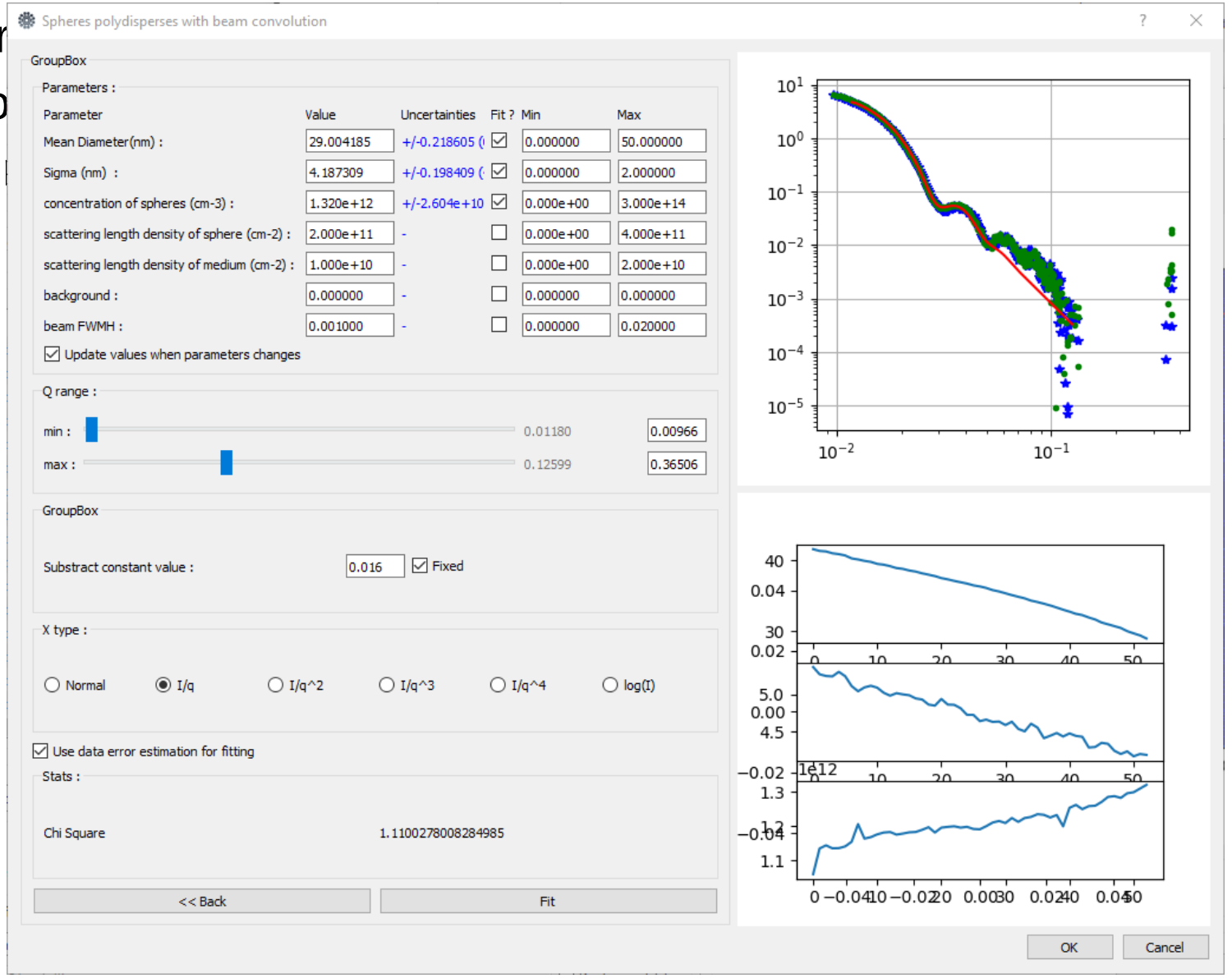
BEAM AND GEOMETRY DETERMINATION



Tetradecanol ring

PYSAXS DEMO

- Pysaxs intr
- Pysaxs mo
- Pysaxs Su



CONCLUSION

- Home made tool
- Difficult to distribute (documentation, models)
- Available on pypi repository

- pyFAI integration necessary
  - -mask tool integration
  - -PONI definition not very usefull

-> definition of Intensity / q standard for exchanging files

npSize participants proposed of HDF5 file NeXus / NXcanSAS ?