Size and concentration of nanoparticles in suspensions: Comparison of laboratory methods to SAXS and spICPMS

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Introduction

EMPIR EURAMET

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

INNANOPART

Innovative Nanoparticle Metrology

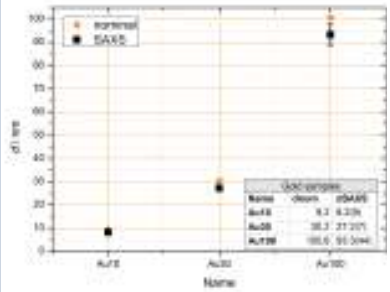
The InNanoPart project focuses on the major unmet metrological needs in the production of high quality nanomaterials: measuring the concentration of particles and measuring the surface chemistry. These two measurements are critical to the performance of these novel materials in products and the development of valid measurement approaches. Supported by documentary standards they will underpin trade and the supply chain for these novel products. Within 14IND12 InNanoPart project "Metrology for innovative nanoparticles", which is part of EMPIR and EURAMET initiatives, the goal was set to develop traceable measurement and calibration protocols for particle number concentration in liquid suspensions. A target of relative uncertainty u = 10 % was specified for spherical particles with diameters in the range from 1 to 1000 nm.

Methods and laboratories

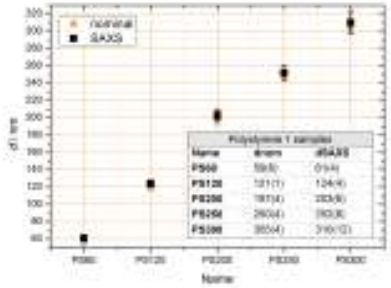
Method	Short	Laboratory
Small Angle X-Ray Scattering	SAXS	PTB
Single Particle Inductively Coupled Plasma Mass Spectroscopy	spICPMS	LGC
Particle Tracking Analysis	PTA	LGC
Single Particle Inductively Coupled Plasma Mass Spectroscopy	spICPMS	DLO
Small Angle X-Ray Scattering	SAXS	CEA
Dynamic Light Scattering	DLS	RISE
Ultraviolet – visible spectroscopy	UV-vis	NPL
Differential Centrifugal Sedimentation	DCS	NPL
Tunable Resistive Pulse Sensing	TRPS	NPL
Electrospray Differential Mobility Analysis	ES-DMA	METAS
Raman Spectroscopy with Hollow Fiber	HC-PCF	DFM

Sample sizes

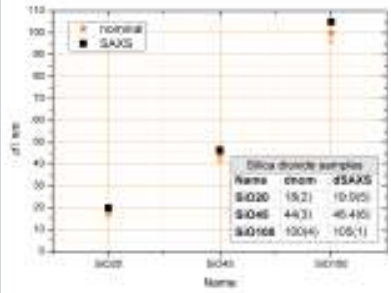
Gold, $\rho = 19.3\ \mathrm{g/cm^{-3}}$



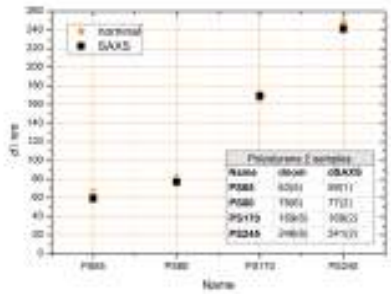
Polystyrene 1, $\rho = 1.05\ \mathrm{g/cm^{-3}}$



Silica dioxide, $\rho = 2.2\ \mathrm{g/cm^{-3}}$



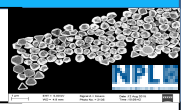
Polystyrene 2, $\rho = 1.05\ \mathrm{g/cm^{-3}}$

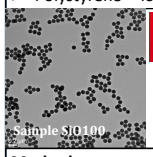


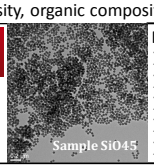
Challenges

Samples:

- Gold – sedimentation
- Silica dioxide – dissolution, uncertain density, porosity
- Polystyrene – low density, organic composition





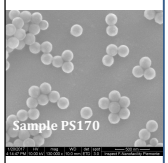


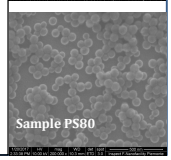
Batches:

- Transportation
- Leakage
- Sedimentation
- Aging
- Coordination of measurements

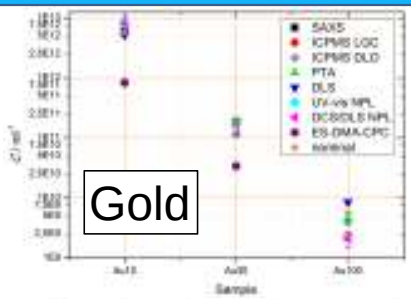
Methods:

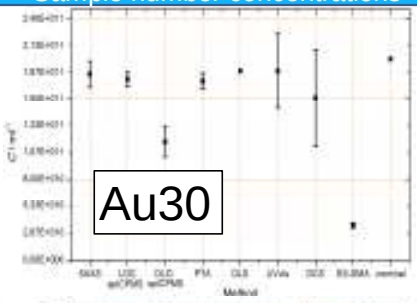
- SAXS : – sedimentation (strong for $d > 100$ nm)
  – effects of dissolution, assumption of sphere
  – higher uncertainty for low contrast
- spICPMS : – only inorganic samples
  – dissolution sensitive
  – size limits ➔ material and instrument
- PTA: – detection limit material dependent
  – for gold $d < 10$ nm
  – sedimentation for $d > 500$ nm
- DLS : – black box
  – volume concentration output
  – size distribution essential for outcome
  – different algorithms available
- UV-vis – opaque or photosensitive samples
- DCS – highly dependent on density
  – knowledge of RI, losses in the system
- TRPS – need of calibration materials
- ES-DMA – dependent on sample matrix
- HC-PCF – $d < 100$ nm, no silica, no gold

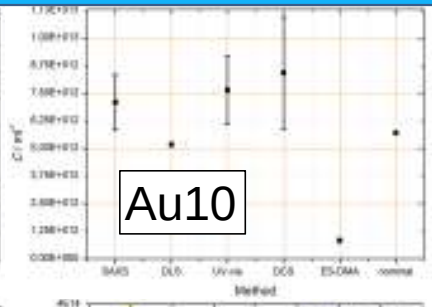


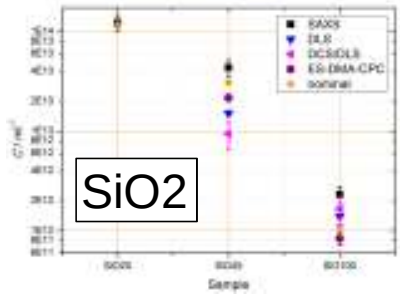


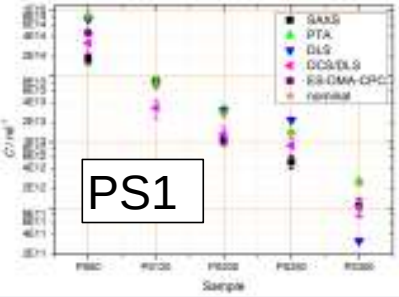
Sample number concentrations

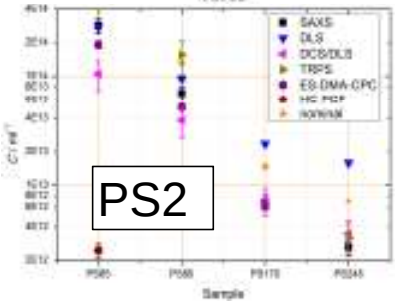












Conclusions

- SAXS and spICPMS (LGC) agree within standard uncertainties on Au30
- SAXS relative uncertainties:
  - Au30 <10%, Au10 <15%, SiO <20%, PS < 20% (except PS300)
- spICPMS (LGC): u_r<5%, spICPMS (DLO): u_r<15% ➔ only gold samples
- spICPMS measurements performed at different facilities show large deviation
- DCS – measured all samples, agrees best with reference methods
- DLS measured all samples, but no uncertainties, volume concentration
- PTA showed reliable results with relative uncertainties <10%
- UV-vis provided reliable results for high density samples
- TRPS only samples stable in high ionic media
- ES-DMA with reliable results for silica and polystyrene, but not for gold
- HC-PCF worked only on low density and $d = 60$ nm, shows too low values
- DCS and PTA first choice as laboratory methods
- DLS for volume concentration as stand alone method

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