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COMPARISON OF SIZE-DETERMINING TECHNIQUES FOR NANOPARTICLES IN SUSPENSION: APPLICATION TO Ag NPs

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PLATE-FORME NANO SÉCURITÉ

INTRODUCTION

Context

- Need to develop techniques that should provide the relevant information on the size of all types of particle populations (counting & size distribution)

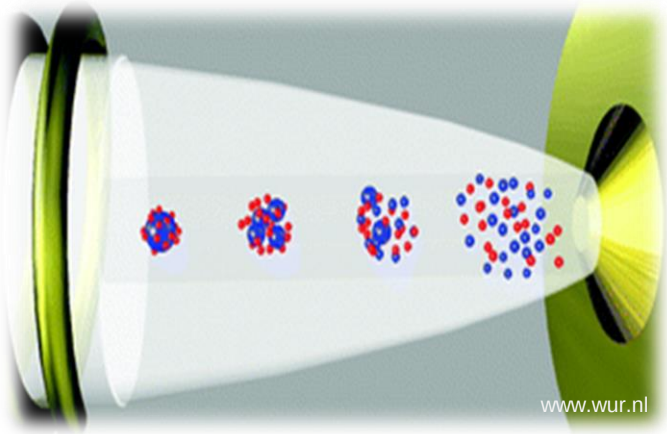
Characterization techniques of nano-suspensions

- Microscopy techniques (SEM, TEM) D_{geom}, chemical composition
  - "real" particle image, individual particle probing
- Techniques based on light scattering (MALLS, DLS) D_{rms}, D_h
  - Ease of use, representative of the whole population
- Novel techniques (sp-ICP-MS, AF4(-MALLS-ICP-MS)) D_{rms}, D_h, D_{mass}, chemical composition
  - Very complete information, representative of the whole population

➢ **Are all methods equivalent, accurate, and reliable?**

ANALYTICAL TECHNIQUES: PRINCIPLE

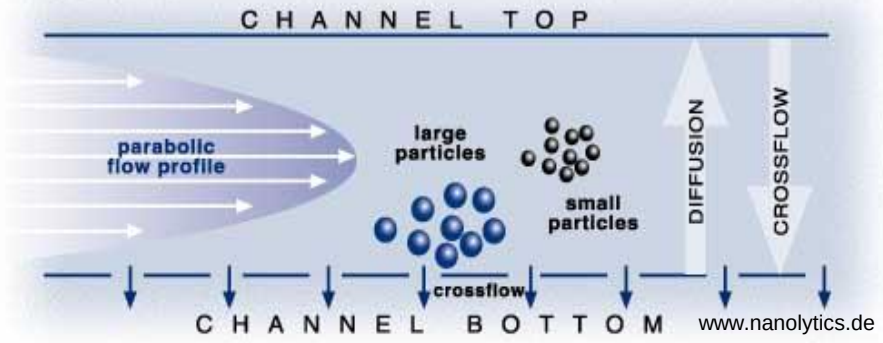
sp-ICP-MS



- Advantages
  - **Feasible with any ICP-MS device**
  - Very sensitive (ng/L)

➢ **D_{mass}, mass distribution**
⇨ **Distribution in number**
➢ **Quantification**

AF4

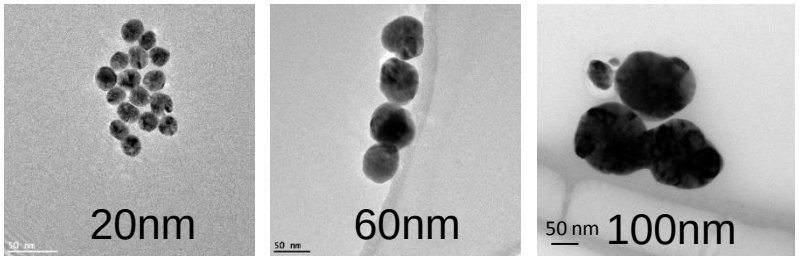


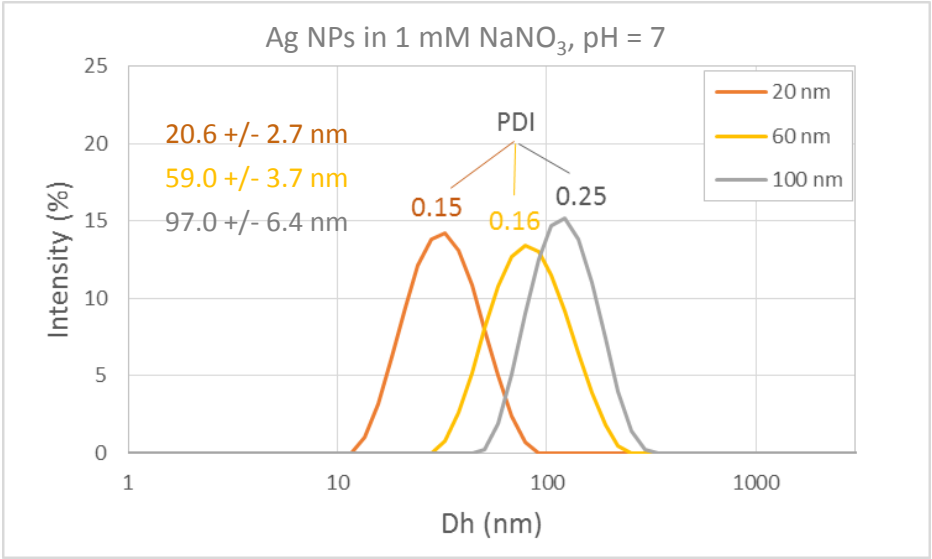
- Advantages
  - **Efficient physical separation of the particles**
  - Coupling with detectors (UV-Vis, MALLS, RI, ICP-MS,…)

➢ **D_h and D_{rms}, mass distribution**
⇨ **Distribution in number**
➢ **Quantification**

CASE STUDY: Ag NPs

TEM & DLS analyses

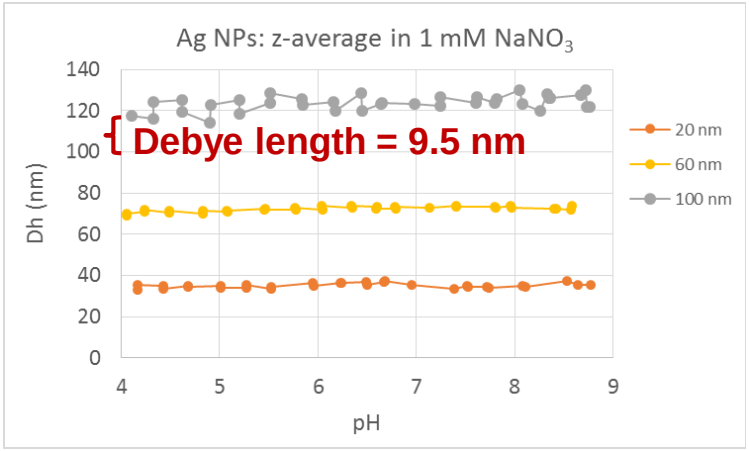




- TEM observations
  - Spherical particles
  - Little agglomeration
  - More heterogeneity for 100 nm NPs

- DLS analyses
  - ~ Monodisperse for 20 and 60 nm NPs
  - Broader distribution for 100 nm NPs
  - Stable suspensions in the pH range 4-9
  - $D_h = D_{geom}$ + (10-20 nm)

➢ **One single mode**

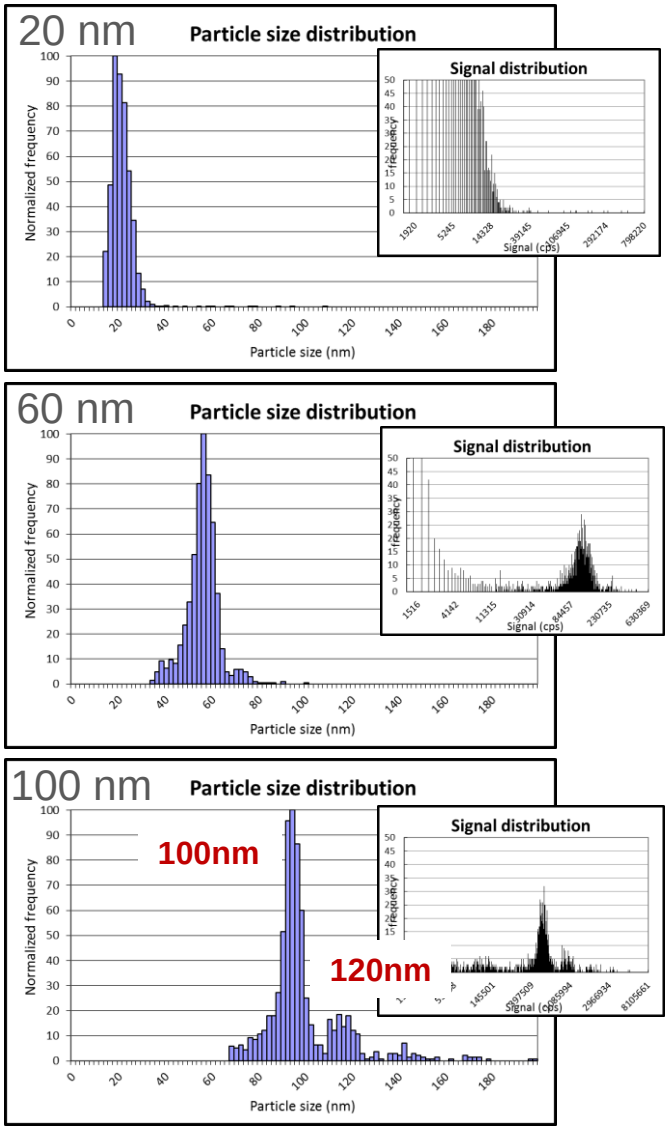


CASE STUDY: Ag NPs

sp-ICP-MS analyses

- Observations
  - High electronic/ionic background (20 nm NPs)
    - ↳ Definition of threshold?
  - Well-defined peaks for 60 and 100 nm NPs
  - More than one mode ⇨ resolution

➢ **Two modes (100 nm NPs)**



Experimental conditions:

- Dwell time 3 ms, acquisition 1 min
- Standard Au NPs ⇨ Transport efficiency
- Ionic Ag calibration ⇨ Particle mass, D_{mass}
- Data processing: spreadsheet from Rikilt(1)

(1) www.wur.nl/en/show/Single-Particle-Calculation-tool.htm

CASE STUDY: Ag NPs

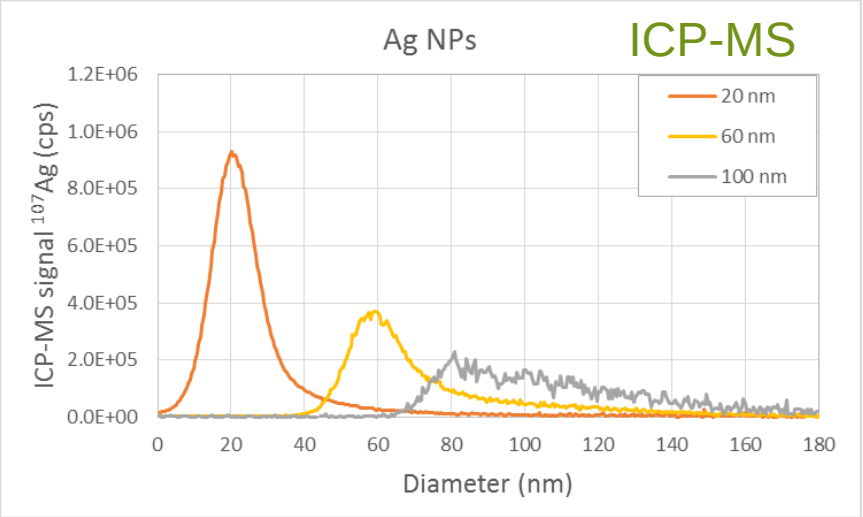
AF4 analyses

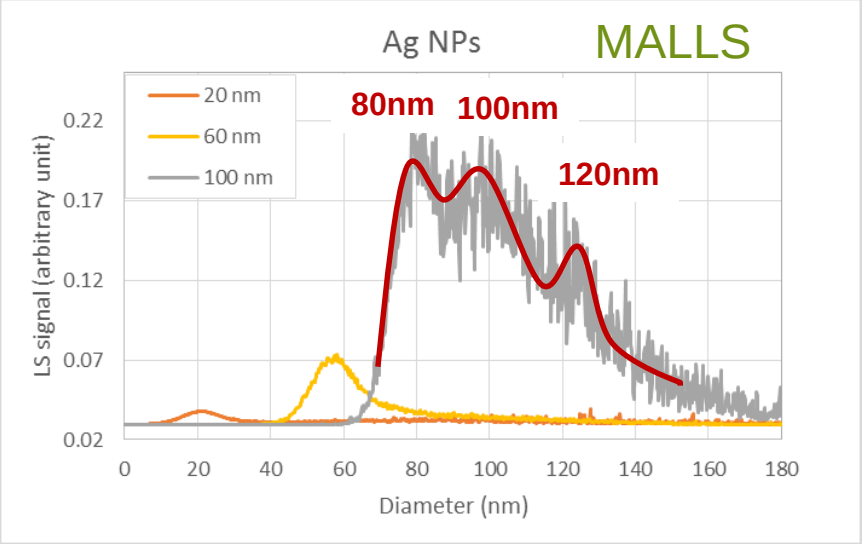
- ICP-MS monitoring
  - Signal ↘ with NP size
  - Tailing
    - ↳ Agglomeration and/or interactions with the membrane
    - ↳ Sample loss ⇨ ~~quantitative analysis~~
- LS monitoring
  - Sensitivity ↗ with NP size (r^6)
  - "Waves" on the 100 nm NPs peak

➢ **Three modes?**

Experimental conditions:

- NaOH pH = 10, 10kDa RC membrane
- Time calibration with Ag NPs standards

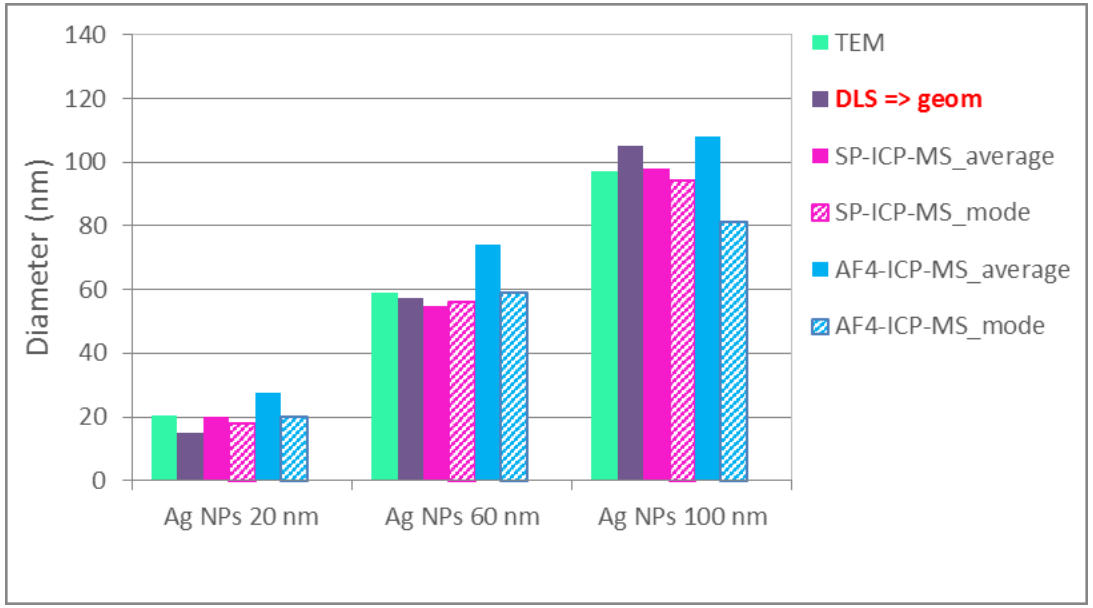




CASE STUDY: Ag NPs

In summary:

- DLS ⇨ largest D (D_h)
- sp-ICP-MS
  (D_{mass}) ~ D(TEM) mode ~ average
- AF4-ICP-MS
  Difference mode < average
  - ↳ Indication of the distortion of the size distribution



- **Size estimates are close one another for 20 nm and 60 nm NPs**
- **Up to 150% difference between Dmin and Dmax for 100 nm NPs**

CONCLUSIONS

- Well- and monodisperse suspensions
  - Consistent results, correlation of the “sizes”
  - D(DLS) > D(other techniques)

- Polydisperse (polymodal) populations
  - The higher the population polydispersity, the larger the difference in “size”
  - TEM ⇨ Small number of particles, possible bias of mean size
  - DLS ⇨ Insufficient resolution, serious risk of overestimation of mean size
  - Size distribution: sp-ICP-MS (D > 20 nm) and AF4-MALLS-ICP-MS (membrane interactions?)

- Next?
  - sp-ICP-MS based on mass ⇨ metal oxides, multi-element particles (core-shell)
    ⇨ underestimation of the size
    ↳ need for more information: XRD, XPS
  - AF4-MALLS-ICP-MS more complete… but more complex

➢ **Not one single method: size and morphology can only be described by combining complementary techniques**
… to AF4-sp-ICP-MS

Financial support:

Thank you for your attention !

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