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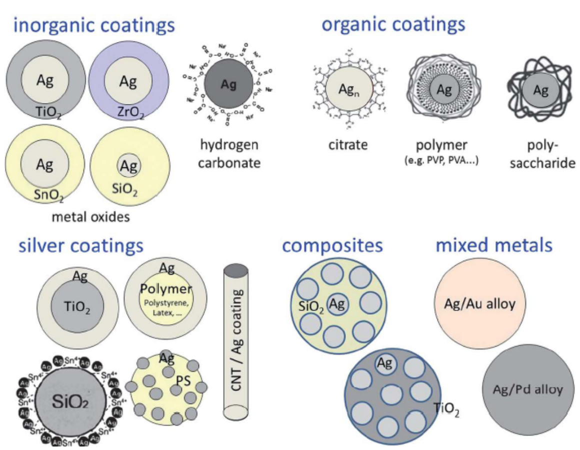
Evaluation of Field Flow Fractionation-ICP-MS and Single Particle-ICP-MS for Nanoparticle Characterization

Wei Liu, Richard Jack, Daniel Kutscher, Shona McSheehy-Ducos

Nanoparticles

- Natural or Engineered (ENPs)
- Exceptional properties - high surface to mass ratio
- Added in Foods, packaging, hygiene products, clothes etc...
- Widespread industrial uses



A. Ulrich and co. *JAAS* 2012, **27**, 1120

New Scientist 14 Aug 2010

Environmental impact clouds benefits of bug-killing silver

ANTIBACTERIAL nanoparticles may have more of an impact on the environment than we thought, including potentially raising levels of greenhouse gases.

Silver nanoparticles are used as an antibacterial agent in a wide range of products, from odour-free socks to wound-healing bandages (see diagram, below). They can find their way into waste water, and have been shown to reduce the activity of bacteria used to remove ammonia when the water is treated.

So far most of the research on the environmental impact of nanoparticles has been carried out on single nanoparticles get into the real environment," says Colman. "These particles are developed with the express purpose of killing things."

Two months on, the microbial population in the outdoor tub containing silver had significantly declined relative to the lab sample measured after one week. What's more, the activity of the enzymes they produce to break down organic *matter was 34 per cent lower in* the tub that had been dosed with nanoparticles than in the tub to which only sludge had been added.

Given that the outdoor tub containing nanoparticles had a much

Potential effects in the environment are not clear!

spICP-MS – Current status

• Evolution of the Technique

JAAS

PAPER — View Article Online | View Journal | View Issue

A signal deconvolution method to discriminate smaller nanoparticles in single particle ICP-MS

Cite this: *J. Anal. At. Spectrom.*, 2014, **29**, 134

Geert Cornelis* and Martin Hassellöv

Single particle ICP-MS (spICP-MS) analysis of inorganic nanoparticles (NPs) cannot accurately distinguish dissolved ion signals and signals from relatively small NPs, although these particles are often more reactive than their larger counterparts. A signal deconvolution method was developed for spICP-MS analysis using gold (Au) NPs of nominally 10, 15 or 30 nm diameter. The signal distributions of dissolved Au standards were parameterised as a function of concentration using a mixed Polyagaussian probability mass function. Dissolved curves were fitted using this parameterisation to the low-intensity signals of samples containing NPs to subtract and deconvolute the dissolved signals from the particle signals. The dissolved signals were quantified in this process. The accuracy of the deconvolution method was confirmed for all NP suspensions studied when comparing the size and number concentration obtained with the deconvolution method with values based on transmission electron microscopy. This method thus allows analysis of NP suspensions with spICP-MS where it was hitherto not possible. The applicability domain lies predominantly with relatively small NPs and/or when a relatively high concentration of dissolved ions of the element of interest is present, where overlapping between dissolved and particulate signals occurs.

Received 5th May 2013
Accepted 2nd October 2013

DOI: 10.1039/c3ja50160d

www.rsc.org/jaas

analytical chemistry — Article — pubs.acs.org/ac

Capabilities of Single Particle Inductively Coupled Plasma Mass Spectrometry for the Size Measurement of Nanoparticles: A Case Study on Gold Nanoparticles

Jingyu Liu,[†,‡] Karen E. Murphy,[†] Robert I. MacCuspie,[‡,§] and Michael R. Winchester*[,†]

[†]Chemical Sciences Division and [‡]Materials Measurement Science Division, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

• Real World Applications

analytical chemistry — Letter — pubs.acs.org/ac

Quantitative Imaging of Gold and Silver Nanoparticles in Single Eukaryotic Cells by Laser Ablation-ICPMS

Daniela Drescher,*[,†,‡] Charlotte Giesen,[†,‡,§] Heike Traub,[†] Ulrich Panne,[†,‡] Janina Kneipp,[†,‡] and Norbert Jakubowski*[,†]

[†]BAM Federal Institute for Materials Research and Testing, Richard-Willstätter-Str. 11, 12489 Berlin, Germany
[‡]Humboldt-Universität zu Berlin, Department of Chemistry, Brook-Taylor-Str. 2, 12489 Berlin, Germany

Nanomedicine & Nanotechnology

Nia et al., J Nanomed Nanotechnol 2015, 6:2
http://dx.doi.org/10.4172/2157-7439.1000269

Research Article — Open Access

Determination of Ti from TiO_2 Nanoparticles in Biological Materials by Different ICP-MS Instruments: Method Validation and Applications

Yacine Nia[1], Sandrine Millour[1], Laurent Noël[1], Petra Krystek[2], Wim de Jong[3] and Thierry Guérin[1]*

[1]*Anses, Food Safety Laboratory–Maisons-Alfort, Chemical Food Contaminants Department, Metallic Trace Elements and Minerals Unit, Maisons-Alfort, France*
[2]*Philips Innovation Services (PInS), High Tech Campus 11, Eindhoven, The Netherlands*
[3]*National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands*

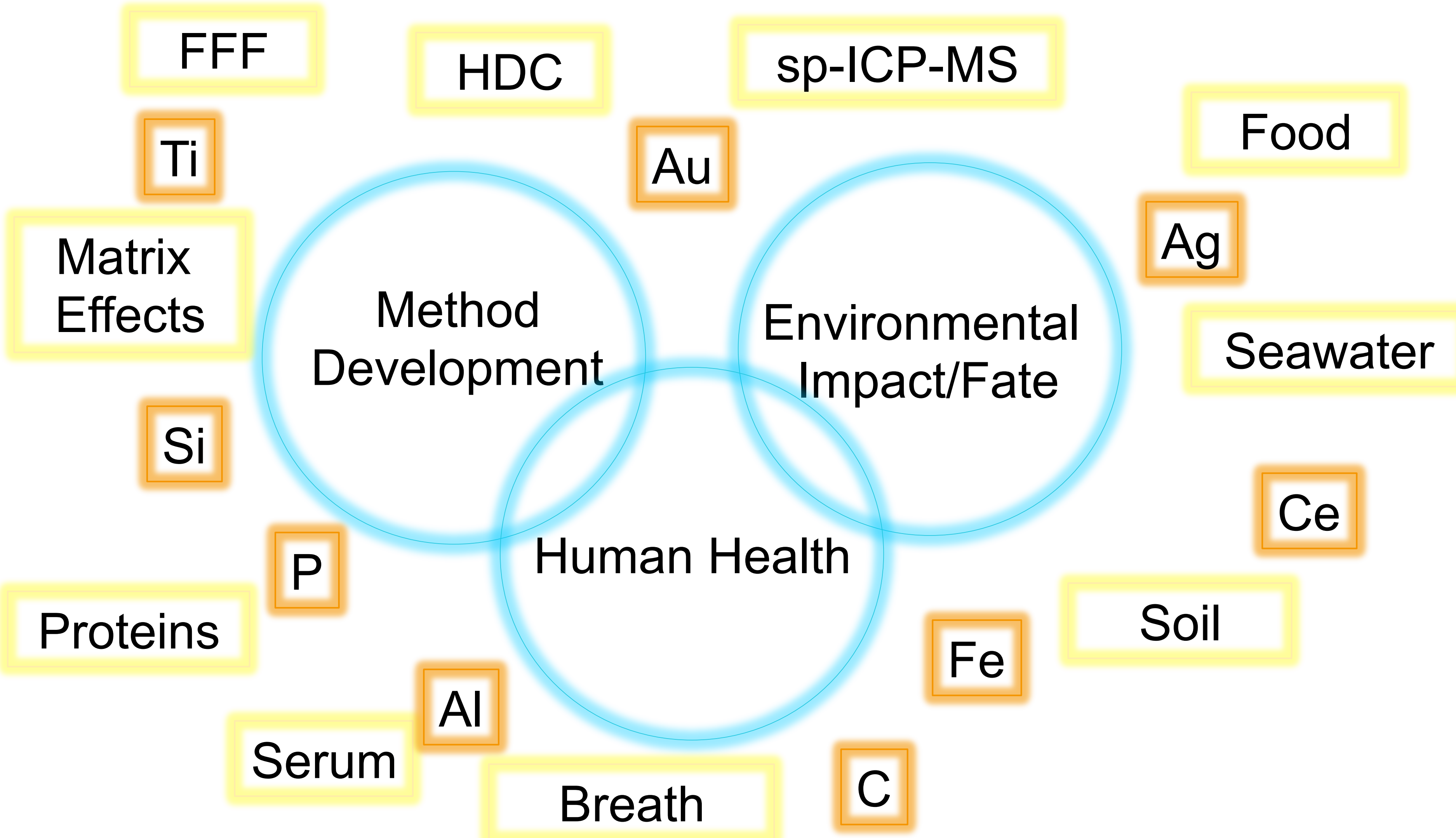
The Nanodefine EU project

- **Scientific project financed by the European Comission with the objective to develop analytical tools to verify "Nano-content" in different sample types (consumer products, environmental etc.)**
- **Thermo Fisher Scientific is one partner among many others, both academic and industrial**

NanoDefine

www.nanodefine.eu

Nanoparticle Characterization…



Thermo Scientific iCAP Q ICP-Q-MS

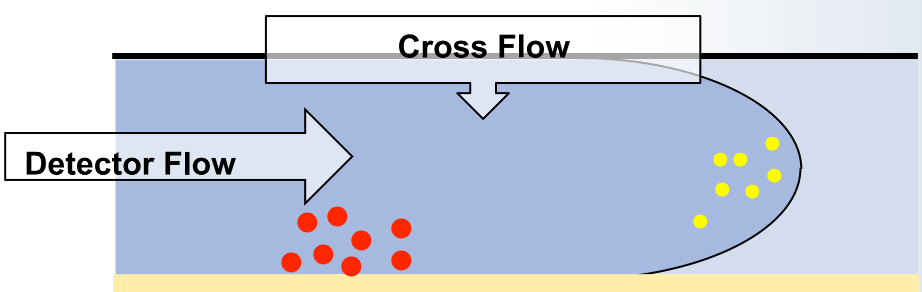
- **Instrumental Parameters**
  - High Detection Sensitivity
  - Fast data acquisition and real-time display during measurement in the single particle mode

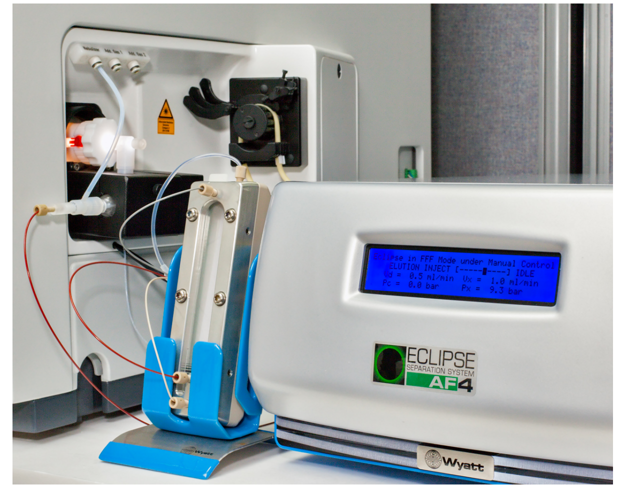
- **Powered by Qtegra ISDS**
  - Dedicated software plug-ins for seamless control and data evaluation for both FFF and spICP-MS

Field-Flow-Fractionation (FFF) coupled to ICP-MS

- Also known as AF^4 (Asymetric Flow-Field Flow Fractionation)
- Separation based on the different mobilities of particles or molecules of different sizes

Sample focussed on membrane through cross flow, but opposed by diffusion (hydrodynamic radius)



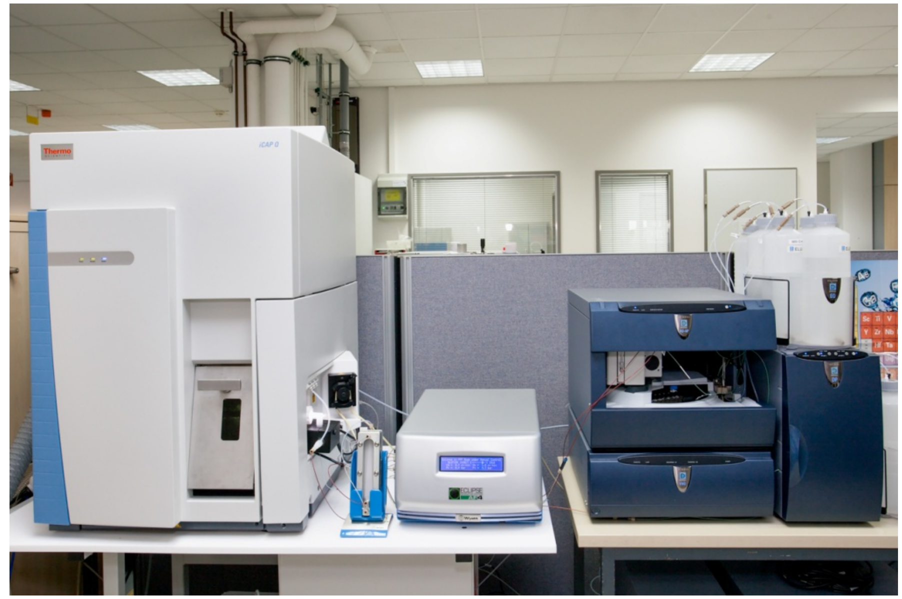


Similar to chromatography, but…

- Ions are separated through cross flow
- No stationary phase, no interaction
- FFF theory allows to calculate size from retention time

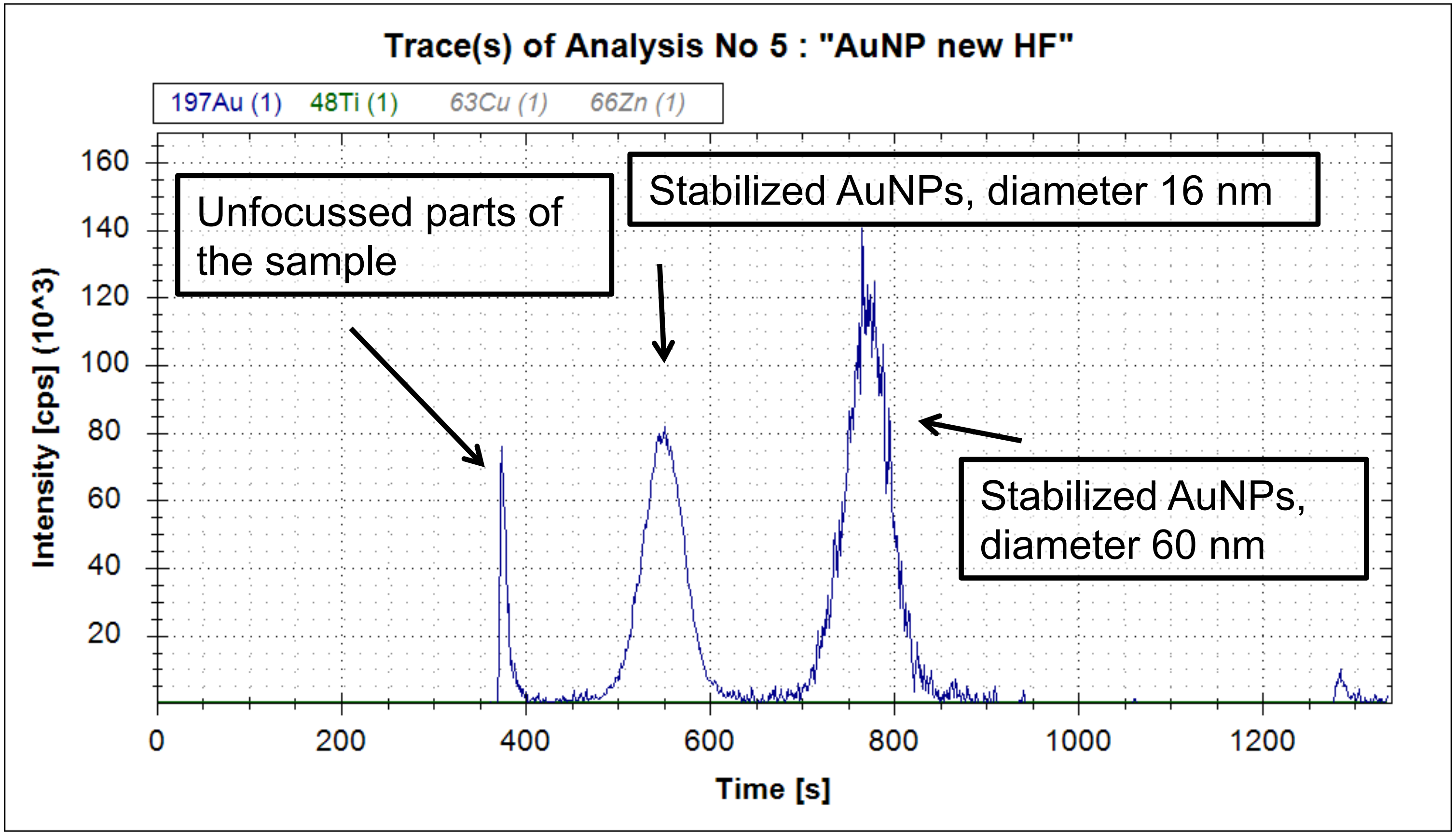
Wyatt Technology Eclipse - Thermo Scientific iCAP Q ICP-MS

- **Wyatt Eclipse FFF**
  - Integrates with any existing IC/HPLC equipment
  - Uses only 1 pump to deliver detector, cross and injection flow
  - Uses AS of IC system to inject sample
  - Fully integrated with ICS-5000 and iCAP Q through Qtegra software



- Thermo Scientific IC systems are completely metal free
- Fully metal free version of Eclipse available
- Eclipse switch option allows easy switch over from FFF to IC analysis and vice versa

FFF-ICP-MS Analysis of AuNP



Conditions for Separation in PES hollow fibre (HF):
Eluent: 0.02% SDS; **Detector flow:** 0.5 mL min^{-1}
Focus flow: 0.4 mL min^{-1} for 5 minutes
Cross flow: 0.2 ml min^{-1} to 0 in 15 minutes

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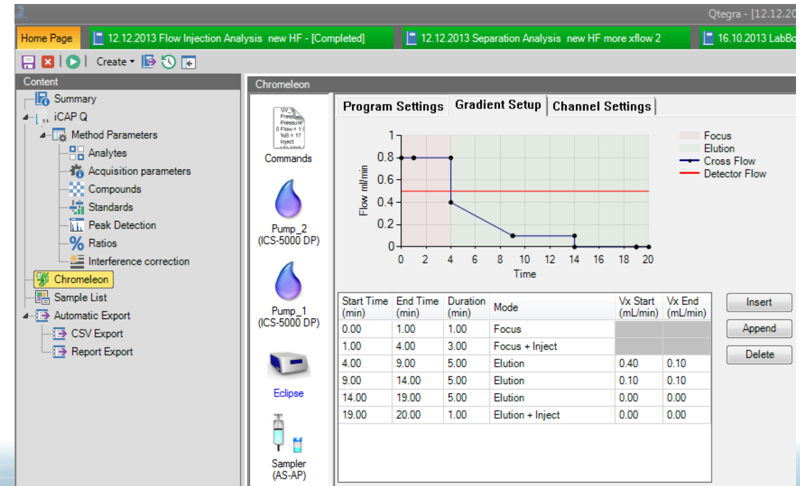
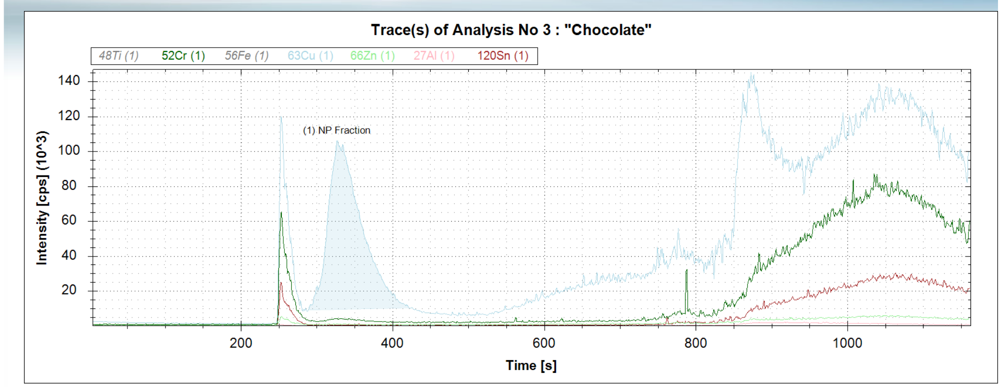
FFF-ICP-MS in real samples

- Versatile tool to fractionate different kinds of samples
  - Fractionation
  - Flow-Injection

- Characterisation of “nano“-content of different materials
  - NP containing Cu found in red tattoo ink





Real-Life: Particle Aggregation, Loss etc.

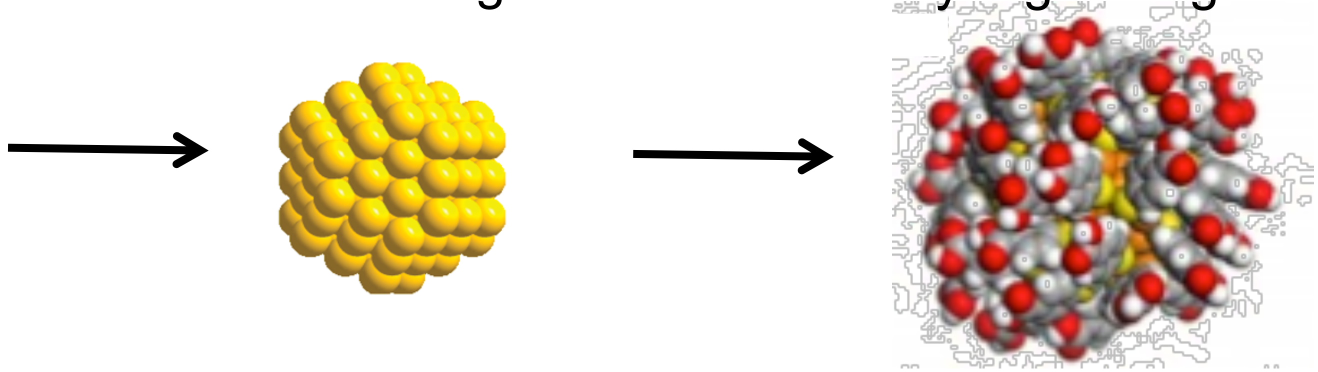
Chemical background

- Structure of Ag, Au nanoparticles similar
- Synthesis: Mild reduction of Ag^{+}, Au^{3+} in presence of suitable stabilizing ligands

Core of Ag^{0}

Surface of Ag^{+} "protected" by organic ligands

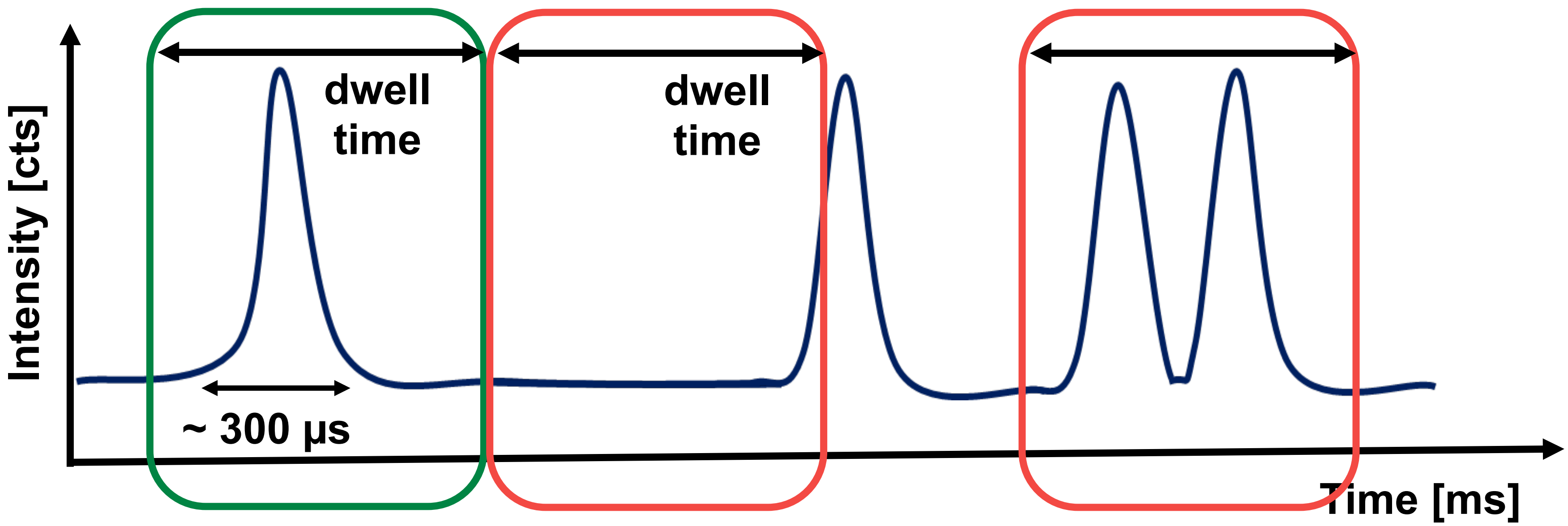
Ag^{+}



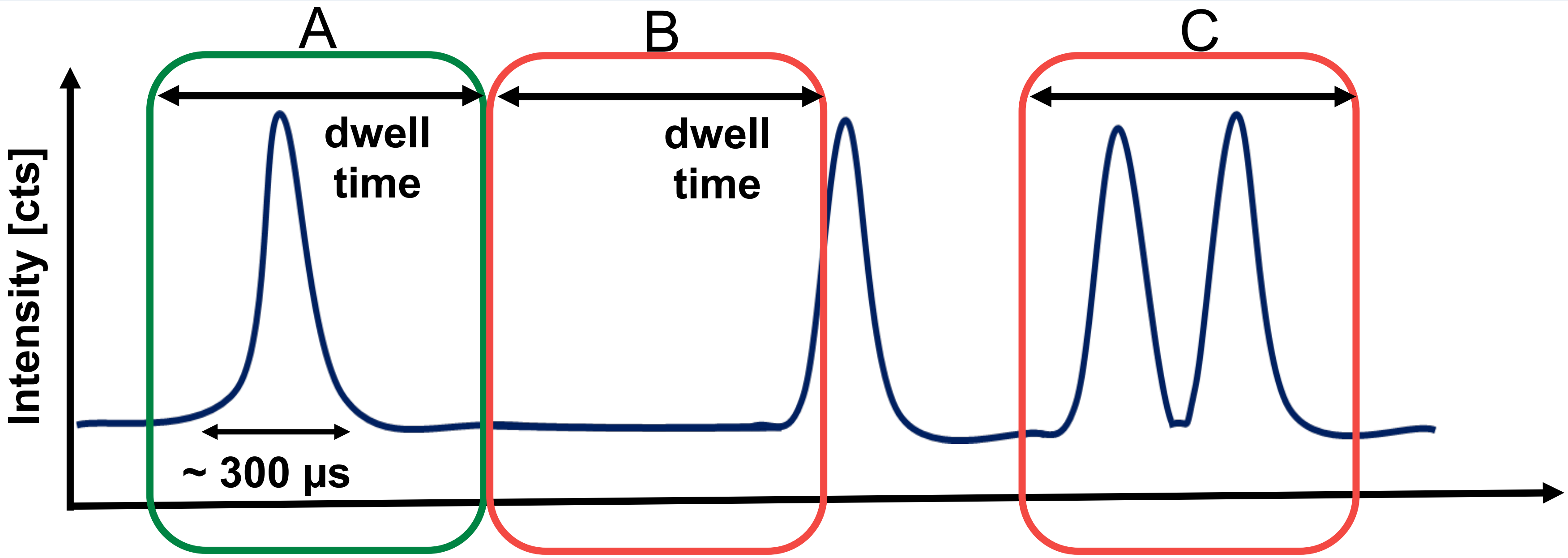
- Sample Preparation: AgNPs are best stabilized in 2mM sodium citrate solution; AuNPs can be handled in UPW
- All solutions need to be sonicated (5-15 minutes) to avoid coagulation of the particles

Basics of spICP-MS

- Introduced single nanoparticle produces an ion plume in the plasma. Process duration ~ 300 µs.
- For the discrimination of various particles short dwell times (~ 3-10 ms) are applied.
- Chosen dwell time is a critical parameter in spICP-MS.



Artifacts in spICP-MS

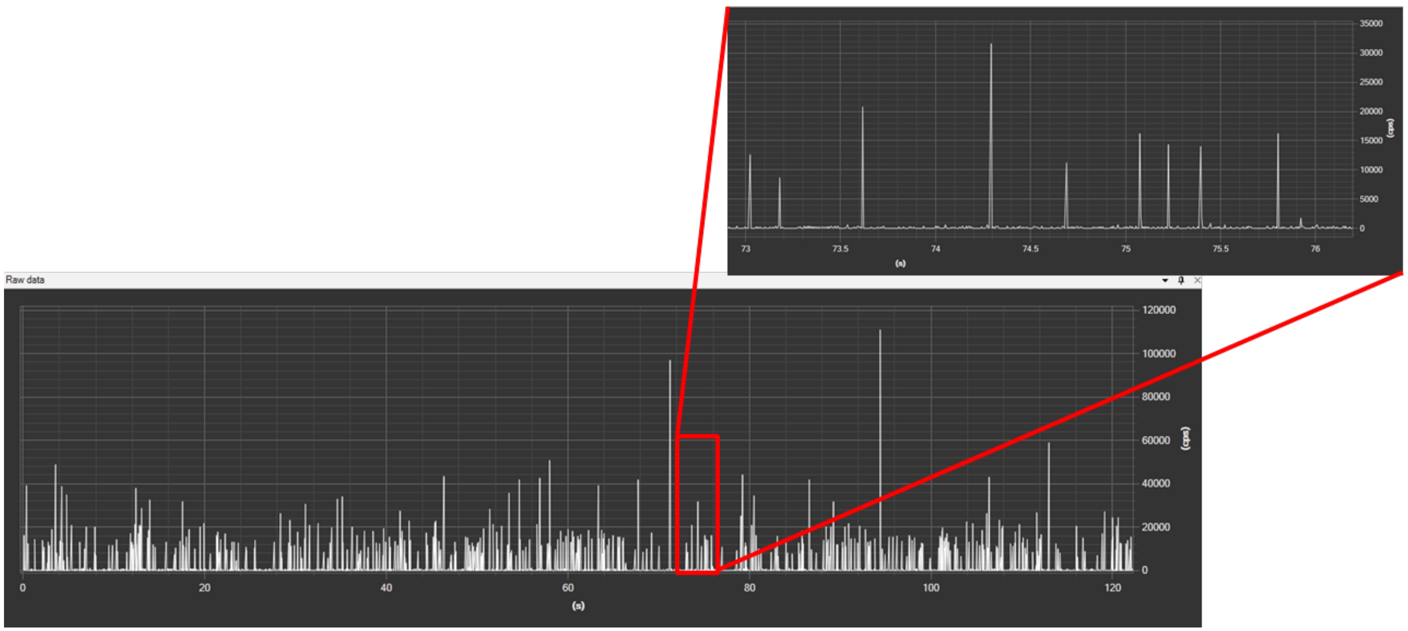


- **Split Particle Events (B):** A nanoparticle signal is observed in two adjacent measurement slots. The extent of split particle events depends on the nanoparticle pulse duration and the applied dwell time, and can be reduced by using longer dwell times.

- **Double or Multiple Particle Events (C):** Two or more particles are observed in one measurement slot, leading to an overestimation of the particle size. The occurrence of such events can be estimated using Poisson statistics and can be reduced by sample dilution.

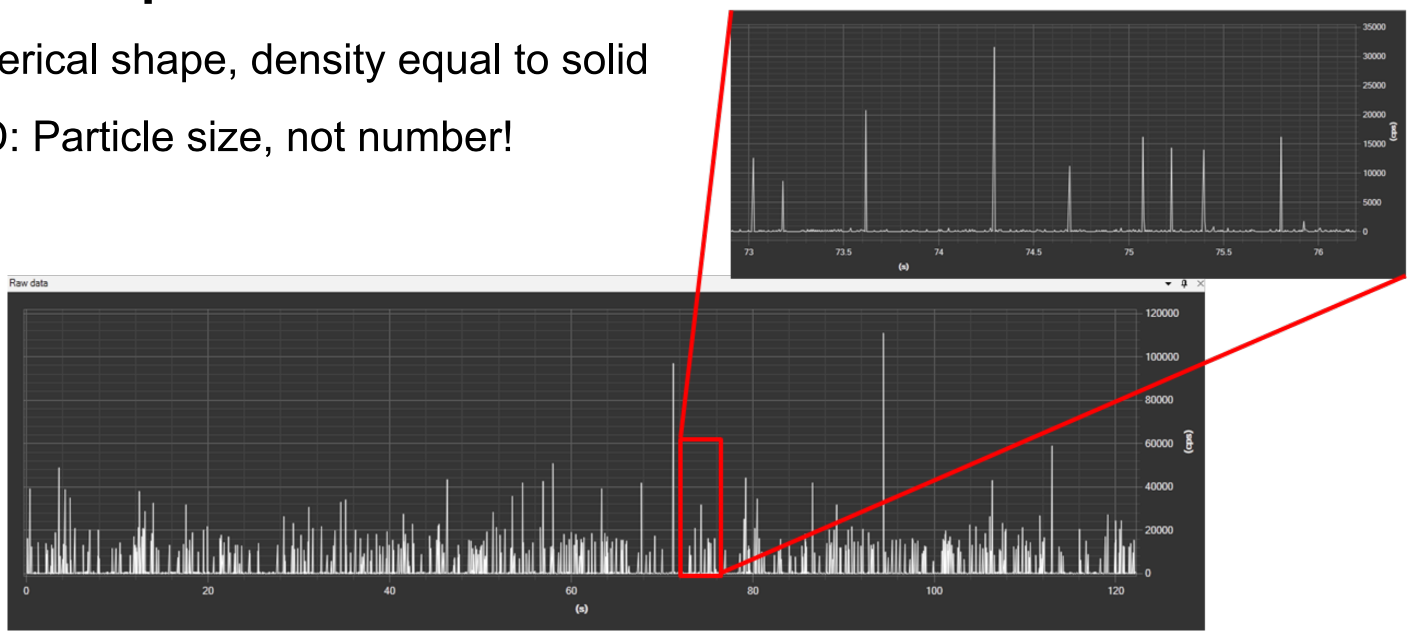
Single particle ICP-MS for characterization of AgNPs

- **Background signal ~ Concentration of dissolved species**
- **Number of events ~ Particle number concentration**
- **Signal intensity of events ~ Particle mass → Particle Volume and Shape**

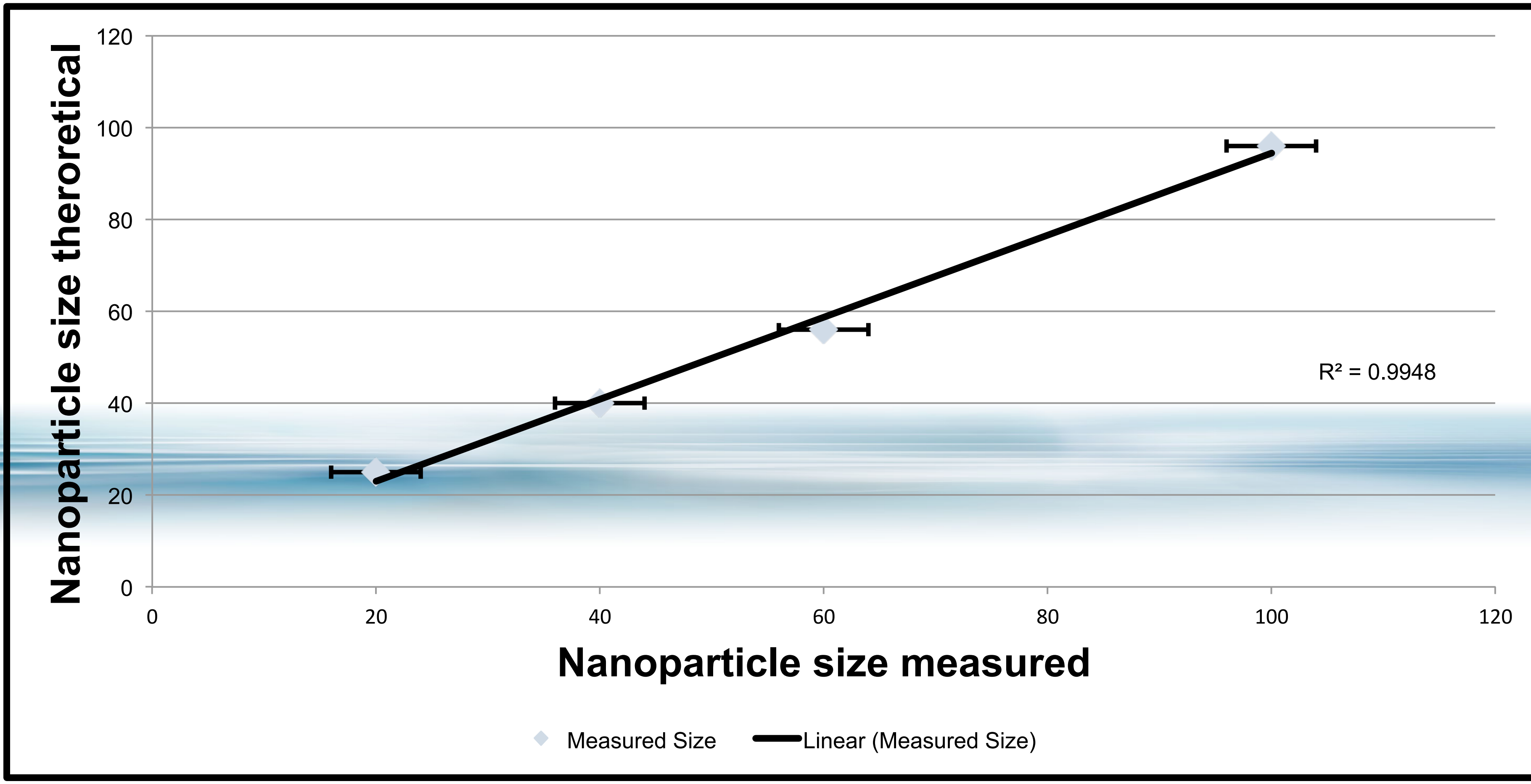


Single particle ICP-MS for characterization of AgNPs

- **Filter sp events from background → Intensity threshold values**
- **Calculate mass of element observed in the event**
  - Knowledge of detection sensitivity, transport efficiency
- **Calculate particle diameter**
  - Spherical shape, density equal to solid
  - LOD: Particle size, not number!



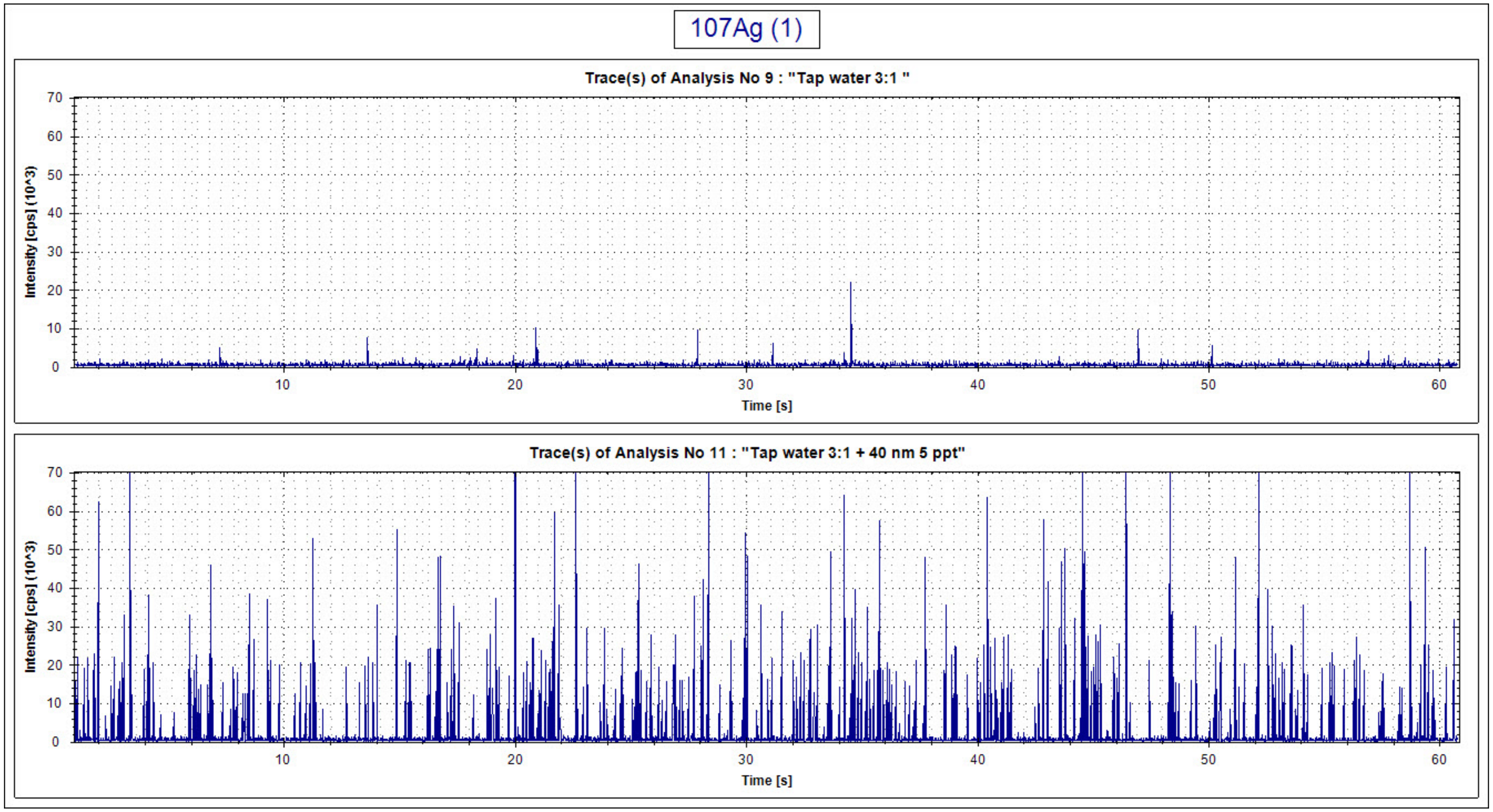
Measuring the nanoparticle size



Particle size LOD depending on detection sensitivity!

Analysis of NPs in tab water

- Tab water spiked with AgNPs, diluted 3:1 with 2mM sodium citrate
- Determined NP size: 41 ±3 nm [Nominal diameter 40 nm]



The highlight

- Simple setup, no separation unit
- High throughput analysis
- Information about low-molecular metal species, number of particles, metal mass in a particular particle, particle size

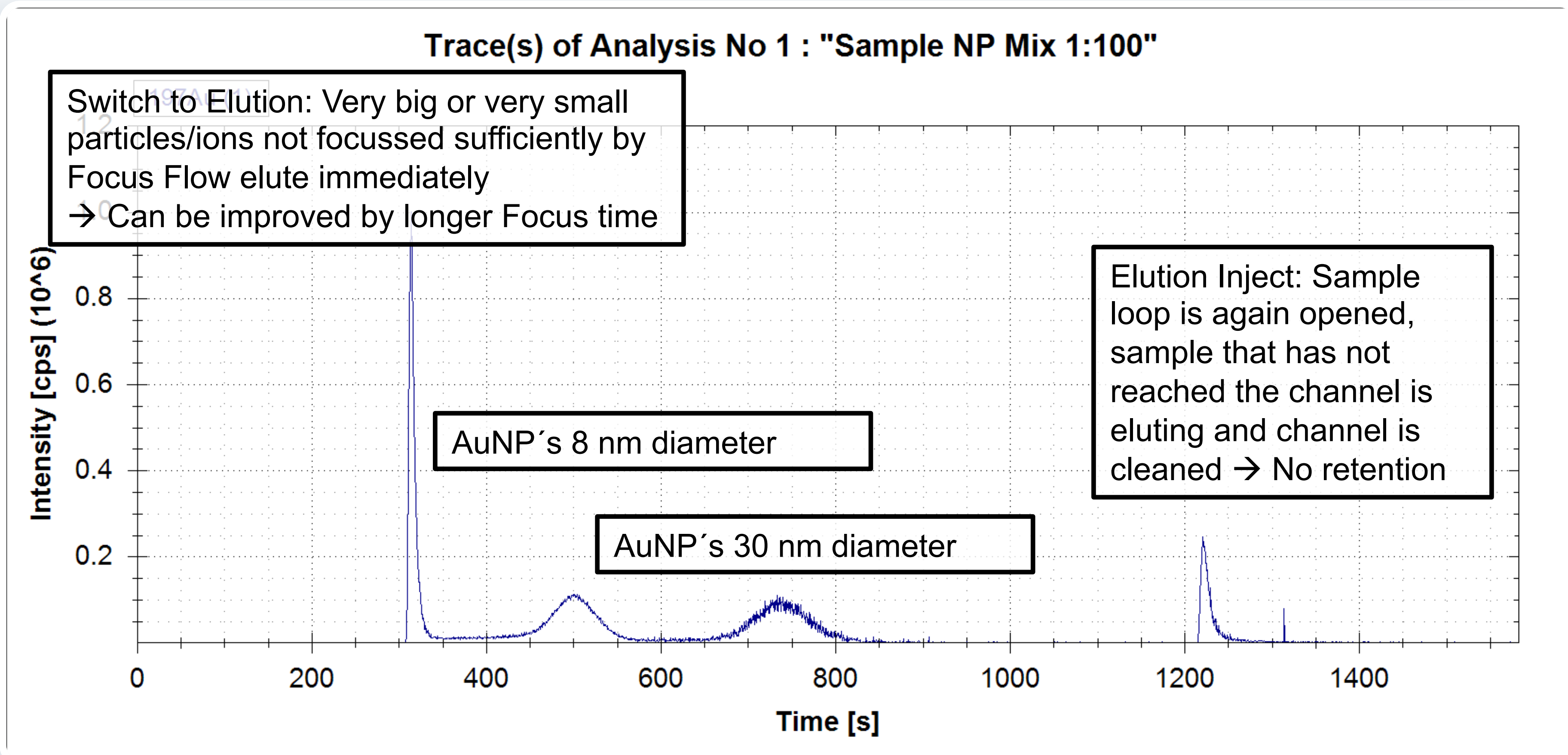
- Dwell times in the low ms range are sufficient for monoelemental NP´s
  - Faster scanning is required for multielement/isotopic information
- Obtainable LOD (iCAP Q) approx. 20nm for Ag

Outlook: combine FFF and spICP-MS

spICP-MS	FFF-ICP-MS
☑ Direct characterization of particle size	☑ Fractionation of different particle regimes in a sample
✘ Difficult for samples with more than one particle fraction	✘ Direct size characterization only with complementary technique like MALS

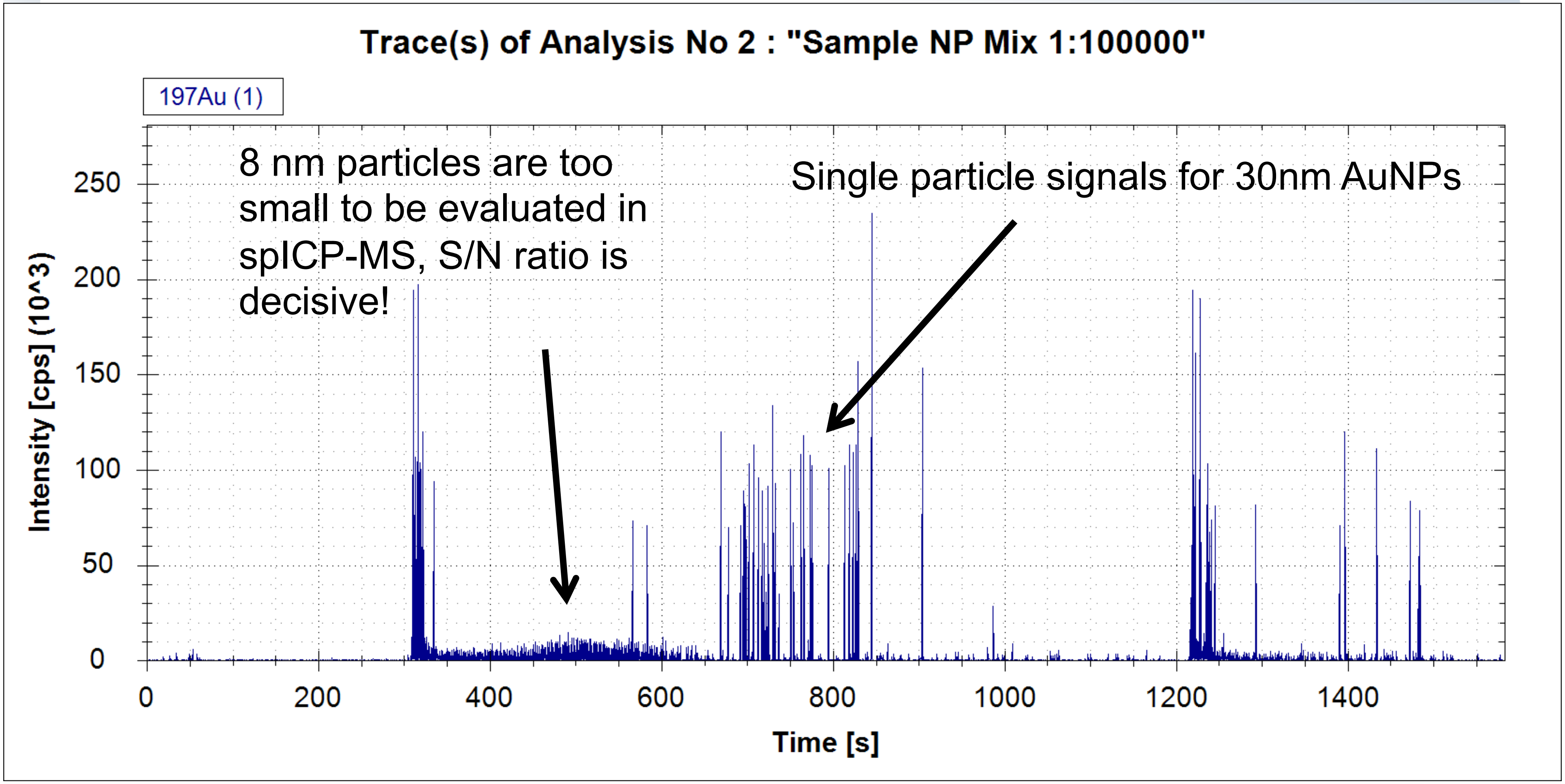
- Inject diluted sample to elute single particles instead of particle fractions
  - → Fractionation of different particle regimes in a sample
  - → Direct particle size characterization in one run

FFF-spICP-MS



Trace(s) of Analysis No 1 : "Sample NP Mix 1:100"
Switch to Elution: Very big or very small particles/ions not focussed sufficiently by Focus Flow elute immediately
→ Can be improved by longer Focus time
Elution Inject: Sample loop is again opened, sample that has not reached the channel is eluting and channel is cleaned → No retention
AuNP´s 8 nm diameter
AuNP´s 30 nm diameter
Intensity [cps] (10^6)
0.8
0.6
0.4
0.2
0
200
400
600
800
1000
1200
1400
Time [s]

FFF-spICP-MS



Trace(s) of Analysis No 2 : "Sample NP Mix 1:100000"
197Au (1)
8 nm particles are too small to be evaluated in spICP-MS, S/N ratio is decisive!
Single particle signals for 30nm AuNPs
Intensity [cps] (10^3)
0
50
100
150
200
250
0
200
400
600
800
1000
1200
1400
Time [s]

Summary

- Both spICP-MS and FFF-ICP-MS have their advantages and drawbacks
- Combination of both can give additional insights into the Nanoworld and helps to overcome the drawbacks of both techniques
- Instrumentation to get a complete picture:
  - spICP-MS, FFF-ICP-MS and Speciation Analysis
  - Fast scanning for elevated periods allows to combine both techniques

Thank you for your attention!

Further references:
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Krystek et al., J. Anal. At. Spectrom. **26** (2011), 1701
Ulrich et al., J. Anal. At. Spectrom. **27** (2012), 1120