Apport de l’ICP MS a haute resolution et en temps de vol pour l’analyse de nanoparticules

Dr Ariane Donard
Dr Lukas Schlatt

Commission européenne

Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° *952306*

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Nu Instruments is a market leading designer and manufacturer of high-performance mass spectrometers. Our highly specialised instrumentation includes; Multi-Collector ICP-MS (MC-ICP-MS), Time-of-Flight ICP-MS (TOF-ICP-MS), High Resolution ICP-MS (HR-ICP-MS), Glow Discharge Mass Spectrometry (GD-MS), Isotope Ratio Mass Spectrometry (IRMS), Gas Analysis Mass Spectrometry, Thermal Ionisation Mass Spectrometry (TIMS).

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Introduction

- **AttoM ES**

The AttoM ES HR-ICP-MS is **a double-focusing single-collector instrument** of forward Nier-Johnson geometry which features the unique FastScan Ion Optics.

The instrument is entirely purpose designed and built to provide the best performance and reliability coupled with flexibility and ease-of-use for precise and accurate **elemental and isotope ratio analysis**.

AttoM ES is an instrument of choice for Earth Sciences, Environmental Science, Nuclear Research, Archaeology, Forensics, Nanoparticle characterisation…

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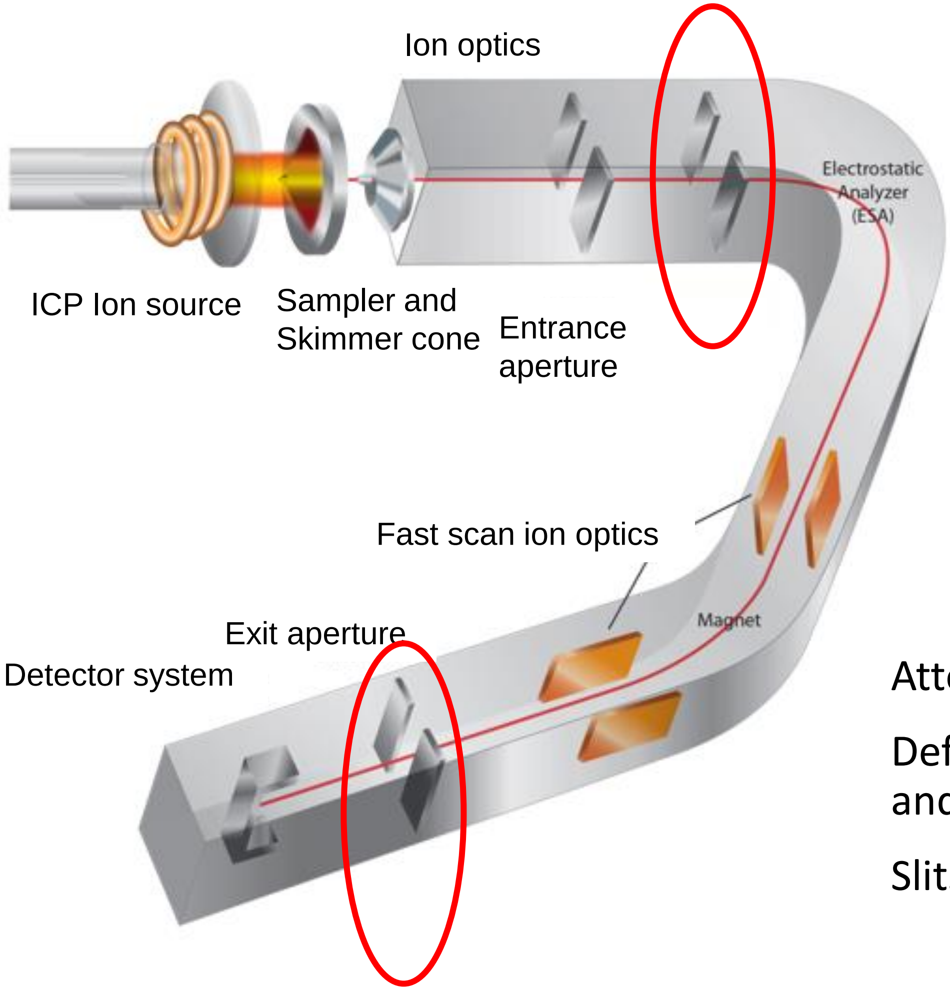
General layout



Resolution
(source slit)

Attom uses fixed width slits for resolution

Default resolutions are: 300, 2500, 4000, 10000 and >10000 (not specified)

Slits positions are 12 for source and 5 for collector

Source: LR 500, MR 40, HR 10 and UR 6µm

Collector: 900, 65, 45, 15 and 8µm

Forward Nier-Johnson geometry

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High Resolution

- To be able to deal with interferences, two major modes of operations in the ICP-MS world:

- Improve the signal to background ratios using collision/reaction cell technology with analyte/interference shifts, energy transfers and losses
- Using the exact mass difference between analyte and interference for physical separation using high resolution

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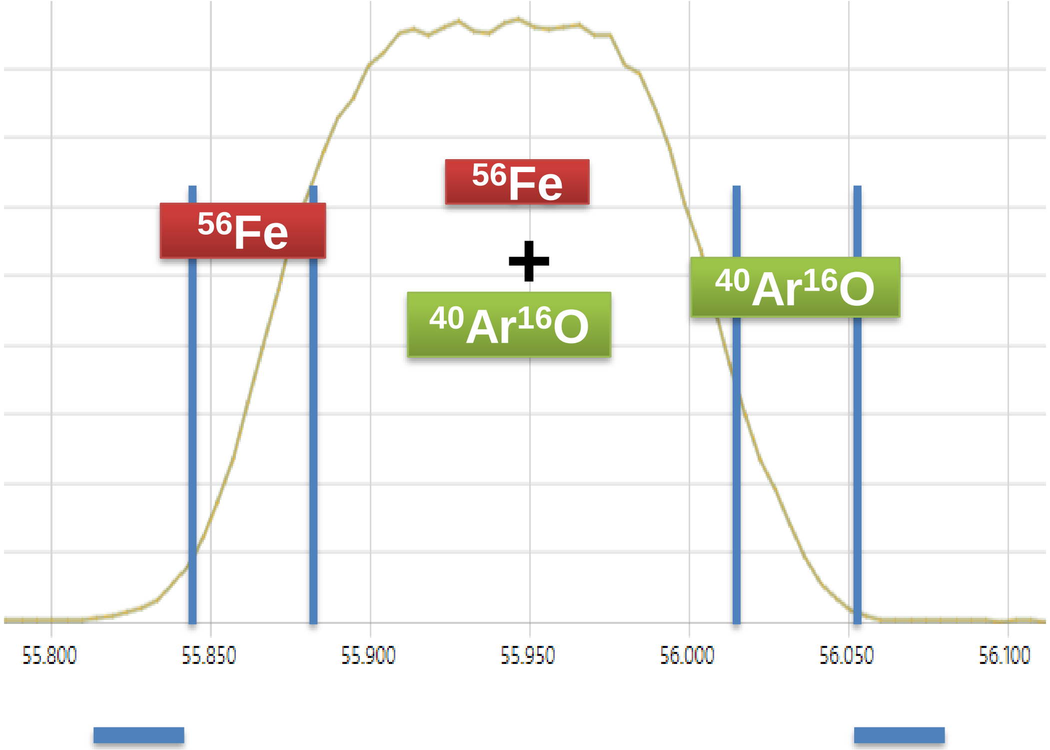
High Resolution

High resolution : example for Fe



Full ionic beam

^{56}Fe

$^{40}Ar^{16}O$

Low resolution slit

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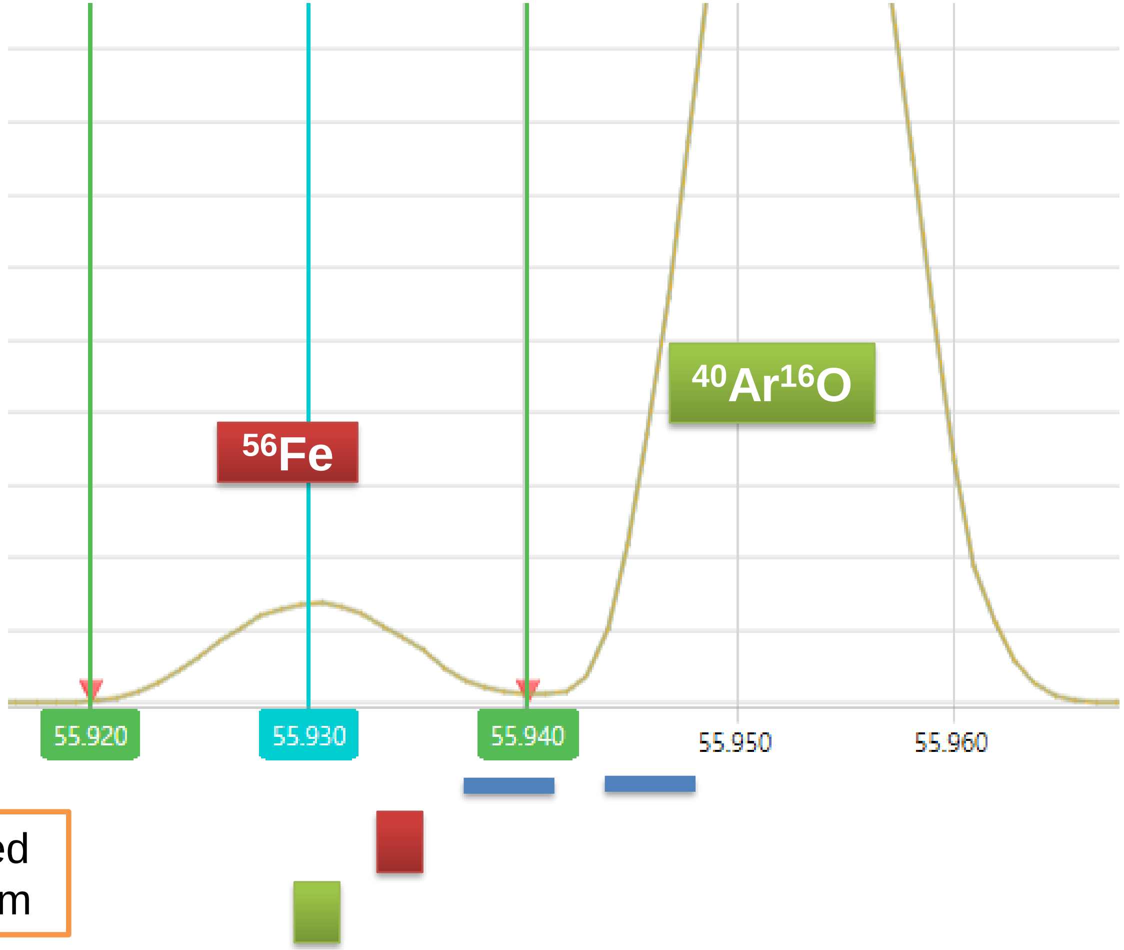
High Resolution

High resolution : example for Fe



Reduced ion beam

High resolution slit

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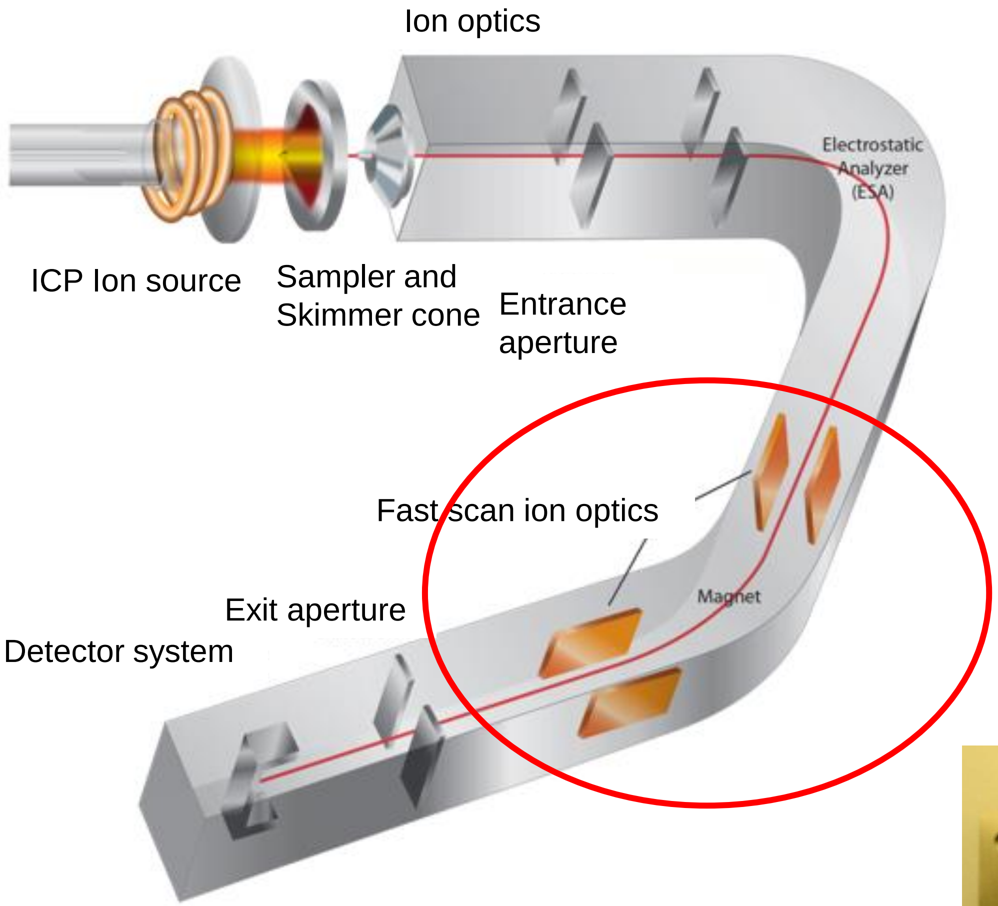
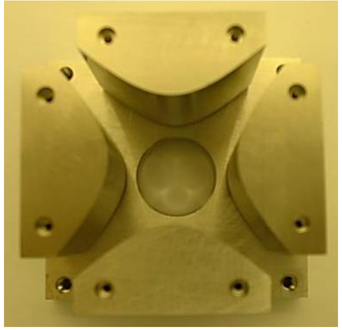
General layout

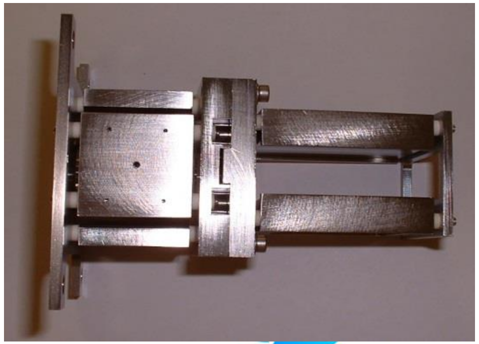


Deflector Ion Optics:

- Pair of quadrupoles for beam shaping
- Two sets of parallel plates, before and after magnet

Able to deflect the incoming ion beam into magnetic field so that ions take a different path, effectively changing the radius inside the field.





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General layout

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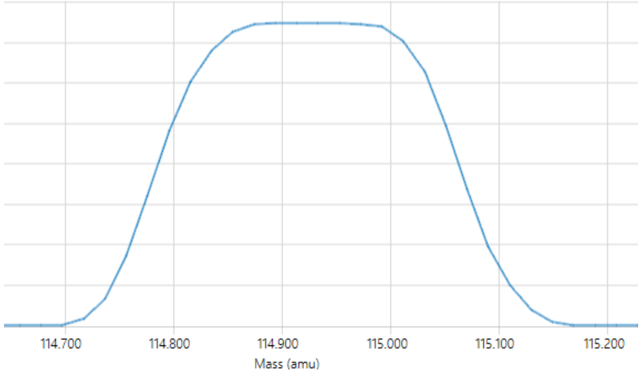
Analysis method

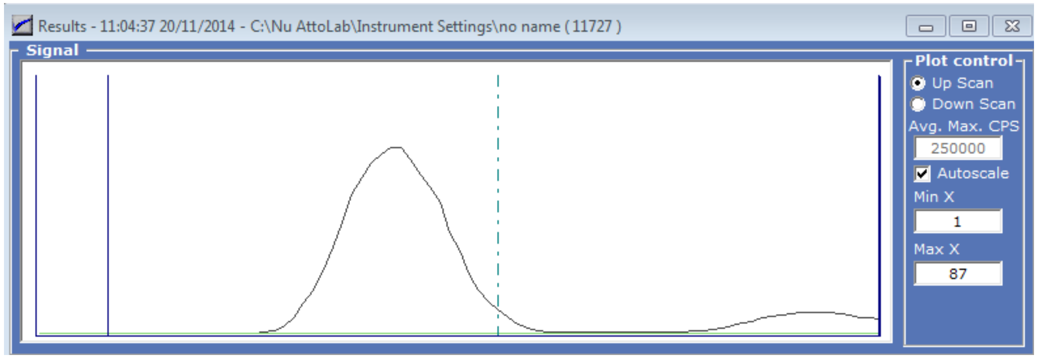
Deflector jump (LR)

Measure on the centre of the peak (due to flat top peak).
10µs timeslots

Deflector scan (HR)

Scan a mass window around the peak centre
100µs timeslots




Results - 11:04:37 20/11/2014 - C:\Nu AttoLab\Instrument Settings\no name (11727)

Plot control

● Up Scan
○ Down Scan

Avg. Max. CPS: 250000

☑ Autoscale

Min X: 1

Max X: 87

R=300

R=4000 or R=10 000

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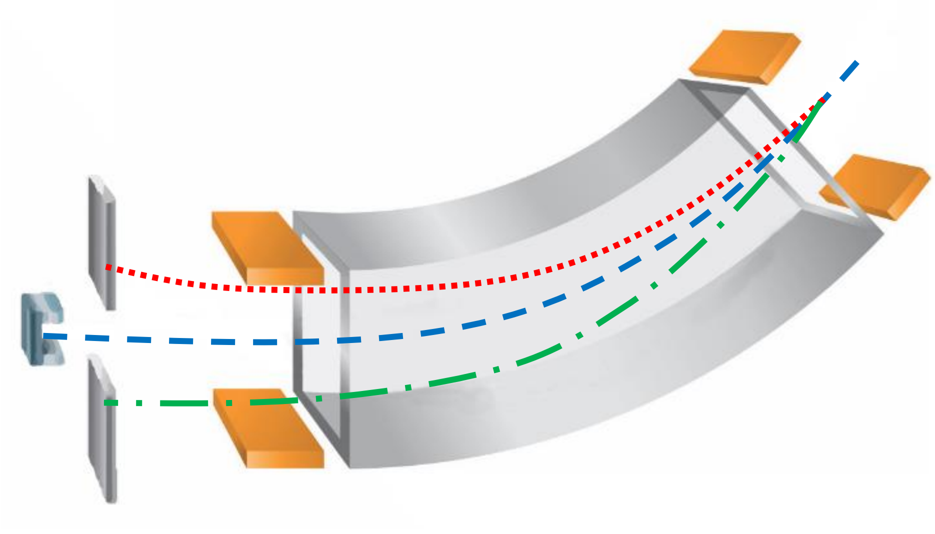
General layout

Deflector jump (LR)



With no deflection

↓

only the magnetic field dictates which m/z goes to the detector

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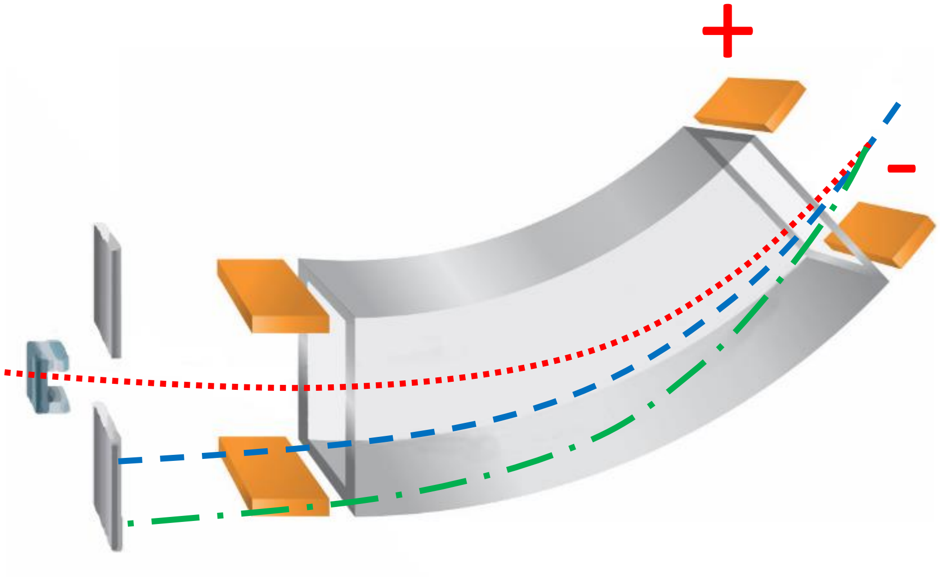
General layout

Deflector jump (LR)



Fixed magnetic field
but voltages applied to the deflectors:

↓

Ion beam deflected,
different m/z are detected..

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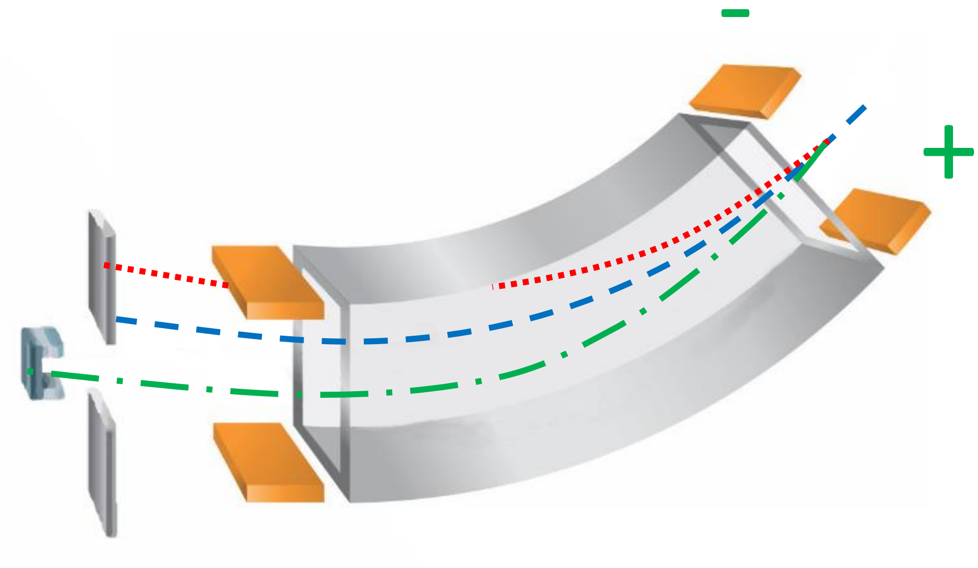
General layout

Deflector jump (LR)



Fixed magnetic field
but voltages applied to the deflectors:

Ion beam deflected,
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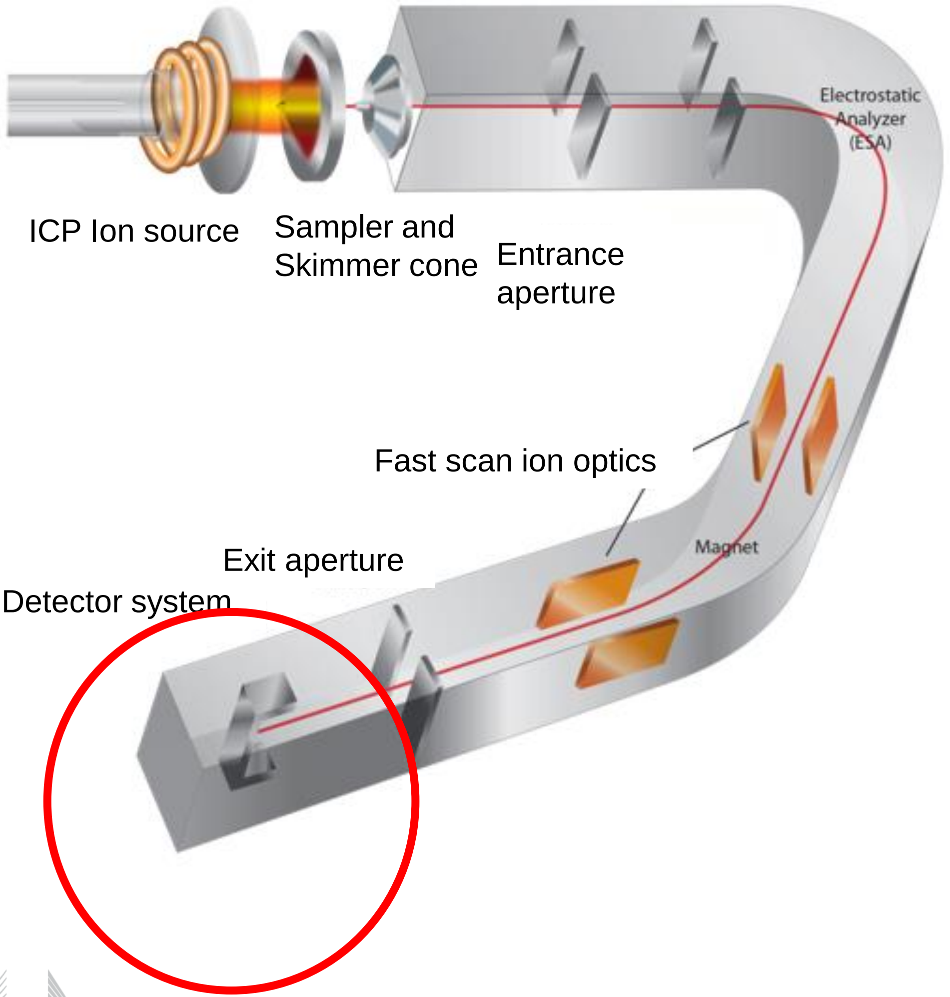
General layout



Ion optics

ICP Ion source

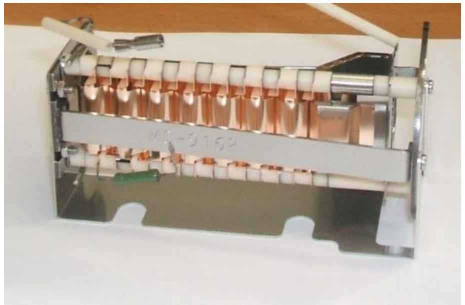
Sampler and Skimmer cone

Entrance aperture

Fast scan ion optics

Exit aperture

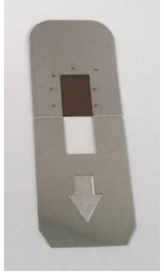
Detector system



(0) to 10^6 cps → Discrete dynode detector

10^6 to 10^9cps → Discrete dynode detector with Attenuation mode

The attenuation is usually between ~30 and ~600 depending on size of holes



10^9 to 10^{12}cps → Faraday cup

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AttoM ES for nanoparticle analysis applications

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Main features

Dwell time > 10 µs
Continously (no settling time)

Flexible data processing software

High sensitivity

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Nanoparticles analysis with AttoM – HR-ICP-MS

Dwell time > 10 µs
Continously (no settling time)

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Nanoparticles analysis with AttoM – HR-ICP-MS

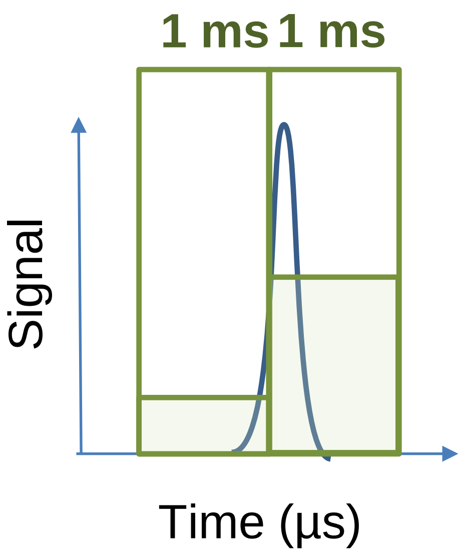
Dwell time > 10 µs
Continously (no settling time)

Why do we want to use a short dwell time ?

Arrival of the ion cloud on the detector = 300-400 µs

1 ms (dwell time)

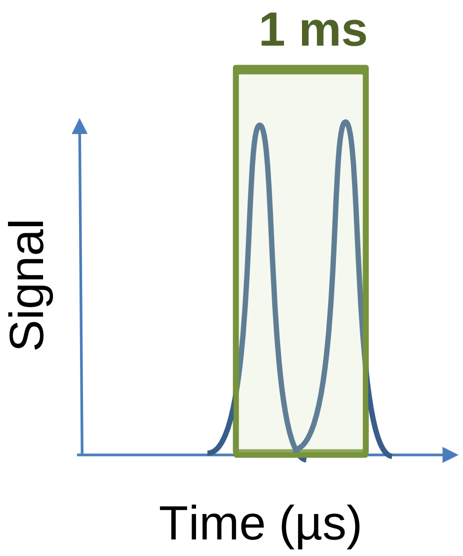
Adapted from Strenge et al JAAS 2015



2 Nps detected

Overestimation of the Np number

Shift in the distribution



1 Np detected

Understimation of the NP number

Shift in the distribution

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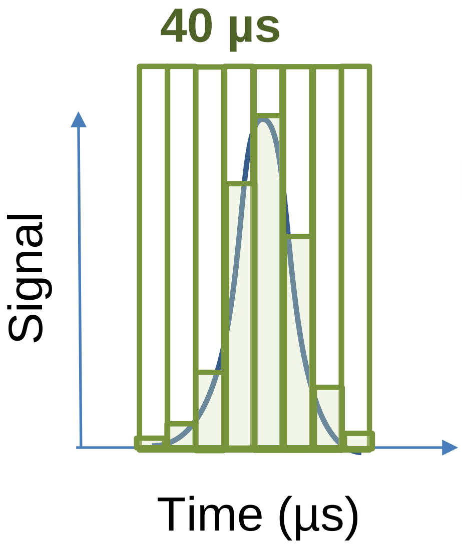
Dwell time > 10 µs
Continously (no settling time)

Why do we want to use a short dwell time ?

Arrival of the ion cloud on the detector = 300-400 µs

40 µs (dwell time)



For a NP measured in 400 µs

10 points defined peak

No overestimation or underestimaiton of the NP number

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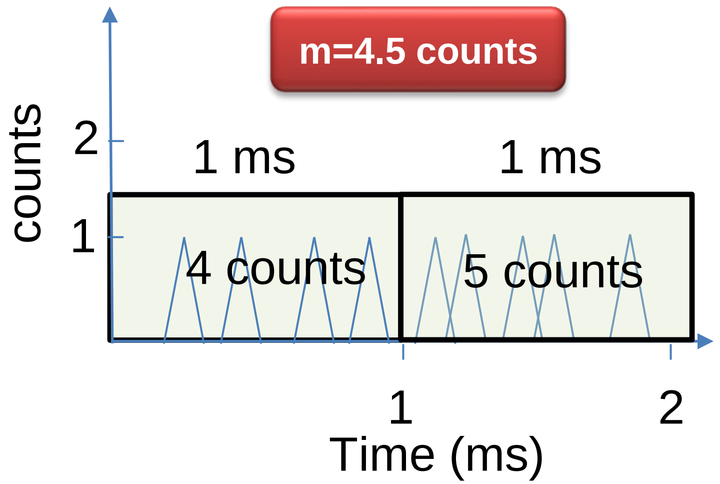
Nanoparticles analysis with AttoM – HR-ICP-MS

Dwell time > 10 µs
Continously (no settling time)

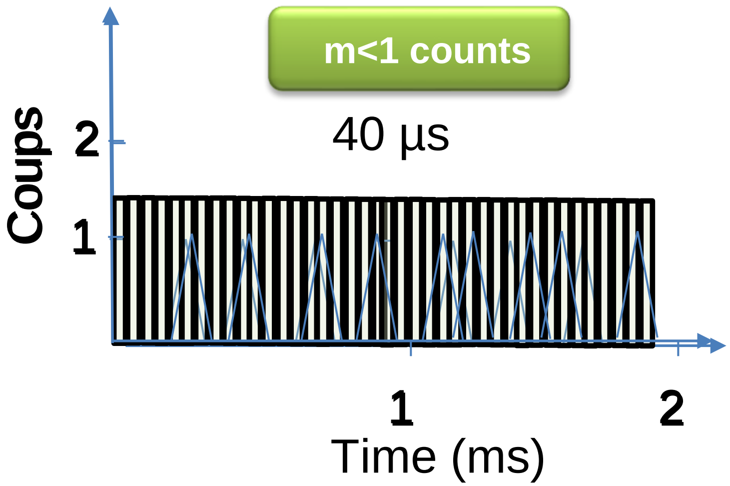
Why do we want to use a short dwell time ?

➡ Improvment of detection limit

1 ms (dwell time)



40 µs (dwell time)



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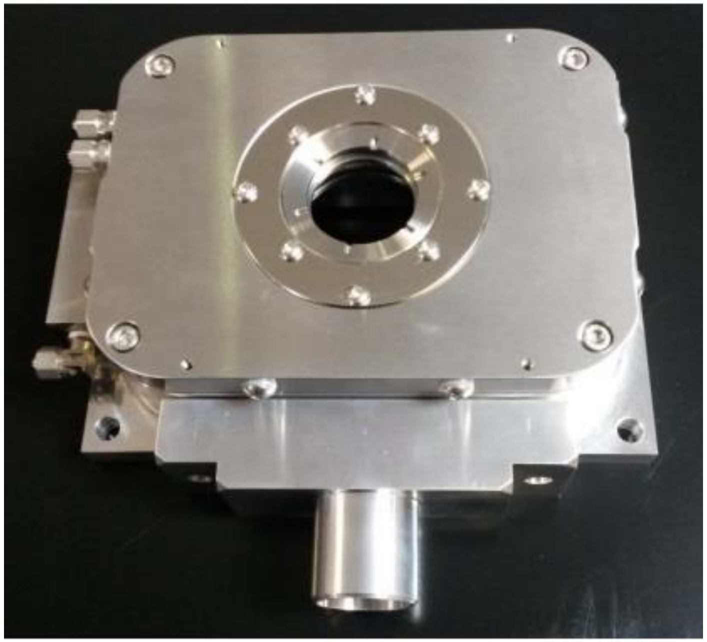
Nanoparticles analysis with AttoM – HR-ICP-MS

High sensitivity

- The interface region between the sampler and skimmer cones is pumped using an (earthed) 50 m3h-1 rotary pump, to give a working pressure in this region of <1 mbar.
- The Enhanced Sensitivity interface provides **very high efficiency** for dry sample introduction systems whilst not compromising performance for normal “wet” sample introduction systems.



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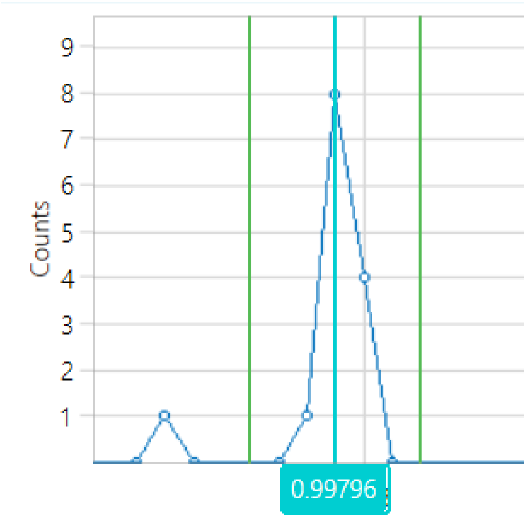
High sensitivity



Signal example Au **5nm**
(Aridus, 40 µs dwell time)

Detection limit with desolvator (Aridus, CETAC):

- Au : 4.5 nm
- Ag : 4.5 nm
- CeO :4 nm

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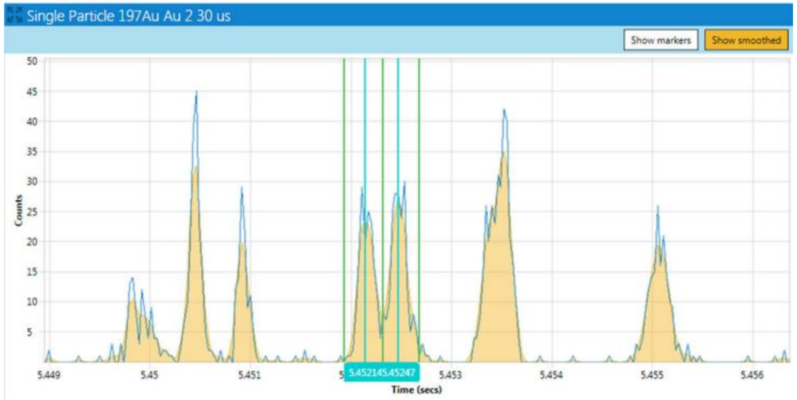
Nanoparticles analysis with AttoM – HR-ICP-MS

Flexible data processing software

The software NuQuant is designed to easily handle nanoparticles measurement :

- Automatic peak search and adjustable peak width



Smoothing of the data and research of the peak maxima and minima with criteria that allow different:

- Peak size,
- Peak widths
- Partially merged peaks
- Continuous background signals

to be distinguished easily

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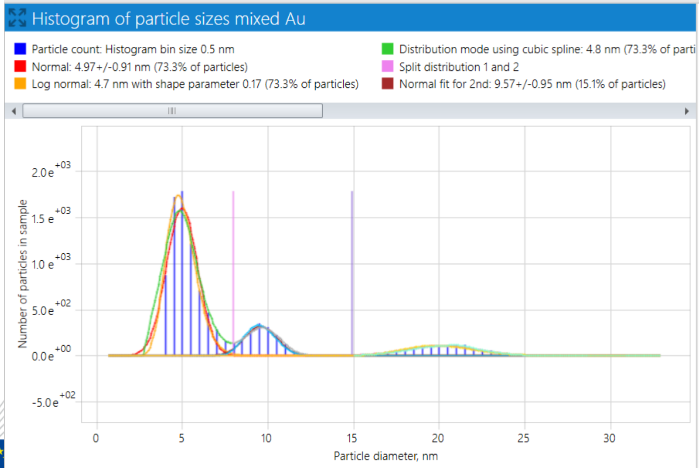
Nanoparticles analysis with AttoM – HR-ICP-MS

Flexible data processing software

The software NuQuant is designed to easily handle nanoparticles measurement :

- Automatic peak search and adjustable peak width
- Ready to use script to detect and measure nanoparticle size distribution, concentration, ionic background…



Possibility to use different calibration methods:

- Ionic standard
- Nanoparticle standard

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Nanoparticles analysis with AttoM – HR-ICP-MS

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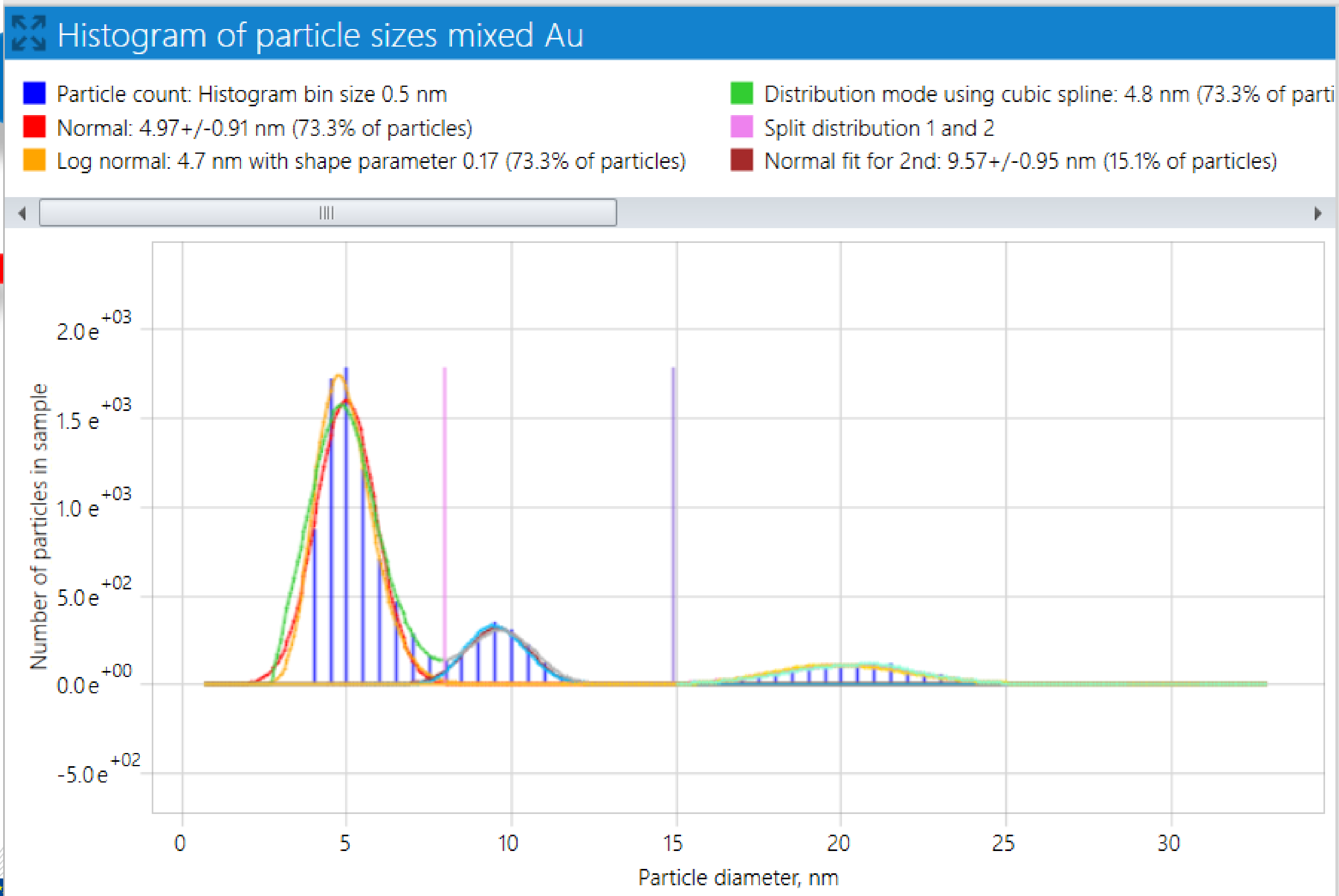

Histogram of particle sizes mixed Au

🟦 Particle count: Histogram bin size 0.5 nm
🟥 Normal: 4.97+/-0.91 nm (73.3% of particles)
🟧 Log normal: 4.7 nm with shape parameter 0.17 (73.3% of particles)
🟩 Distribution mode using cubic spline: 4.8 nm (73.3% of parti
🟪 Split distribution 1 and 2
🟫 Normal fit for 2nd: 9.57+/-0.95 nm (15.1% of particles)

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Flexible data processing software

The software NuQuant is designed to easily handle nanoparticles measurement :

- Automatic peak search and adjustable peak width
- Ready to use scripts to detect and measure nanoparticle size distribution, concentration, ionic background…
- Possibility for the user to access the scripts to read / modify / create them. Calculations are transparents

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Nanoparticles analysis with AttoM – HR-ICP-MS

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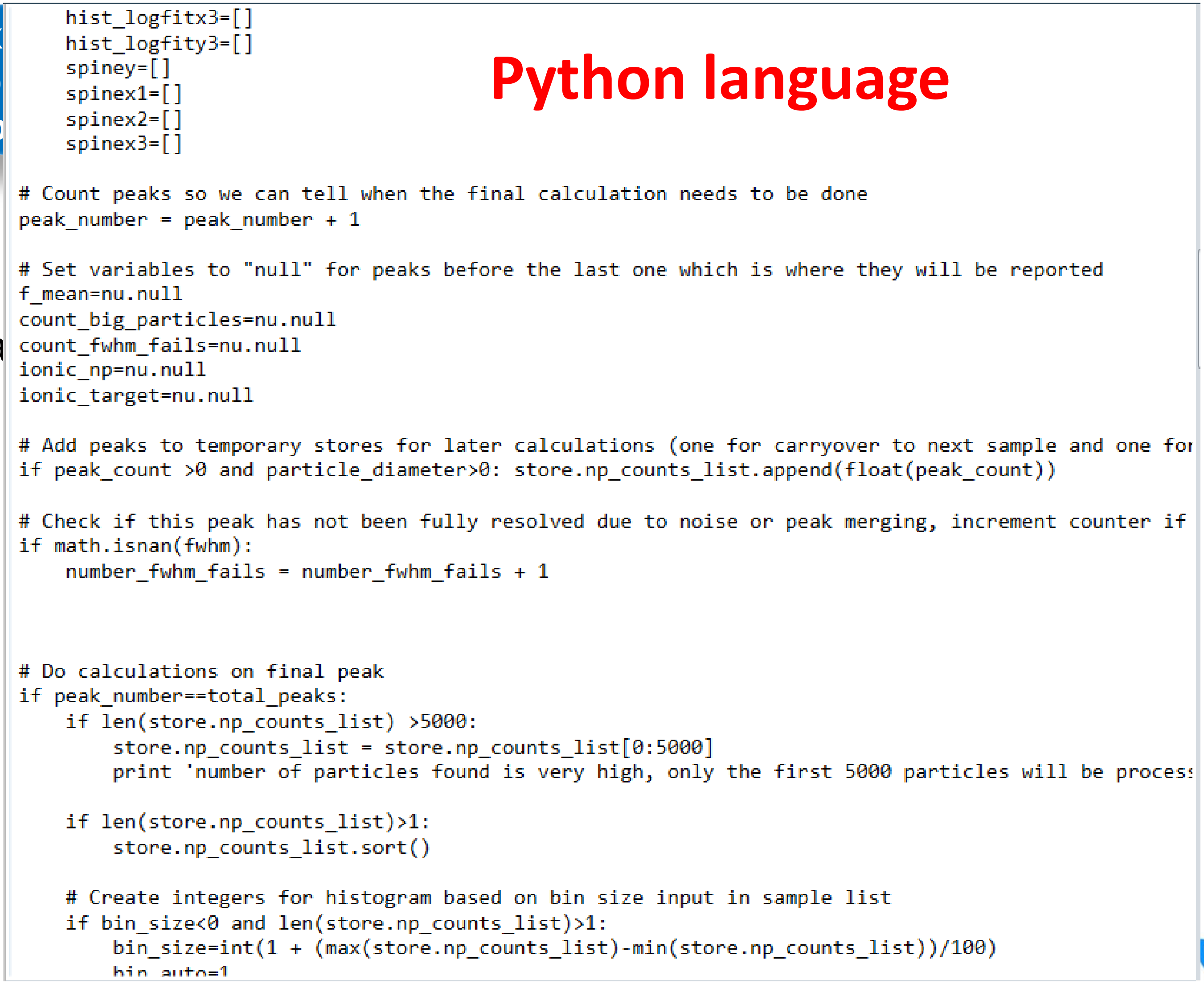

Python language

```
    hist_logfitx3=[]
    hist_logfity3=[]
    spiney=[]
    spinex1=[]
    spinex2=[]
    spinex3=[]

# Count peaks so we can tell when the final calculation needs to be done
peak_number = peak_number + 1

# Set variables to "null" for peaks before the last one which is where they will be reported
f_mean=nu.null
count_big_particles=nu.null
count_fwhm_fails=nu.null
ionic_np=nu.null
ionic_target=nu.null

# Add peaks to temporary stores for later calculations (one for carryover to next sample and one for
if peak_count >0 and particle_diameter>0: store.np_counts_list.append(float(peak_count))

# Check if this peak has not been fully resolved due to noise or peak merging, increment counter if
if math.isnan(fwhm):
    number_fwhm_fails = number_fwhm_fails + 1



# Do calculations on final peak
if peak_number==total_peaks:
    if len(store.np_counts_list) >5000:
        store.np_counts_list = store.np_counts_list[0:5000]
        print 'number of particles found is very high, only the first 5000 particles will be process

    if len(store.np_counts_list)>1:
        store.np_counts_list.sort()

    # Create integers for histogram based on bin size input in sample list
    if bin_size<0 and len(store.np_counts_list)>1:
        bin_size=int(1 + (max(store.np_counts_list)-min(store.np_counts_list))/100)
        bin_auto=1
```

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UNTOIN

NP applications

Improved limit of detection with desolvator

- In classical mode (ionic solution measurement), use of desolvator improve sensitivity by factor ~ 10

Transport efficiency

Ions non extracted

Transmission efficiency

- Desolvator useful for SP-ICP-MS ?

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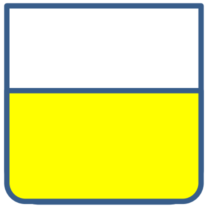
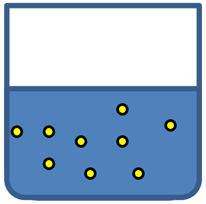
Improved limit of detection with desolvator

- **Comparison of calibrations for wet and dry plasma**

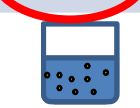


1 ppb Au



4-7 nm / 10 nm Au NP solutions

	Ionic sensitivity, cps/ppt	Sample transport rate, µL/sec
Wet sample introduction, standard cones	330	0.124
Dry Aridus II, ES interface	3180	0.434
Enhancement	9.6	3.5



Improvement in ion transport expected : **~2.7.**

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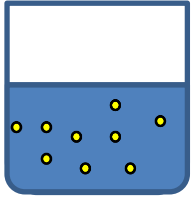
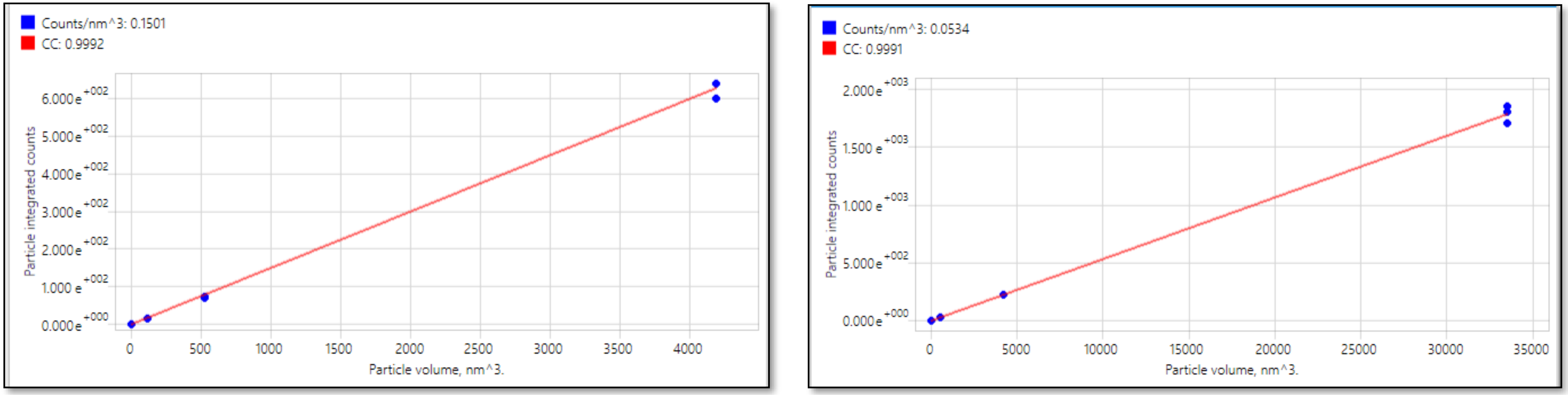
Improved limit of detection with desolvator

- **Comparison of number of counts per particle for DRY and WET**



Calibration curve for particle counts per particle volume for wet and dry sample introduction system



Wet, 10, 20 and 40nm

0.0534 cts/nm^3

Dry, 5, 10 and 20nm.

0.15 cts/nm^3

~ 2.8

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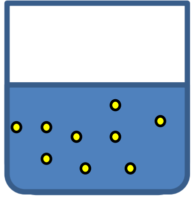
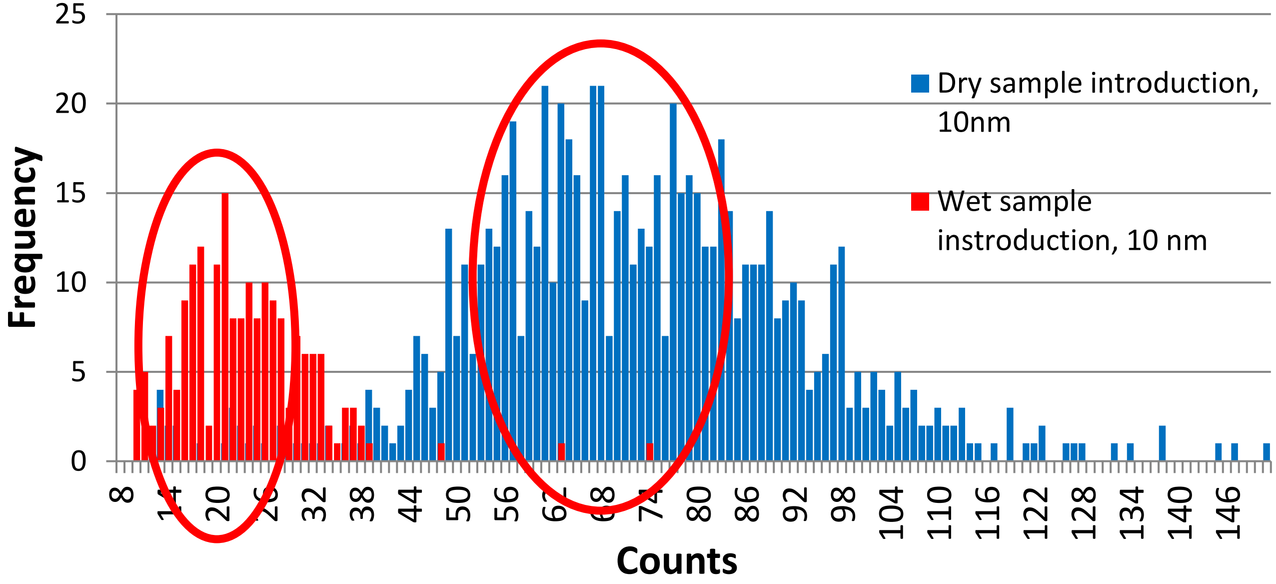
Improved limit of detection with desolvator

- **Comparison of number of counts per particle for DRY and WET**



Particle count distributions for 10nm standard using wet and dry sample introduction systems



25 cts

70 cts

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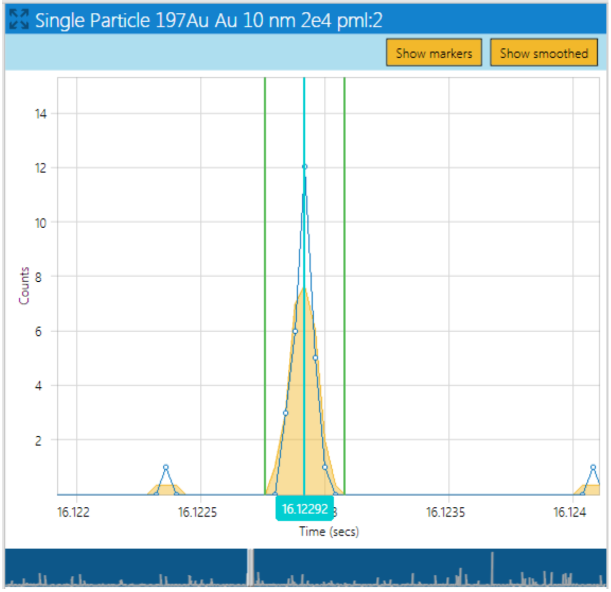
Improved limit of detection with desolvator

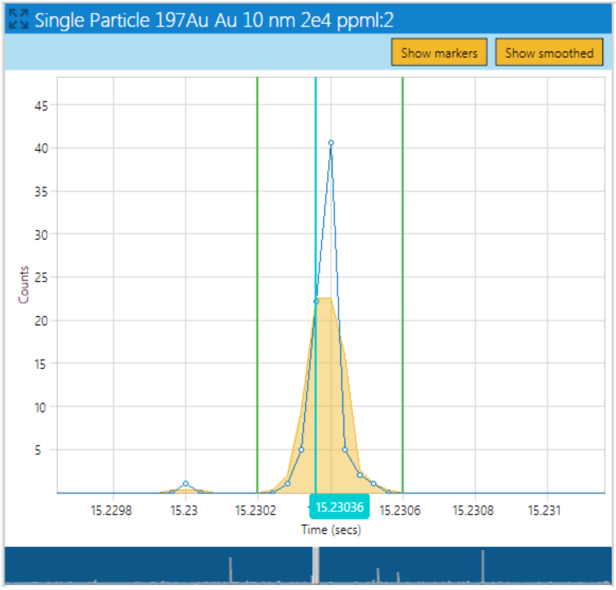
- **Comparison of detection limits for DRY and WET**

Wet – nominal 10nm Au
27 counts

Dry – nominal 10nm Au
76 counts



Single Particle 197Au Au 10 nm 2e4 pml:2



Single Particle 197Au Au 10 nm 2e4 ppml:2

Detection limits based on baseline plus 3 SD noise:

Wet: **6** nm

Dry: **4** nm

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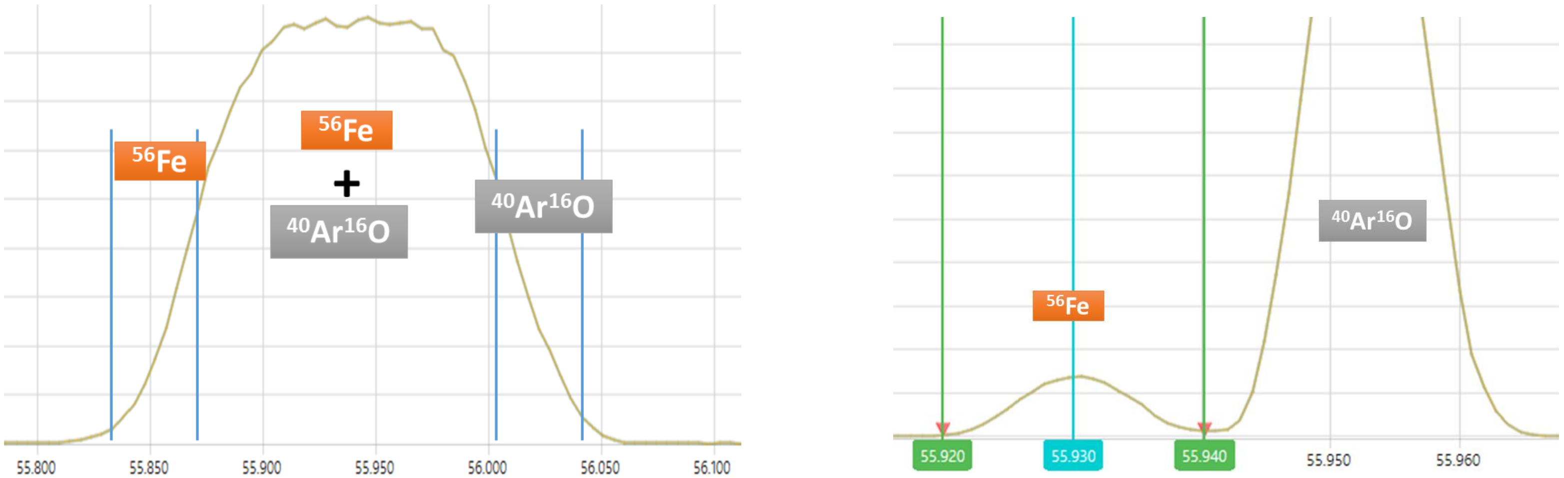
Handling elements with interferences

- Some elements have degraded detection limits in ICP-MS due to interferences at the mass of interest from molecular species found in the plasma

Example of ^{56}Fe interfered by ^{40}Ar^{16}O



Resolution 300

Resolution 4000

Resolution increase

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Handling elements with interferences

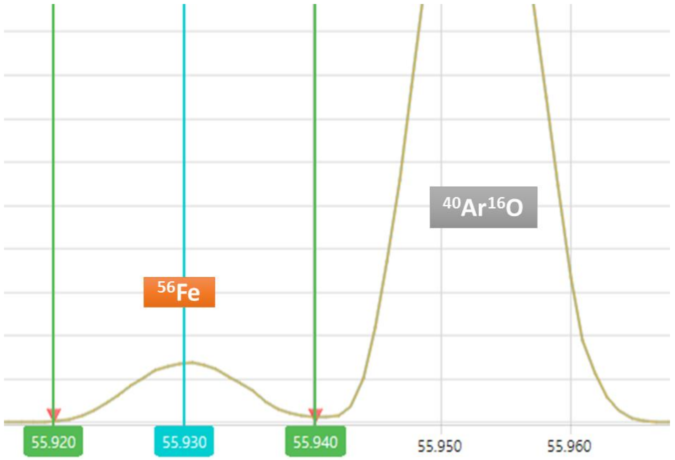
- Some elements have degraded detection limits in ICP-MS due to interferences at the mass of interest from molecular species found in the plasma

Example of ^{56}**Fe** interfered by ^{40}**Ar**^{16}**O**

Disadvantage of using higher resolution

- Loss of transmission
- Loss of the flat peak

Pseudo Resolution



Resolution 4000

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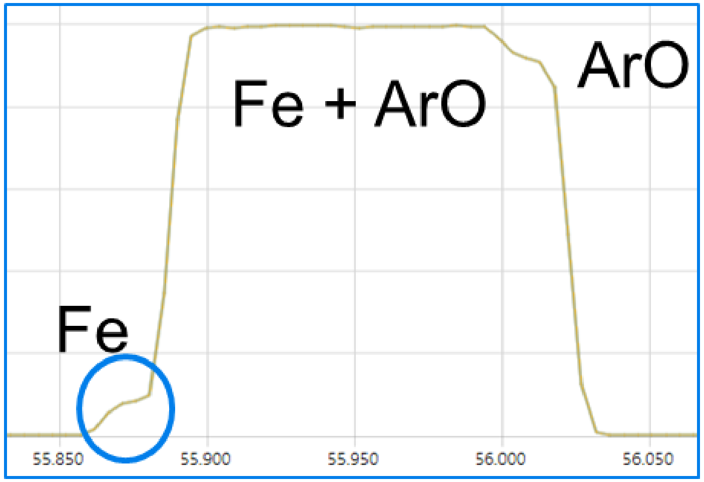
Handling elements with interferences

- Some elements have degraded detection limits in ICP-MS due to interferences at the mass of interest from molecular species found in the plasma

Example of $^{56}\mathbf{Fe}$ interfered by $^{40}\mathbf{Ar}^{16}\mathbf{O}$

Pseudo Resolution

- Source slit narrowed (4000)
- Collector slit left wide open (300)



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Handling elements with interferences

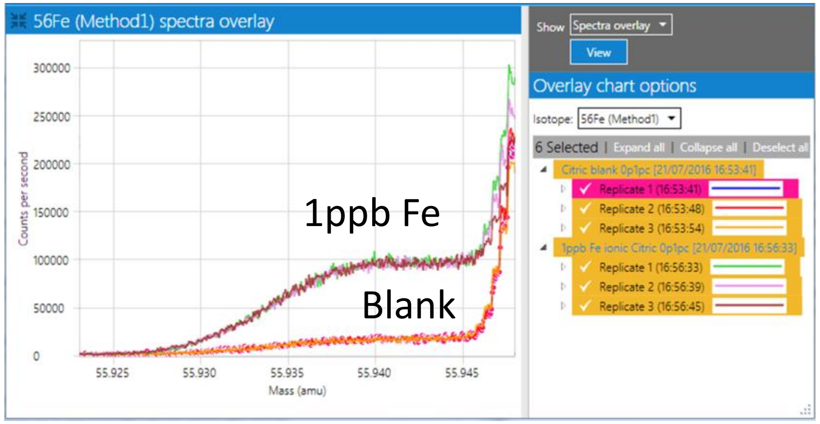
- Some elements have degraded detection limits in ICP-MS due to interferences at the mass of interest from molecular species found in the plasma

Example of $^{56}\mathbf{Fe}$ interfered by $^{40}\mathbf{Ar}^{16}\mathbf{O}$

Pseudo Resolution

- Source slit narrowed (4000)
- Collector slit left wide open (300)

➡ Possibility to measure on flat top peak without interferent influence



Show: Spectra overlay

Isotope: 56Fe (Method1)

6 Selected

Citric blank 0p1pc [21/07/2016 16:53:41]
- ✓ Replicate 1 (16:53:41)
- ✓ Replicate 2 (16:53:48)
- ✓ Replicate 3 (16:53:54)

1ppb Fe ionic Citric 0p1pc [21/07/2016 16:56:33]
- ✓ Replicate 1 (16:56:33)
- ✓ Replicate 2 (16:56:39)
- ✓ Replicate 3 (16:56:45)

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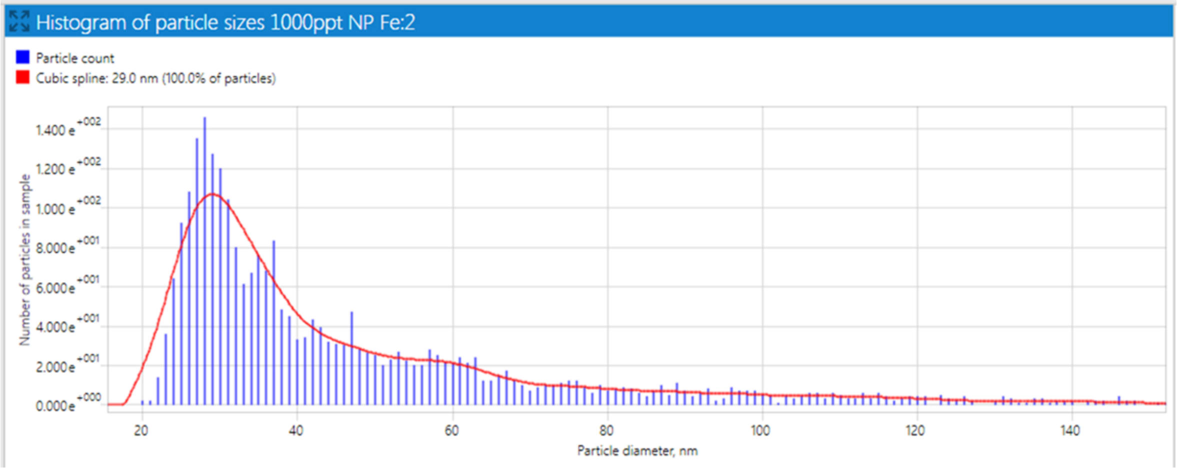
Handling elements with interferences

- **Measure of 30 nm Fe3O2 nanoparticles**

  - Ionic calibration
  - Agglomeration problem
  - Detection limit calculated : 21 nm



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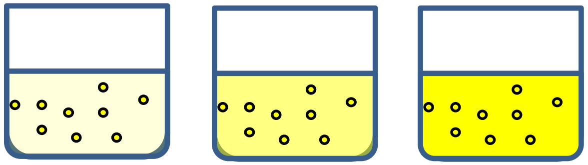
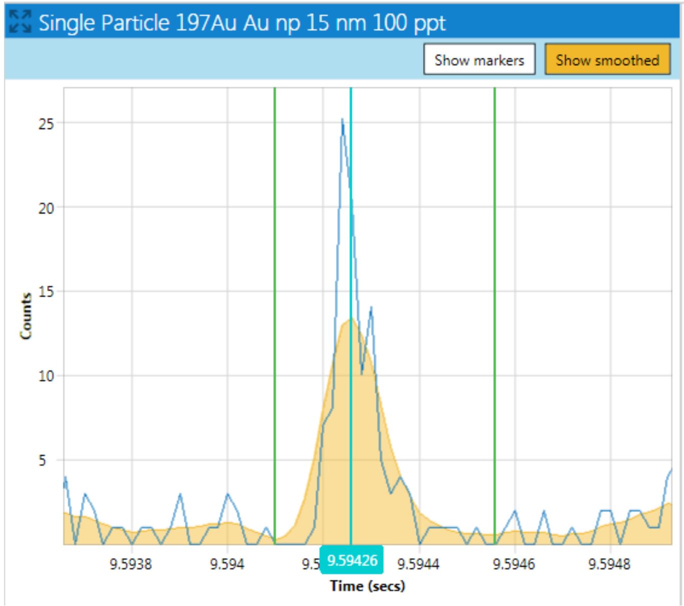
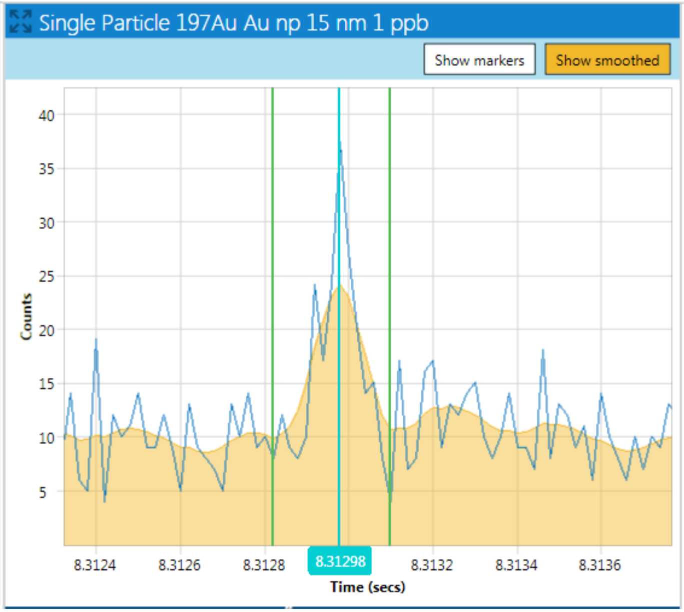
NP detection with high ionic background

Analysis of : Np 15 nm Au in ionic background (10 ppt, 100 ppt, 1 ppb)







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Improvements in single particle analysis using a time-of-flight mass analyzer

Vitesse TOF-ICP-MS

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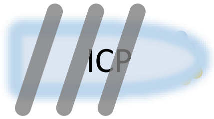
ICP-TOF-MS Principle

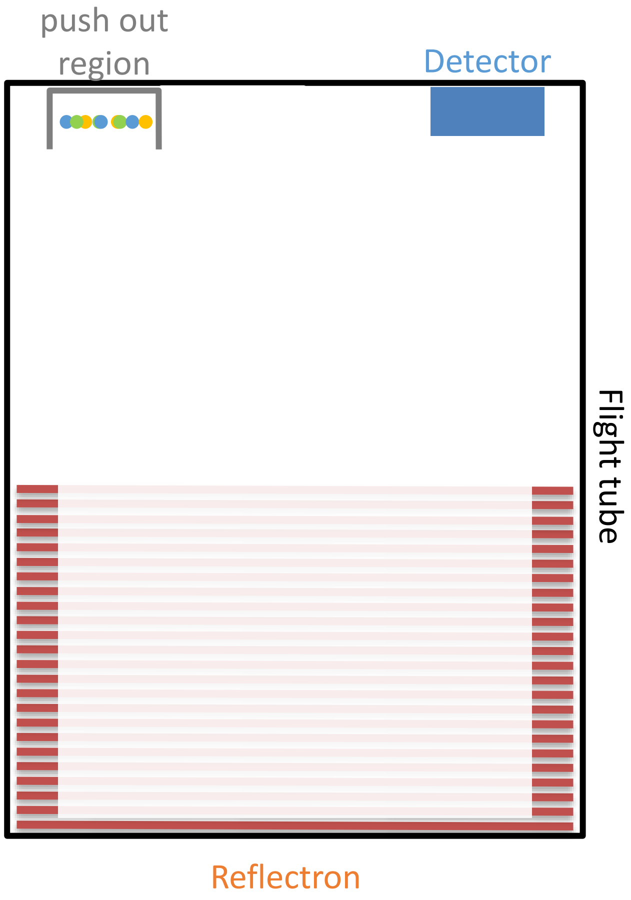


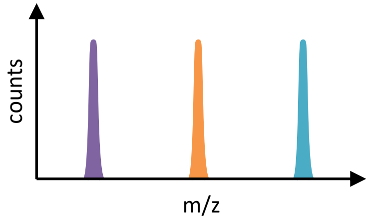
1. Incoming flow of ions from ICP

2. Extraction of ion packets in the push out region

3. Acceleration of the ions with equal energy

4. Ions travel thought the fly tube with a speed depending on m/z
   - ● lighter ions
   - ● heavier ions





5. Full spectra recorded **<30 µs**

time of flight	**quadrupole**
Full mass spectrum	Single isotope
Fast acquisition (50-100 µs)	Slower acquisition (1-2 ms)

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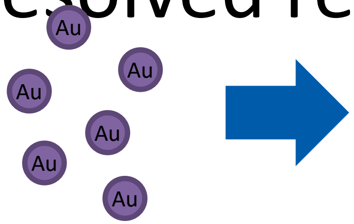
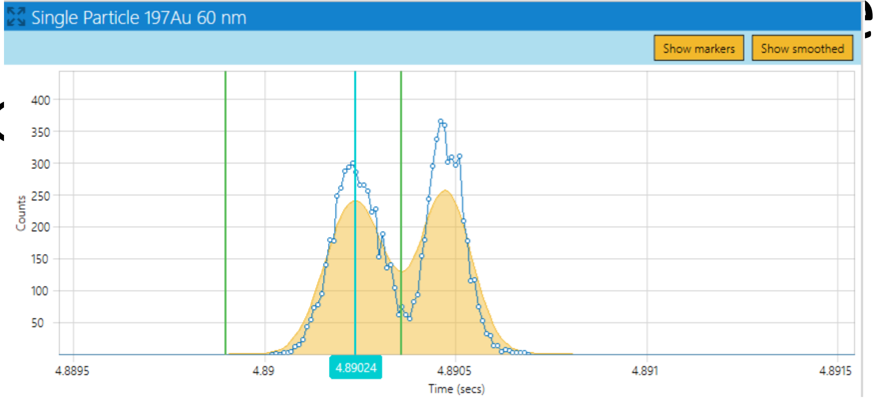
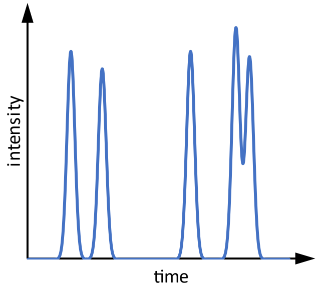
Single Particle Analysis – Acquisition Speed

- Ionic solution gives constant tim
  resolved resp

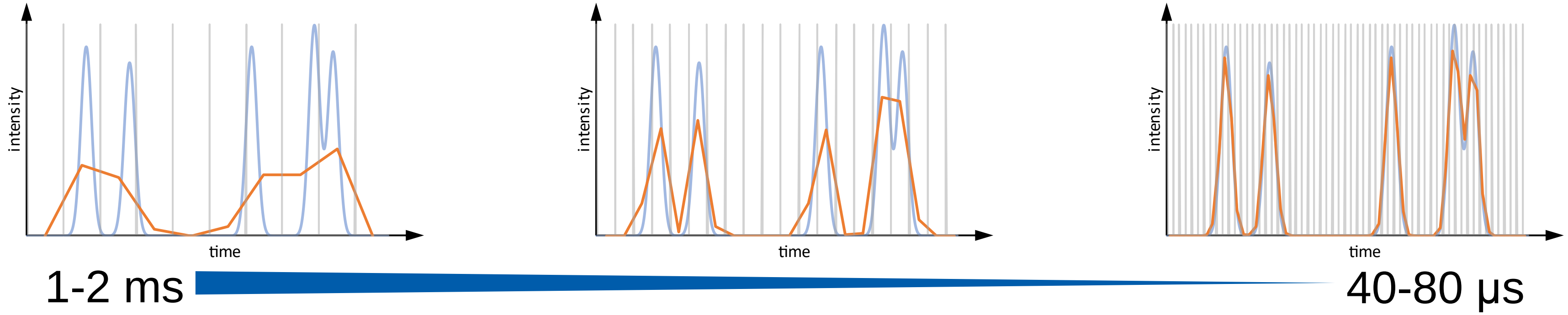
- Nanoparticles
  e bursts of







A high time resolution is crucial to most accurately measure the single bursts of signals



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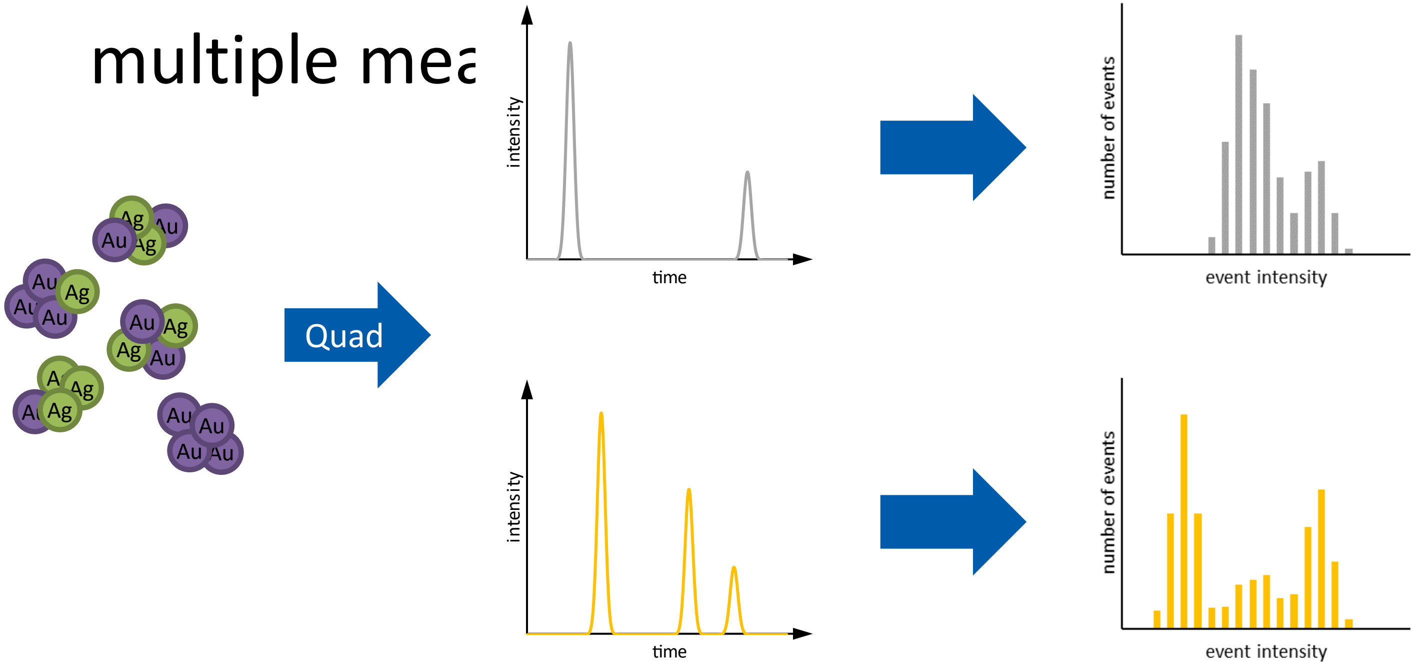
Single Particle Analysis – Multi Element Capability

- Quadrupole: No multielement information obtainable
  - Elemental composition of entire population in multiple mea



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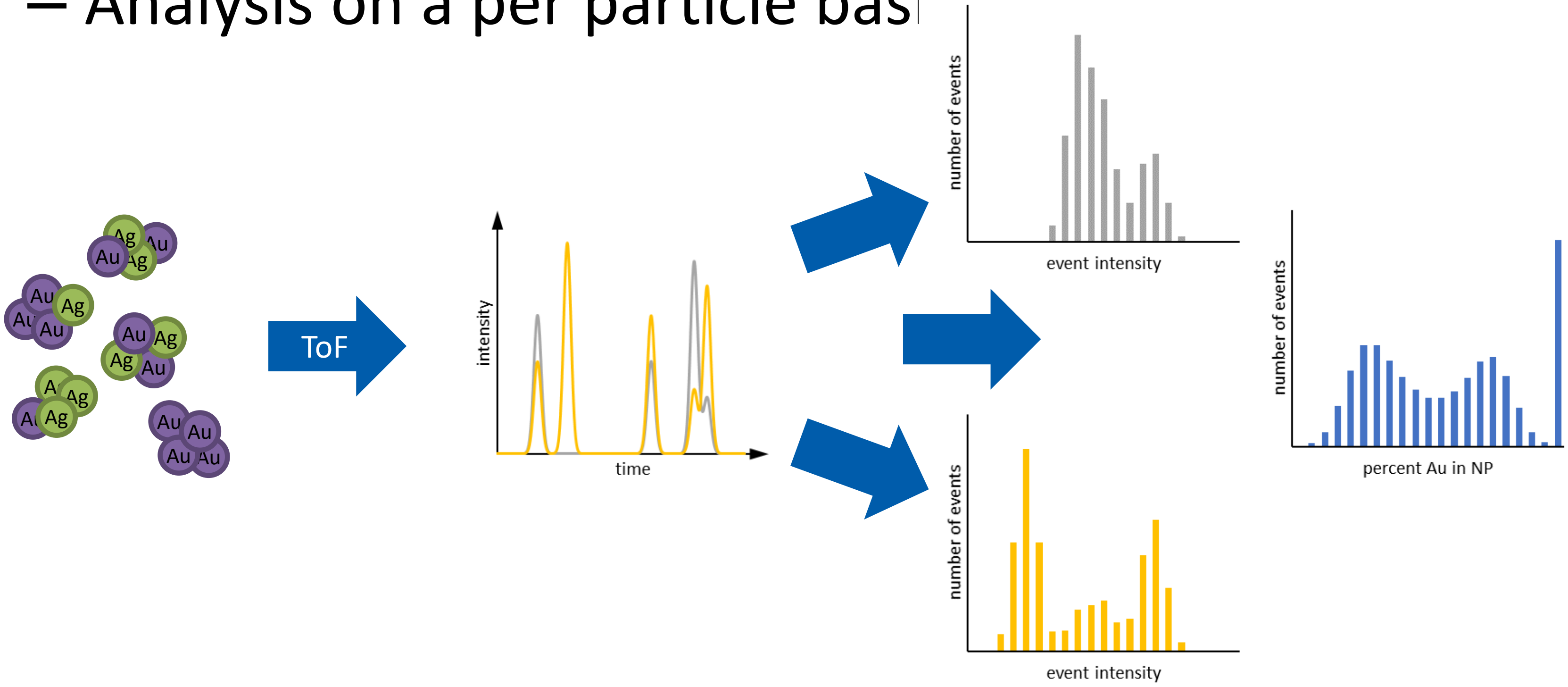
Single Particle Analysis – Multi Element Capability

- Vitesse: Full elemental information for every event detected
  - Analysis on a per particle basi



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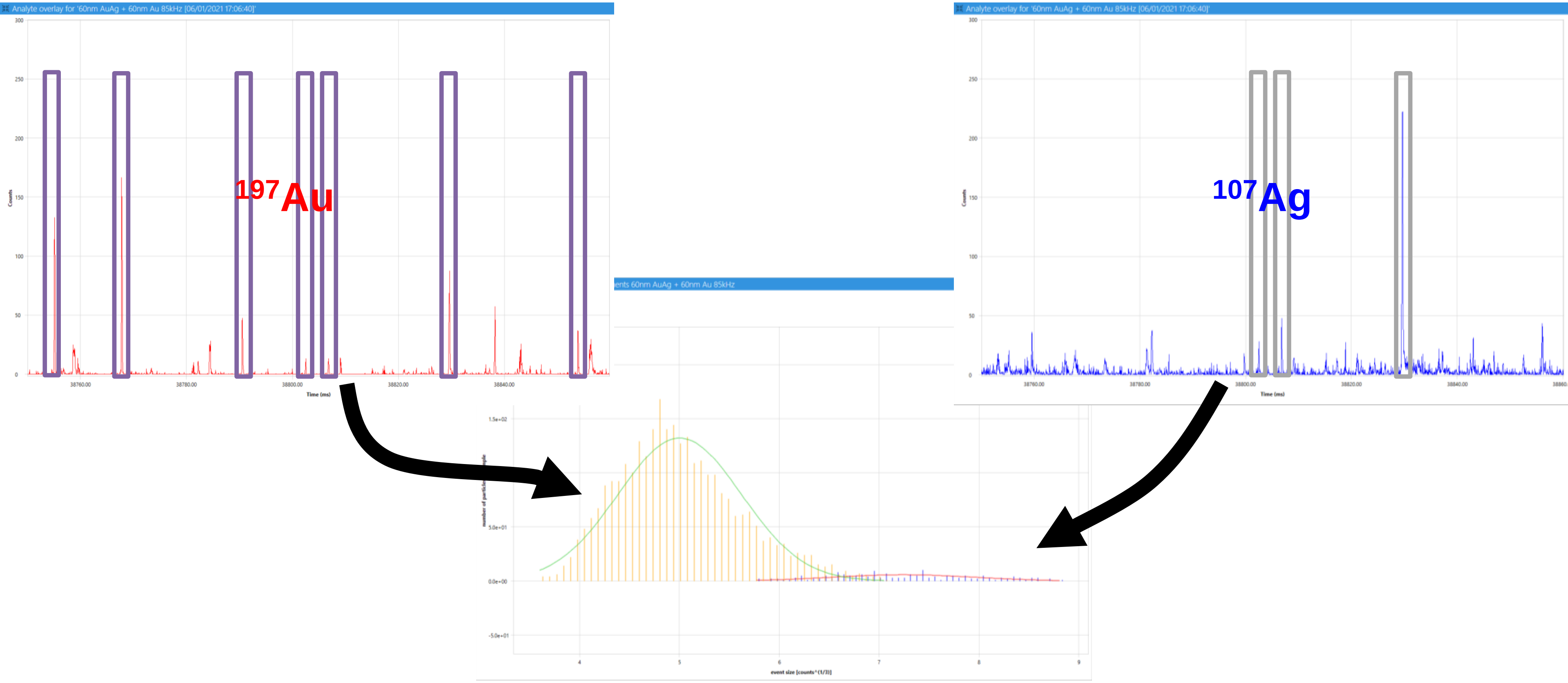
Single Particle Analysis Example

- Mixture of Au core Ag shell and pure Au NPs



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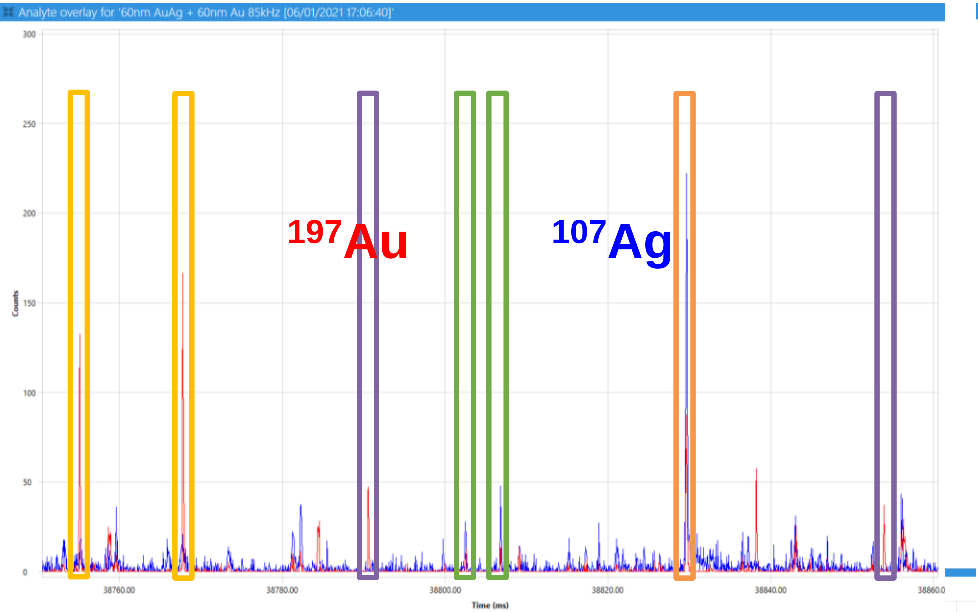
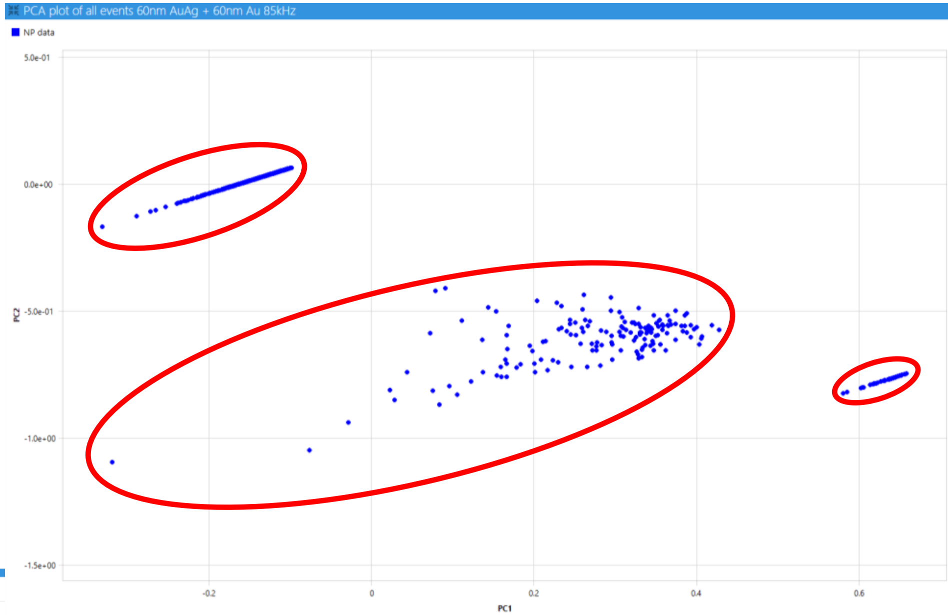
Single Particle Analysis Example

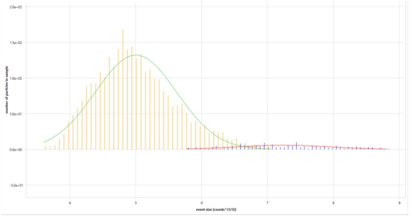
- Mixture of Au core Ag shell and pure Au NPs



Analyte overlay for '60nm AuAg + 60nm Au 85kHz [06/01/2021 17:06:40]'



PCA plot of all events 60nm AuAg + 60nm Au 85kHz



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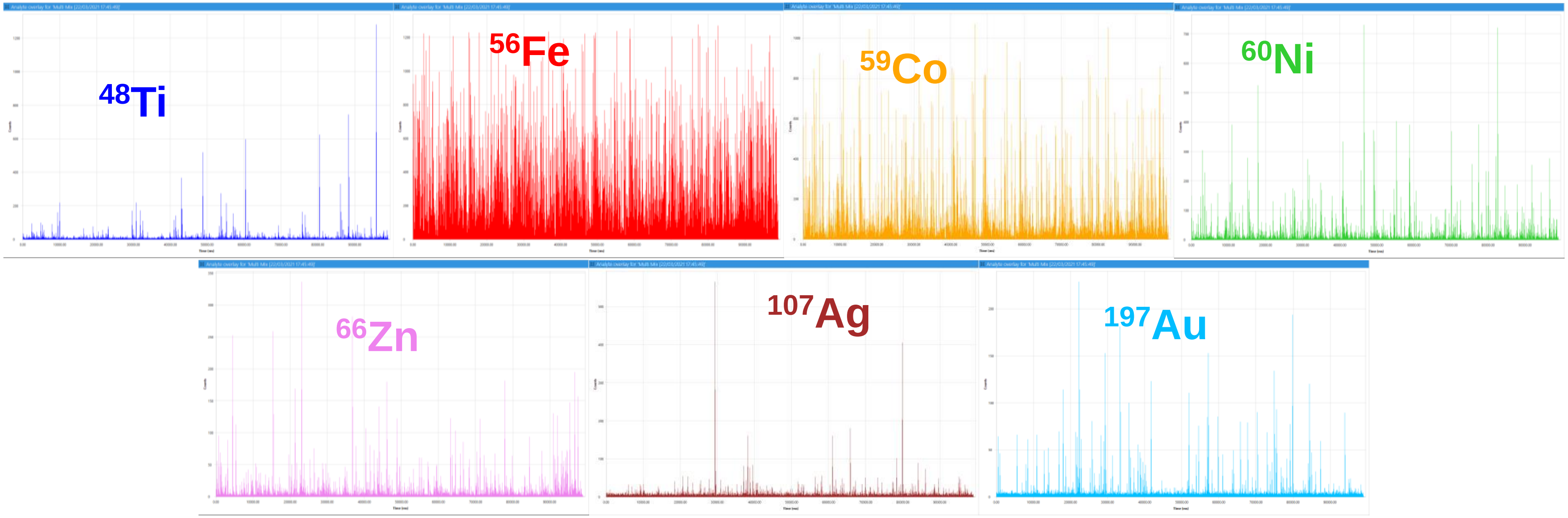
Single Particle Analysis Example

- Various types of NPs:
  - FeCoZn, FeCoNi, Au, Ag, AuAg, Natural NPs



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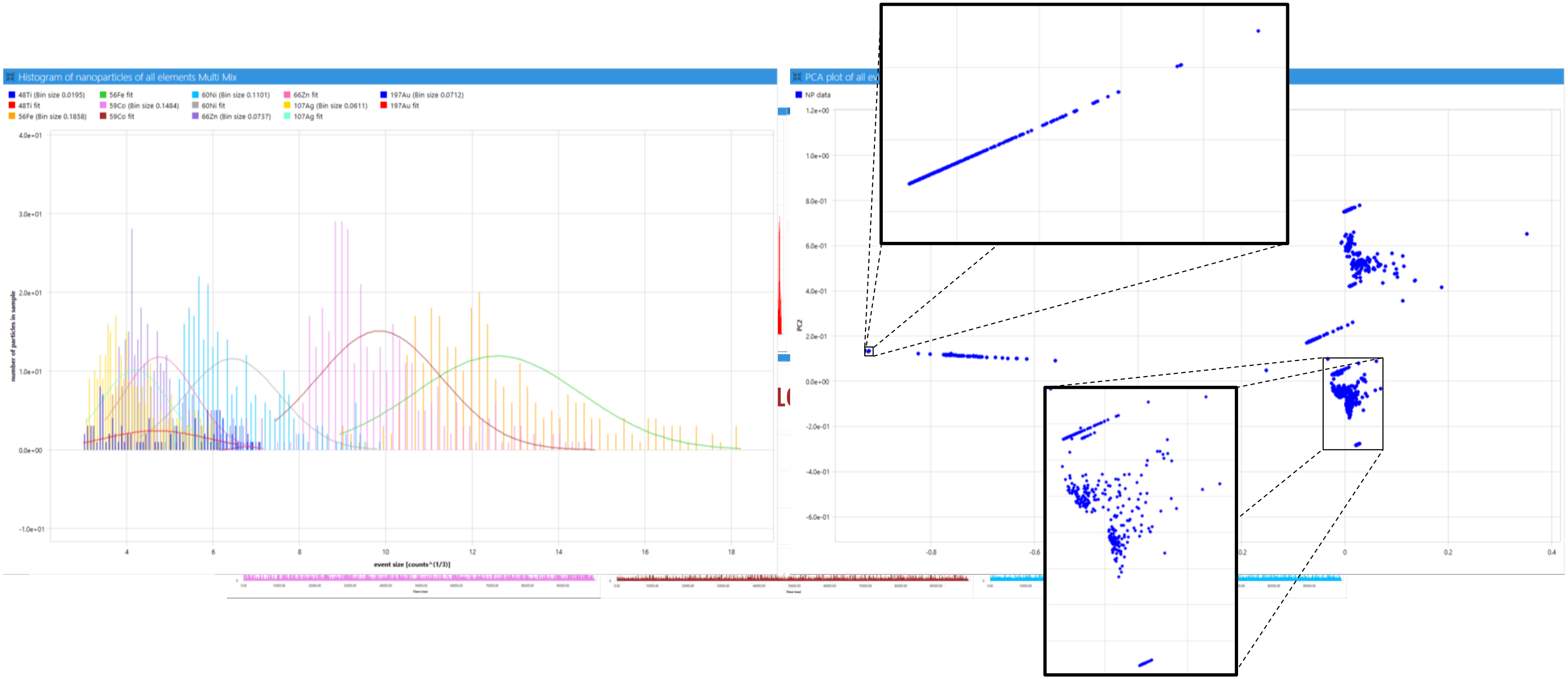
Single Particle Analysis Example

- Various types of NPs:
  - FeCoZn, FeCoNi, Au, Ag, AuAg, natural clay NPs



Commission européenne

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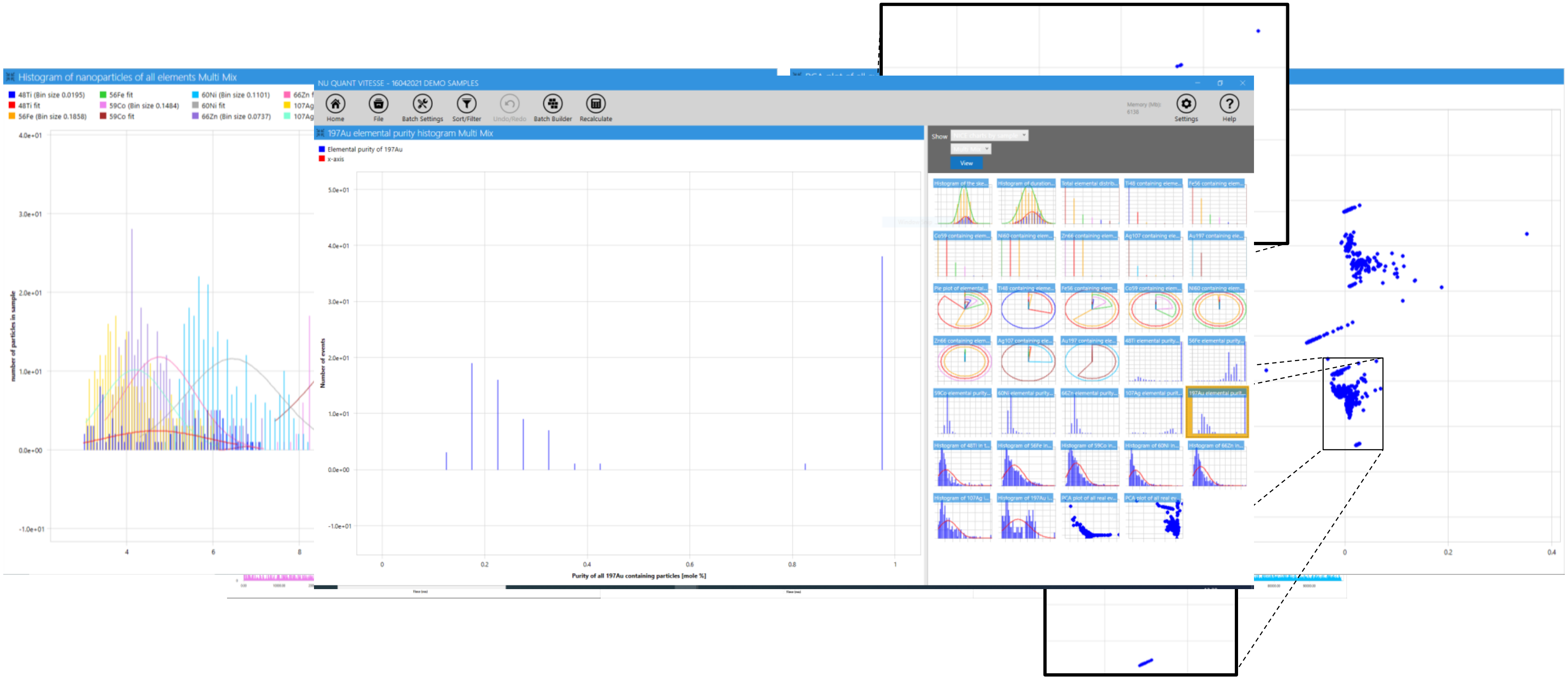
Single Particle Analysis

- Various types of NPs:
  - – FeCoZn, FeCoNi, Au, Ag, AuAg



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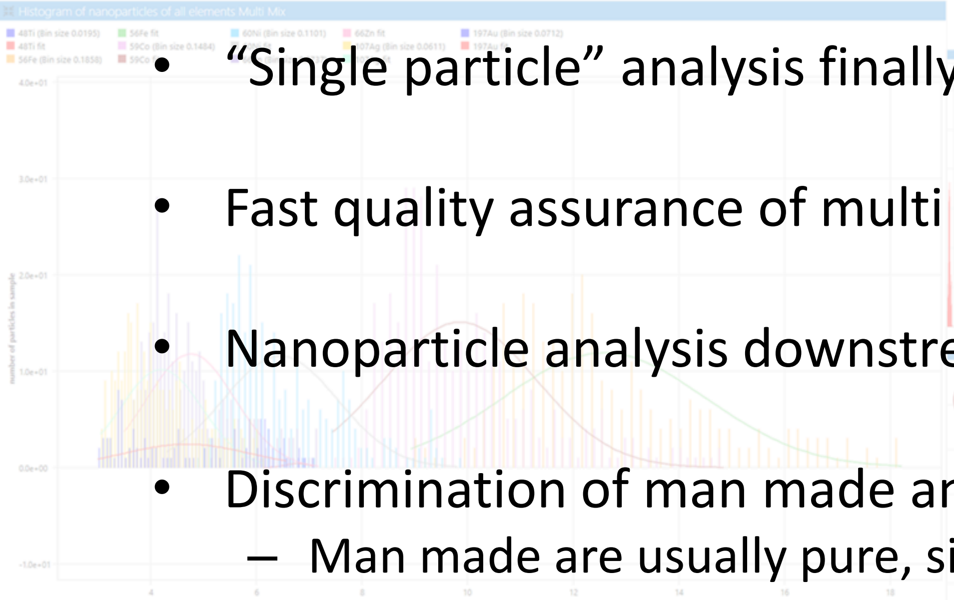
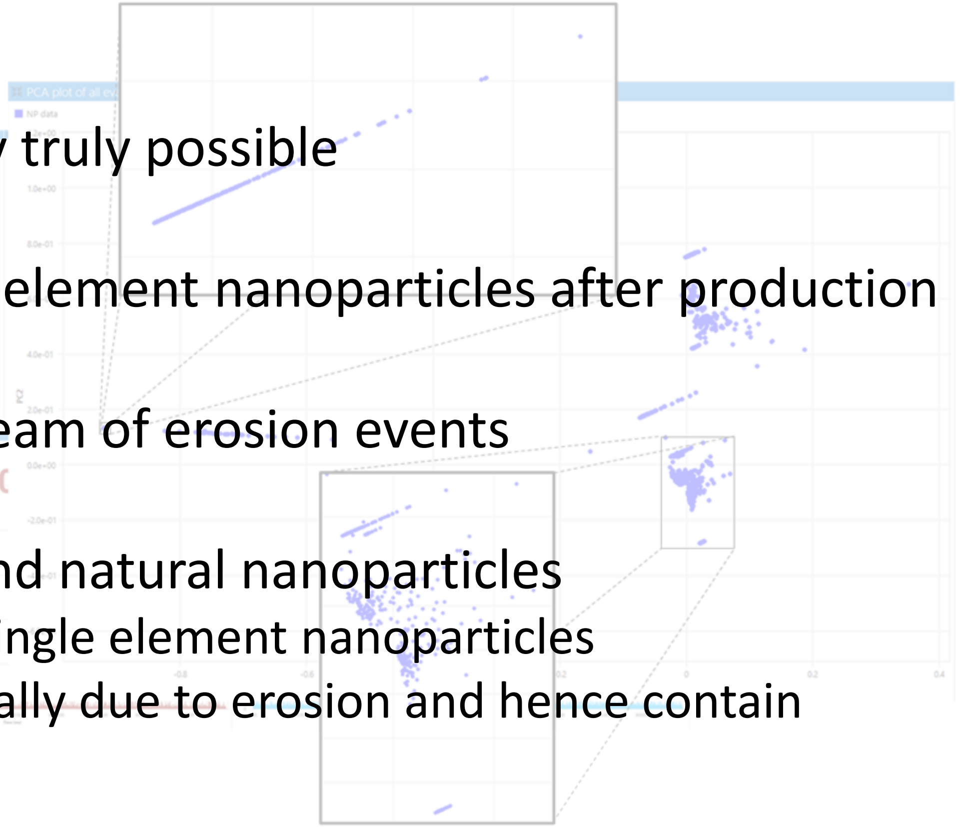
Single Particle Analysis Uses





- “Single particle” analysis finally truly possible
- Fast quality assurance of multi element nanoparticles after production
- Nanoparticle analysis downstream of erosion events
- Discrimination of man made and natural nanoparticles
  - Man made are usually pure, single element nanoparticles
  - Natural nanoparticles are usually due to erosion and hence contain multiple elements

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