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Interactive spICPMS data treatment using Nanocount

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spICP-MS: pros and cons

Pros:

- Determines
 - polydisperse sizes
 - particle number concentration
 - dissolved concentrations vs. particulates
- uses an existing machine to calculate size
- It can do small sizes fast \Leftrightarrow TEM
- Extremely sensitive for very low number concentrations
- Very little sample preparation or sample disturbance

Cons:

- Assume a spherical shape
- Poor size limits for certain nanoparticles (e.g. SiO_2)
- Works only for inorganic particles and only "sees" the inorganic part
- Only one element at the time (maybe TOF-spICPMS in the future)
- Method optimization (dilution, dwell time)
- **Data treatment**

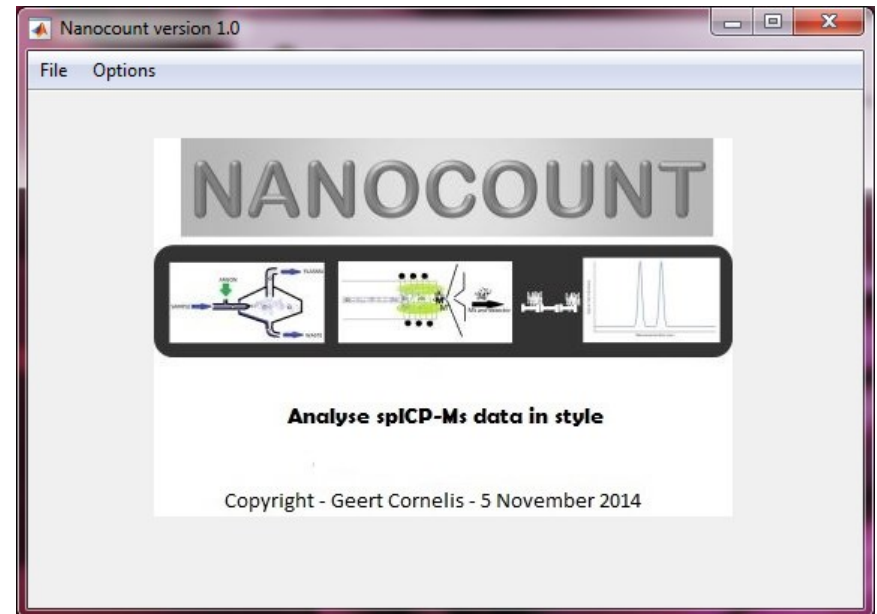


Basic data interpretation steps

- Export data from ICP-MS and import in your tool (e.g. excel)
- Obtain calibration curve
- Calculate histograms from raw data
- Determine dissolved/particulate level and remove dissolved data
- Calculate nebulisation efficiency
- Calculate diameters from signal intensities
- Calculate number concentrations from frequencies

Additional data interpretation steps

- Drift correction
- Signal discrimination
- Nebulisation efficiency determination
- Particle size distribution editing



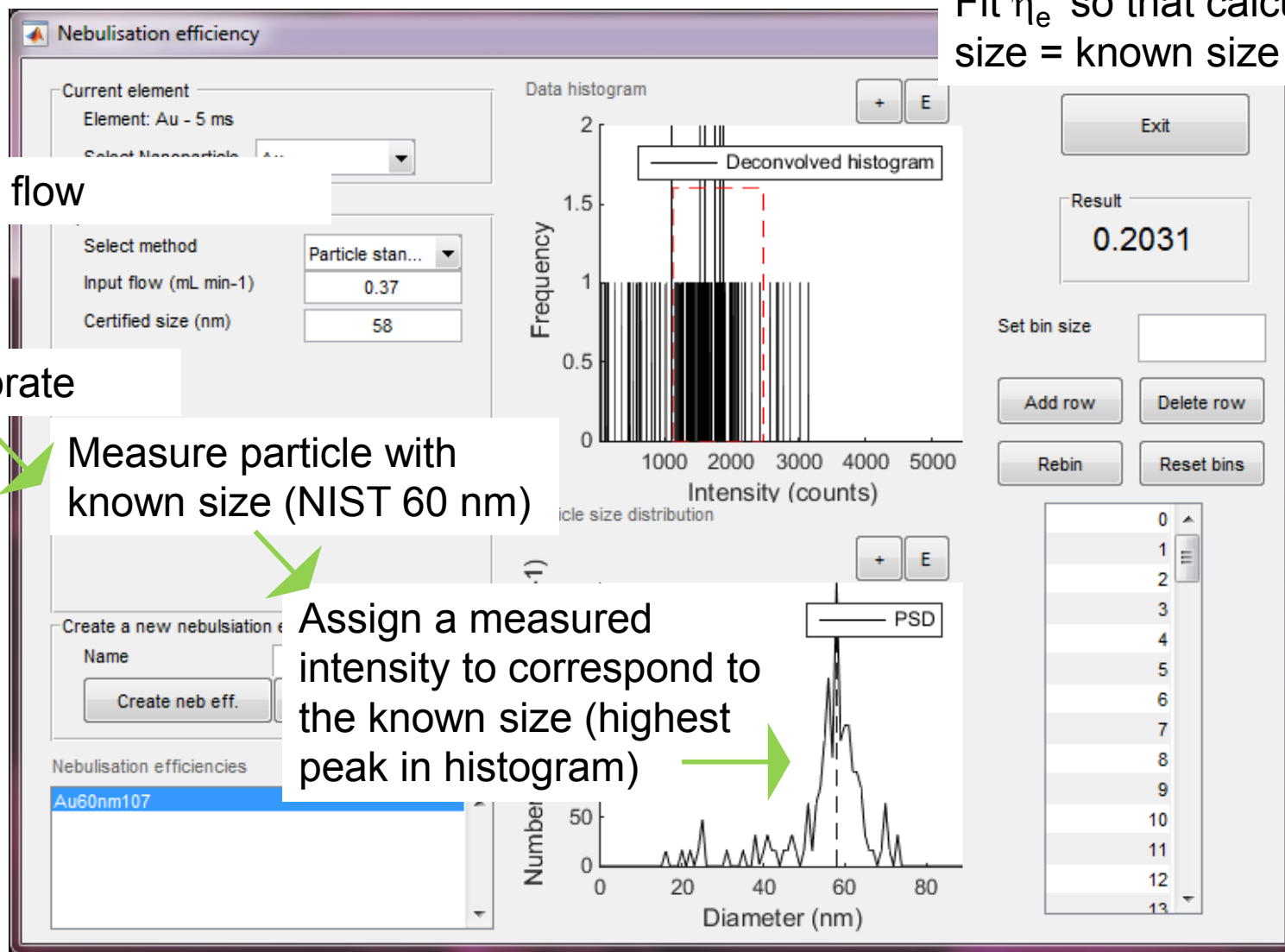
Additional data interpretation

The screenshot displays a 'Data treatment' software window with the following components:

- Element:** Au - 5 ms
- Edit data:** Intensity anchors are set to 'None'.
- Drift correction:** Checked, with a p-value of $1.5e-07$.
- Remove outliers:** Checked, with a count of $n = 10.3$.
- Select dataobject:** 1
- Components list:** A list of data objects including b1-Au, b2-Au, b3-Au, b4-Au, b5-Au, Au1ppt, Au10ppt, Au5ppt, Au30ppt, Au100ppt, Au1000ppt, b1-Ag, and b2-Ag.
- Top Plot:** 'Raw data' showing signal intensity (counts) vs Time (s) from 0 to 10000. The signal is highly noisy and shows a downward drift from approximately 50 counts to 35 counts.
- Bottom Plot:** 'Corrected data' showing signal intensity (counts) vs Time (s) from 0 to 8000. The signal is noisy but stable around 50 counts.
- Controls:** 'Exit' and 'Apply to all' buttons are on the right. A legend at the bottom right shows 'Data' selected and 'Histogram' unselected.

Nebulisation efficiency

Fit η_e so that calculated size = known size



Measure flow

Calibrate

Measure particle with known size (NIST 60 nm)

Assign a measured intensity to correspond to the known size (highest peak in histogram)

Current element
Element: Au - 5 ms
Select Nanoparticle: Au

Select method: Particle stan...
Input flow (mL min⁻¹): 0.37
Certified size (nm): 58

Data histogram
Frequency vs Intensity (counts)
Deconvolved histogram

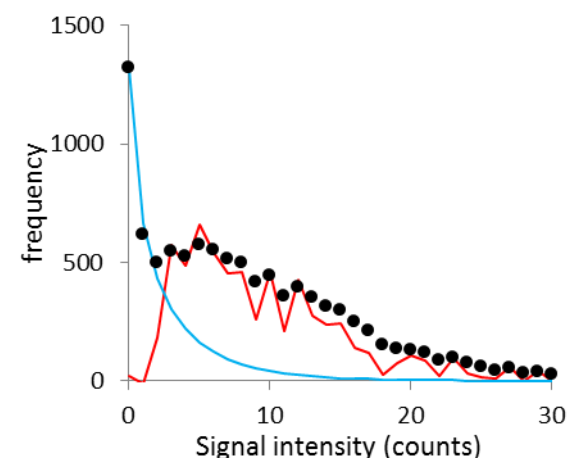
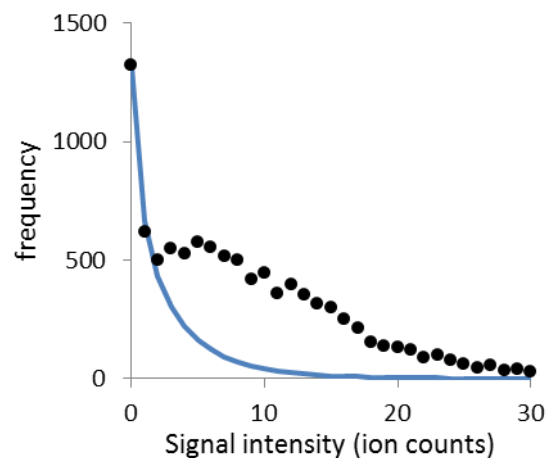
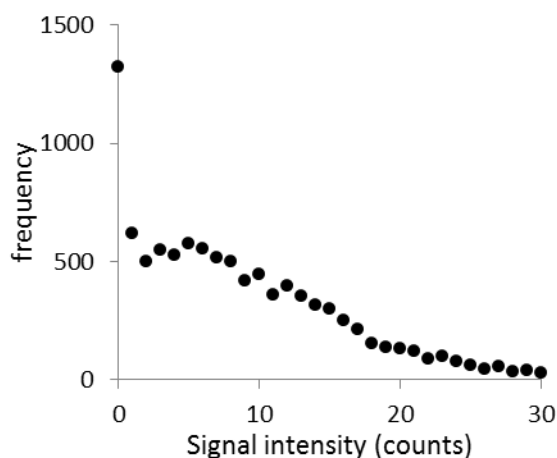
Result: 0.2031

Set bin size: []
Add row, Delete row, Rebin, Reset bins

Nebulisation efficiencies
Au60nm107

Particle size distribution
Number vs Diameter (nm)
PSD

Signal discrimination: Deconvolution



If one has perfect knowledge how dissolved signals look like in histograms they could be subtracted to provide a histogram free of dissolved signals

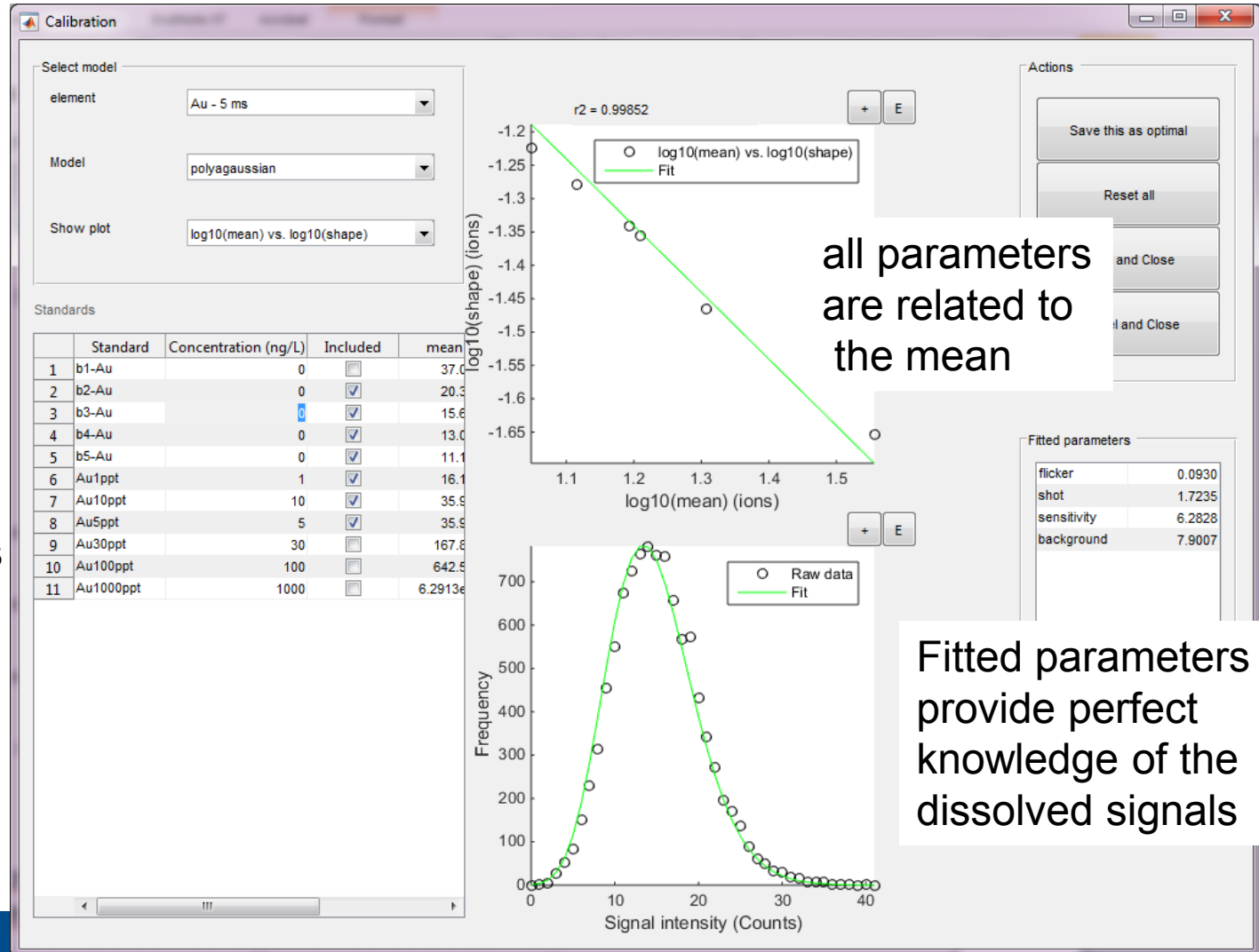
Cornelis, G.; Hasselov, M., A signal deconvolution method to discriminate smaller nanoparticles in single particle ICP-MS. *Journal of Analytical Atomic Spectrometry* **2014**, 29 (1), 134-144.

Calibration in the deconvolution method

Different models

- Basic
- Normal
- Polyagaussian
- Poissongaussian

Model parameters are fitted to several dissolved standards



all parameters are related to the mean

Fitted parameters provide perfect knowledge of the dissolved signals

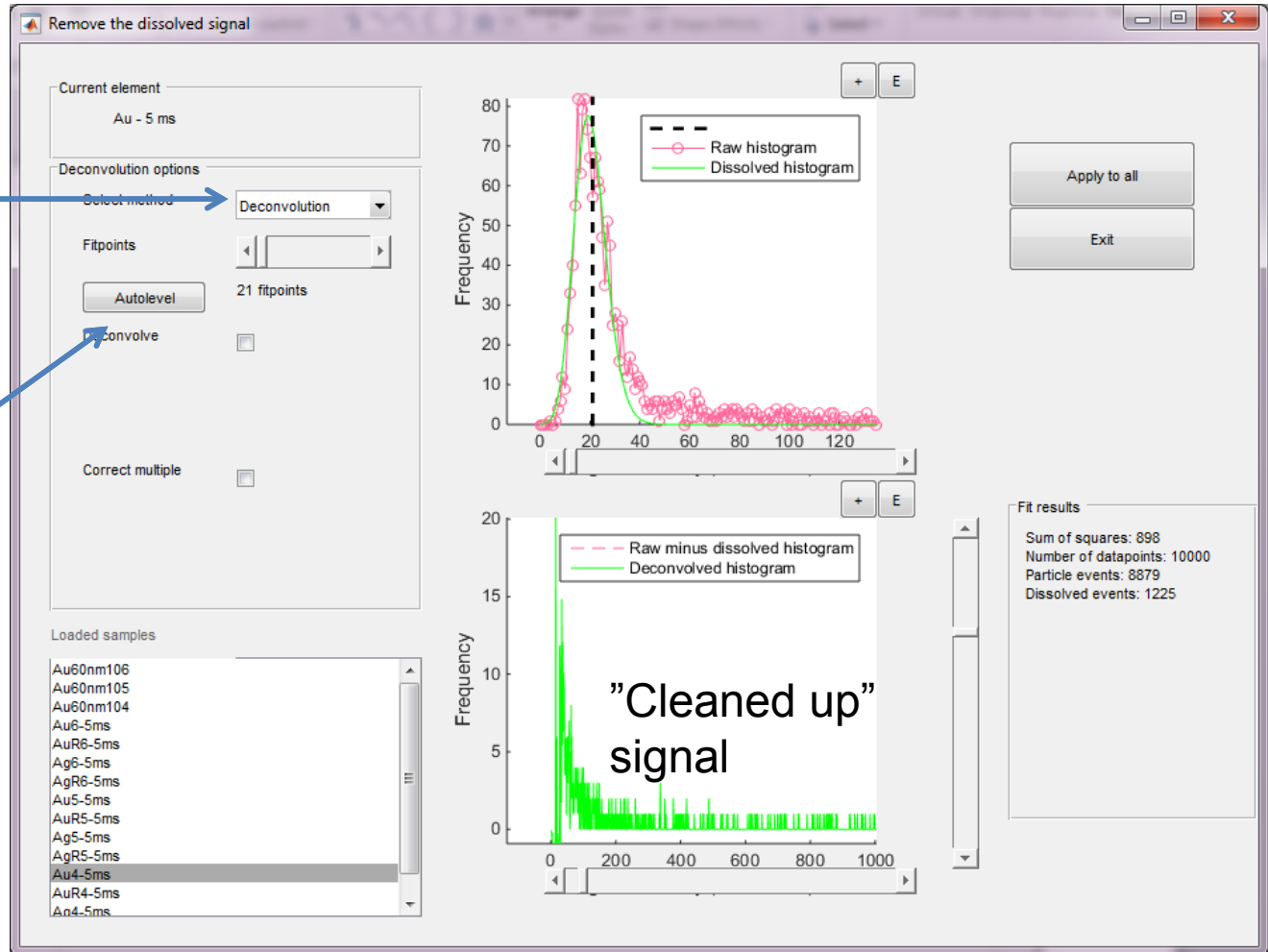
Dissolved signal removal

Several methods:

- "None"
- Outlier analysis
- Deconvolution
- K-means

Choice of number of fitpoints

- manual
- Do a sweep





PSD editing

The screenshot shows the 'Particle size distribution' software interface. On the left, there are control panels for 'Current element' (Au - 1 ms), 'Select Nanoparticle' (Au), and 'PSD options'. The 'PSD options' panel includes 'Flow (mL min-1)' (0.4), 'Neb eff 1' (Au60nm1), 'Neb eff 2' (none selected), 'PSD based on' (Number), 'Smooth' (slider), 'Only > 0' (checked), 'X-axis trend' (log(expected...)), and 'Y-axis trend' (log(measure...)). Below these are 'Rebin PSD' and 'Reset bin' buttons. At the bottom left is a 'Loaded samples' table.

	Name	Expected Value
11	12	0.0014
12	13	7.8000e-04
13	14	4.9600e-04
14	15	2.8300e-04
15	16	1.5600e-04

The main area contains two plots. The top plot, 'Particle size distribution', shows 'Particle number concentration (mL⁻¹) × 10⁴' vs 'Size (nm)'. It features multiple colored curves (1-16) and a legend. The bottom plot, 'Sample trend', shows 'd/expected) number (mL⁻¹)' vs 'log(expected number)'. It features a dashed line with open circles. Annotations include blue arrows pointing to 'Neb eff 1' and 'Rebin PSD', and a grey box with an arrow pointing to the 'Sample trend' plot.

Use calculated nebulisation efficiency to calculate diameters and number concentrations

Edit PSD by

- Smoothing
- Rebinning

Plot Log(measured/expected) vs. Log(measured) concentration to establish linear range.

PSD calculation

Particle size distribution

Current element: Au - 1 ms

Select Nanoparticle: Au

PSD options

Flow (mL min⁻¹): 0.4

Neb eff 1: Au60nm1

Neb eff 2: none selected

PSD based on: Number

Smooth: [Slider]

Only > 0:

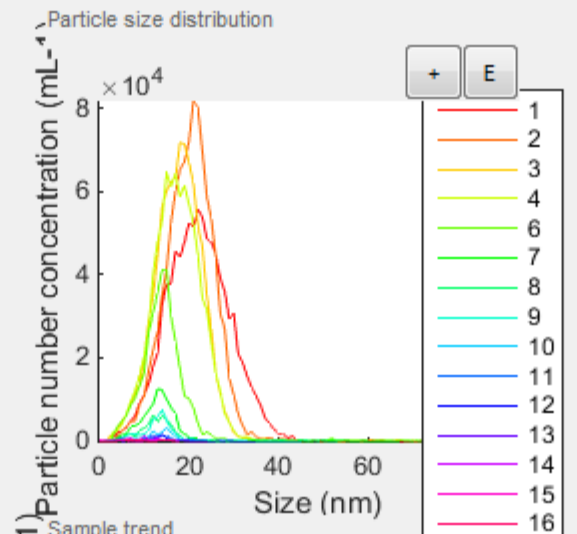
X-axis trend: log(expected...)

Y-axis trend: log(measure...)

Buttons: Rebin PSD, Reset bin

Loaded samples

	Name	Expected Value
11	12	0.0014
12	13	7.8000e-04
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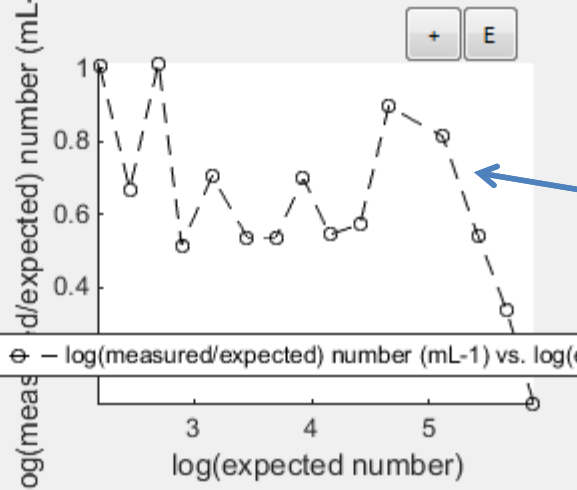


Particle size distribution

Particle number concentration (mL⁻¹) × 10⁴

Size (nm)

Sample trend



log(measured/expected) number (mL⁻¹) vs. log(ε

log(expected number)

Exit

Set bin size: [Input]

Add row Delete row

[List: 0-7]

Use calculated nebulisation efficiency to calculate diameters and number concentrations

Edit PSD by

- Smoothing
- Rebinning

Plot Log(measured/expected) vs. Log(measured) concentration to establish linear range.

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Why ?

- spICP-MS is very promising
- Probably the only technique that can
 - Monitor (inorganic) NMs in complex environments
 - Measure realistically low concentrations
 - Quantify number concentrations
 - Hardly disturbs the sample
- ICP-MS is readily available in many labs
- Data treatment theory is available but will be developed further and is impossible to handle in a spreadsheet format



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Thank you

Contact:

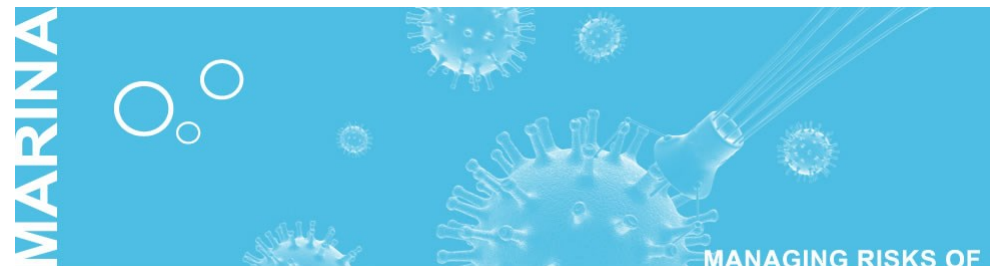
Geert.Cornelis@chem.gu.se



GUIDE *nano* 



Vetenskapsrådet

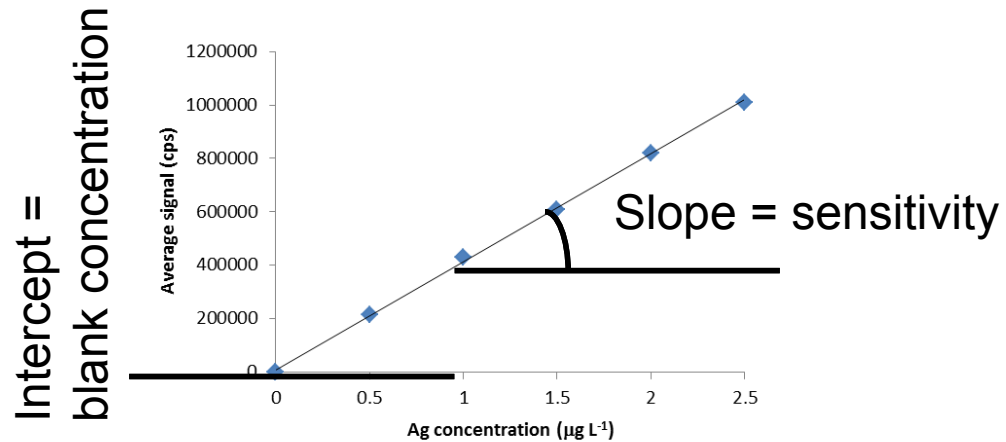


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MANAGING RISKS OF
NANOMATERIALS

Basic data interpretation steps

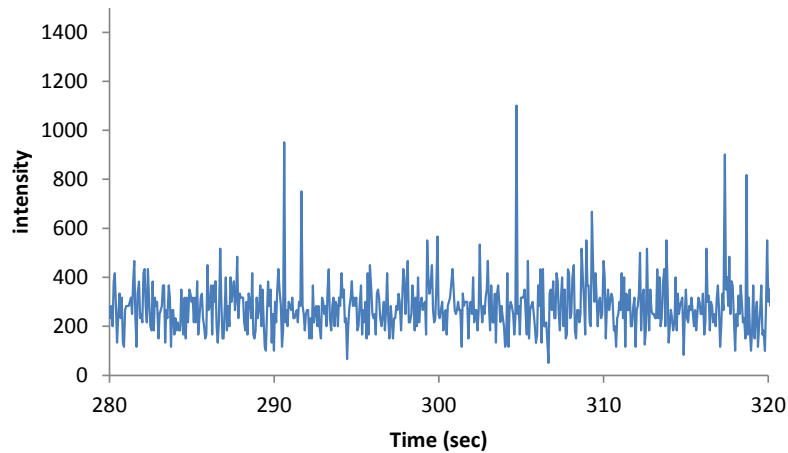
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- Calibration curve



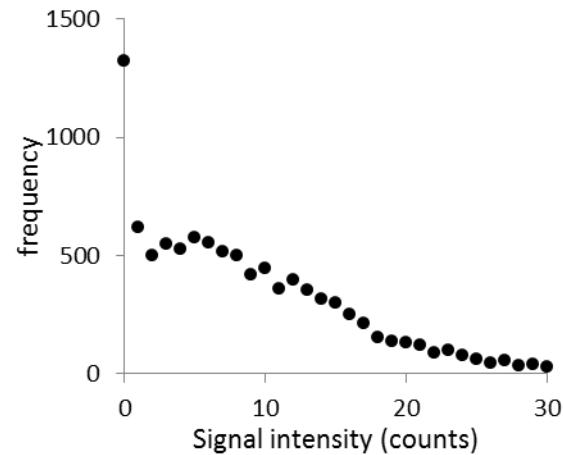
Basic data interpretation steps

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- Calculate histograms from raw data

Particle signal



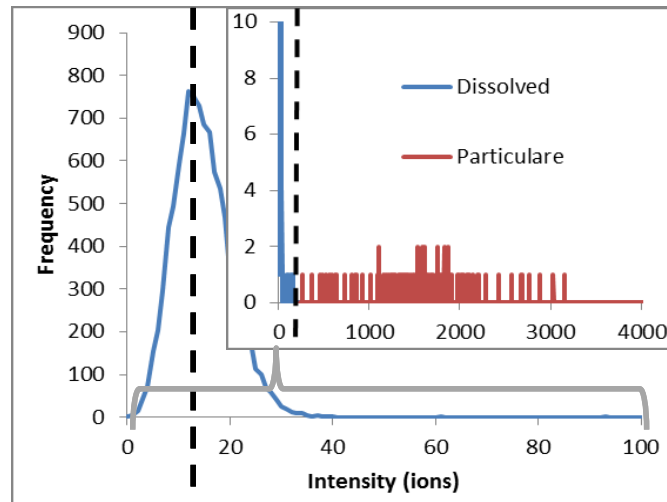
Particle signal histogram



Basic data interpretation steps

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- Determine dissolved/particulate level and remove dissolved data

e.g. 60 nm Au NPs:



Average dissolved intensity

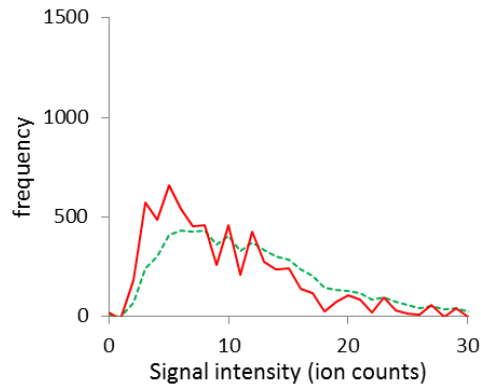


Basic data interpretation steps

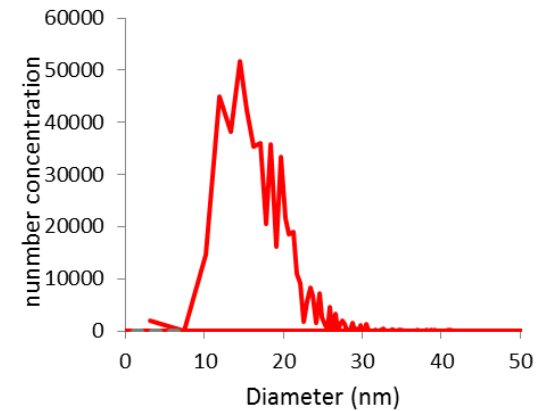
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Basic data interpretation steps

Particle signal histogram



Particle size distribution calculation



$$N_i = \frac{f(P_i)}{\eta_n q D t_d}$$



$$d = \sqrt[3]{\frac{(I - I_d - I_{bkg}) 6 \rho q \eta_e M_w}{\pi m t_d}}$$

