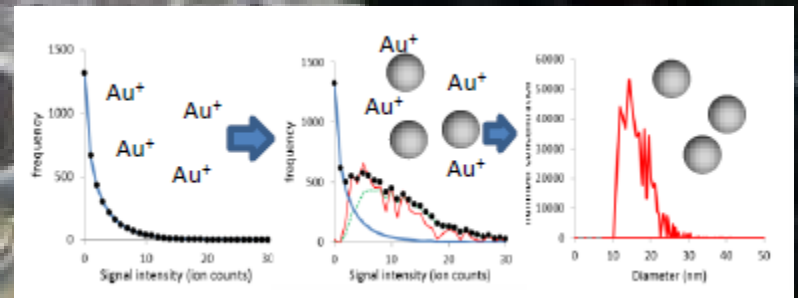


Current challenges in spICP-MS analysis of engineered nanoparticles in environmental samples

Geert Cornelis

ICEENN 2016, Golden, Colorado

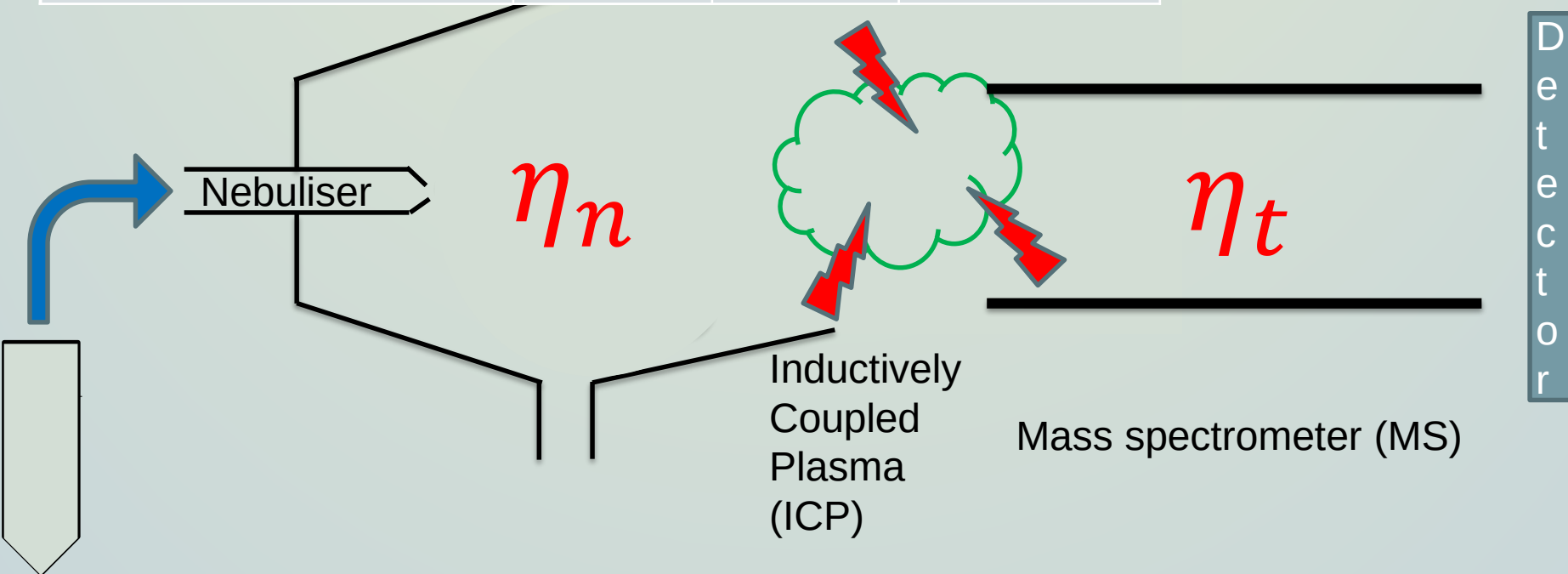
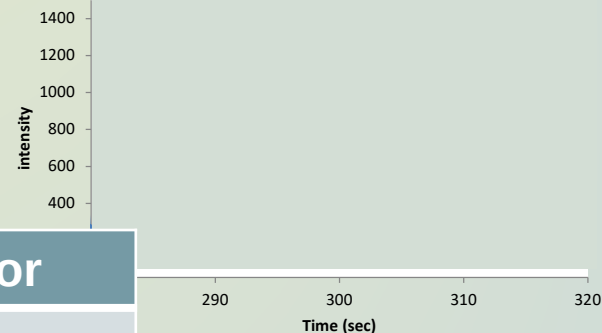


Overview

- Basics
- Signal discrimination techniques
 - Cut-off
 - Outlier analysis
 - K-means
 - **Deconvolution**
- FAST spICP-MS

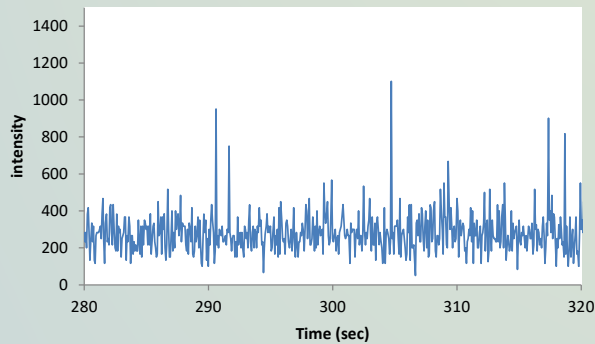
Basics

Parameter	Solution	Plasma	Detector
Particle number	n_p	$\eta_n \times n_p$	$\eta_n \times n_p$
Ions per particle (event)	d	d	$\eta_t \times d$
Dissolved ion number	c	$\eta_n \times c$	$\eta_n \times \eta_t \times c$

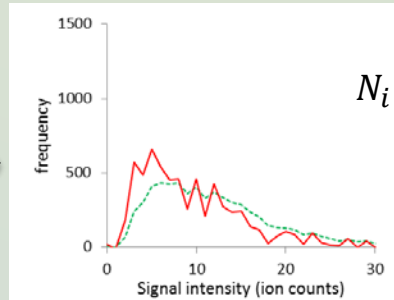


Basics

Particle signal

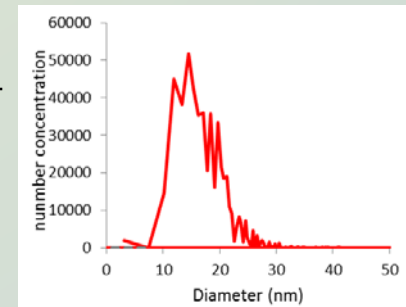


Particle signal histogram



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

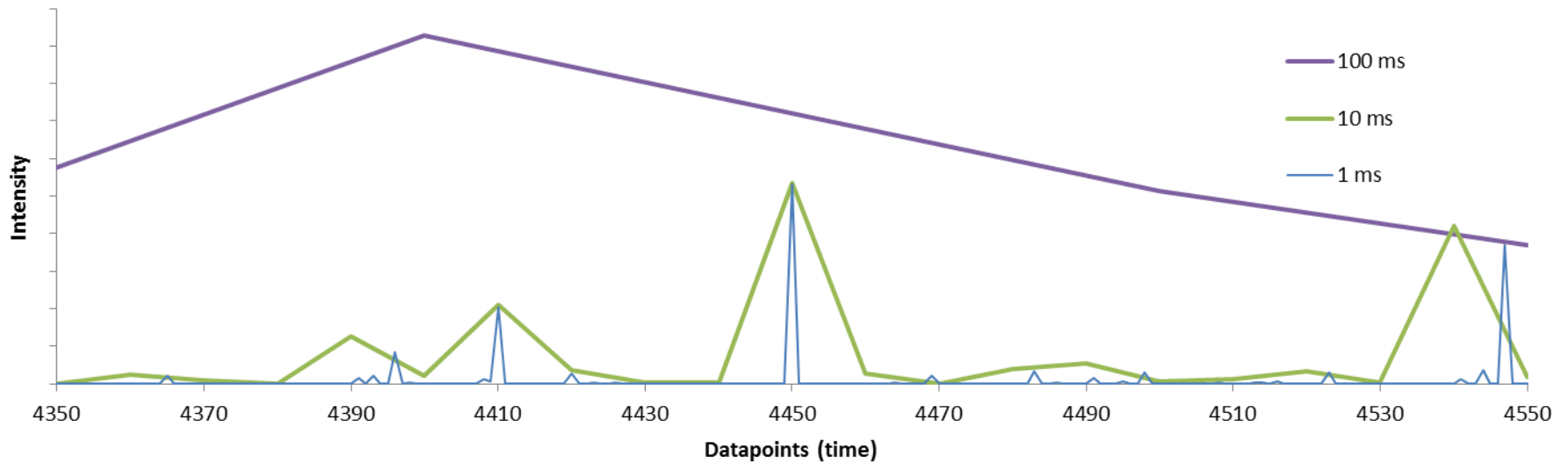
Particle size distribution calculation



$$d_i = \sqrt[3]{\frac{6[(P_i - I_d)\eta_i - I_{bkg}]t_d q_{liq} \eta_n}{m_{fa} \pi \rho}}$$

$$m = \eta_t \times \eta_t$$

Effect of dwell time

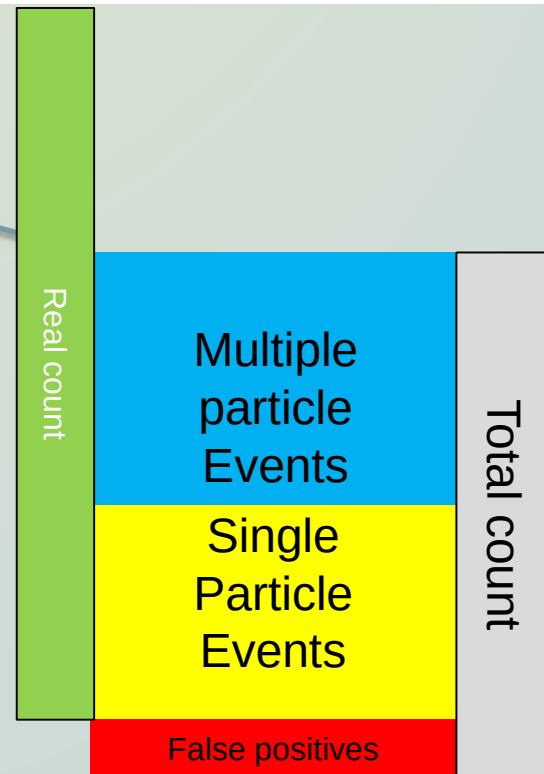
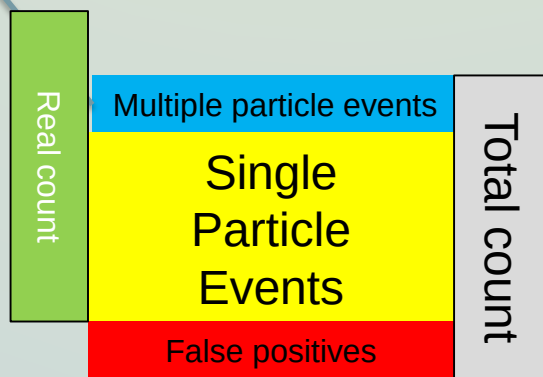
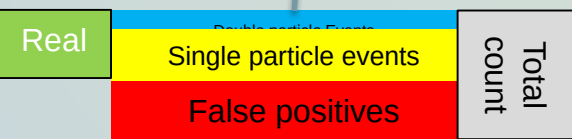
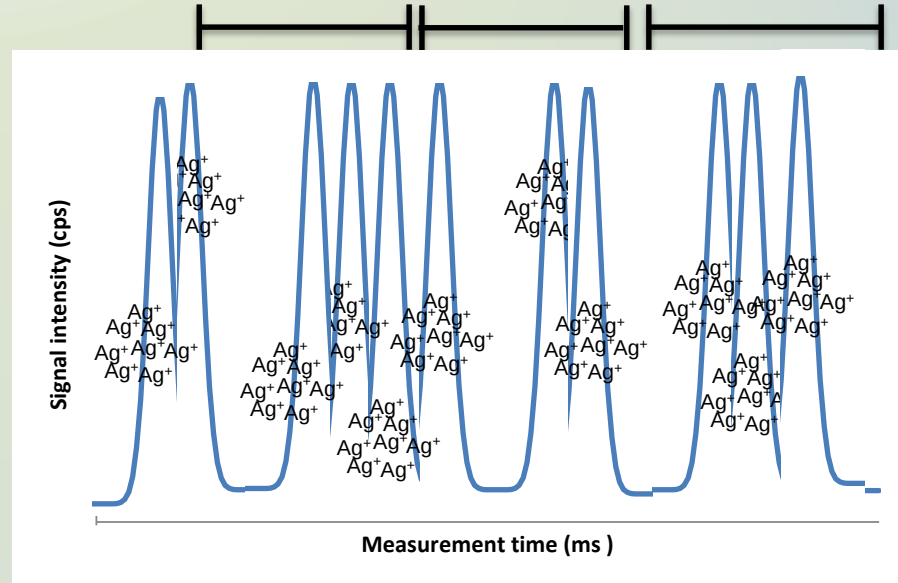
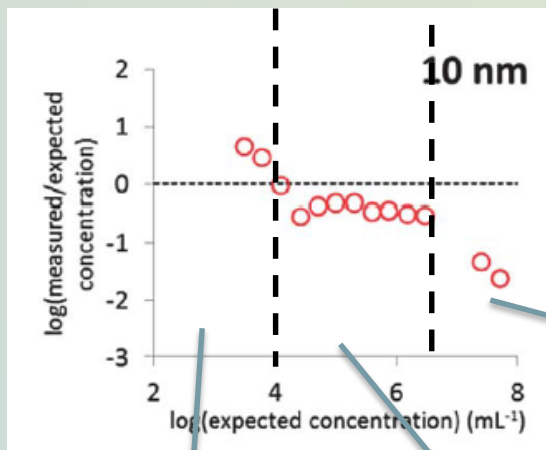


spICP-MS is ICP-MS with short dwell times and some math

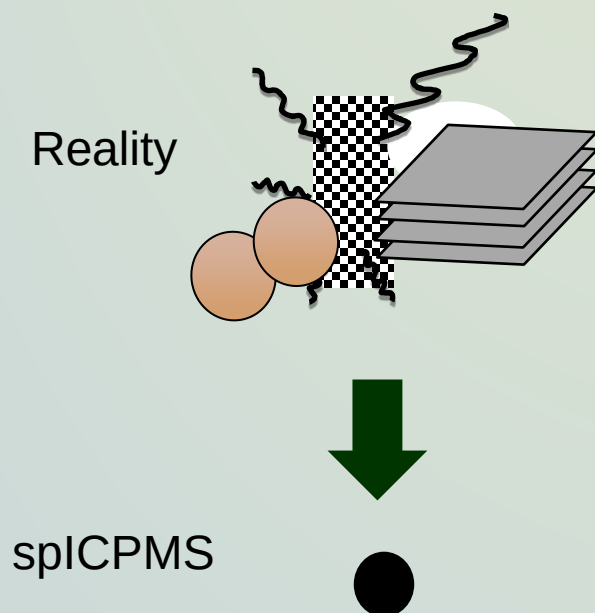
The promise

- Uses existing ICP-MS equipment
- Minimal sample preparation or perturbation
- Fast
- Is element-specific
- Sensitive: **environmentally relevant concentrations**
- Counts particles → **particle number concentrations**
 - Smoluchowski's law: $v_{\text{aggregation}} = k \times n_p^2$
 - Bio-uptake $\sim n_p$
 - European definition based on n_p

Linear range



Size from mass



Single element spICP-MS gives the corresponding spherical diameter

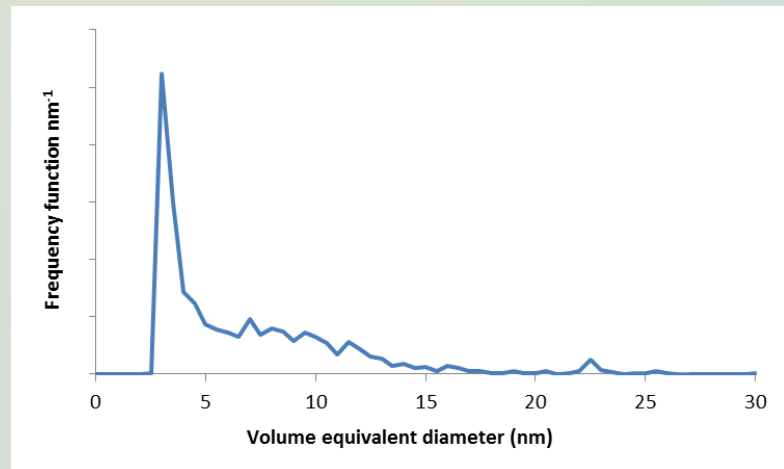
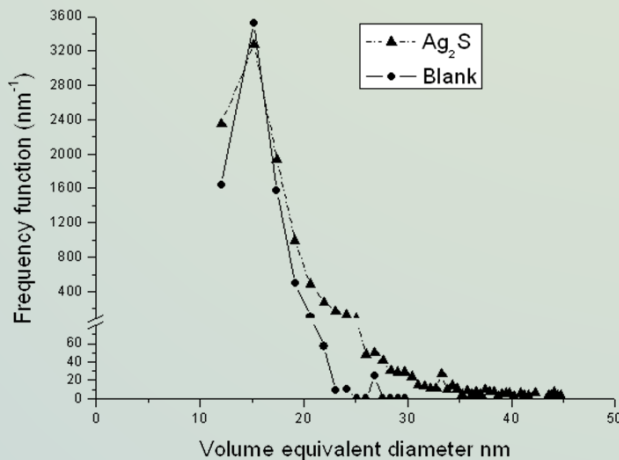
- No shape
- No other particles
- No organics

Solutions:

- FFF - spICP-MS
- TOF-spICPMS

Size detection limits

Minimum size limit:



Analysis of AgNP in a pilot wastewater treatment plant (Fraunhofer Institute): Left: conventional spICP-MS analysis of a WWTP sample ("Ag₂S") compared with a blank sample ("Blank"). SEM analysis of the same sample.

Size detection limits

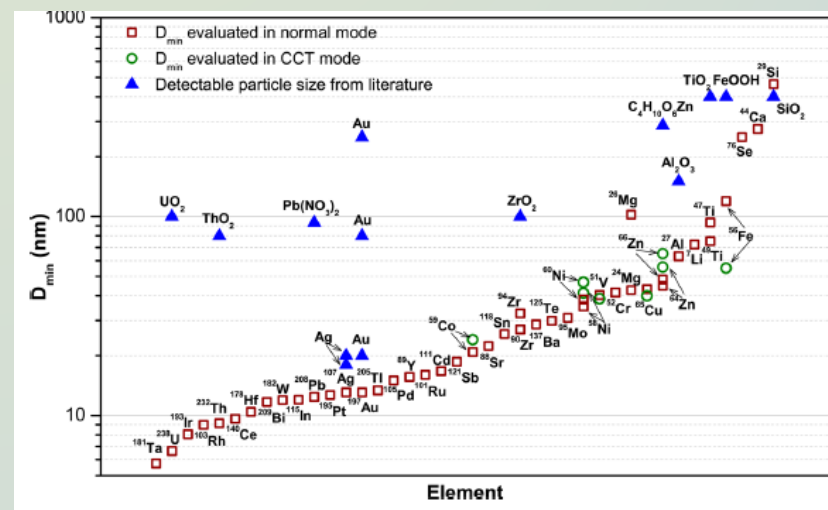
”The size calculated from signals higher than 3 x the standard deviation of the background signal”

Limit depends on:

- Sensitivity
 - Ionisation potential
 - Isotopic composition
- Nanoparticle composition
e.g. Ag vs. TiO_2
- Transport efficiency
- **Dissolved level**
- **Background counts**
- **Carry-over**
- **Interferences**

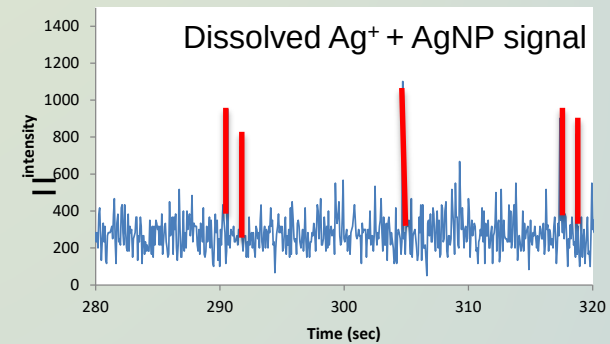
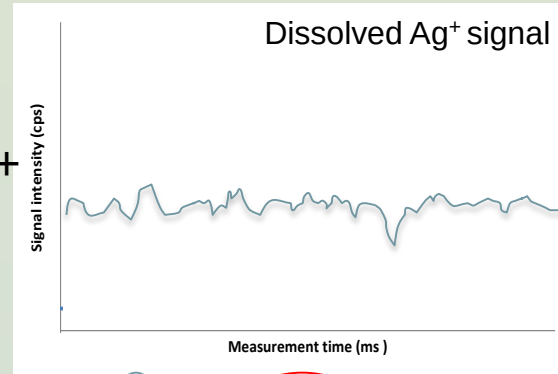
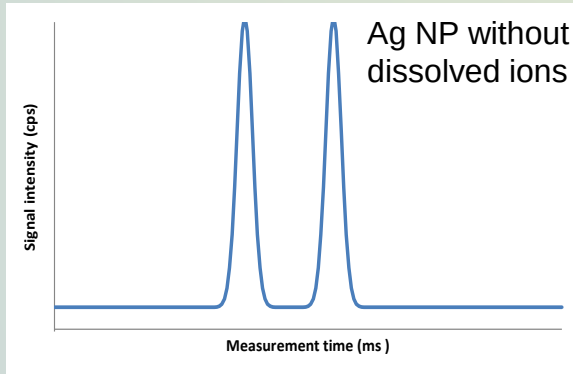
Determine
theoretical
 LOD_{size}

Determine
practical
 LOD_{size}

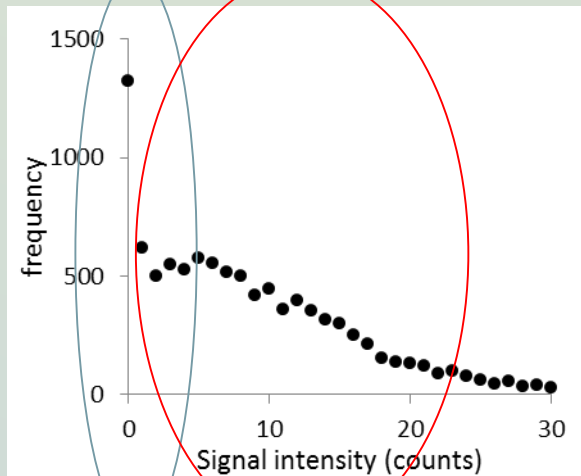


Lee, S.; Bi, X.; Reed, R. B.; Ranville, J. F.; Herckes, P.; Westerhoff, P., Nanoparticle Size Detection Limits by Single Particle ICP-MS for 40 Elements. *Environmental Science & Technology* **2014**, 48 (17), 10291-10300.

Signal overlap



Histogram:

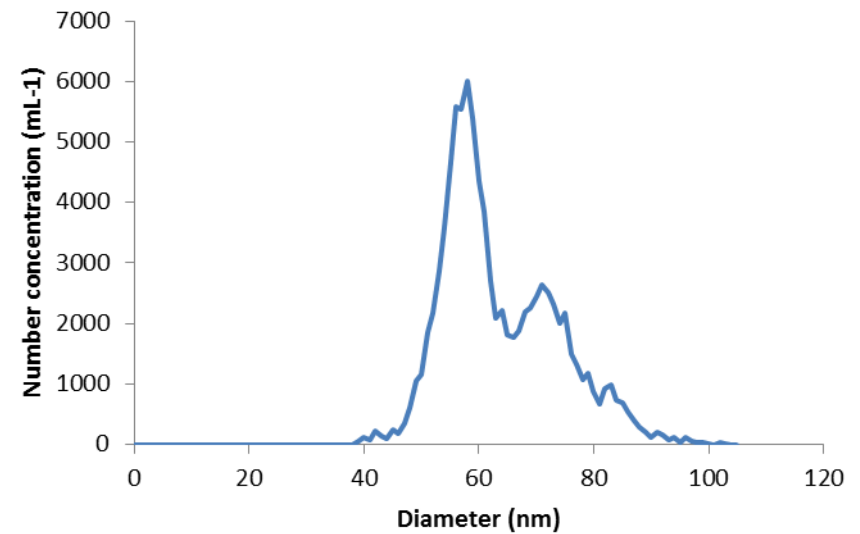
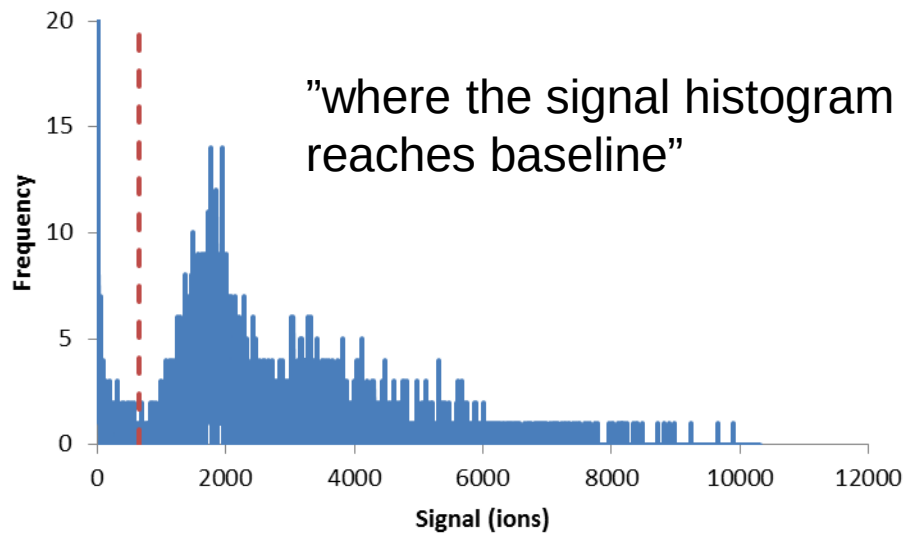
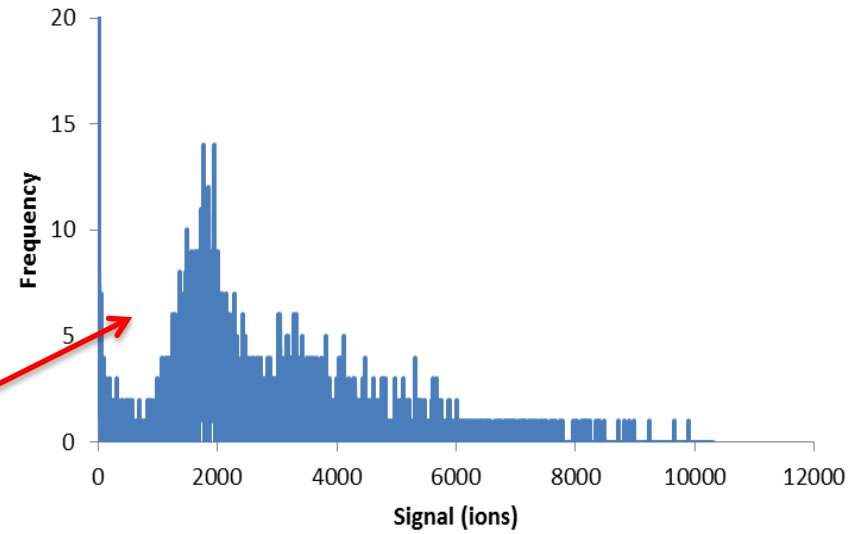
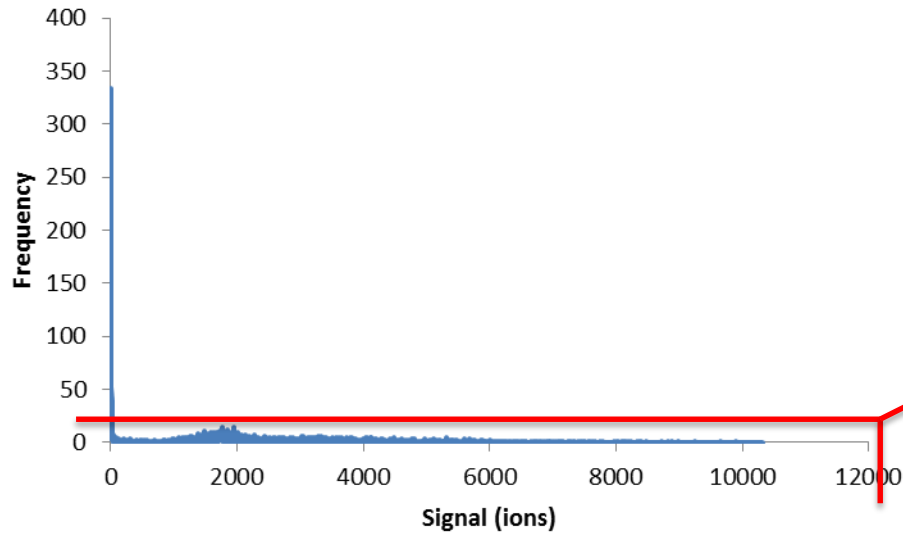


Dissolved
signals

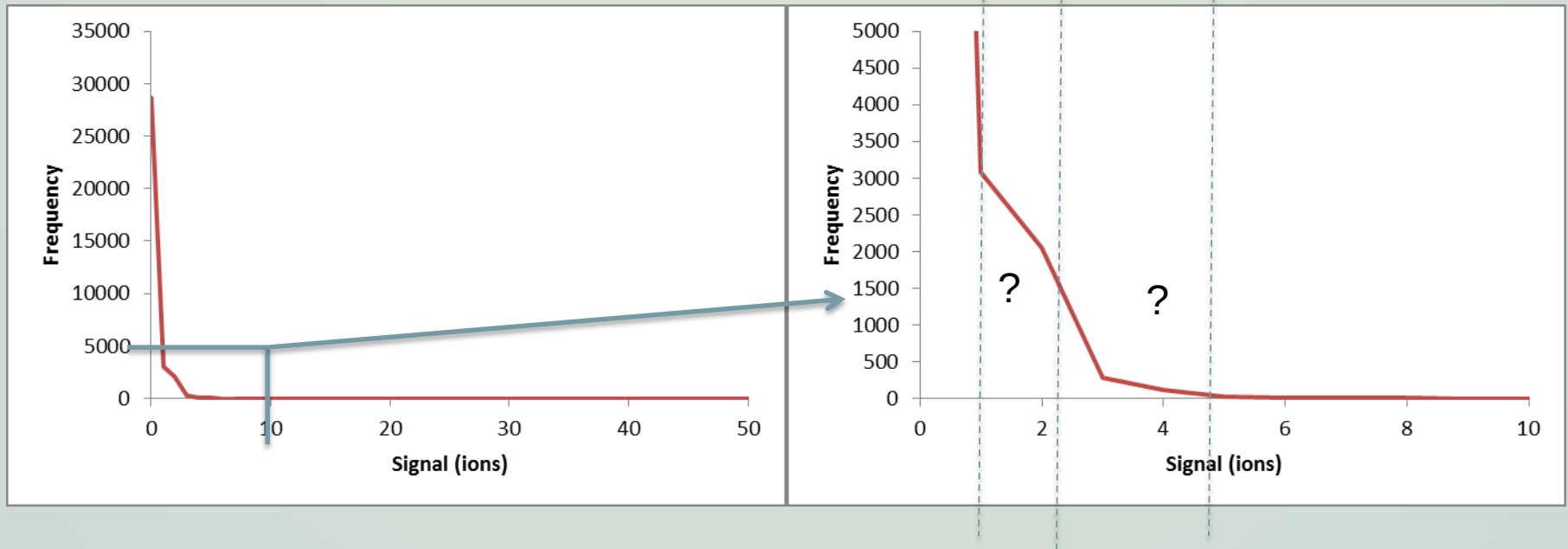
Particle signals



Cut-off

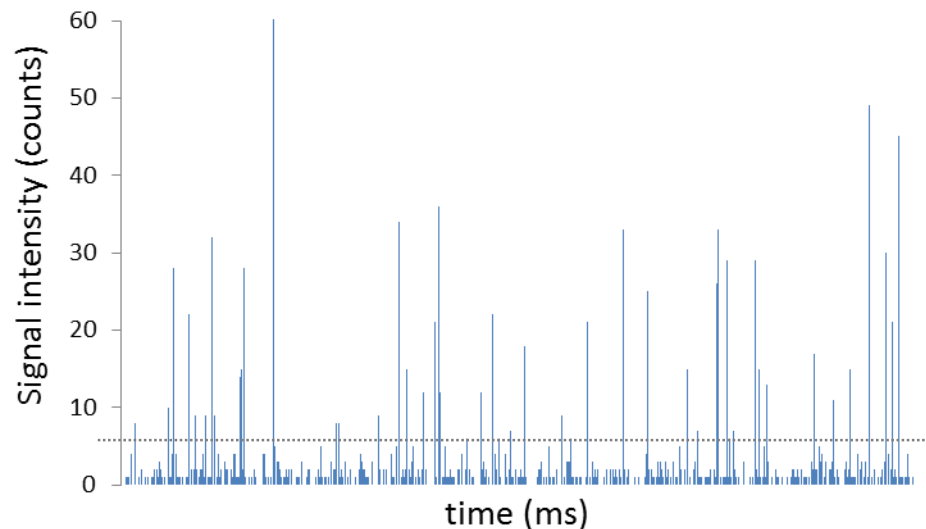


Cut-off

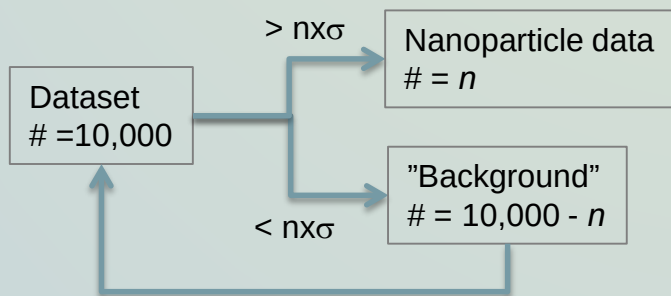


Problematic for overlapping signals

Outlier analysis



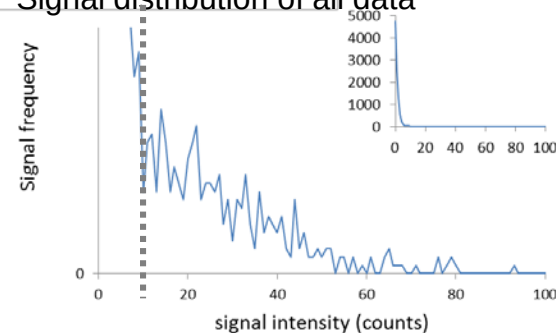
Outlier method



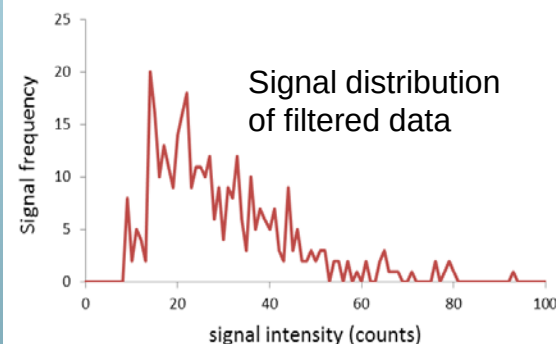
Tuoriniemi et al. 2012. Anal. Chem. 29. 743-752.

30 nm Au NP (NIST)

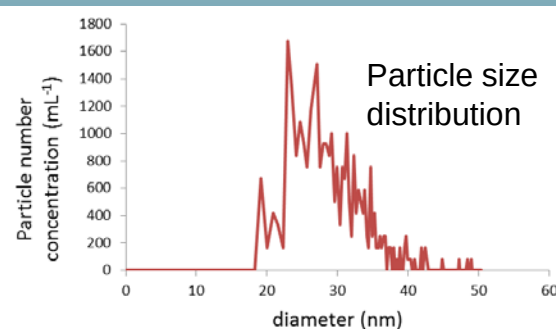
Signal distribution of all data



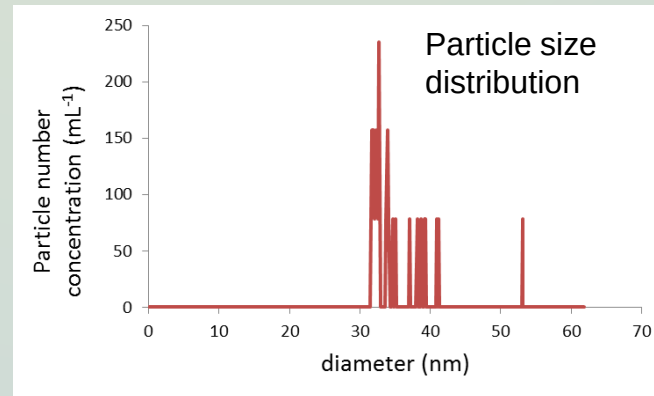
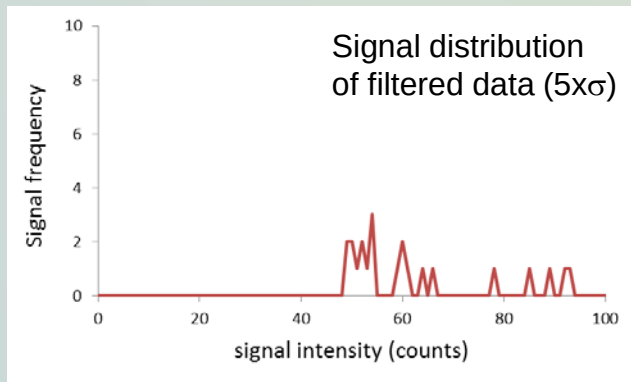
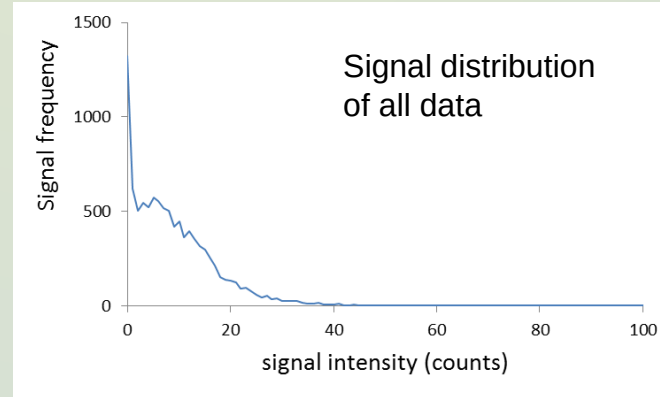
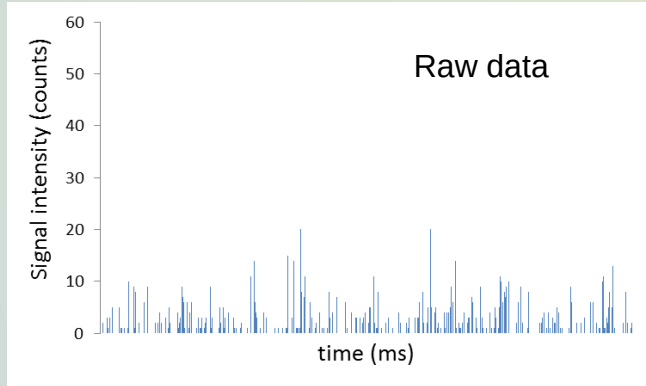
Signal distribution of filtered data



Particle size distribution

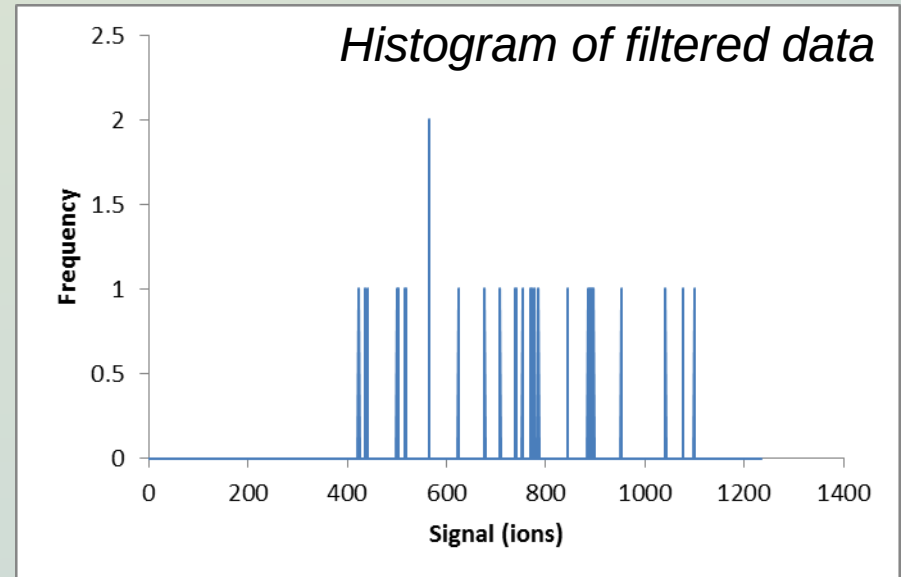
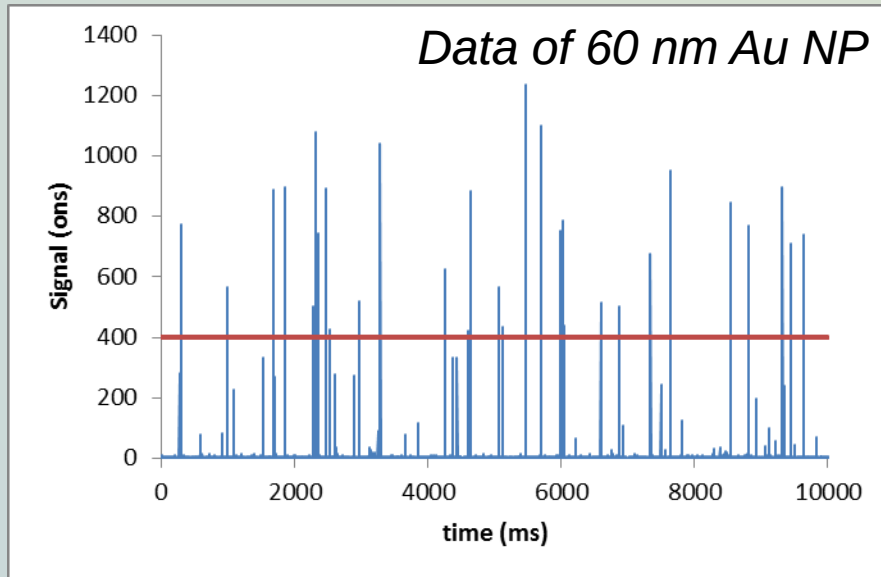


Outlier analysis

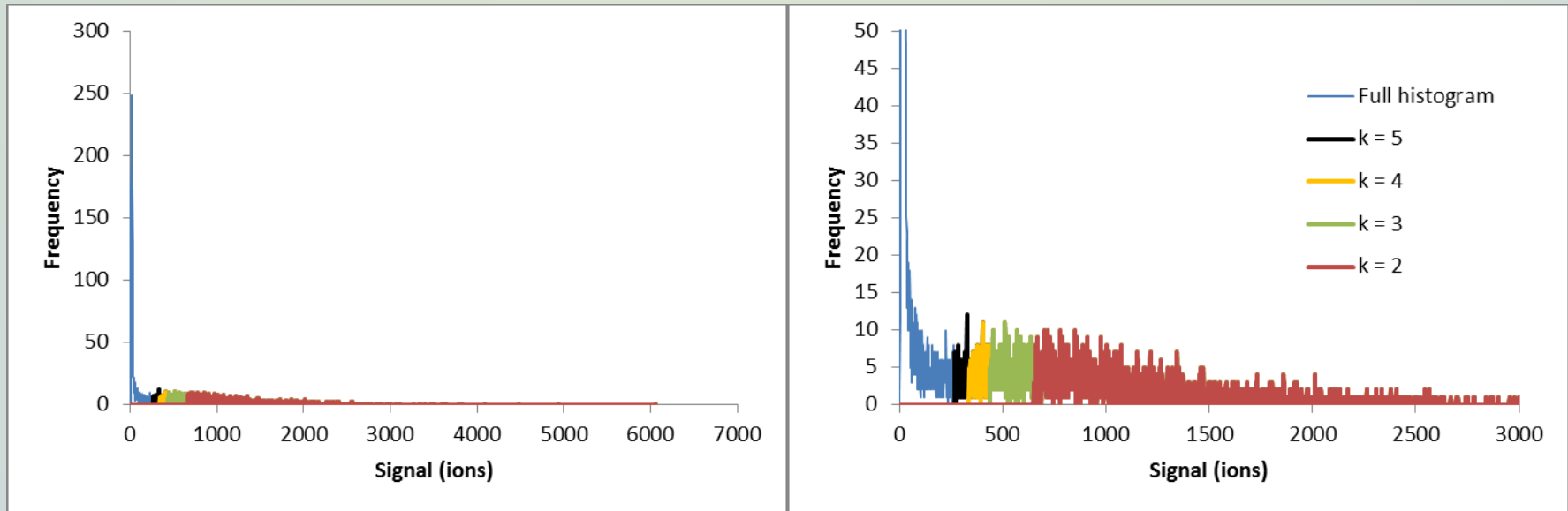


K-means

"Divides data into k clusters, based on minimal squared distance between data and their group centers"

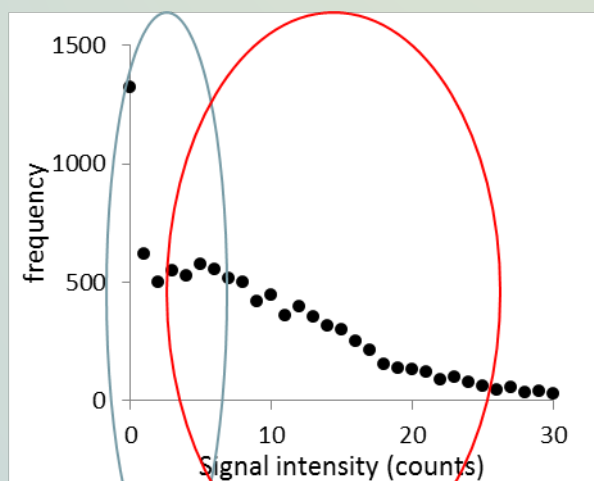


K-means



Polydisperse distributions: big effect of choice of k

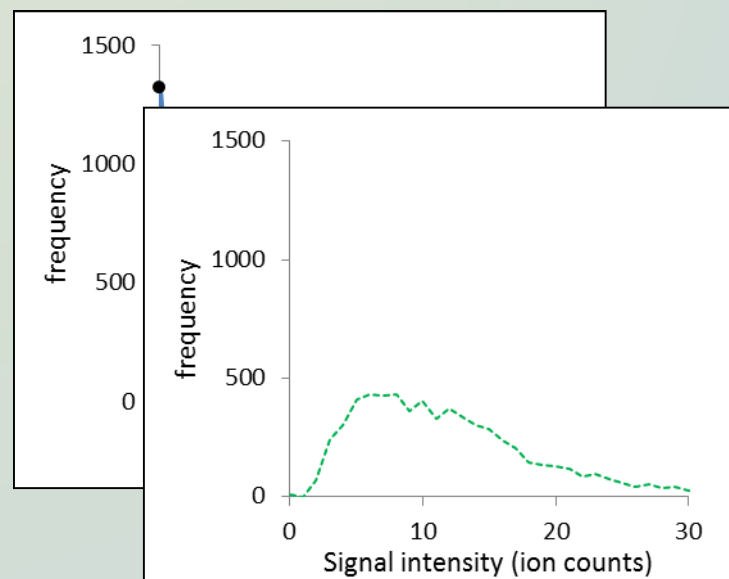
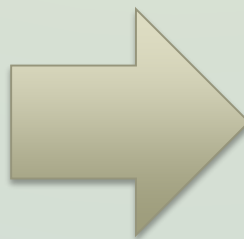
Deconvolution



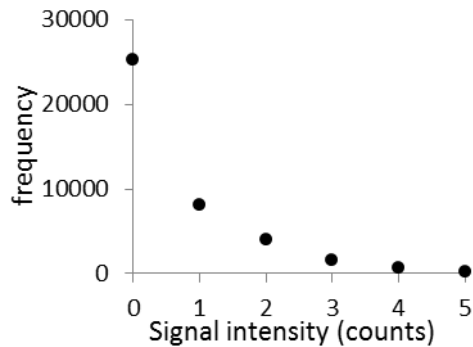
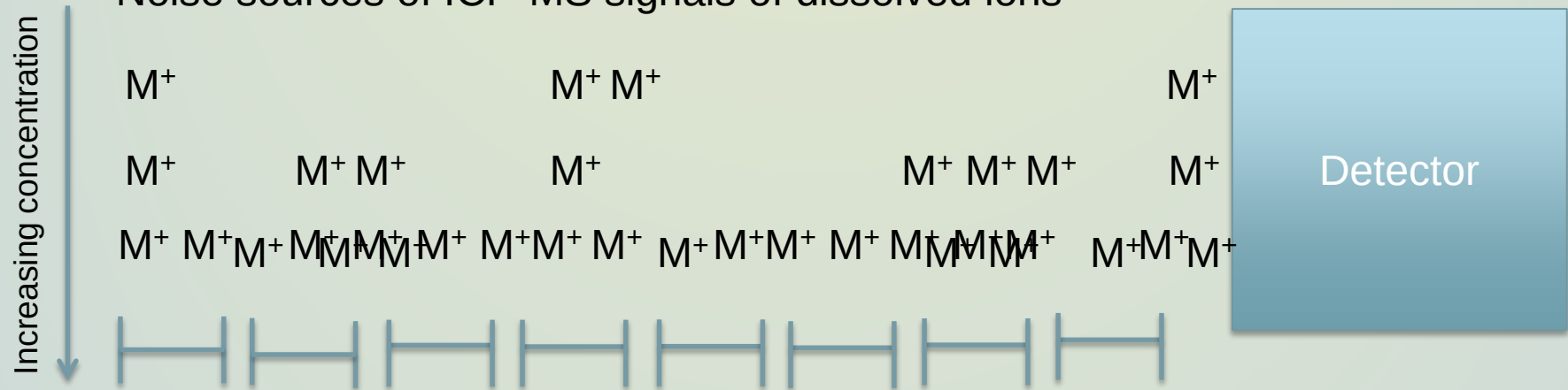
Dissolved
signals

Particle signals

Perfect knowledge
of dissolved signal

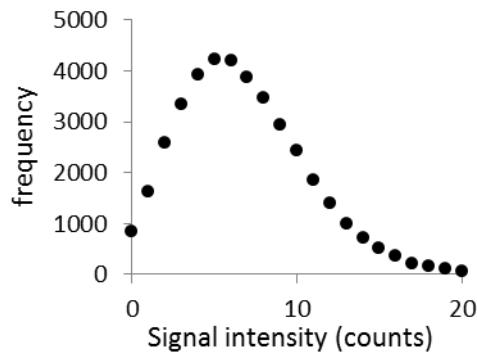


Noise sources of ICP-MS signals of dissolved ions



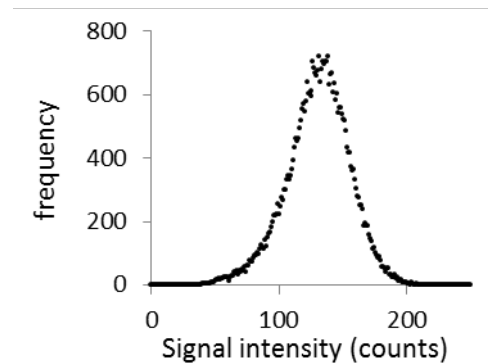
Random arrival of ions
(Shot noise)

Poisson or Polya



Mixed

Polya - gaussian



Plasma flicker

Gaussian

Pmf of dissolved signals: "Compound polya – gaussian"

All signals I have a shot noise and a flicker noise component: $I = S + F$

Shot noise: $S \sim \text{Polya}(\lambda, b)$

Flicker noise: $F \sim \text{Gaussian}(0, \sigma)$

$$I = S + F$$

→ averages: $\lambda_t = \lambda_S + \lambda_F$

→ Standard deviations: $\sigma_t^2 = \sigma_S^2 + \sigma_f^2$

→ Probability distribution:

Convolution of individual distributions

$I \sim [\text{Polya} * \text{Gaussian}]$ with parameters $(\lambda, \mathbf{b}, \sigma)$

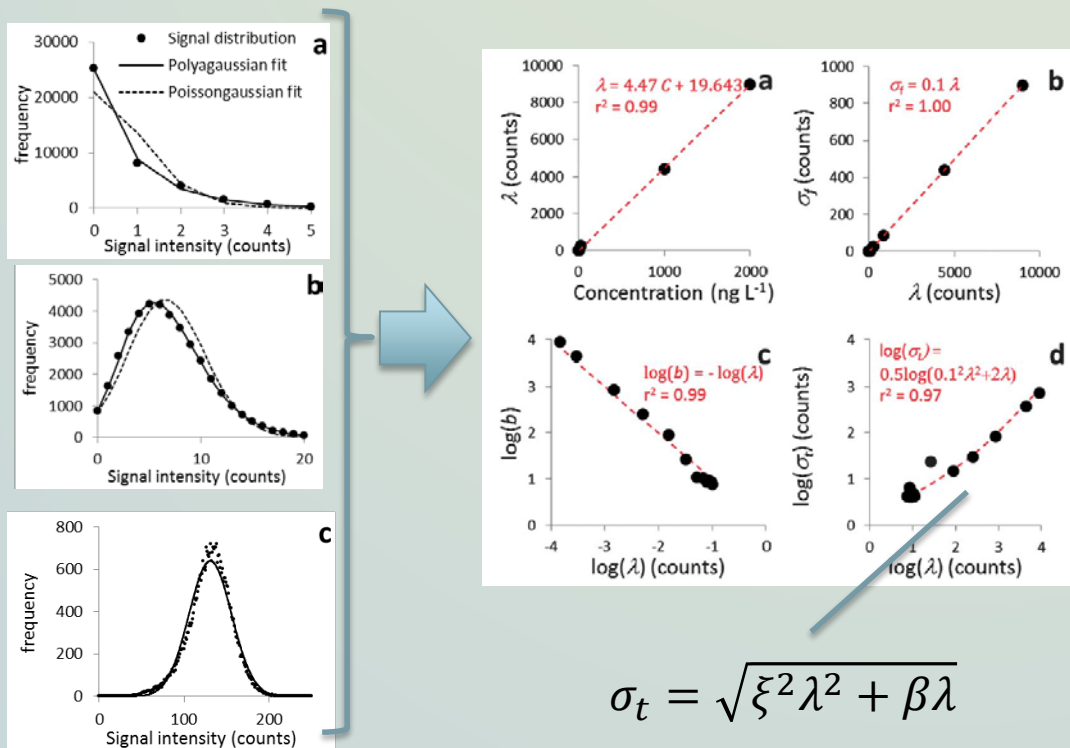
$I \sim \text{Polyagaussian (PG)}$

Fitting noise pmfs

- pmf: probability of measuring a certain signal
 - $\text{sum}(\text{pmf}) = 1$
- histogram: number of times a certain signal was measured
 - $\text{sum}(\text{histogram}) = D$ (e.g. $D = 10,000$)
- Estimating pmf from histogram
 - $\text{pmf} \sim \text{histogram}/D$
 - Fitting pmf models to histogram/ D

Calibration of dissolved model

Relations between parameters for different dissolved standards lead to **sensitivity**, **blank level**, **flicker factor** and **shot factor**



$$\sigma_t = \sqrt{\xi^2 \lambda^2 + \beta \lambda}$$

average (λ) = sensitivity (m) * C + blank level (I_b)

$\sigma_{\text{flicker}} = \text{flicker factor } (\xi) * \lambda$

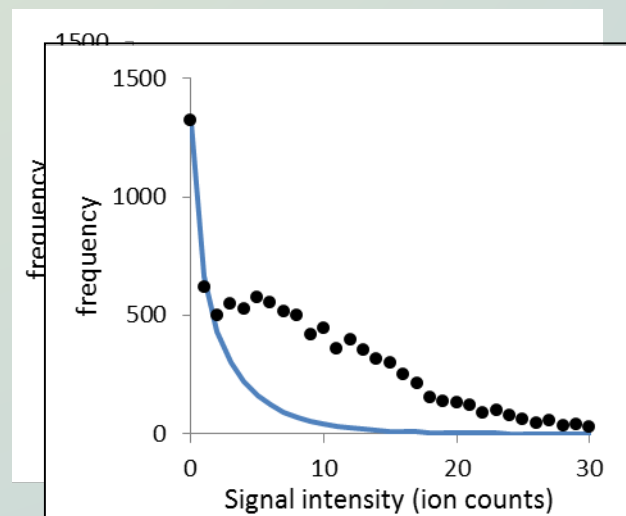
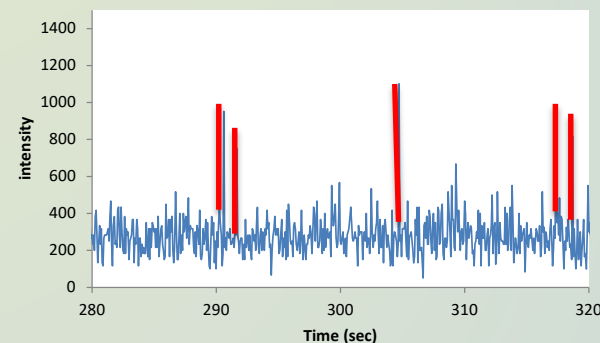
$$\text{shape}(b) = \frac{\text{shot factor}(\beta) - 1}{\lambda}$$



$$\lambda \xrightarrow{m, I_b, \xi, \beta} \left\{ \begin{array}{l} \text{PG}(\lambda, \sigma, b) \\ C \end{array} \right.$$

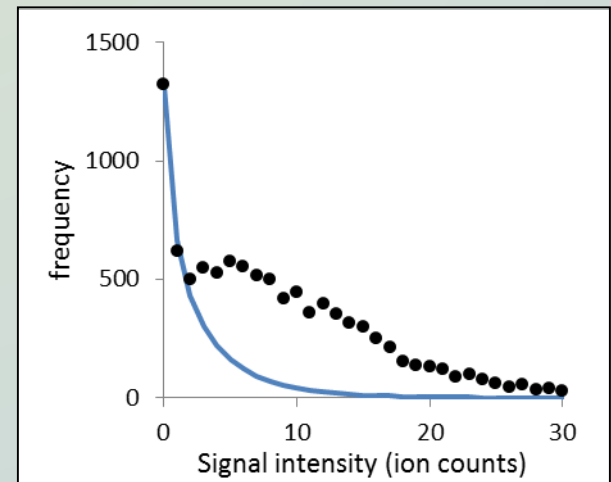
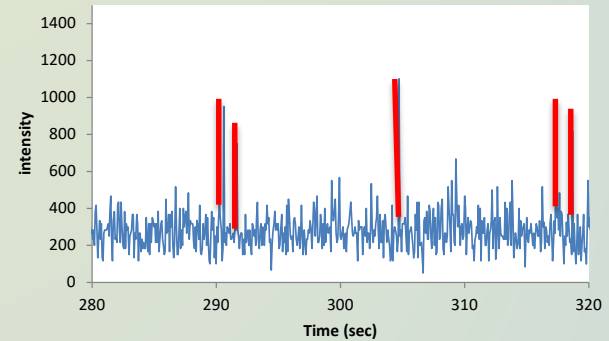
Combined signals

- D data points (e.g. $D = 10,000$)
- For D_p datapoints $I = I_d + P = S + F + P$
- For D_d datapoints, $P = 0$
- Dissolved datapoints on average less intense than particle-containing datapoints
- $D = D_d + D_p$
- $\text{Sum}(\text{total histogram}) = D$
- $\text{Sum}(\text{dissolved histogram}) = D_d$



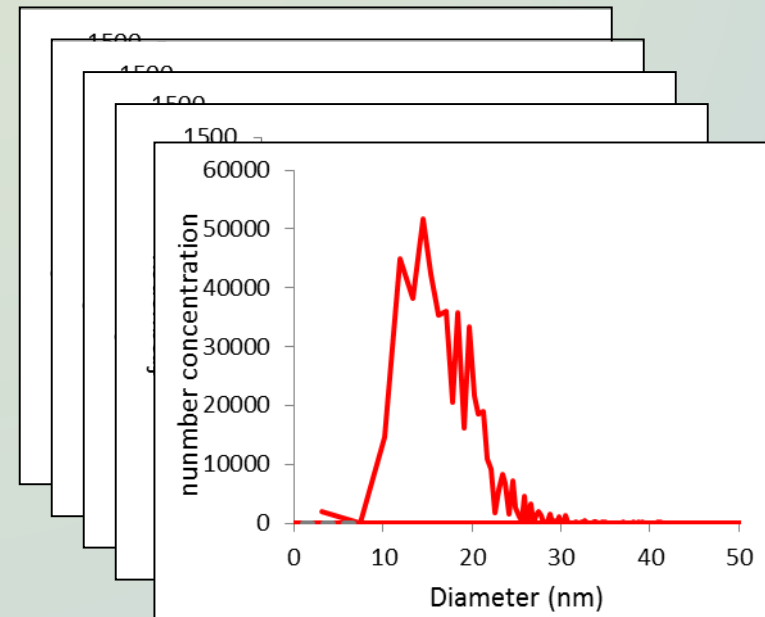
Combined signals

- Not known: D_d , polyagaussian of dissolved part
- Known:
 - $\lambda \sim PG(\lambda, \sigma, b)$
 - Dissolved histogram $\sim D_d \times PG$
- Assuming:
 - Lowest signal intensities come from dissolved signals only
- Fitting $D_d \times PG$ to lowest signal intensities
 - Fitting two parameters: λ and D_d
 - Using $\lambda \sim PG(\lambda, \sigma, b)$ to calculate the PG



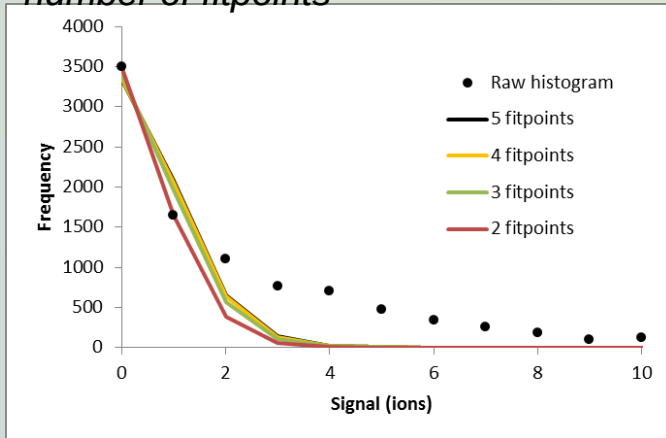
Deconvolution

- Fit polyagaussian x D_d to raw data
- Subtract fit
→ $D - D_d = D_p$ datapoints remain
- for each of these $I = S + F + P$
→ **still a dissolved component (S + F)**
- Deconvolute S + F out of I to get P (reverse of convolution)
- Calculate particle size distribution from P

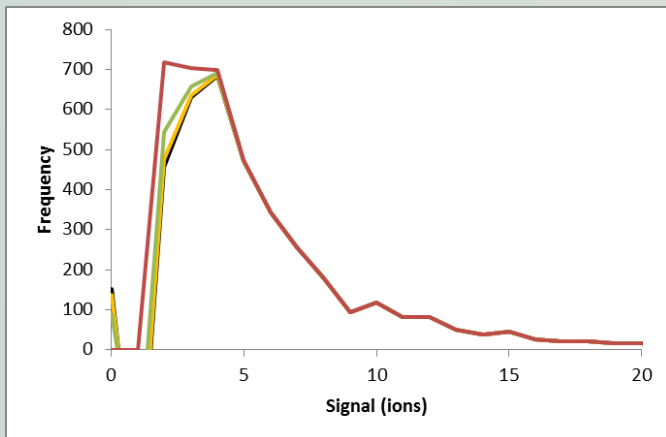


Fitpoints

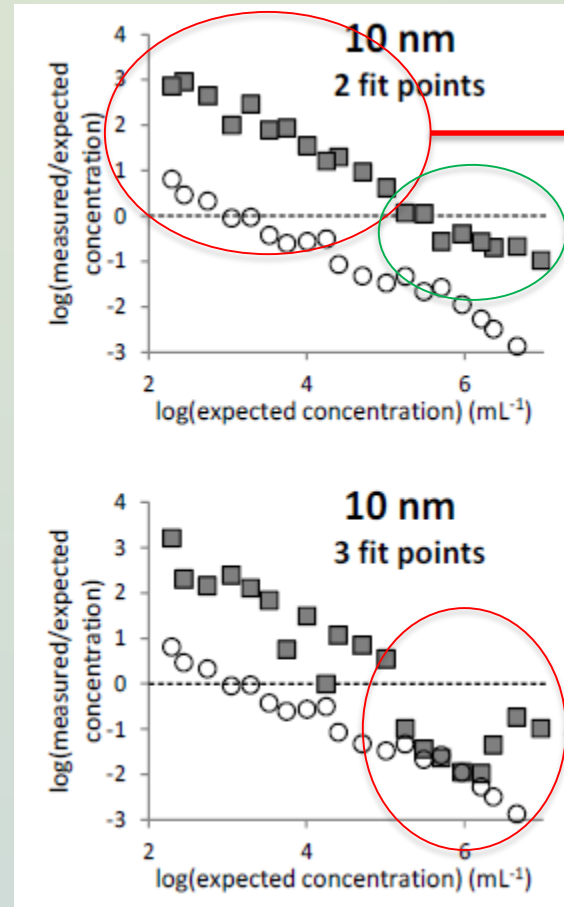
10 nm Au, dissolved fits with increasing number of fitpoints



Raw minus dissolved



Effect of # fitpoints on measured number concentration/expected concentration in a dilution series



too many false positives (too dilute)

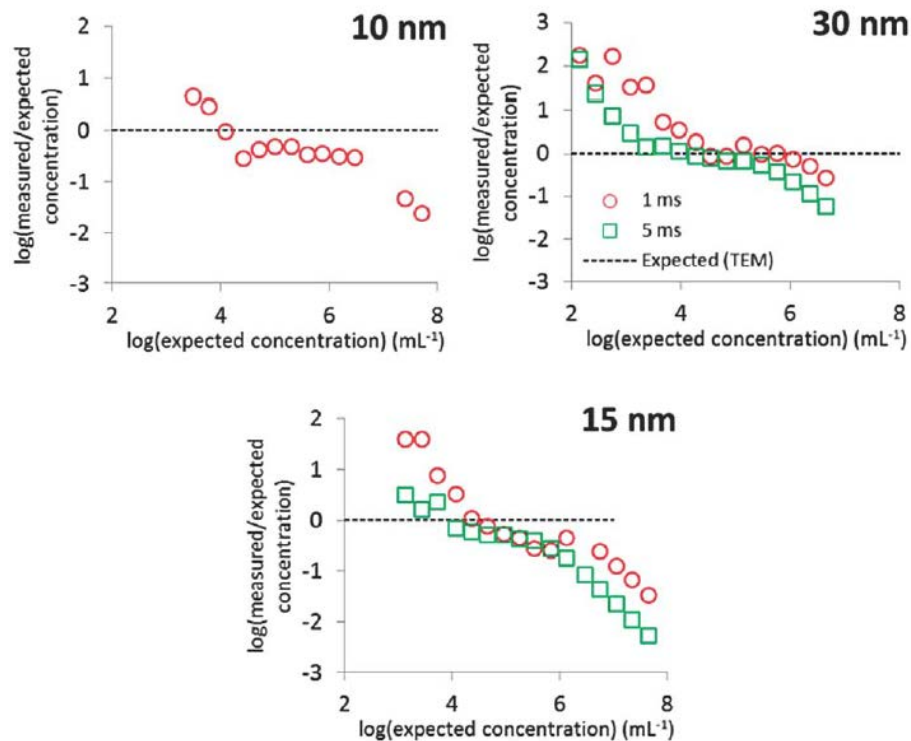
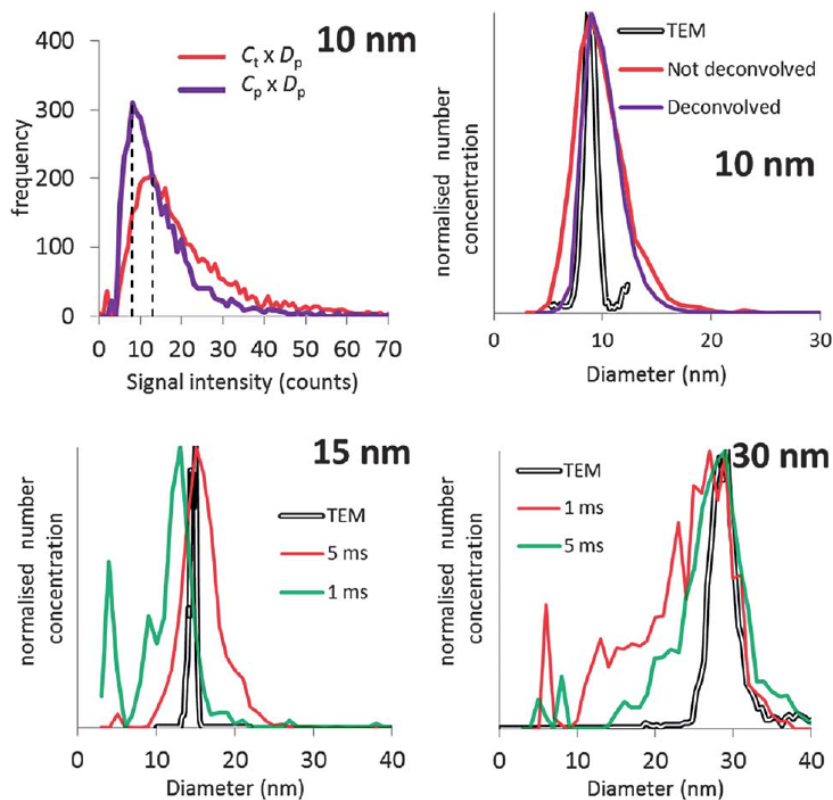
good recovery

too many false negatives (poor dissolved fit)

Performance

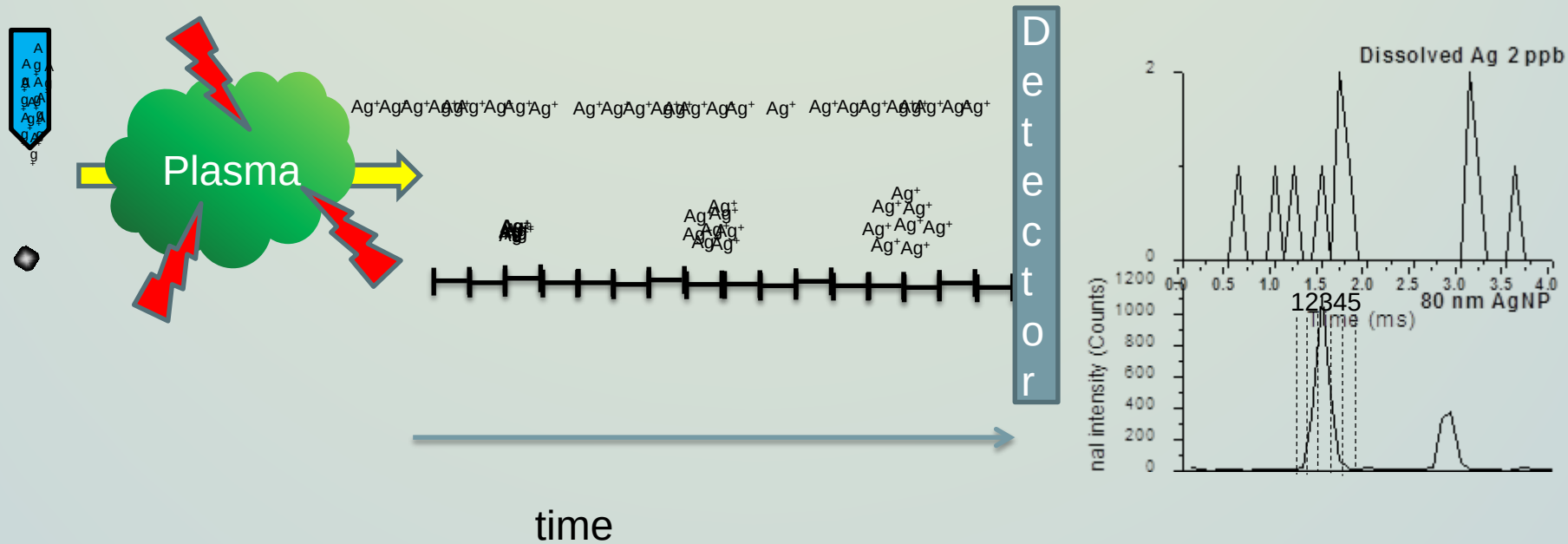
Size

Particle number concentration



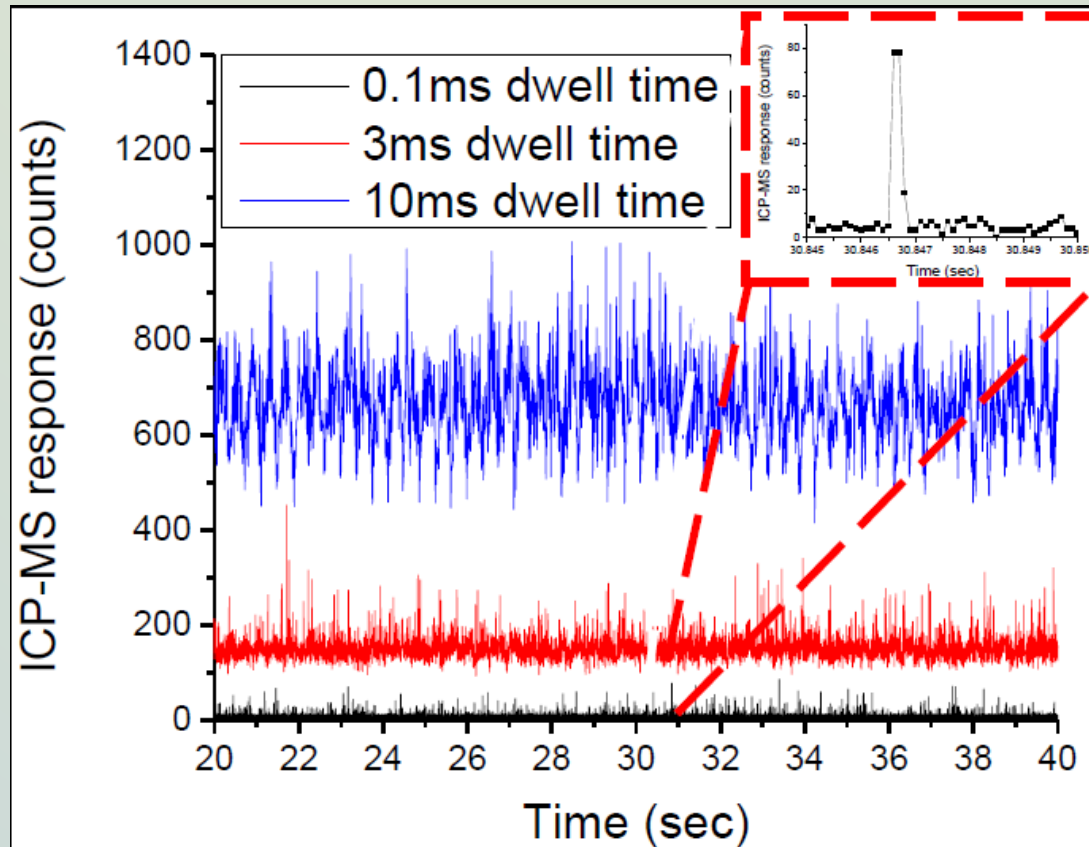
FAST – spICPMS

Dwell time $< t_{\text{nanoparticle event}}$



Effect of dwell time on dissolved signal

500 ppt Ag⁺ and 50 ppt AgNP



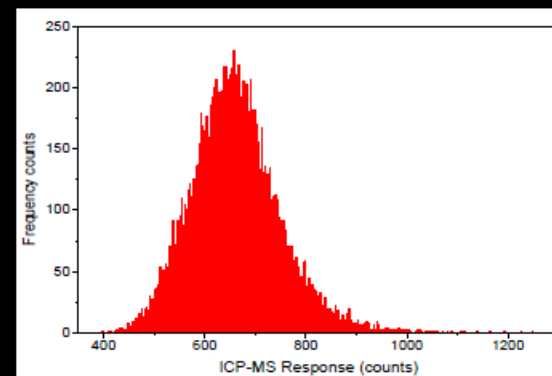
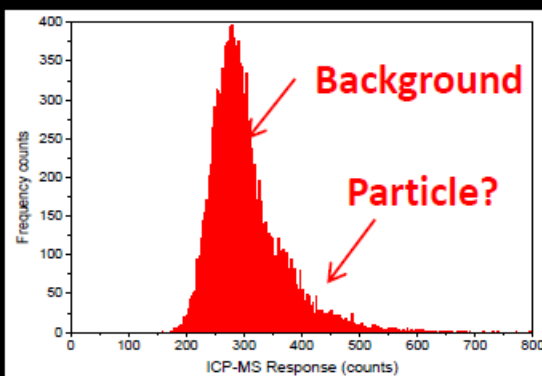
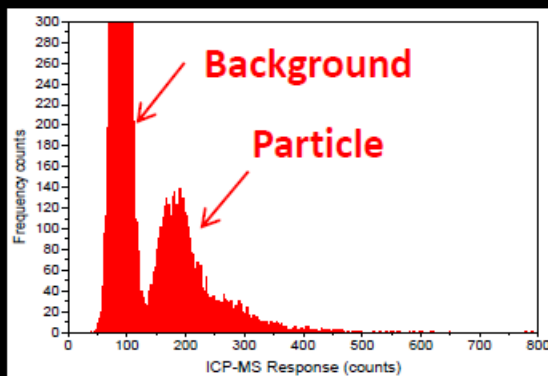
Effect on size detection limit

50ppt Ag⁺ / 50ppt Ag NP

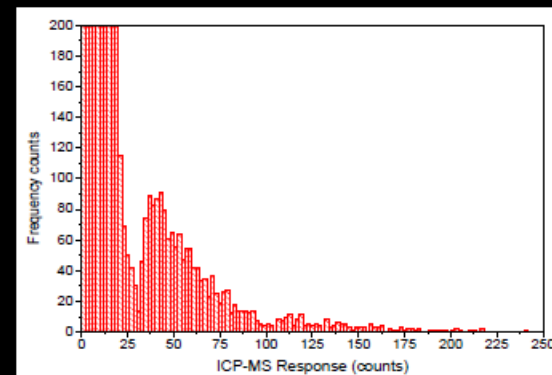
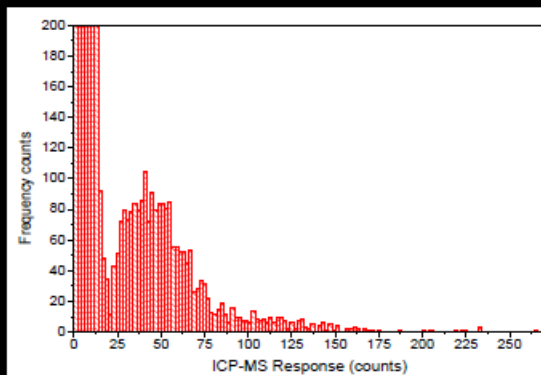
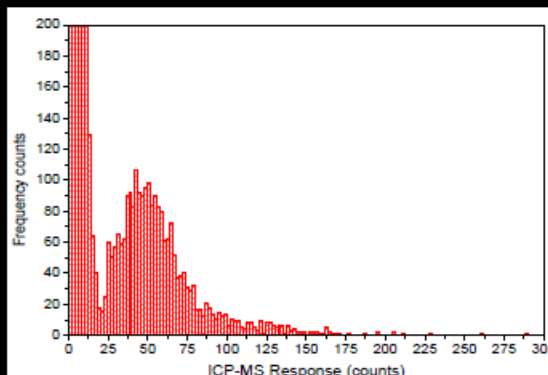
200ppt Ag⁺ / 50ppt Ag NP

500ppt Ag⁺ / 50ppt Ag NP

10ms



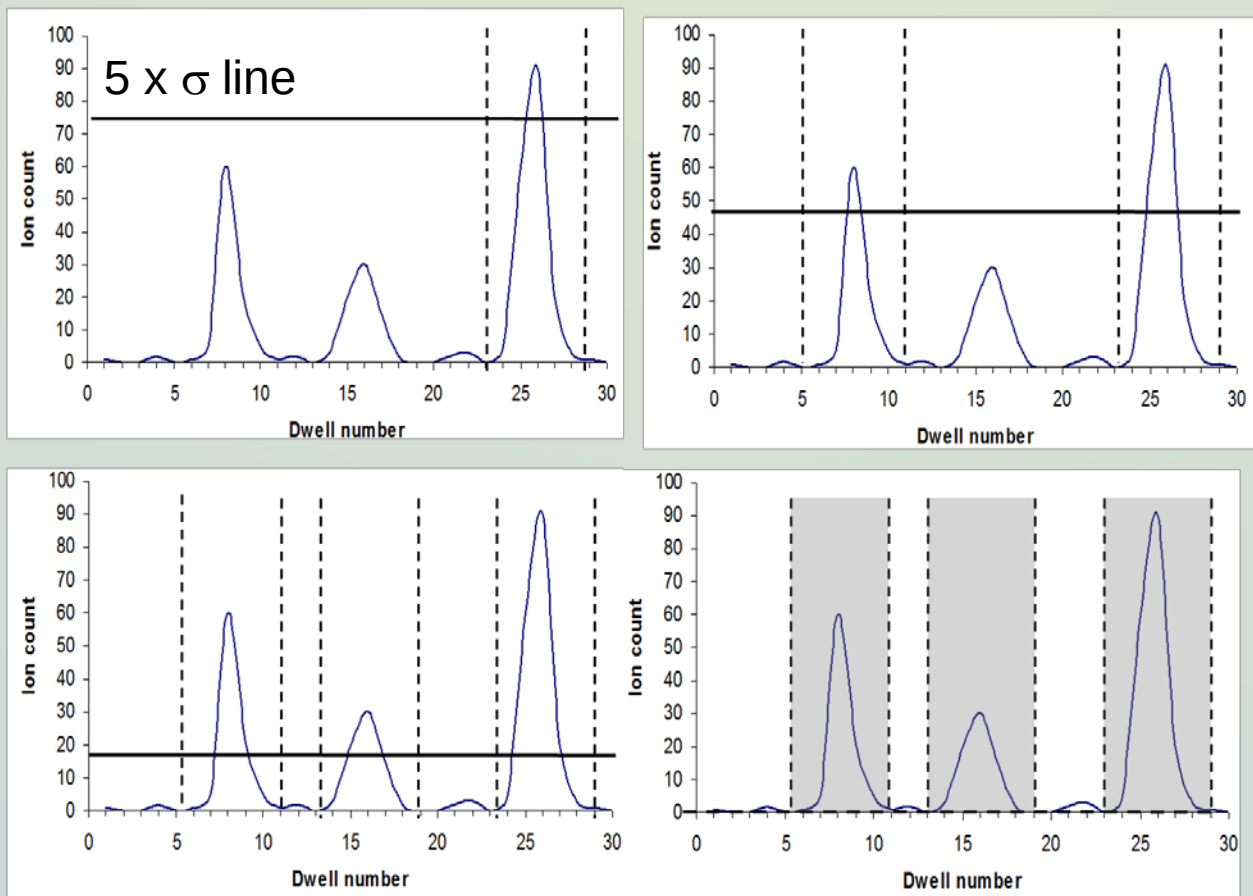
0.1 ms



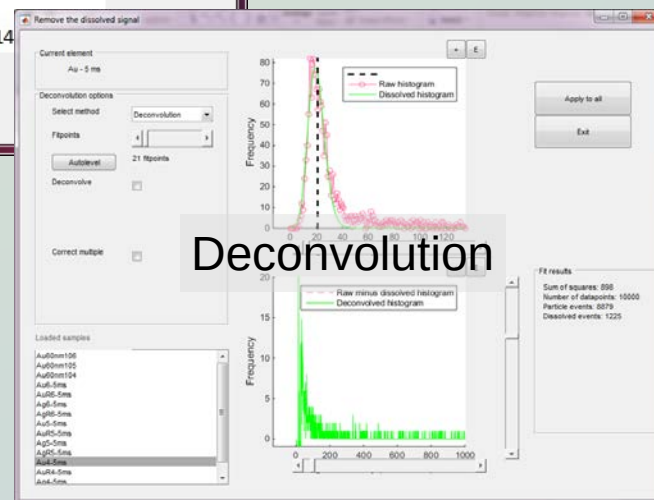
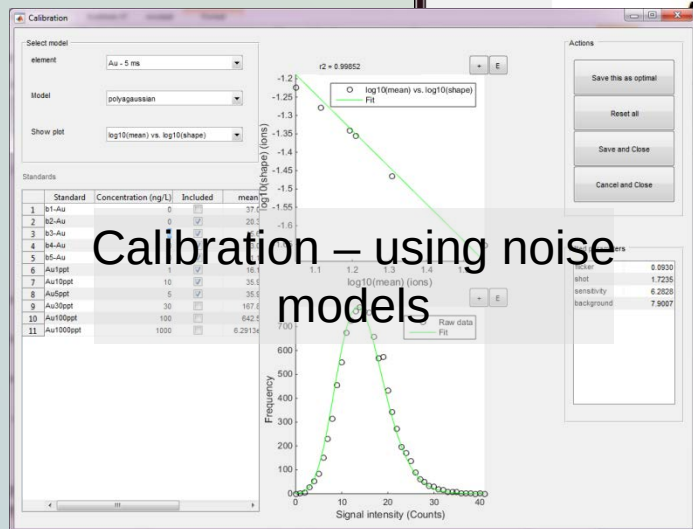
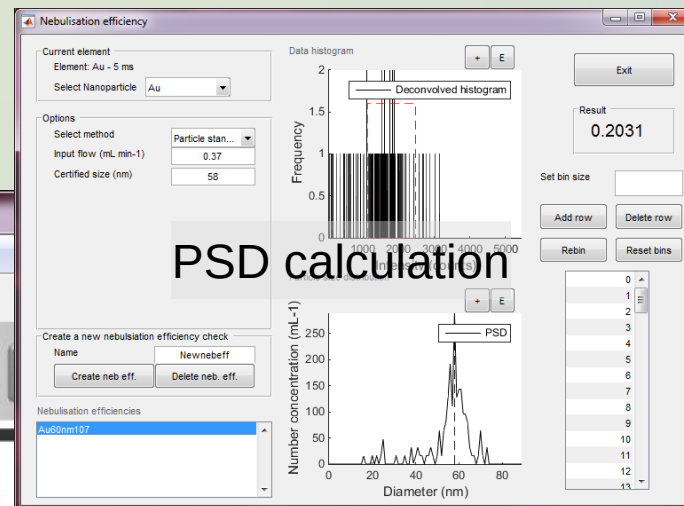
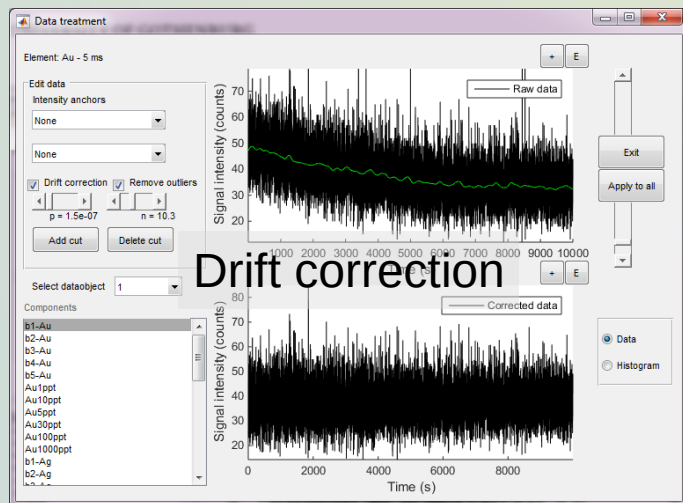
Conclusion

Technique	Advantages	Disadvantages
Cut-off	Simple, possible in spreadsheets	Impossible for overlapping signals
Outlier analysis	Simple	• Risk for false negatives for overlapping signals • Subjective setting of n
K-means	Discriminate different populations of particle peaks	• Impossible for overlapping signals • Difficult for polydisperse samples • Subjective setting of k
Deconvolution	Discriminate overlapping signals	• Not possible in spreadsheets • Subjective settings of number of fitpoints
FAST spICP-MS	Reduction in overlap	• Only ICP-MS with short dwell times • Big datasets

FAST spICP-MS: dissolved versus particulate?



Cornelis and Rauch, 2016. *Anal. Bioanal. Chem.* In press

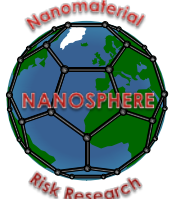


Free Nanocount download (including manual) after filling out survey at:

<https://www.surveymonkey.com/r/Y76JQMF>

Contact: geert.cornelis@slu.se

Acknowledgments

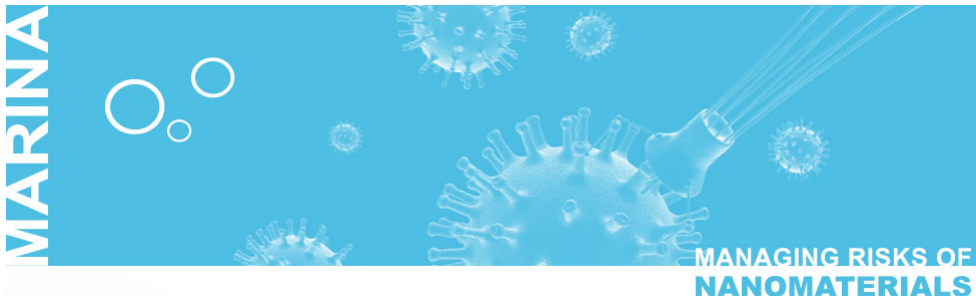


NanOFATE



GUIDE 

NanoFASE



Vetenskapsrådet