Analytical Challenges For Characterization of Nanoparticle Dispersions Posed by Polydispersity

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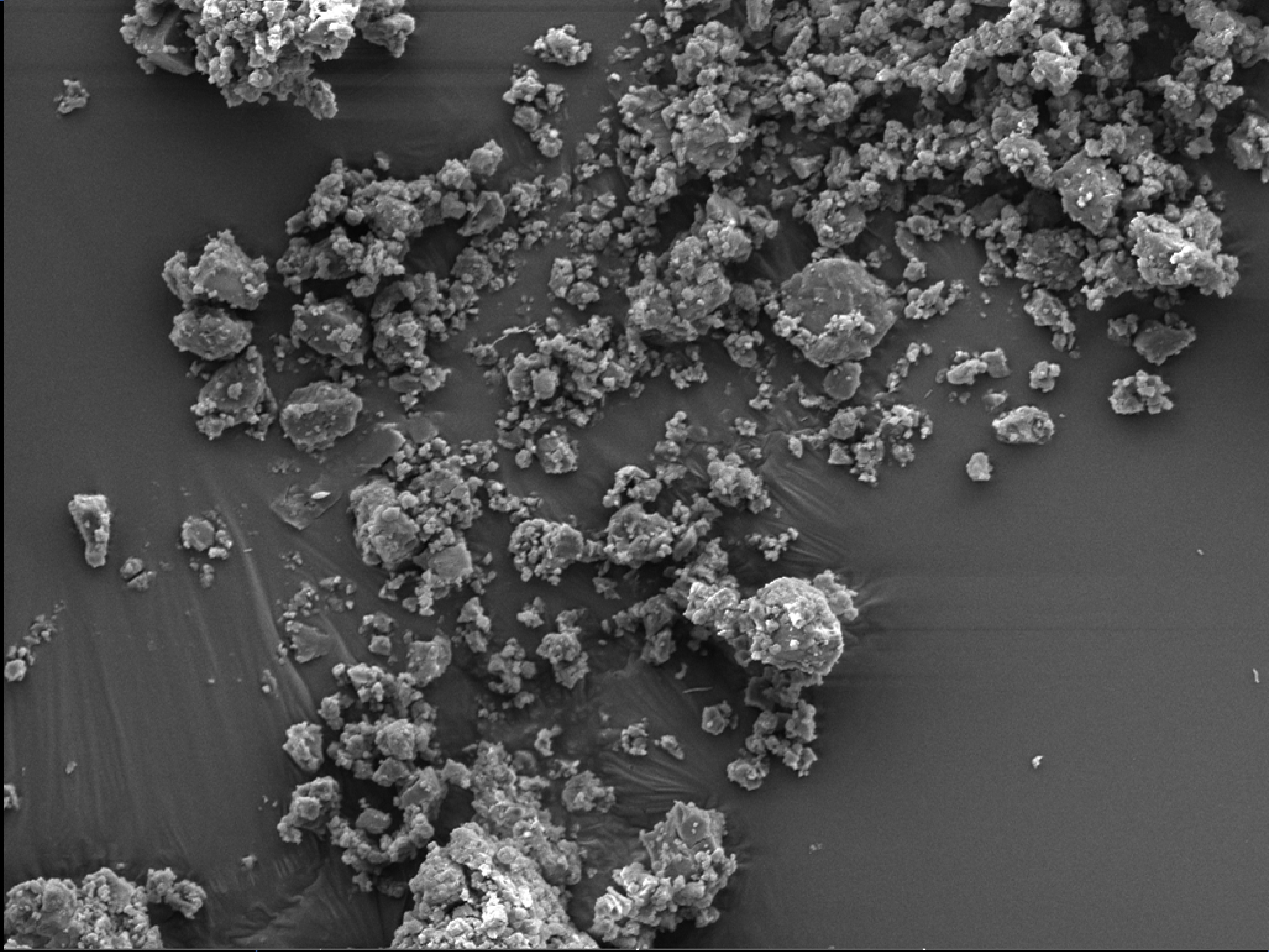


CCQM Particle Metrology Workshop
October 25-27, 2022

What are we all measuring?

Primary

- Size
  - Central tendency
    Mean, mode, median
  - Weighting
    Number, volume, intensity(light scattering)
  - Size distribution
    Normal, log-normal, more complex
- Amount
  - #/ml, (vol/mass)/ml

Secondary

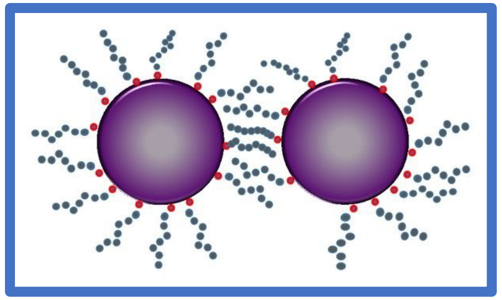
- Composition - more important for complex samples
- Shape - morphology

Approaches

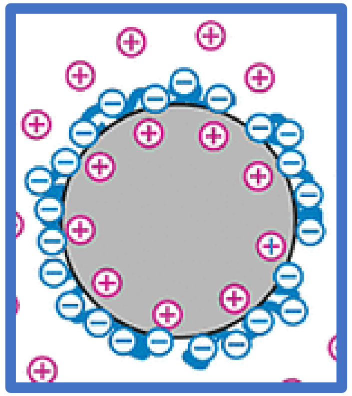
- Ensemble- data extracted from multiple particles
  - Laser diffraction, DLS, sedimentation
  - Theory needed
- Separations
  - FFF, HDC, CE
    - Size by theory/calibration
    - Front end for size detectors
- Individual Particle – measurement of each particle
  - microscopy, NTA, Coulter counter, single particle ICP-MS
  - "seeing is believing"*

* Or is it "If I hadn't believed it, I wouldn't have seen it"

Metrology of particles suspended in water or other liquids – what are the challenges: 1-Stability



Particle and Media Dependent



Ideal World (standards)

- Standard calibration particles are made to be stable in control (calibration) media

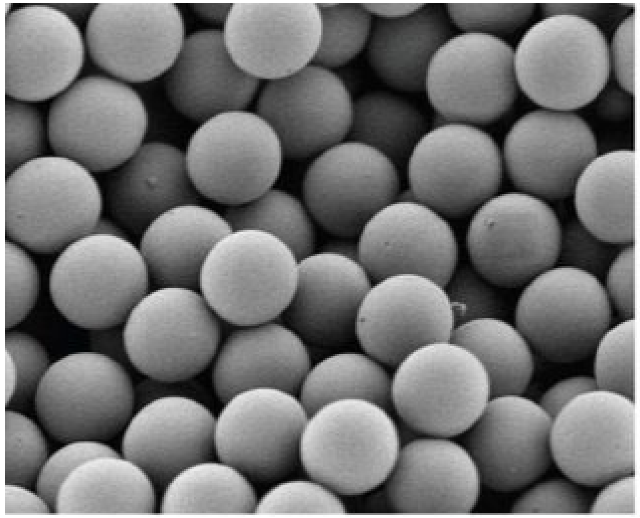
Real World (applications)

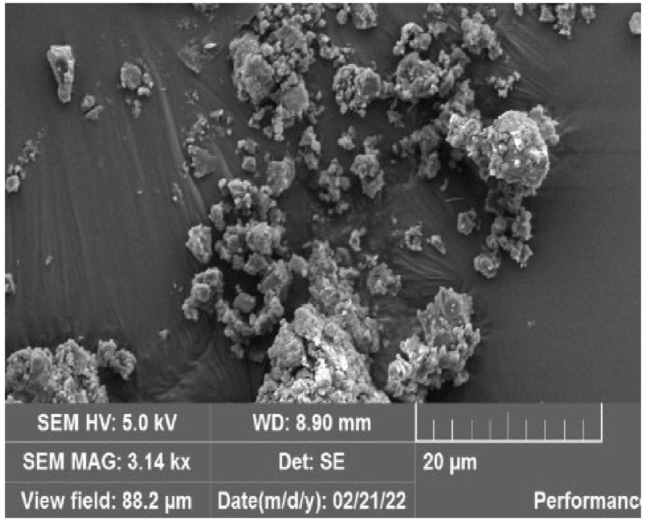
- Test particles may not have stabilizing surfaces
- Test media different than control media (e.g. different ionic strength)
- Stability affects particle size and concentration

Leads to the questions:

- Can (should) we determine the aggregation state <u>for the test particle in the test media</u> or just attempt to measure stable ”primary” size?
- Can a standard dispersant/ionic strength be used?

Metrology of particles suspended in water or other liquids – what are the challenges: 2-Polydispersity





Ideal World (standards)

- Standard calibration particles are monodisperse (or at most mixtures of different sizes)

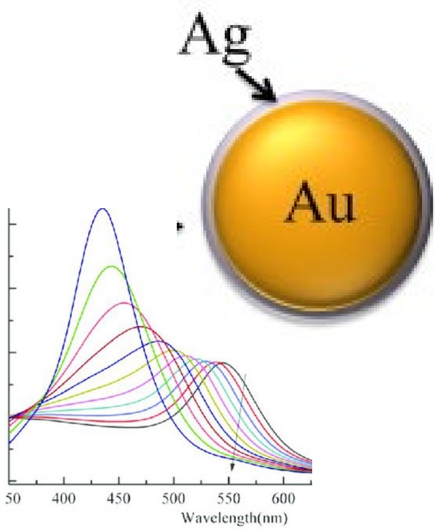
Real World (applications)

- Test particles can be highly polydisperse
- This affects all counting methods but is especially important for single particle ICP-MS

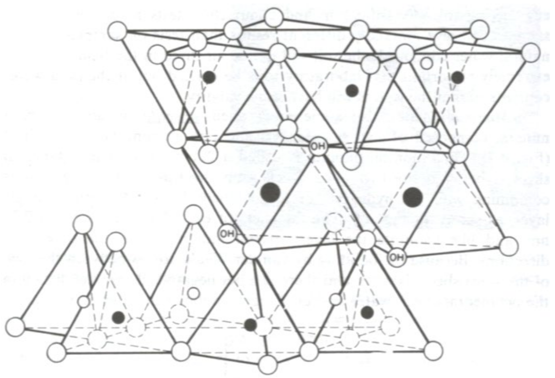
Leads to the questions:

- Mixture of size standards (what proportions)?
- How do we best report size data?
    - How valuable is a single descriptor (diameter, radius)
        - Number, volume or other
        - Mean (average), mode, median
- What is the best approach for reporting broad (polydisperse) size distributions?

Metrology of particles suspended in water or other liquids – what are the challenges: 3- Measuring Composition



$Si_8(Al,Mg,Fe)_{4\sim6}O_{20}(OH)_4 \cdot (K,H_2O)_2$



Ideal World (standards)

- Standard calibration particles are made to be chemically simple ("pure")

Real World (applications)

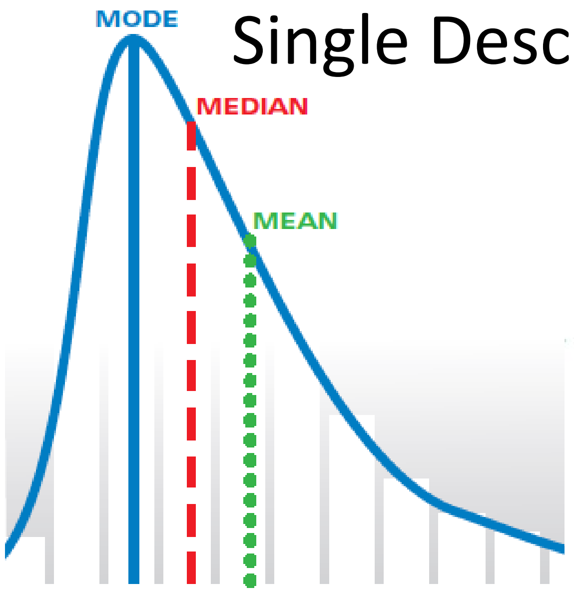
- Test particles may contain multiple elements (especially true for environmental and highly-engineered particles)

Leads to the questions:

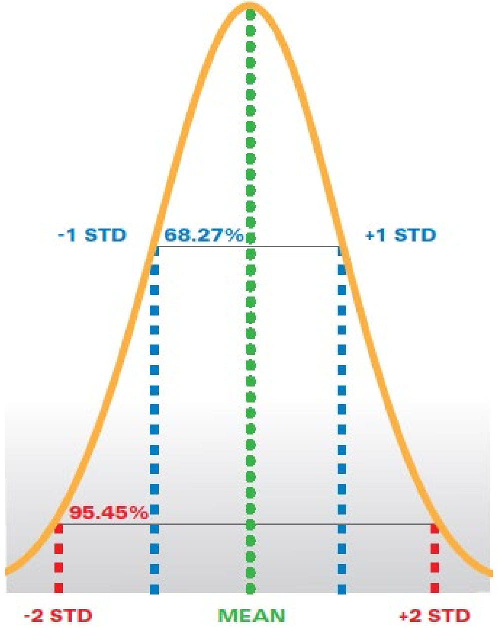
- How do we know an element is absent from a particle or just not detected?
- Related, can a particle be accurately classified (Engineered vs. Natural)?
- If we don't know the complete composition, how do we accurately size particles
    - (Σ element masses → particle mass → size)?

Question: How big is the particle?
Answer: It depends on how you report it

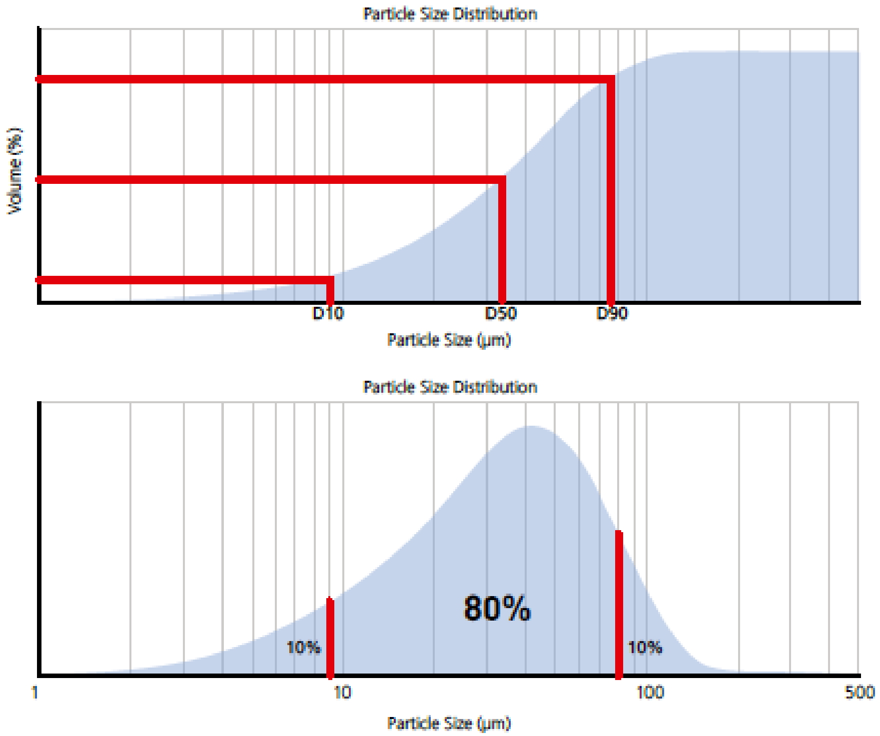
Single Descriptor



Width: Statistics



Span/Particle Size Distribution



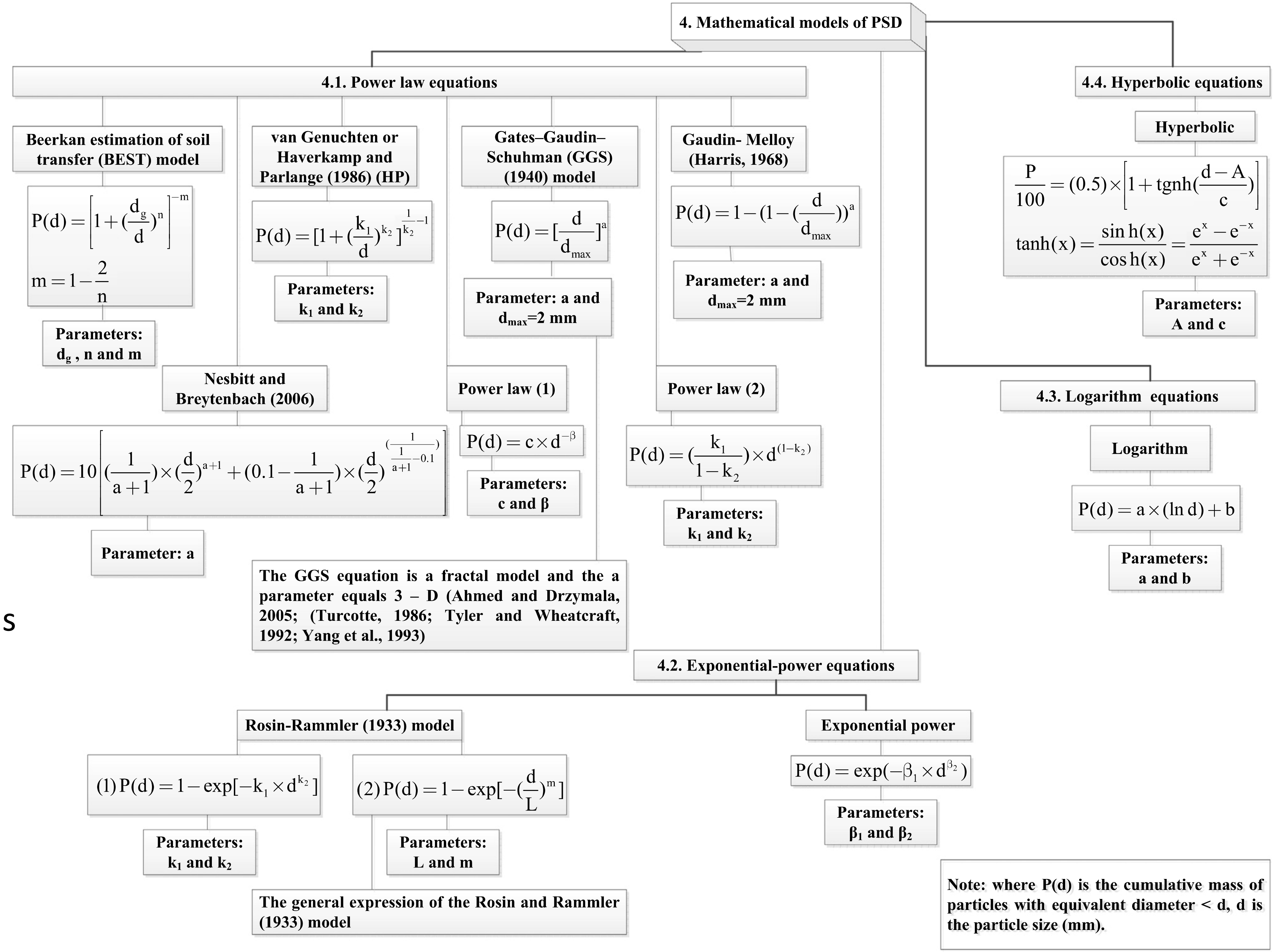
Usual Question: Is the PSD “normal”, Log-normal, other?

Exploring the PSD shape

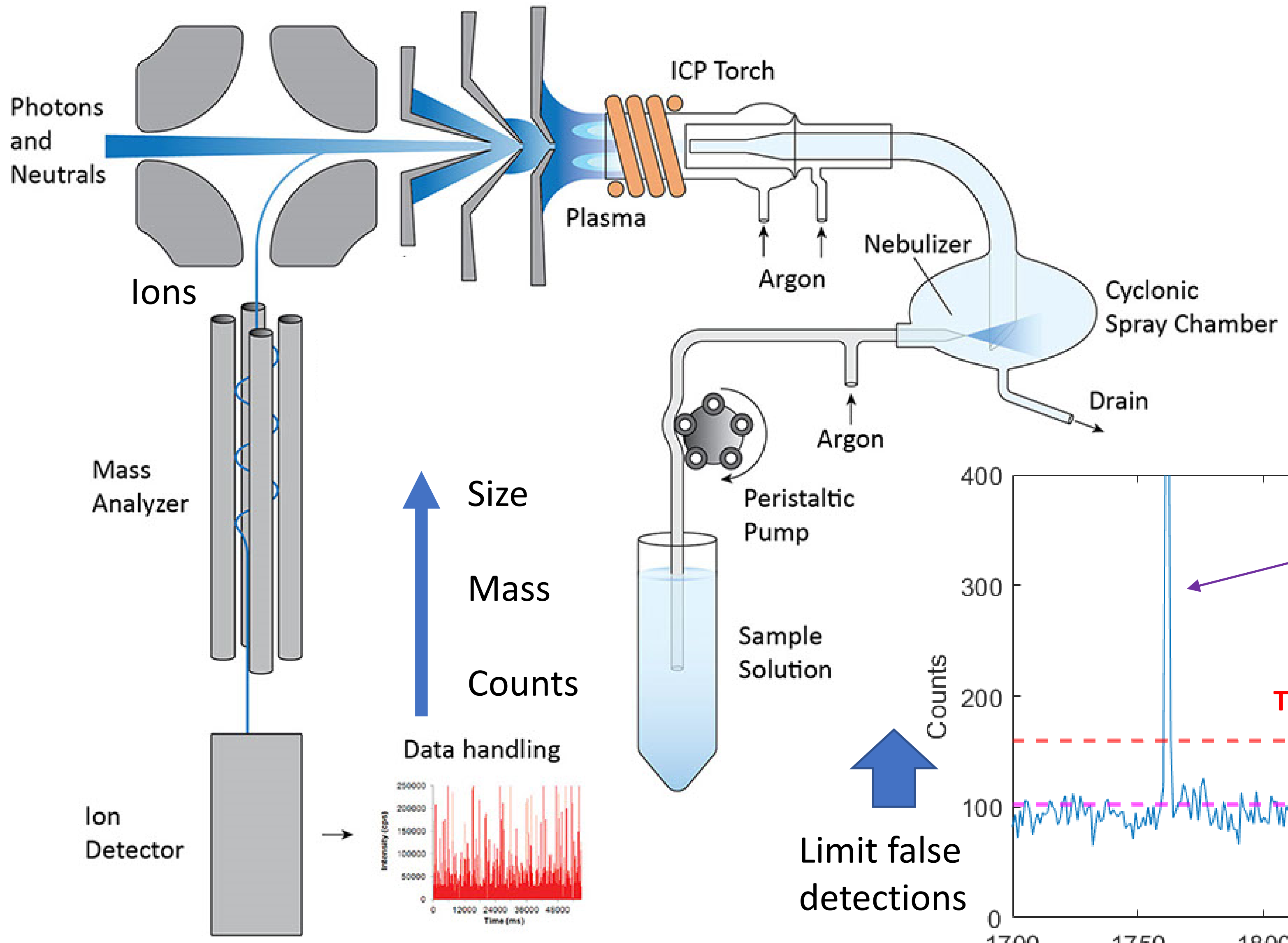
No shortage of models

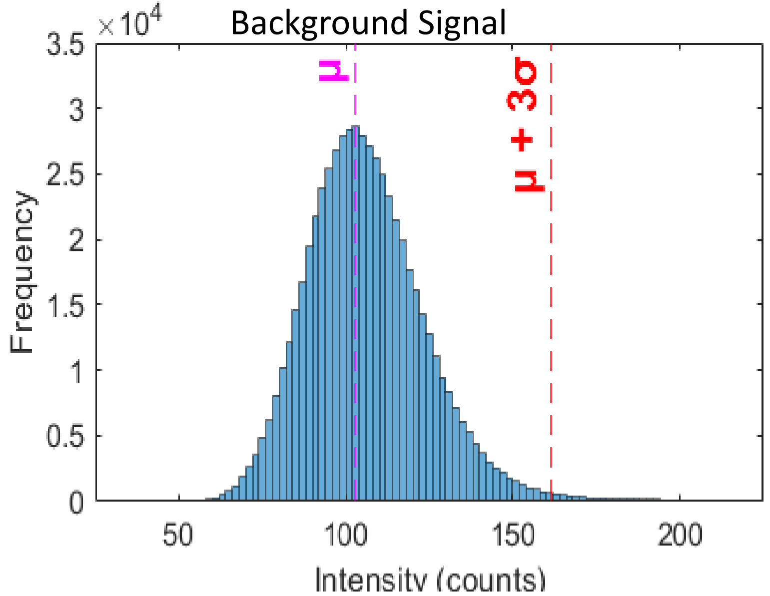
Example from soil analysis

Bayat et al.

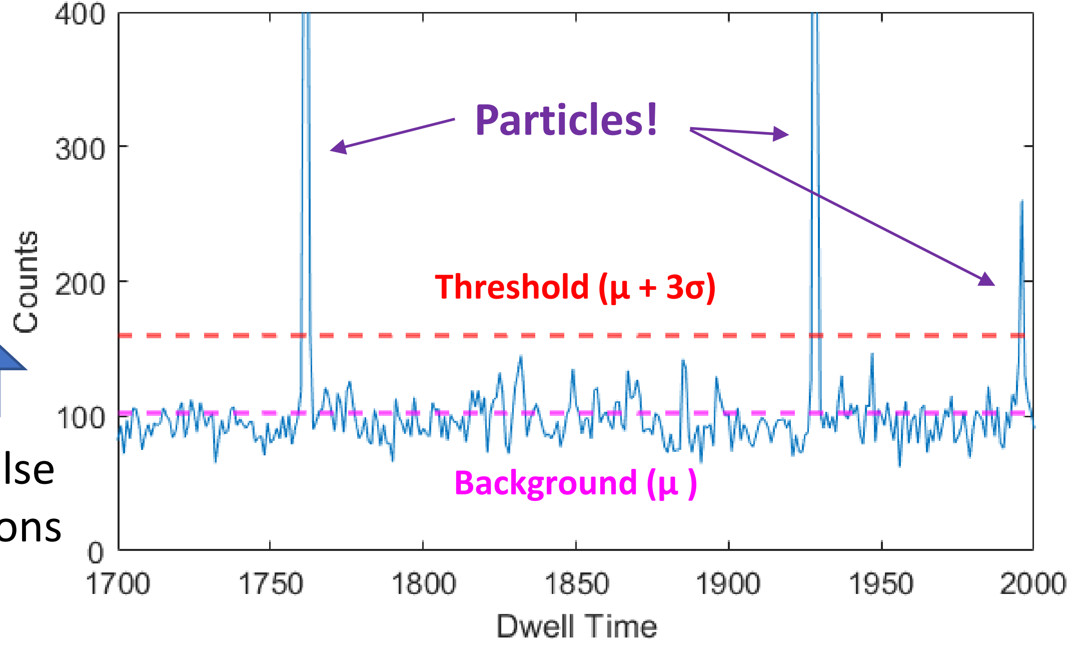


Counting and Sizing Submicron Particles: Single Particle ICP-QMS





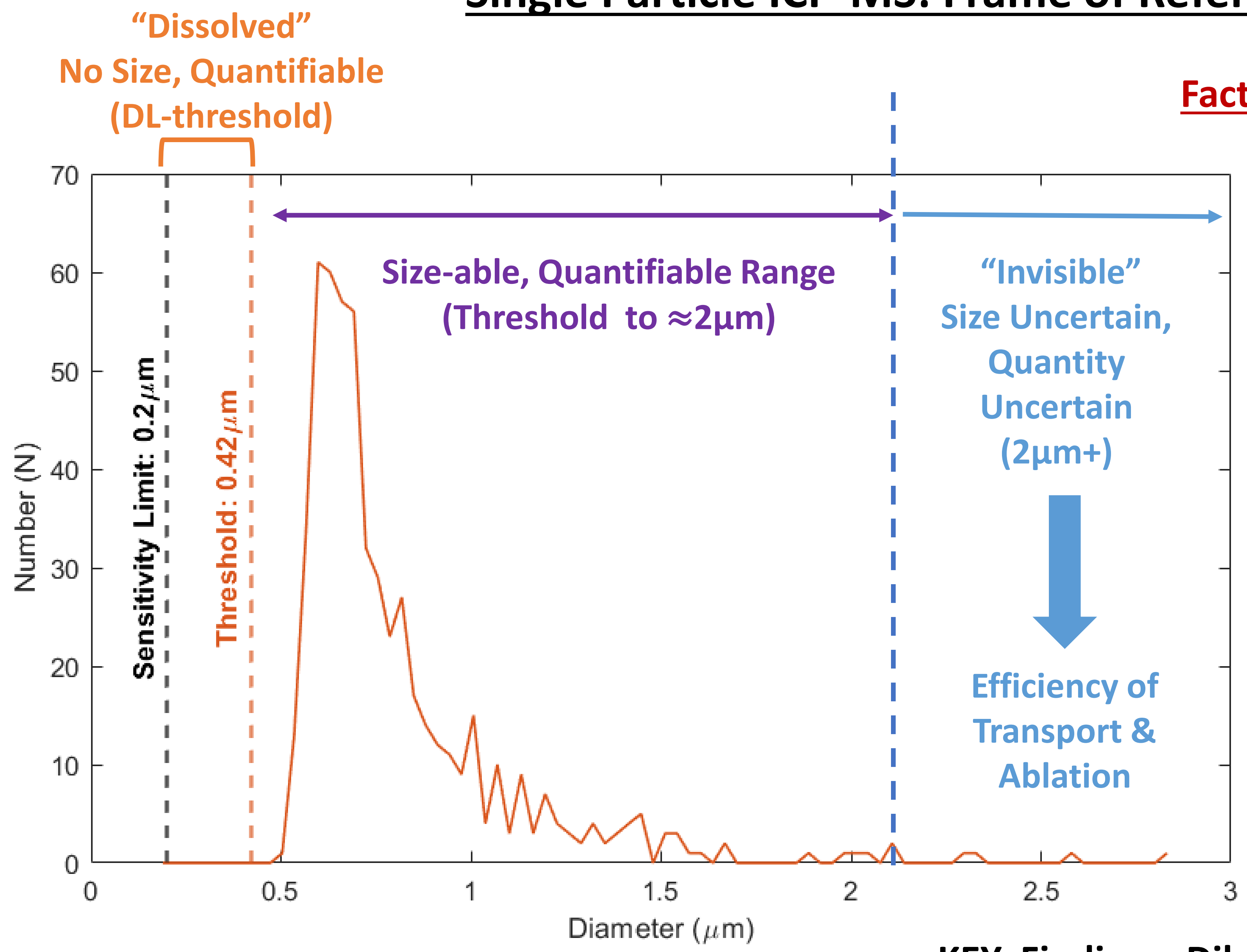
Limit false detections



See smallest particles

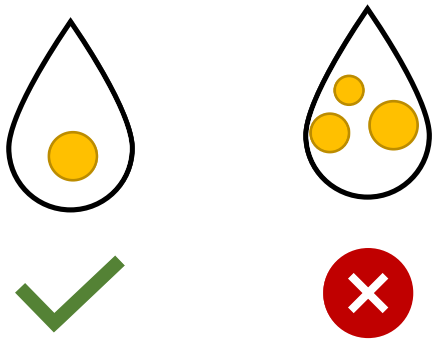
Design by F Herzog. From the Lab Website of K Wilkinson, University of Montreal

Single Particle ICP-MS: Frame of Reference

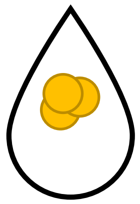


Factors that Artificially Distort the PSD & Affect Number Concentration

Coincidence

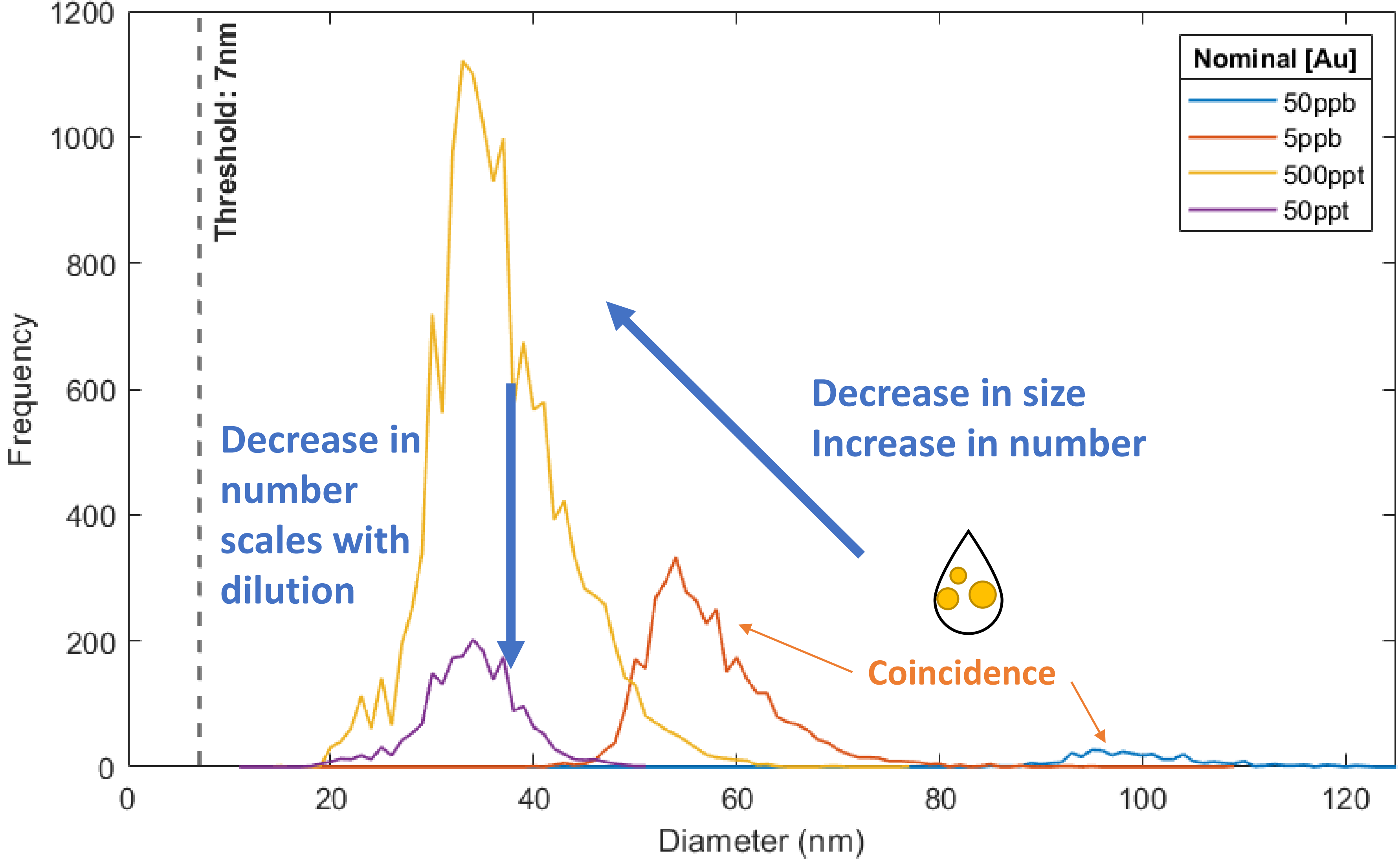


Aggregation



KEY: Finding a Dilution that Minimizes these Effects for Accurate Sizing and Counting!

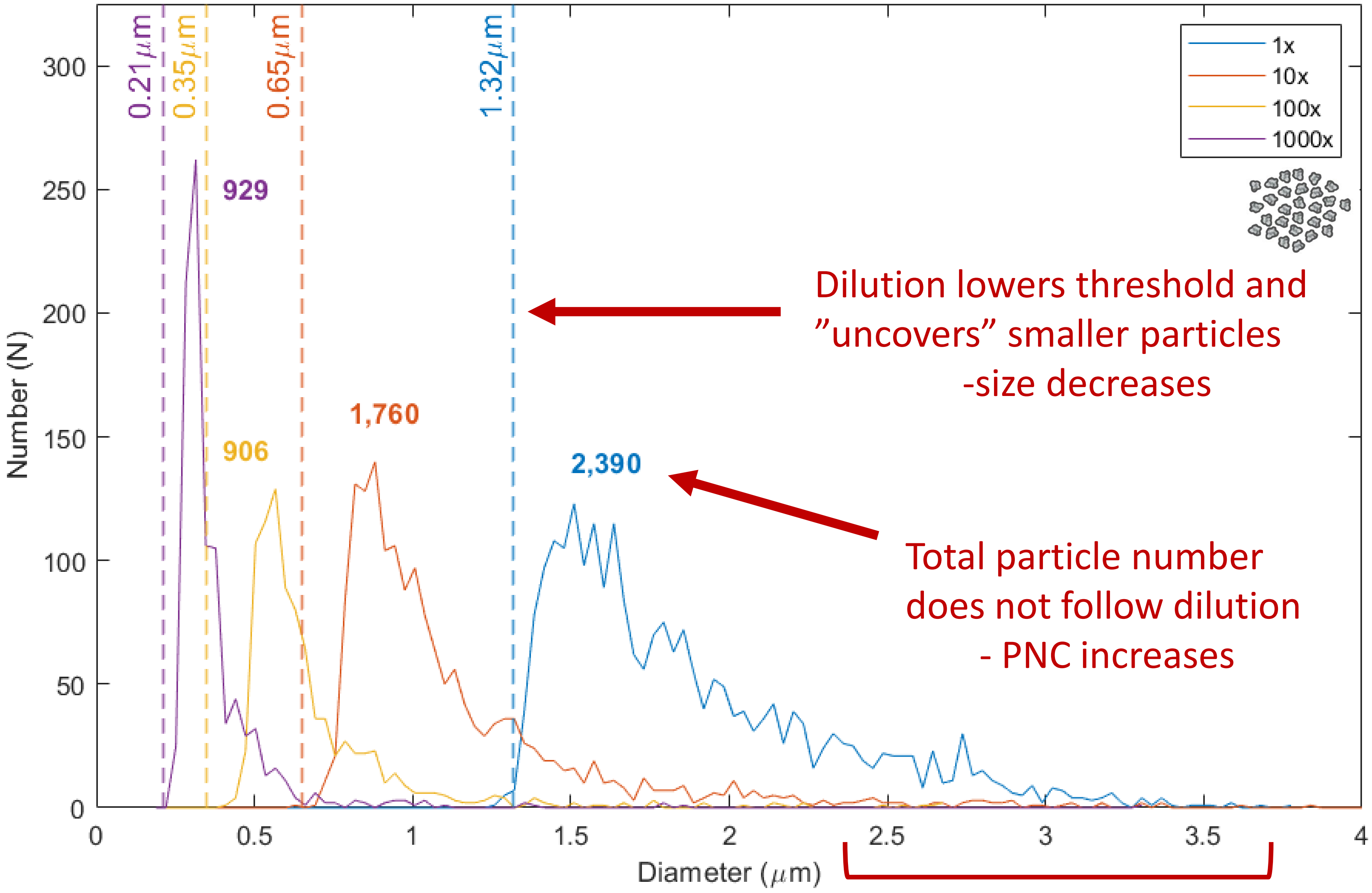
Monodisperse PSD: Dilution is the Solution



nanoComposix Au standard

Threshold has no influence on this dilution - below the smallest observable size

Polydisperse Samples: Particle-Based Background (Dilution is not the total solution)



Dilution lowers threshold and ”uncovers” smaller particles
-size decreases

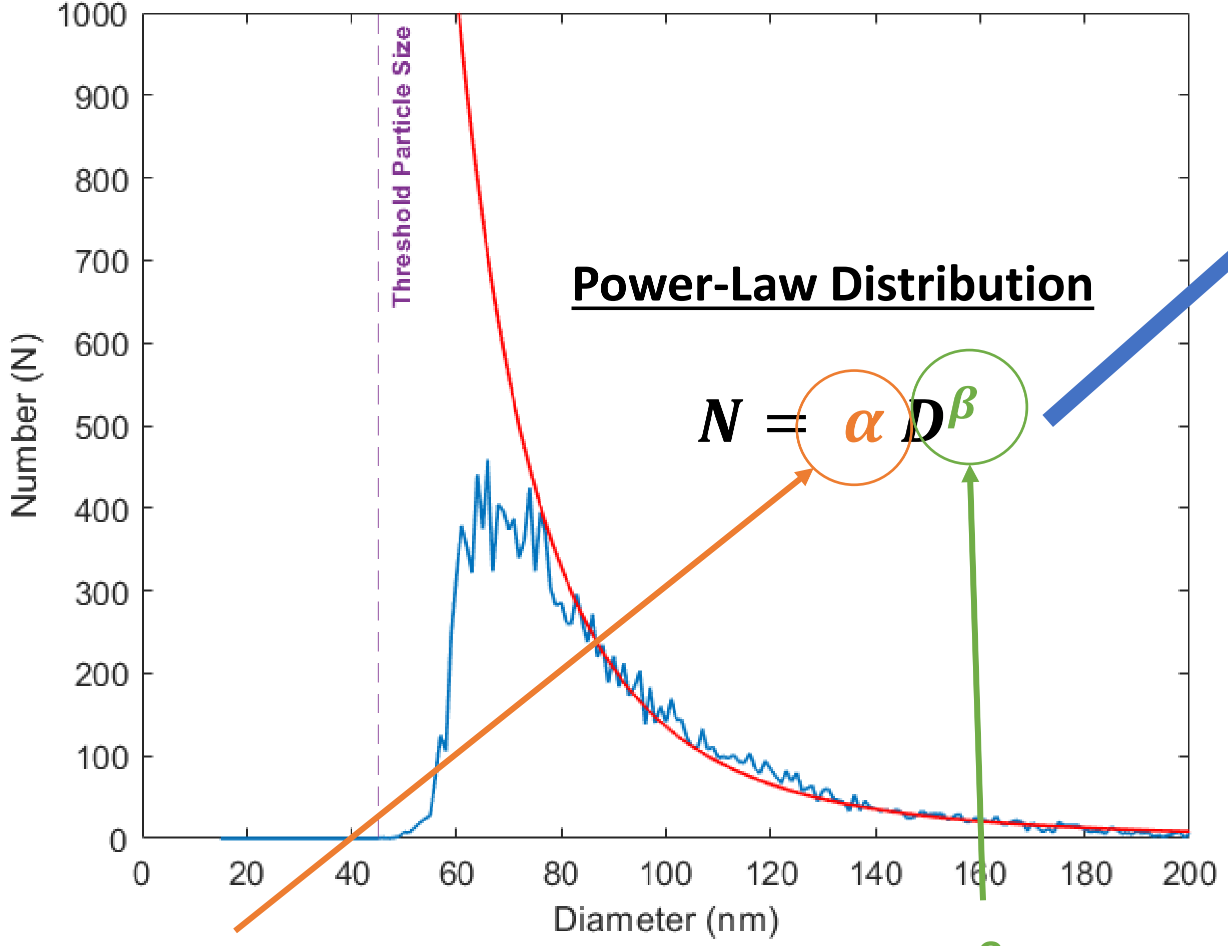
Total particle number does not follow dilution
- PNC increases

Counting Statistics for larger sizes worsen as a function of dilution

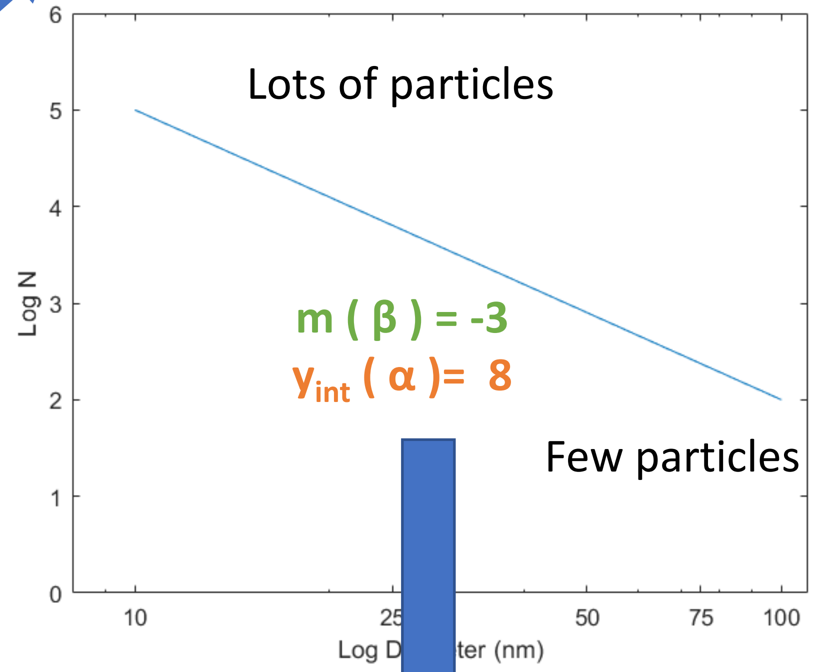
Ta-tagged, polydisperse milled Microplastics

NOT GOOD – results are concentration-dependent!

Modeling Polydisperse PSD with the Power Law



$$\log N = \log \alpha + D \log \beta$$



α
related to total particle number

β
related to the shape of the PSD

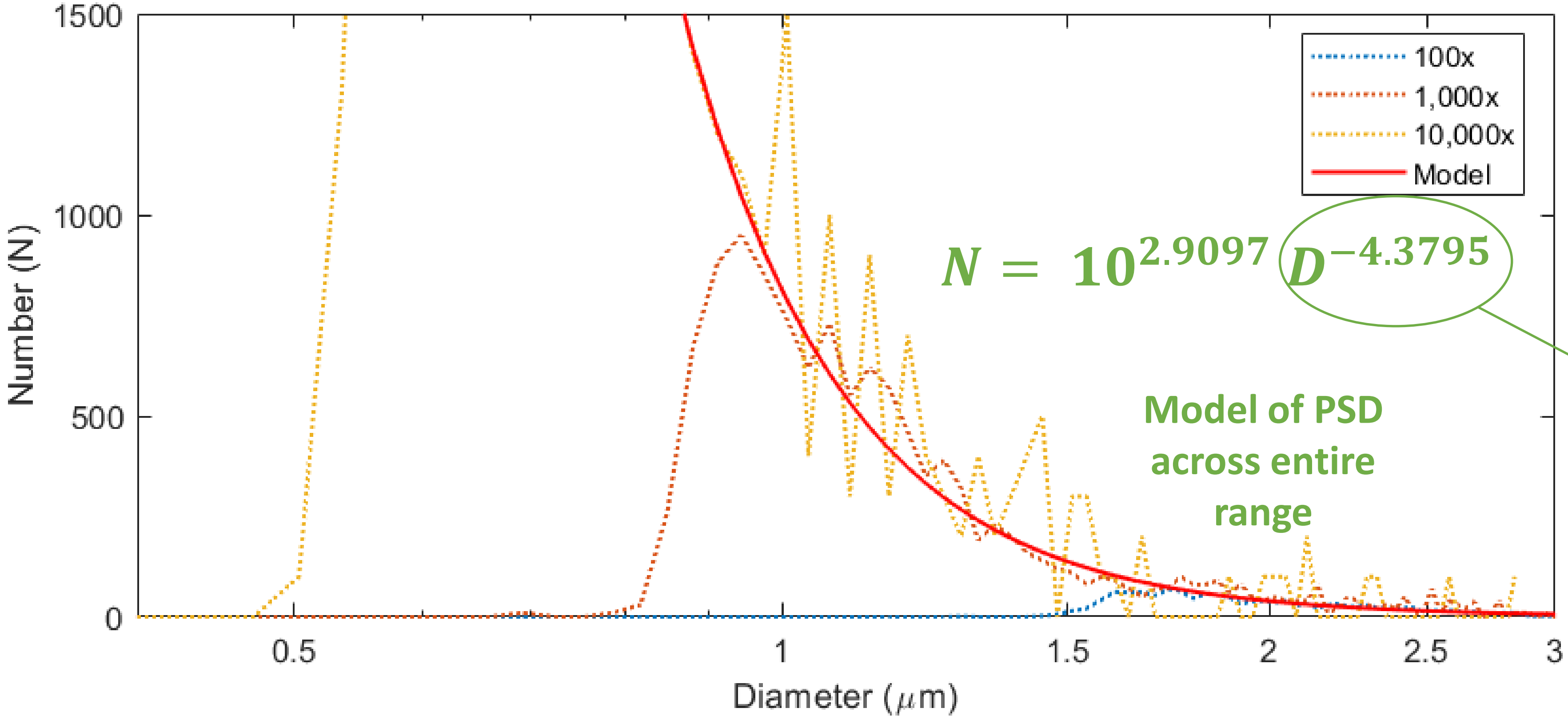
How do we measure a PSD with such a large difference in particle number ?

A Simple Scheme for Comparing Polydisperse Samples?

1. Identify Areas of Proportional Dilution (i.e. areas of the PSD with ideal behavior)

2. “Stitch” the Data for Areas of Proportional Dilution Together in Log Space

3. Model the PSD across the entire size range measured by each dilution

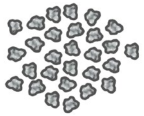


$$N = 10^{2.9097} D^{-4.3795}$$

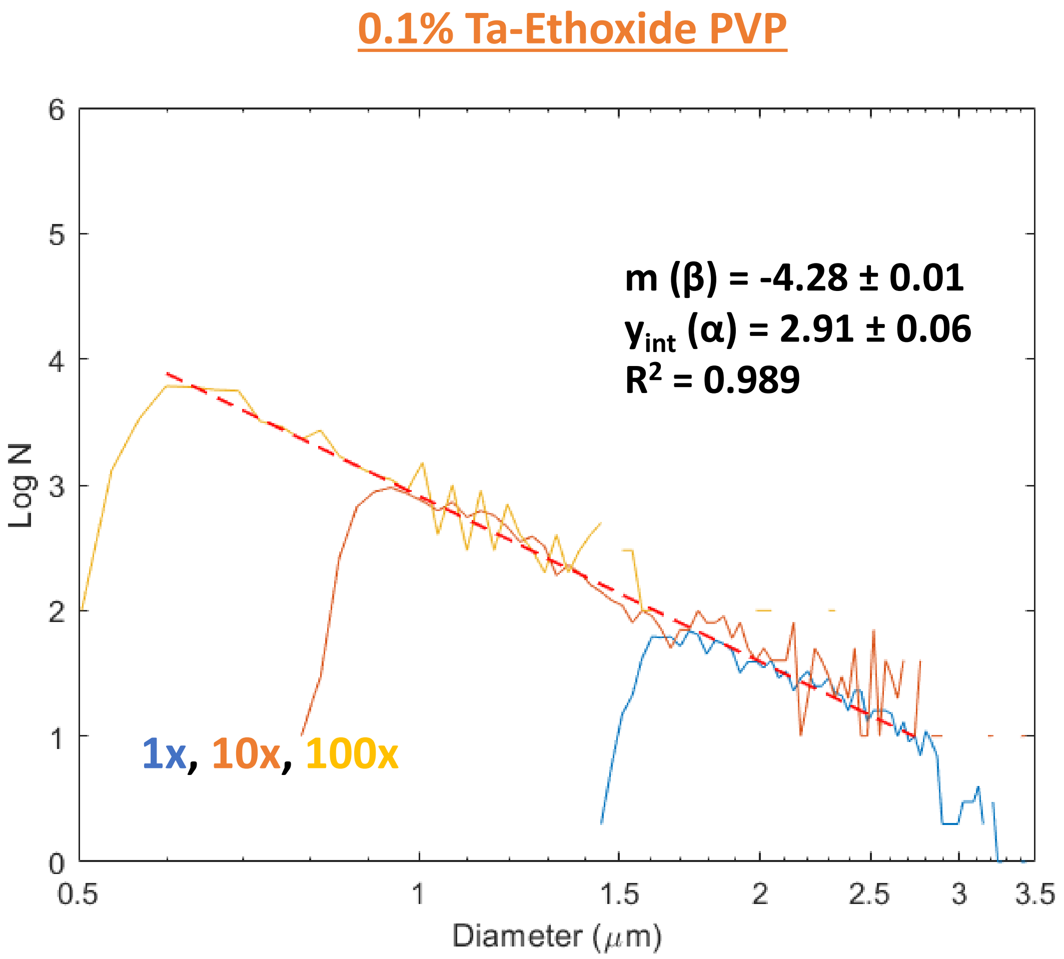
Model of PSD across entire range

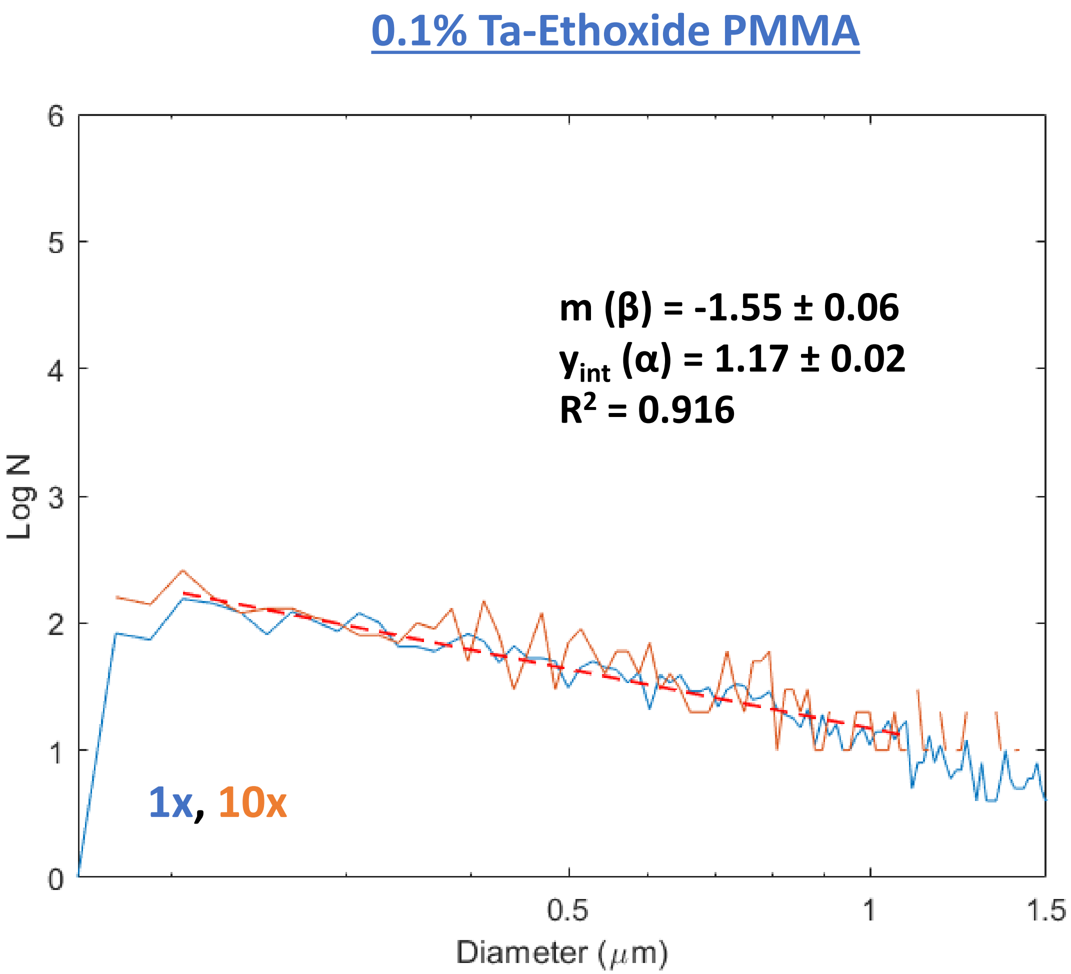
β value that can be used to compare PSD shape between different Polydisperse samples

Log Space Analysis of Size Distributions: Discriminating Between PSDs



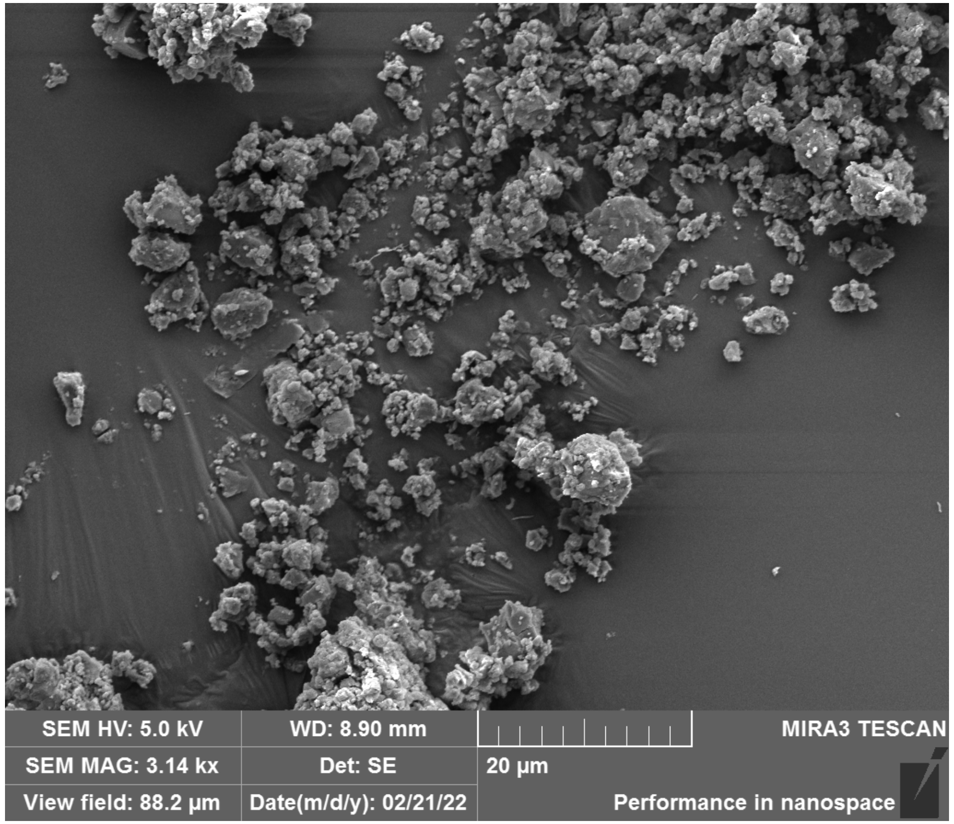
Ta-tagged Microplastics





More Negative β (-) of PVP → More Small Particles per Large Particle than PMMA

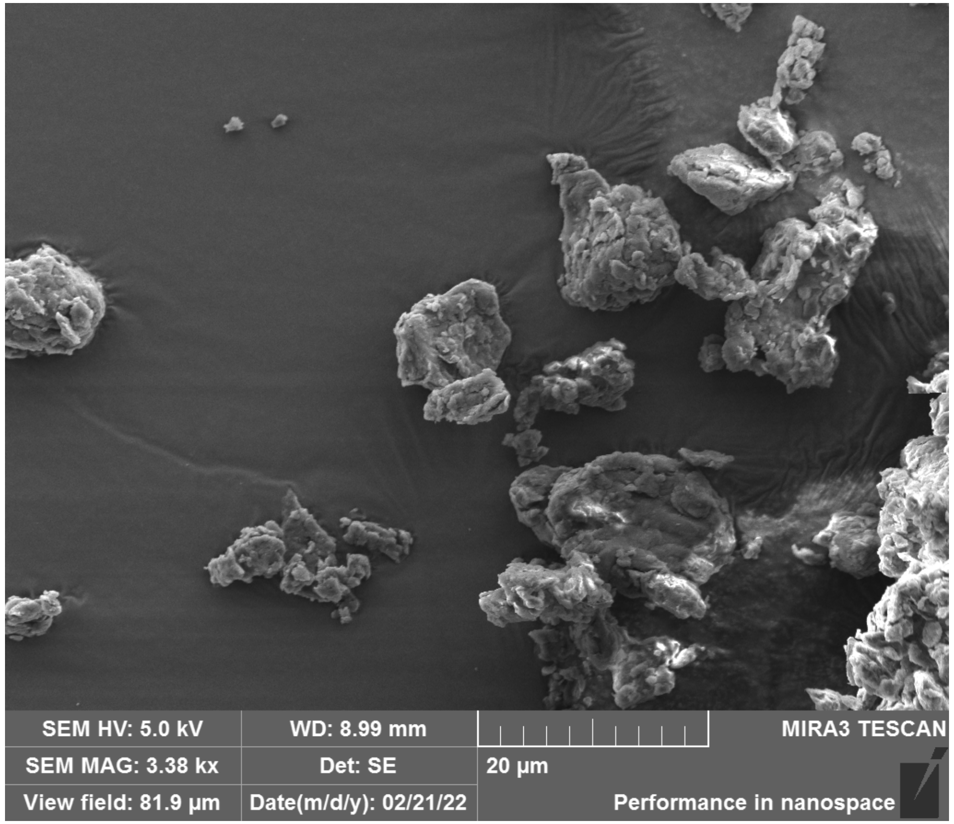
Differences in Slope Reflect Observed Particle Size



0.1% Ta-Ethoxide PVP

β = -4.38

Predicts More Small Particles per Large Particle



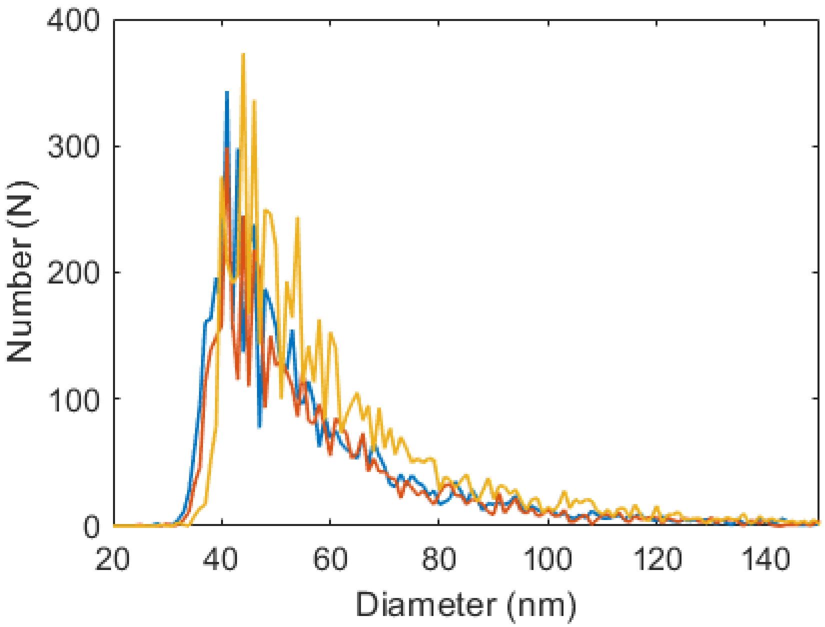
0.1% Ta-Ethoxide PMMA

β = -1.55

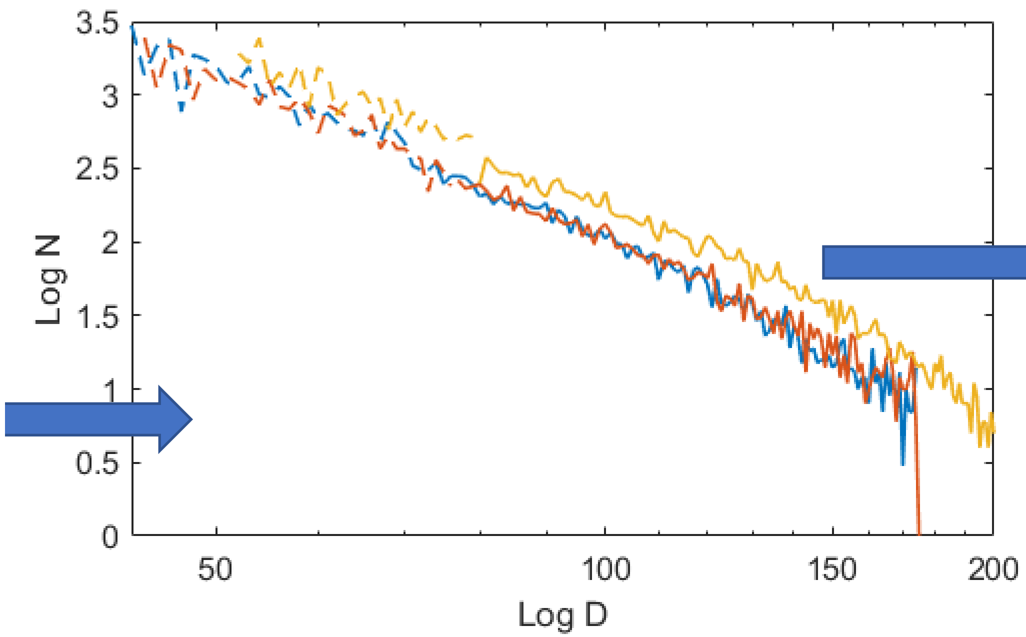
Predicts Fewer Small Particles per Large Particle

Power Law Modeling Conclusions

Number Size Distribution



Log Plot of Size Distribution



Linear Regression

$$N = \alpha D^{\beta}$$

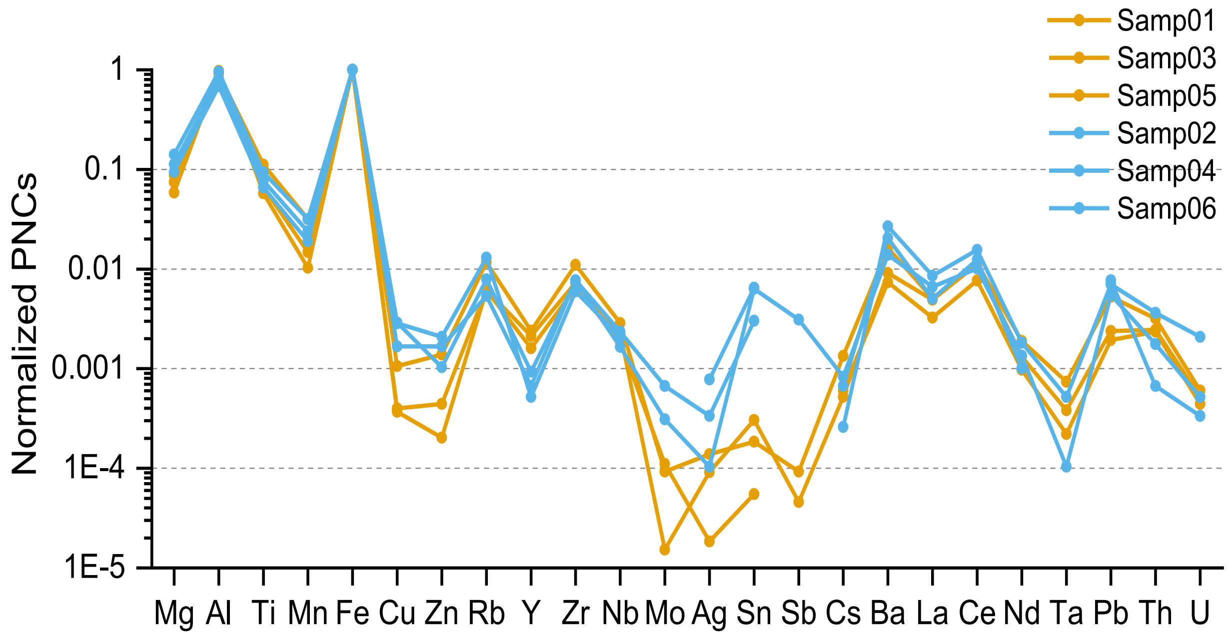
Analysis of Particle Number Size Distributions by Log Plot and Linear Regression

- ✓ Analysis of PSD over a wider range of sizes then possible with one dilution
- ✓ β describing the shape of the PSD can be used to look for size-specific changes across PSD

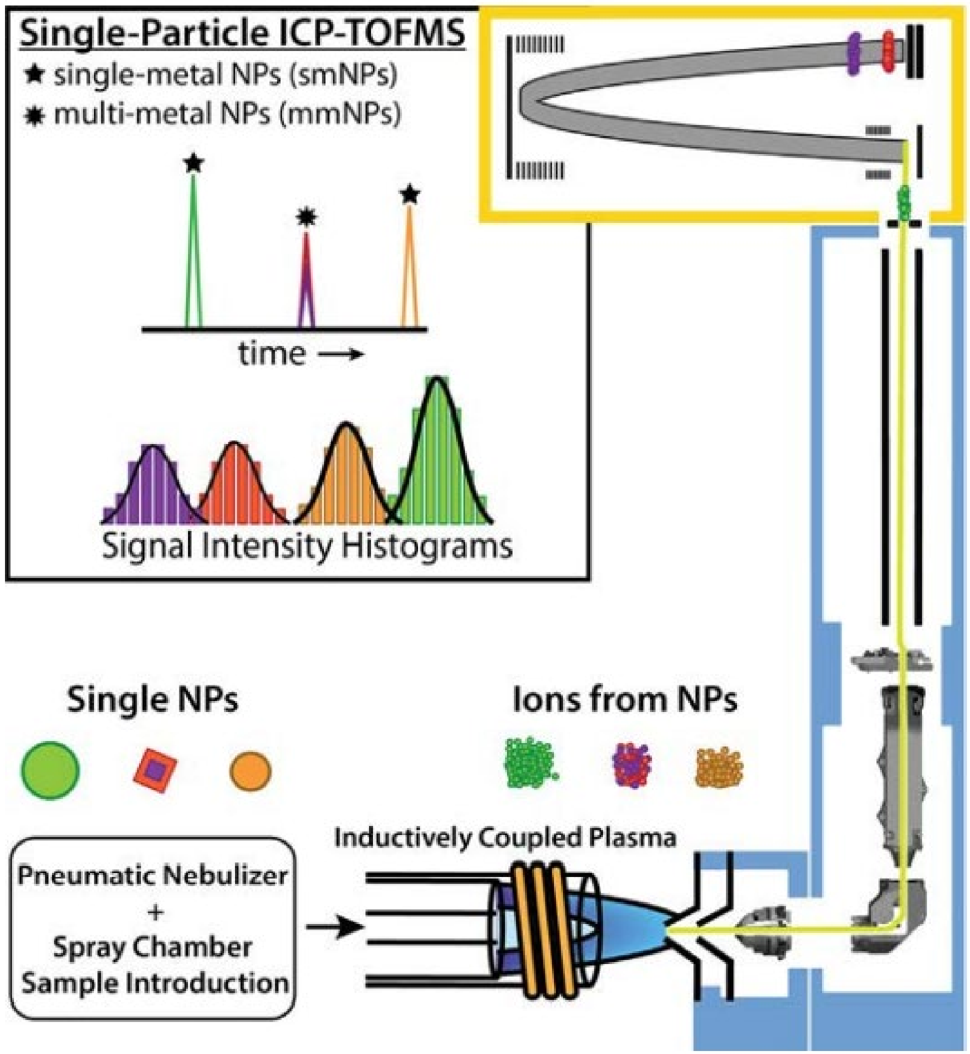
Future Potential: Polydisperse colloids undergoing a reaction (aggregation, dissolution…)

Particle Composition: spICP-Time of Flight-MS

- spICP-QMS detects 1 element at a time
- TOFMS enables detection of multi-elemental NPs
  - Define single metal (SMP) and multi-metal (MMP) particles
- This presents opportunities & analytical challenges

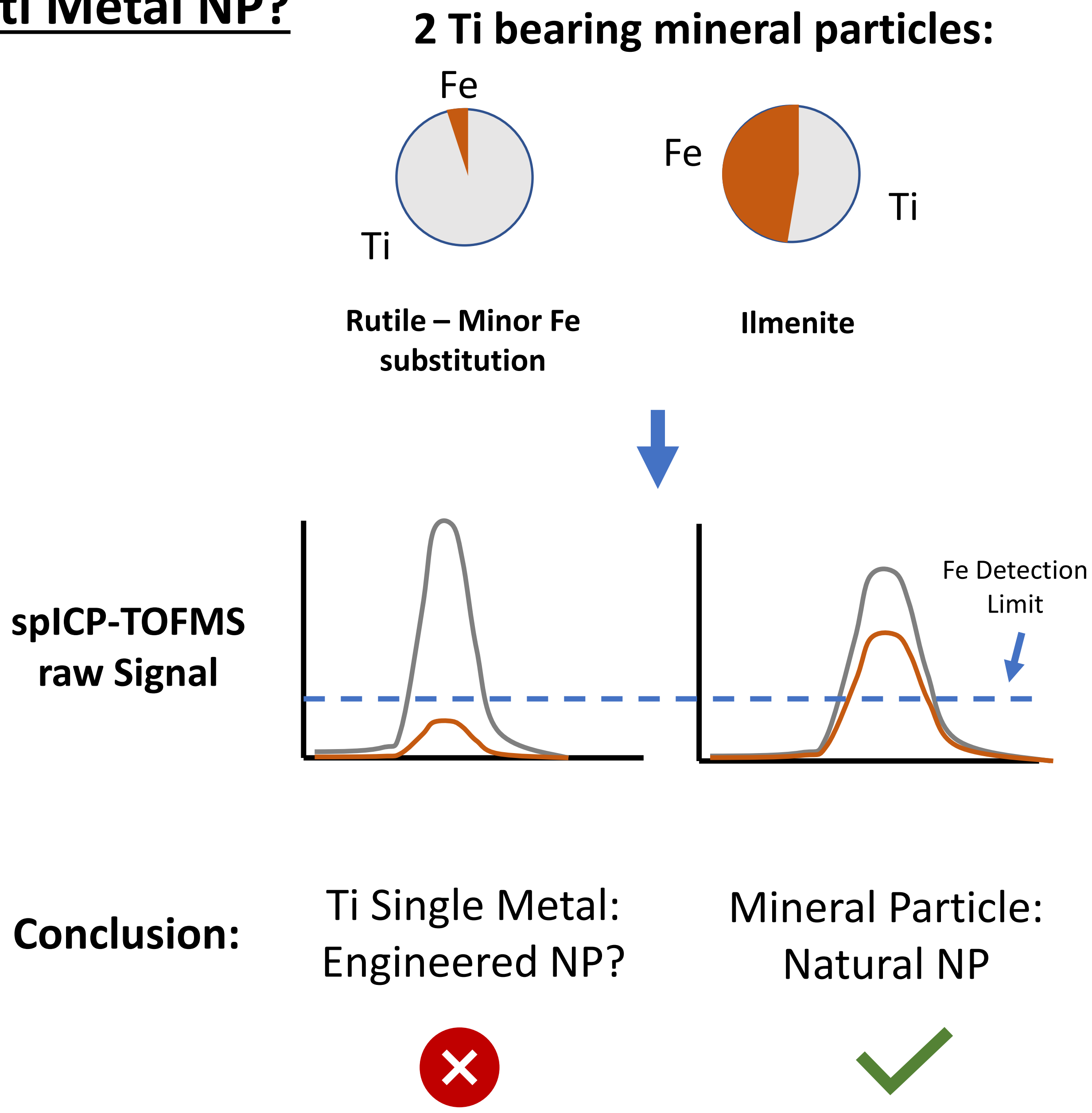


spICP-TOFMS analysis of Mineral Dusts – 24 elements detected simultaneously



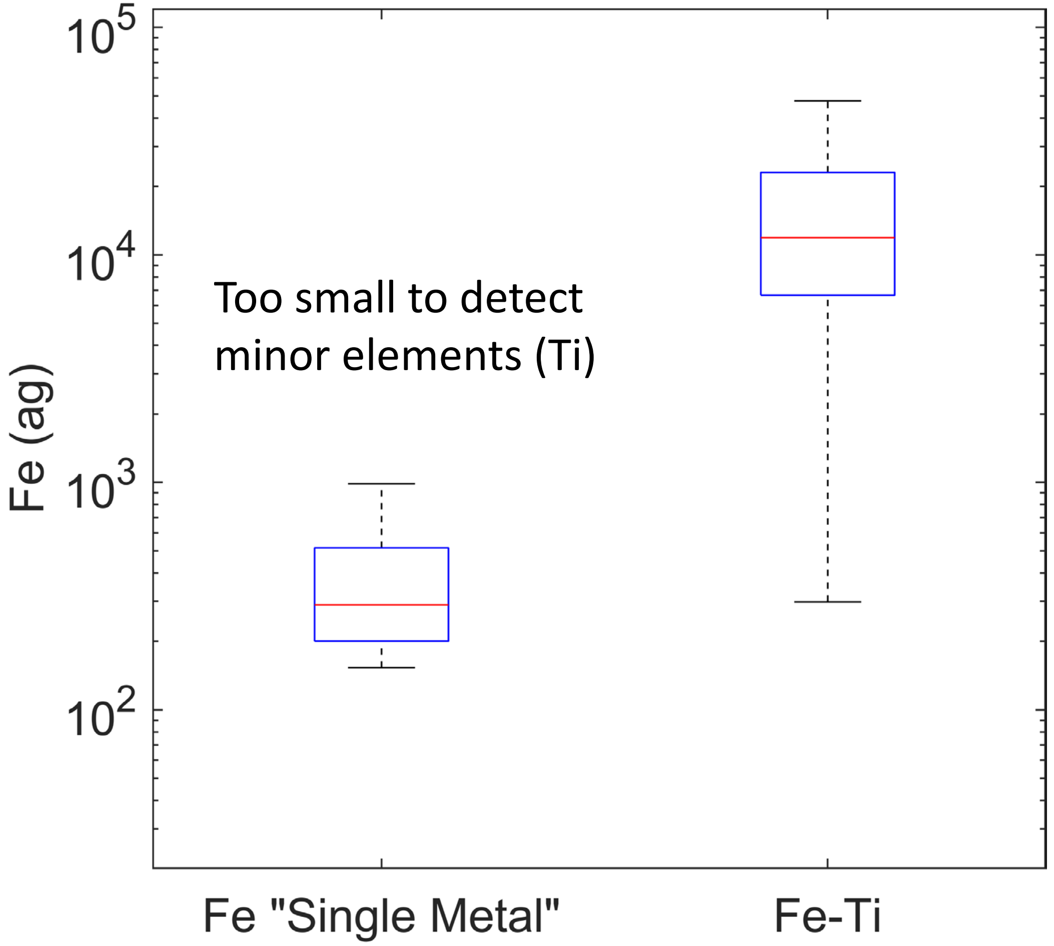
Challenge: Is particle a Single Metal NP or Multi Metal NP?

- Engineered NPs are often "single metal" –
  - Ag - clothing
  - Ti - paint, sunscreen
  - Si - everything
- Natural and incidental NPs are nearly always "Multi-metal"
  - Mineral particles
  - Soils
  - Fly ash
- If we see a single metal particle on TOF-MS, can we be sure we aren't missing something?
- We must be confident in our classification of particles



Case study: Mineral Dusts containing Iron and Titanium

- Question: Do the Fe “only” particles have low amounts of other elements?
- We can miss elements (i.e. a false negative) in some particles for 2 reasons:
  1. Only a small amount of an element in the particle (ilmenite vs. rutile example)
  2. Small particles so the low-abundance element is not detected



How do we quantify this?

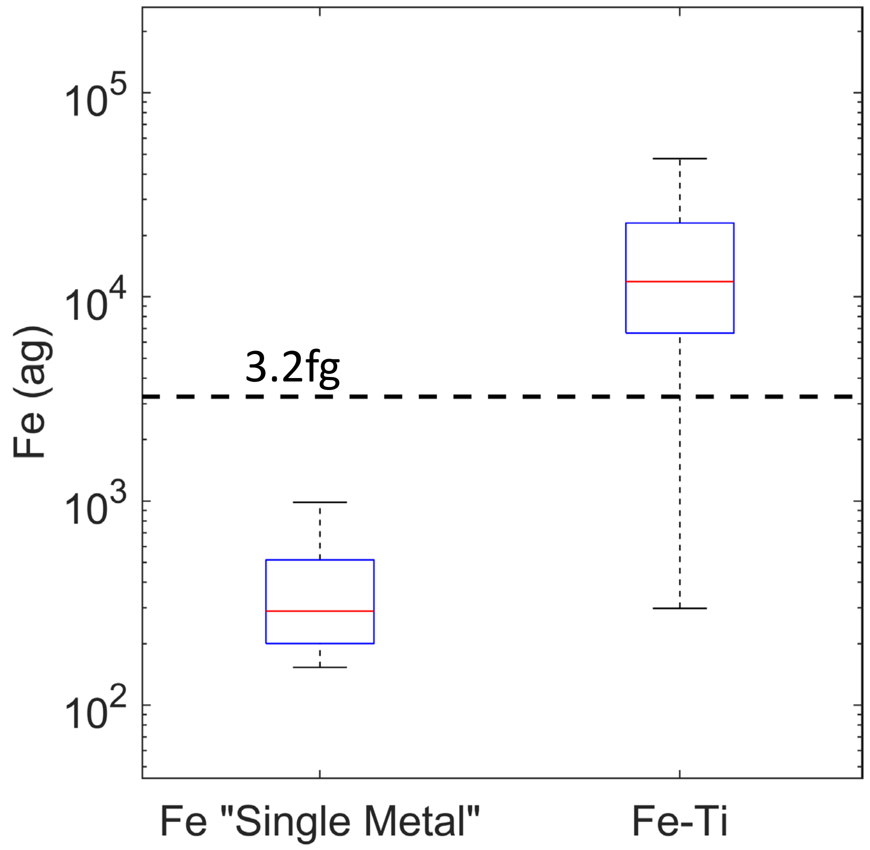
- We need 2 parameters to quantitatively determine false negatives:
  - Particle detection threshold for each element (determined from sensitivity)
  - A known or approximate conserved ratio between elements in question
- For the Mineral Dusts, the median ratio in particles is the earth's crustal ratio (CR)
- For Fe (major element) and Ti (minor element), we can determine how much of Fe is needed to detect Ti

$$L_{D,Ti:Fe} = L_{D,Ti} * CR_{Ti:Fe}$$

Detection limit for Ti based on Fe

Detection limit for Ti alone

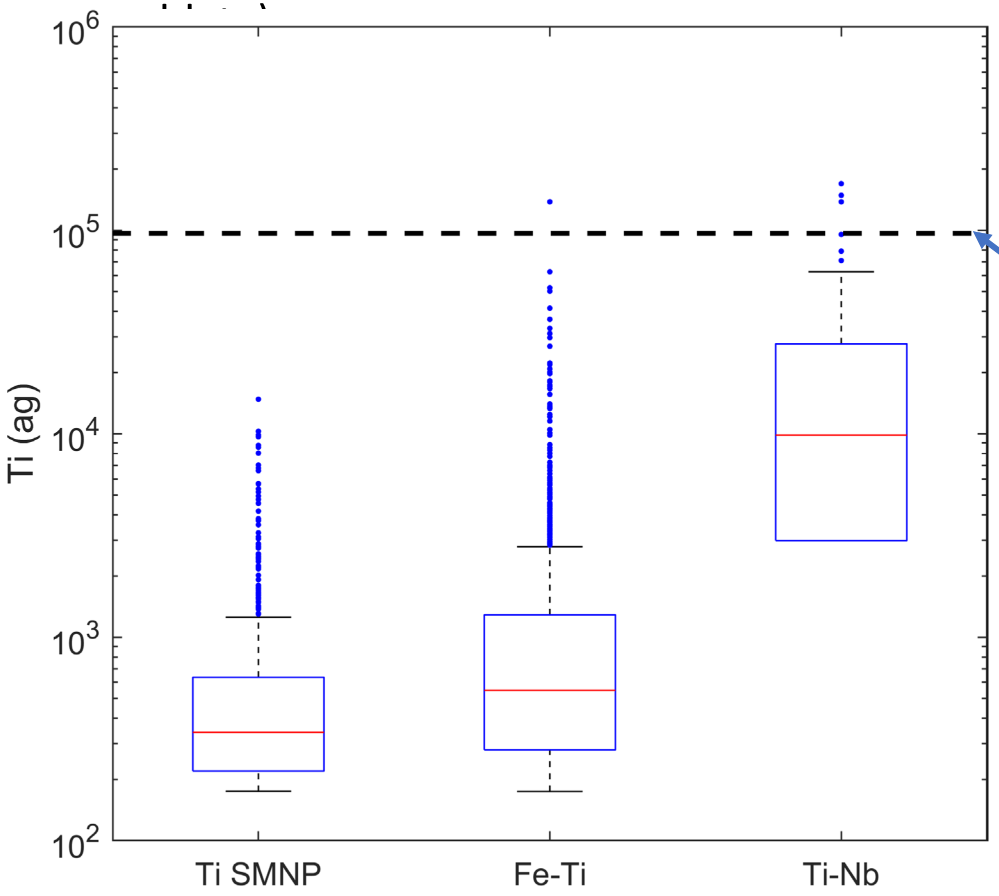
Mass Ratio between Fe and Ti

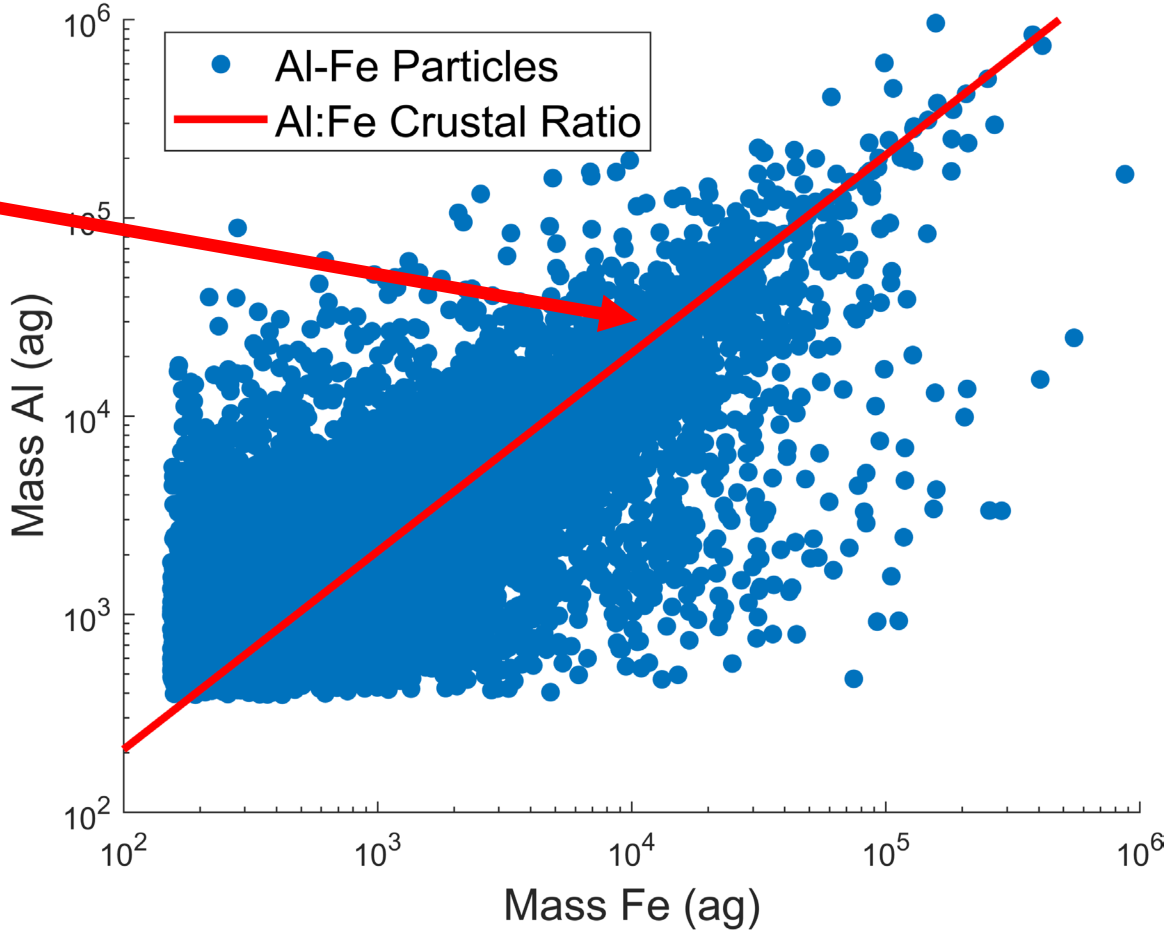


Conclusion: We need 3.2fg of Fe in a particle to know that it truly does not contain Ti (given the crustal ratio)

Challenges:

- Mineral dusts worked nicely – their median elemental ratios can be approximated by the crustal ratio
- Very large element ratios such as Ti:Nb (320) present challenges:
  - To determine that Nb isn't present, you will be nearly at the upper limit of Ti detection (particles too large to

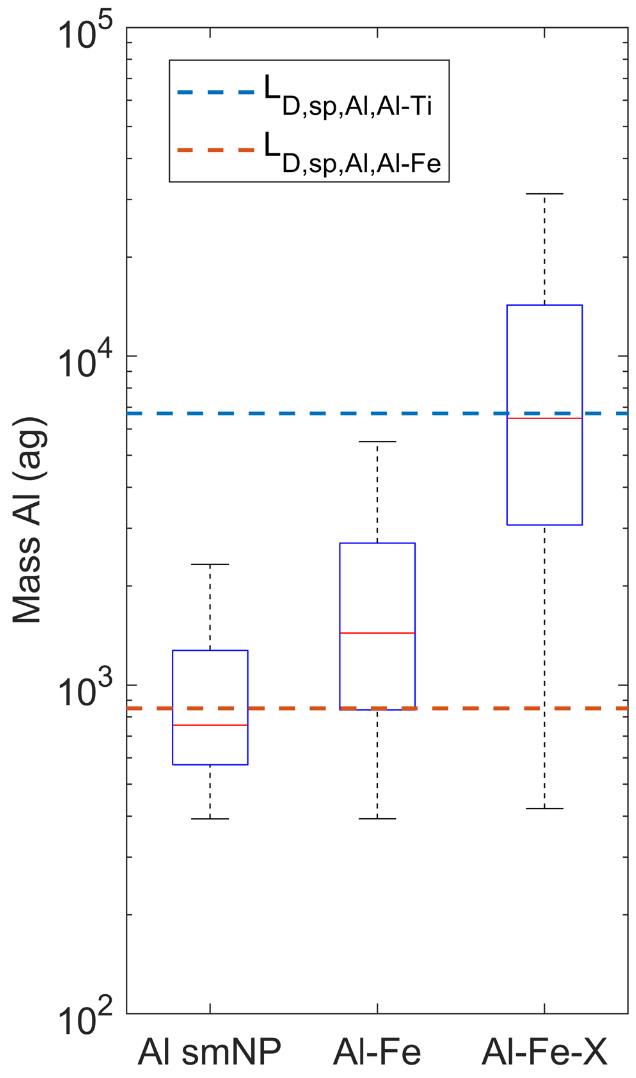


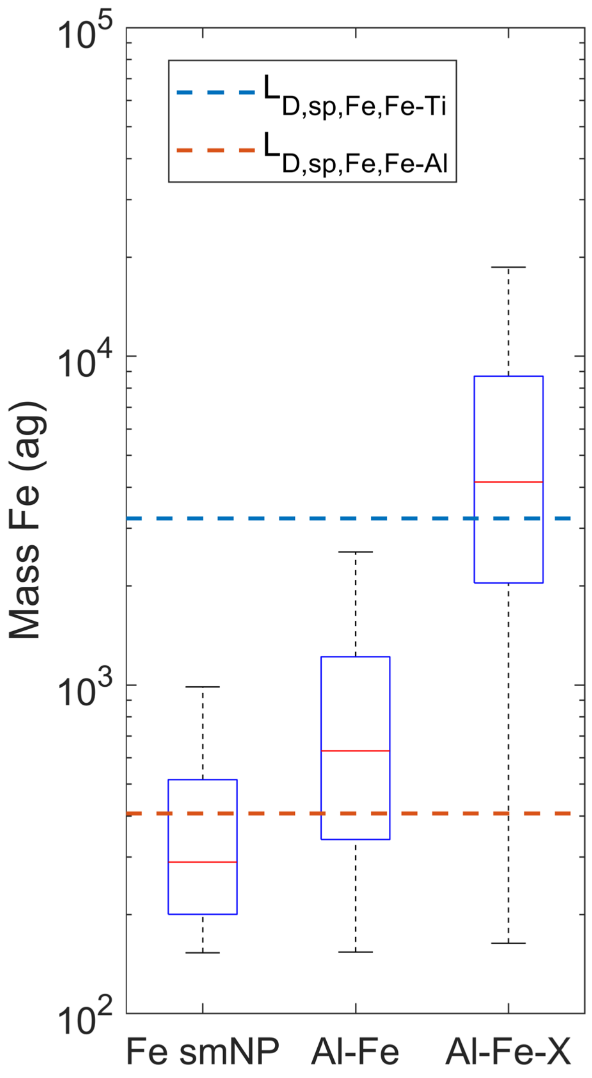


We need 100 fg of Ti to say for sure that no Nb is present – which is almost too big to measure

Particle Composition Conclusions:

- Sp ICP-TOFMS allow classification of particles as Single Element or Multi Element
- To make sure NPs are classified correctly, we need:
    - Sensitivities of each element
    - A known conserved ratio between elements
- In our case study of MDA, we can confidently say:
    - Fe and Al Single Metal NPs are too small to accurately classify them as such
    - Ti Single Metal NPs likely don't contain Al or Fe, but trace elements like Nb largely aren't detected
- **We need to make these determinations even in the absence of known element ratios – how?**





Questions to be explored: Revisited

- Can a standard dispersant/ionic strength be used for test particles to match stability of the standards?
- Can we (should we) determine the aggregation state for the test particle in the test media?
- Standard mixture of sizes (what proportions)?
- For spICP-MS 1-5 micron metal containing standards of different composition to test upper limit of transport and ablation
- What is the best approach for reporting broad (polydisperse) size distributions?
- How do we classify particles if there is no constraining element ratio to establish a size cut off for the major element? (i.e when is the particle too small to contain sufficient mass of minor element)

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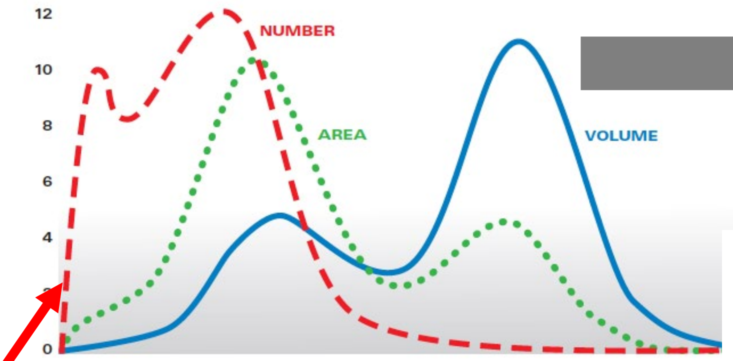
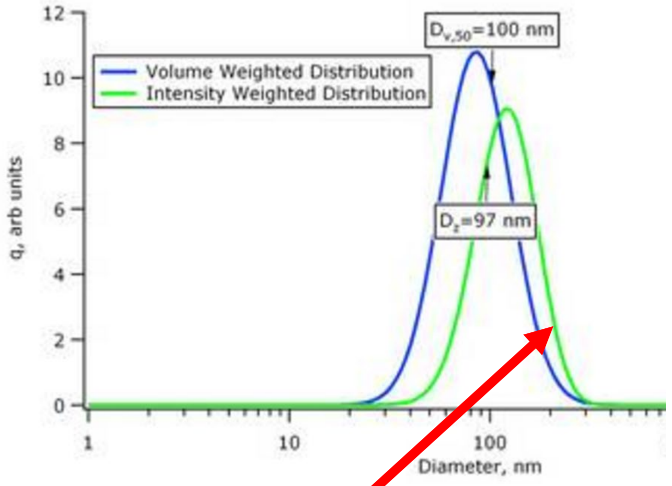
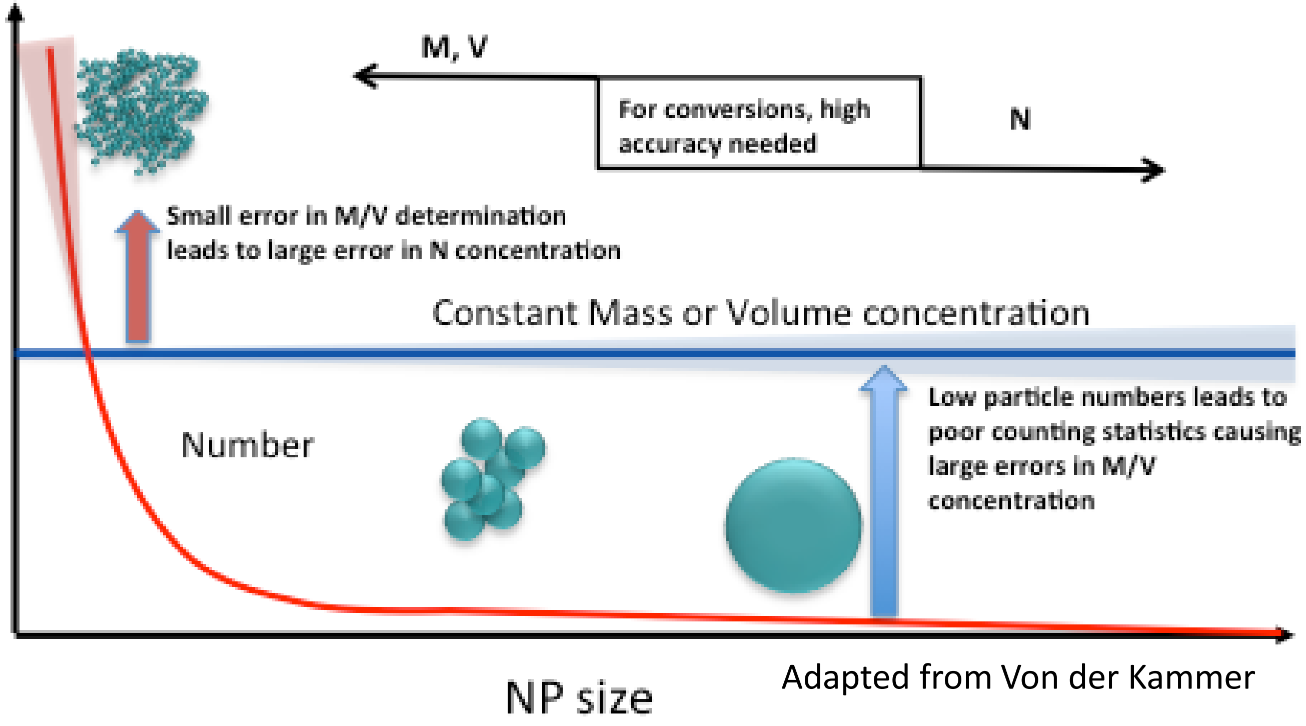


Inter-conversions of Data

- # ⟷ Area ⟷ Volume ⟷ Intensity





Adapted from Von der Kammer

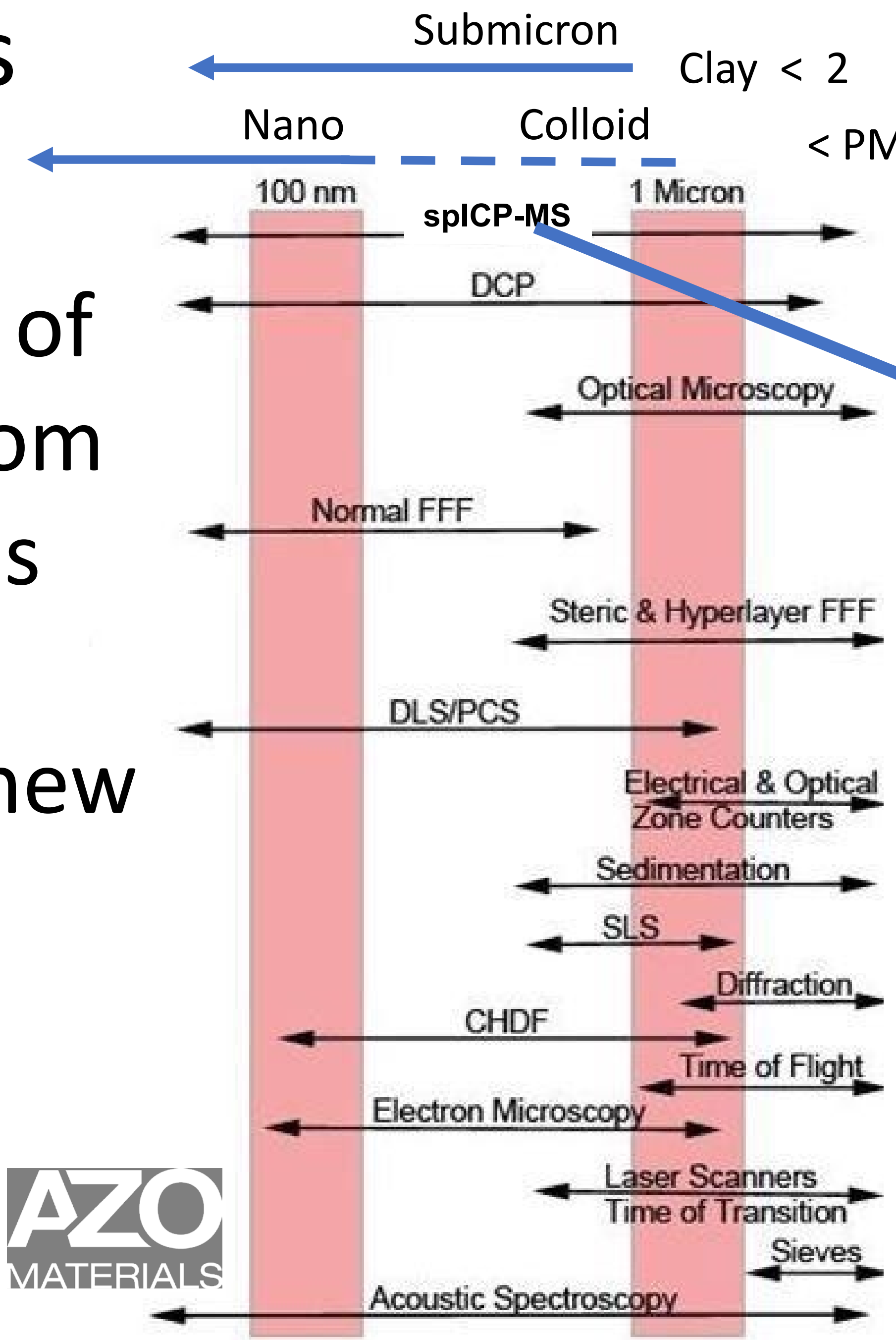
Counting Methods

Light Scattering Methods (Intensity-weighted)

Data Collection Tools

There is an abundance of techniques to chose from for aqueous dispersions

New methods lead to new information & more metrology questions.



Single particle ICP-MS

Counting and sizing by elemental analysis

Legend:
XDC: Scanning X-ray Disc Centrifuge
DCP: Disc Centrifuge Photosedimentometer
FFF: Field Flow Fractionation DLS: Dynamic Light Scattering
PCS: Photon Correlation Spectroscopy
SLS: Static Light Scattering
CHDF: Capillary Hydrodynamic Fractionation