Recent Advances in Nanoparticle Analysis Using ICP-MS

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Detection of Engineered Nanomaterials: Semi-Conductor Facilities and Consumer Devices (*Task Number: 425.040)*

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- Xiangyu Bi, PhD candidate, School of Sustainable Engineering & The Built Environment, ASU
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- Manuel Montano, PhD candidate, Chemistry, CSM
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- Project Goals:
- Develop analytical methods for detecting and quantifying trace quantities nanomaterials relevant to the semiconductor industry in waste and recycled water, in lab air, and leached from packaged semiconductors
- Develop analytical methods for NM size distribution and quantification
- Develop capability to monitor NMs used in semiconducting manufacturing in air and water
- Assess NM release or leaching from electronic devices

CSM Acknowledgements

Current CSM Students working on Nano:
Manuel Montano, Robert Reed, Evan Gray, Denise Mitrano
*Not pictured: JJ. Wang, Emily Lesher, Heather Pace

Collaborators

- ***Christopher Higgins (CSM)***
- ***Paul Westerhoff (ASU)***
- ***Brian Majestic (DU)***
- ***Tony Bednar, Jessica Coleman, & Alan Kennedy (USACE)***
- ***Howard Fairbrother (JHU)***
- ***Ken Neubauer, Andy Salamon, Chady Stephan, and Hamid Badiei (Perkin Elmer)***
- ***Soheyl Tadji (Postnova)***
- ***Scientists at the National Measurement Institute, Sydney Australia***

Funding

- ***National Institute of Health Grand Opportunities (RC2) program Grant DE-FG02-08ER64613***
- ***US Army Corps of Engineers Grant Number W912HZ-09-P-0163.***
- ***USEPA STAR grant program RD-83332401-***
- ***SRC Task Number: 425.040***

NATIONAL INSTITUTES OF HEALTH

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # RD-83332401-0

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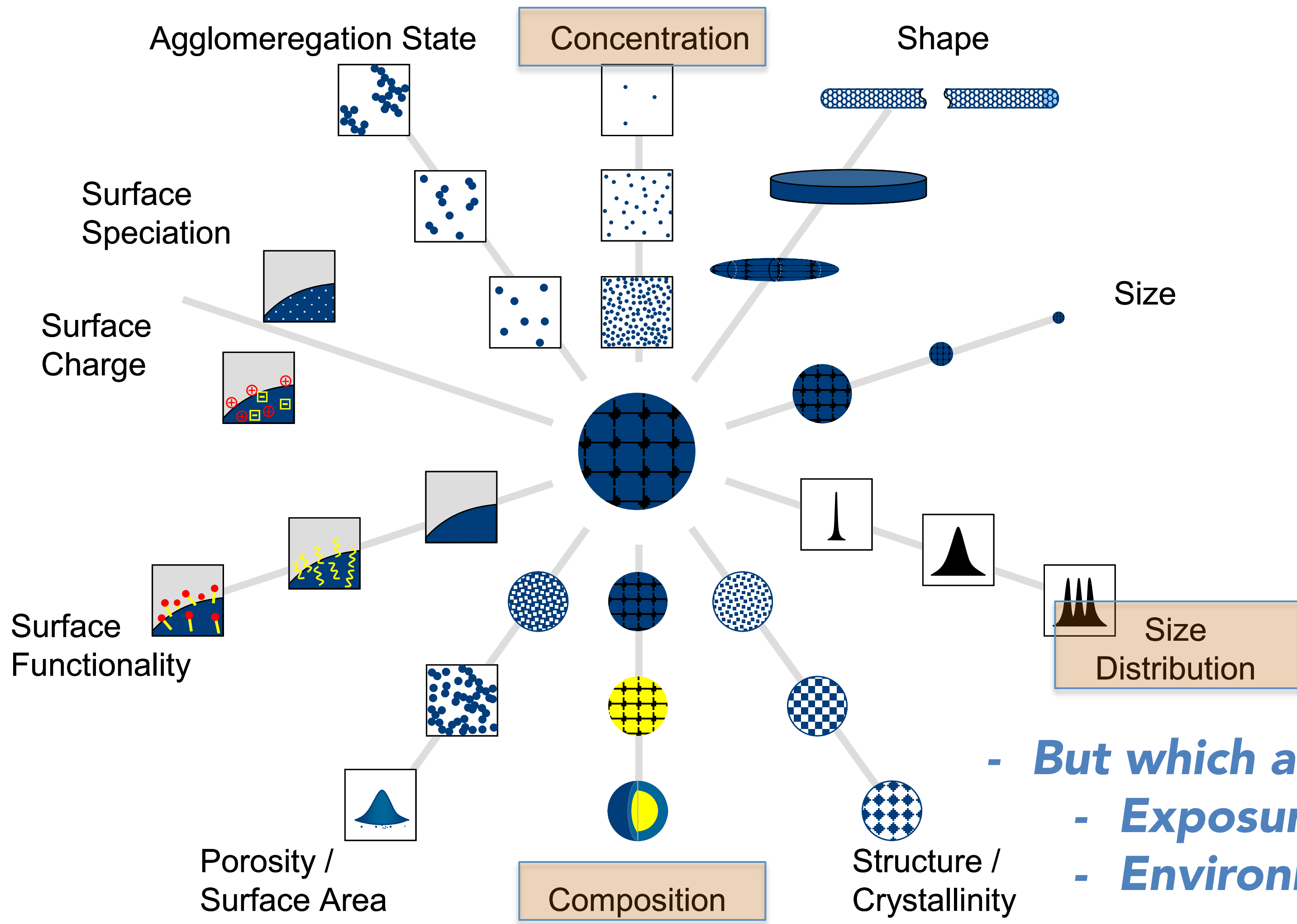
Nanomaterial Characterization: ***There are <u>many</u> parameters that can be measured***



- ***But which are critical to:***
  - ***Exposure assessment***
  - ***Environmental fate ?***

Hassellöv, M. and Kaegi, R. (2009)

There are <u>many</u> nanometrology methods available: what level of analysis is needed?

increasing effort & information

- Detection ((nano)particles are in the sample)
- Characterization (size distribution, composition, …)
- Identification/Differentiation (natural/engineered NPs are in the sample)
- Quantification (how many (# or mass) ENPs are in the sample)

modified from v.d. Kammer et al. ET&C 2012 & TRaC 2011

Topics of the talk

* Development of nanometrology techniques for characterization of metallic NPs
* Comparison of techniques

Method Development

* Implementation of techniques for "real world" studies
  * NP stability (nano Ag)
  * Product release (CNTs)
  * NP biological uptake (nano Au & Ag)

Implementation

* Collaborations with ICP-MS manufacturers

New Approaches

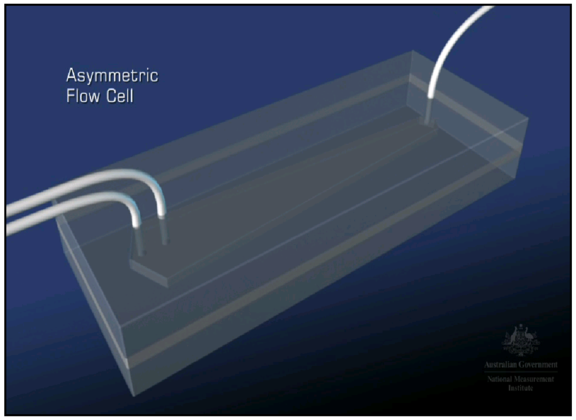
* Development of nanometrology techniques for characterization of metallic NPs
* Comparison of techniques

Method Development

- Characterization by FFF-ICPMS
- Counting and Sizing NPs by spICPMS

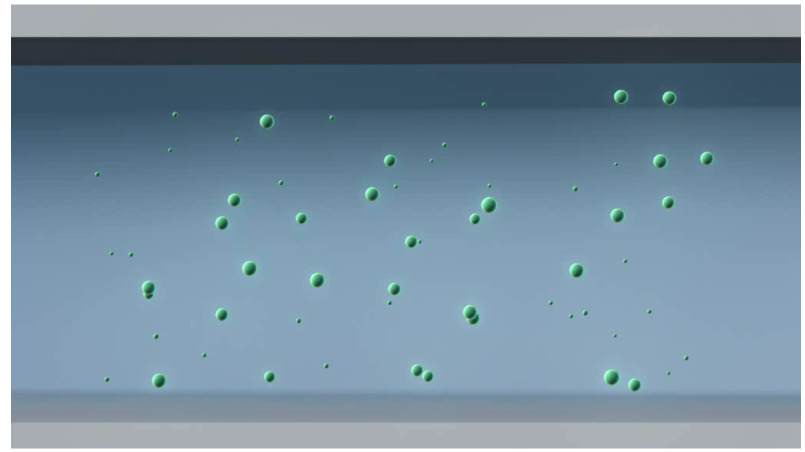
FFF: Diffusion-based method

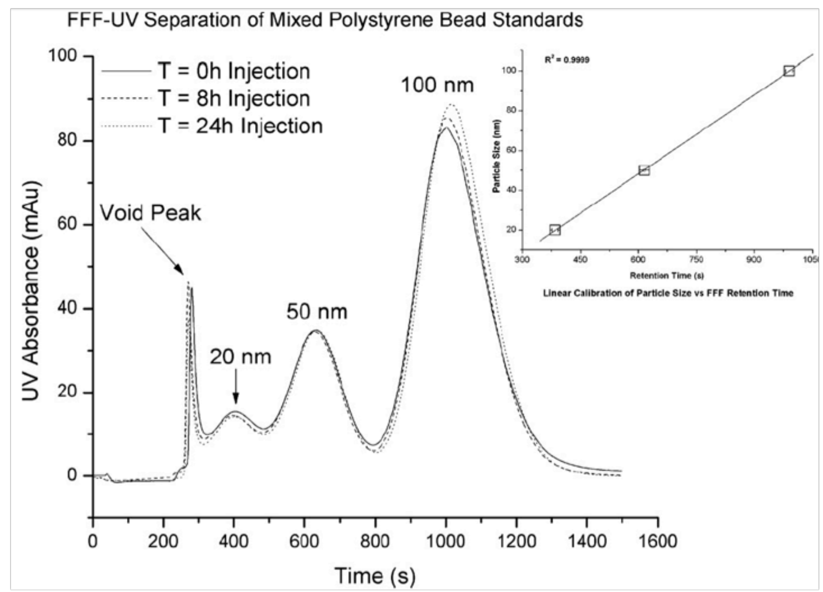
Field flow fractionation



- Applicable from 2-1000nm
- "Size" analysis by theory or calibration
- Multi-element composition data with element specific detectors (ICP)
- Shape analysis by off-line TEM of fractions
- Long analysis times (30-60 minutes) currently limit possibilities for high-throughput applications

Slide courtesy of NMI, Sydney Australia, Animation by MagiPics

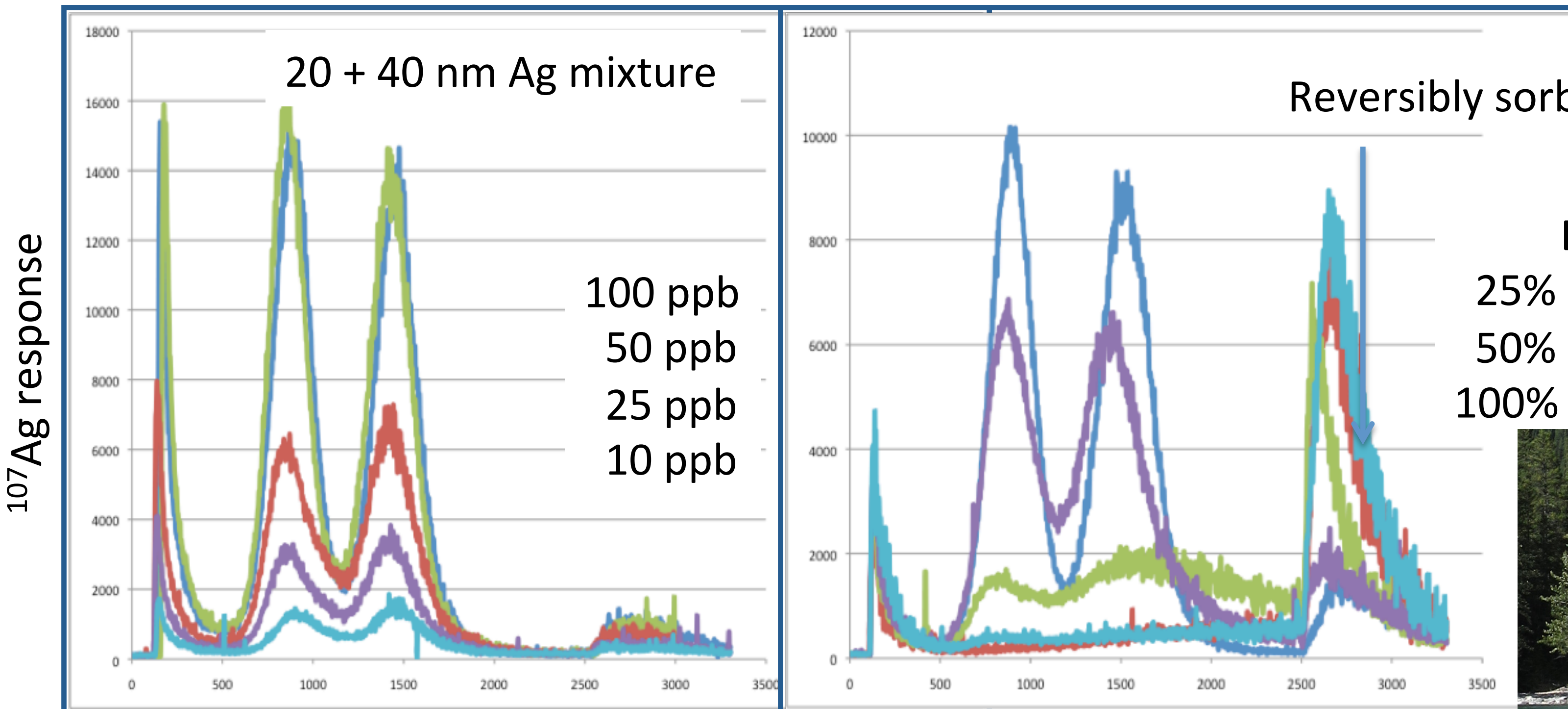




Bednar et al, 2012

Flow field flow fractionation-ICPMS

- ***Complex matrices, in this case cell line fluid (DMEM), can affect recovery and resolution (NP interaction with the AF4 membrane)***
- ***Significant method development can be required for EHS applications***
- ***Improvements in software/hardware allow for "automated" testing of membrane/carrier composition/flow rate to optimize method (see von der Kammer papers)***

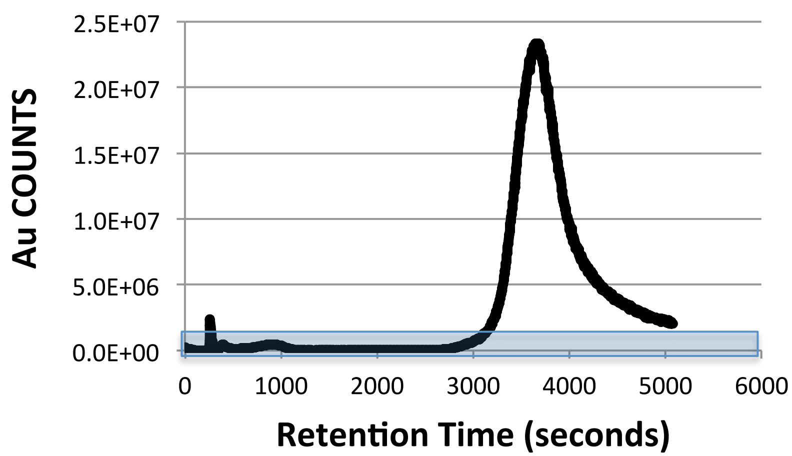


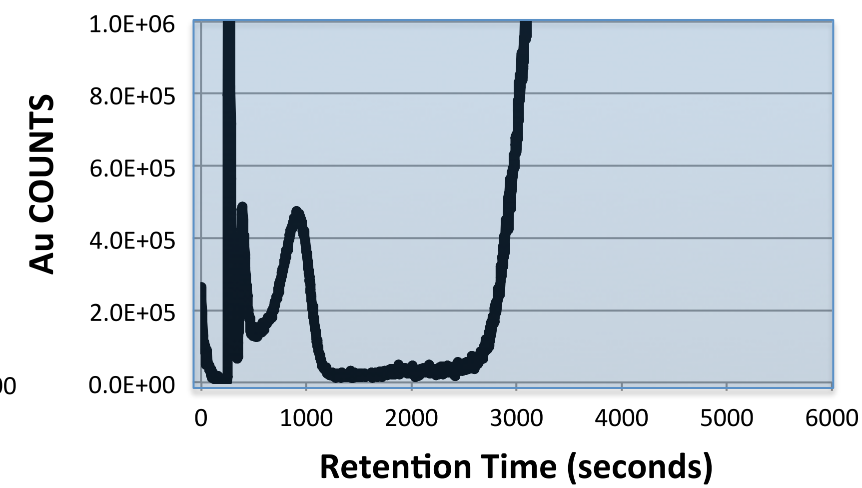
Mitrano et al, JAAS, 2012

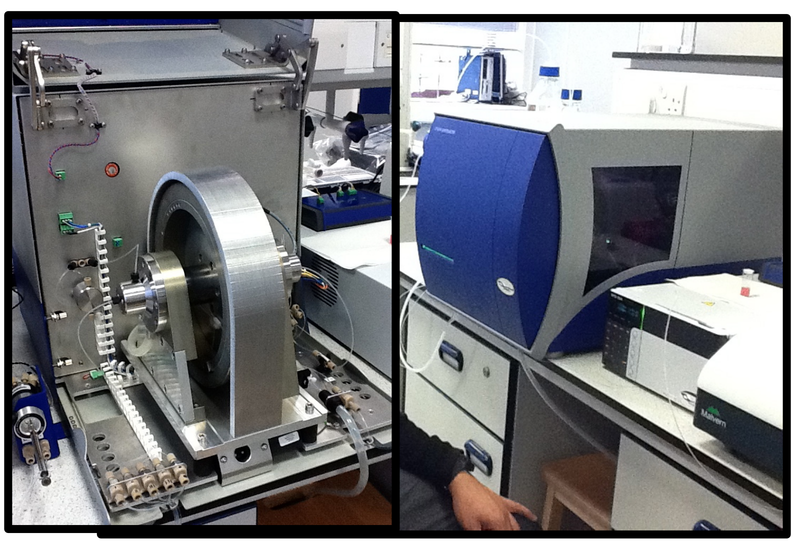
Sedimentation field flow fractionation-ICPMS

NMI (Sydney, AUS) inter-laboratory comparison
Two samples examined: Equal # and equal scattering intensity 20 +100 nm

NPS-4: **Equal number** 20 & 100 nm Au

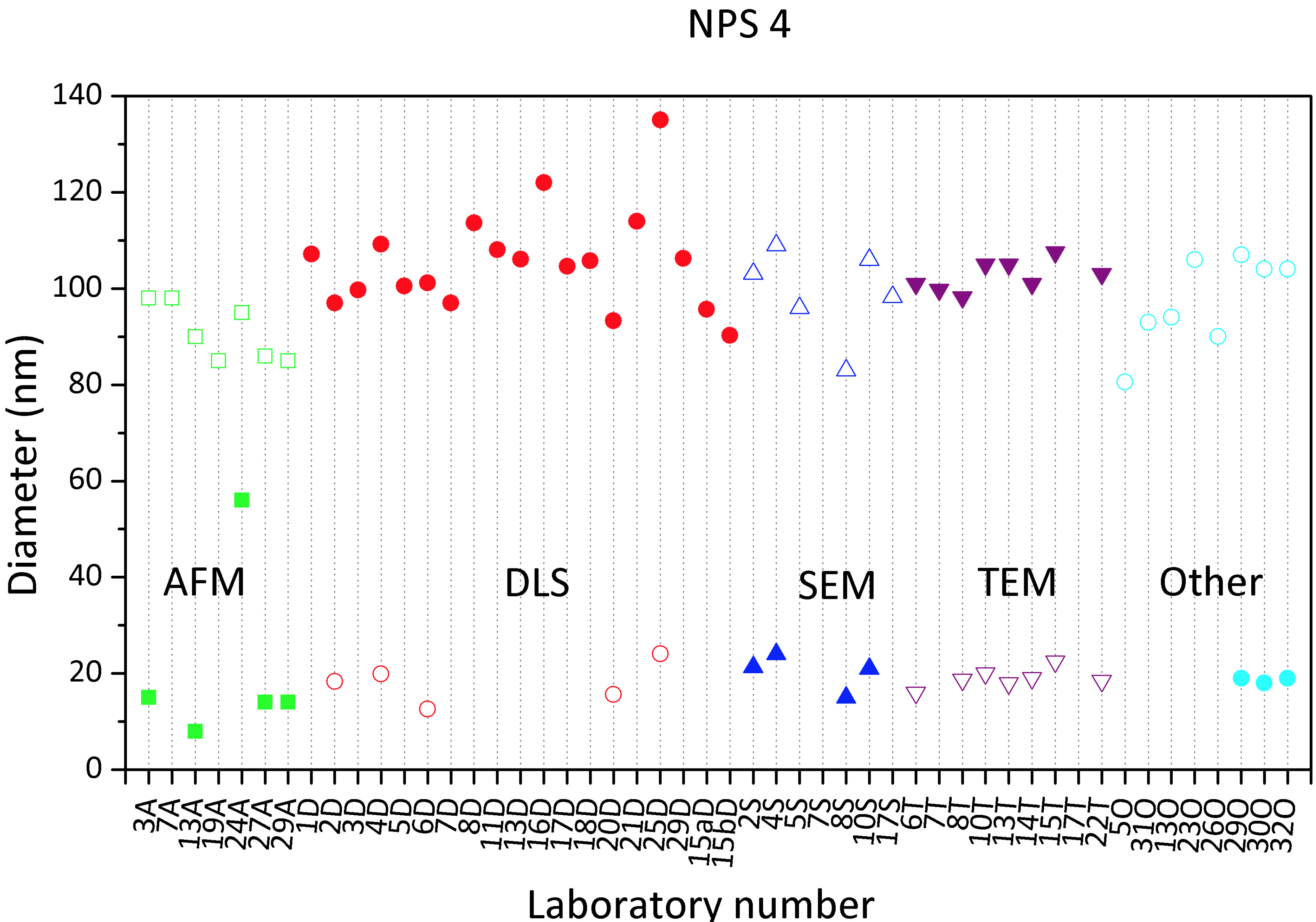






Mass ratio 100nm/20nm: Theoretical 125 (5^3)
Measured 95

- ***Measurement of size and element concentration can be used to compute number-based size distribution for simple ENPs***
- ***Results affected by size-dependent recovery***

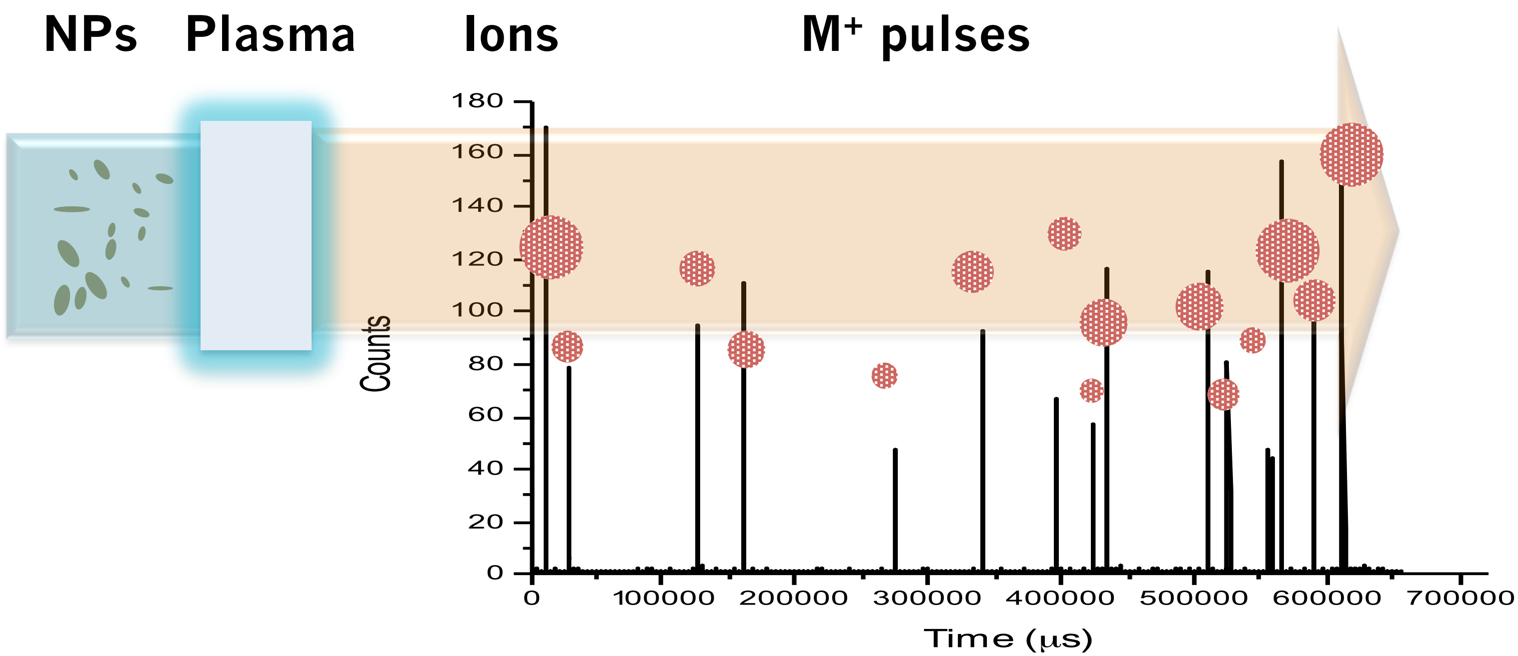


Labs that missed small particle

- 14 out of 19 labs using DLS
- 2 out of 7 labs using AFM
- 2 out of 6 labs using SEM
- 1 out of 8 labs using TEM

A. Jamting, Publication in prep.

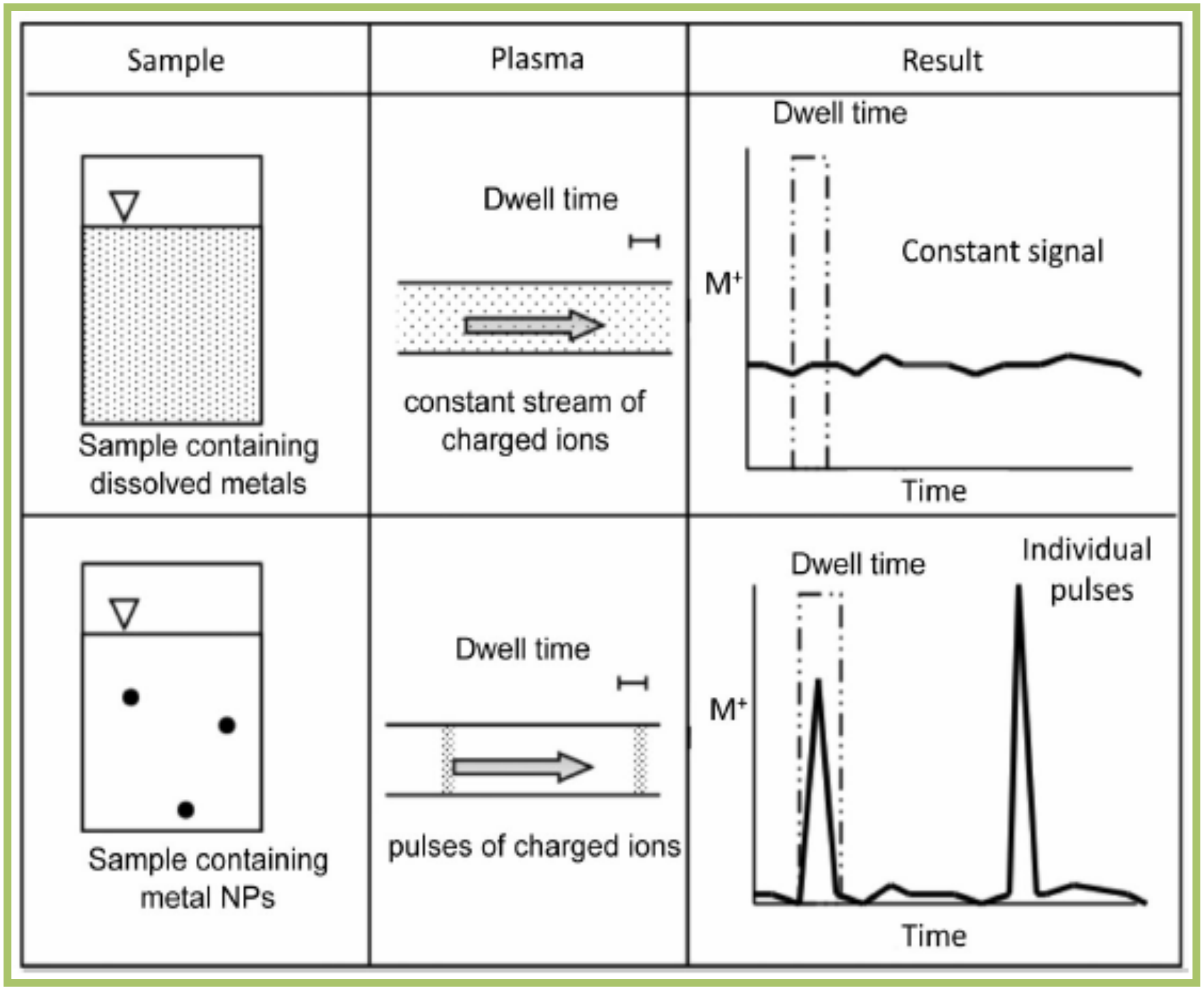
spICPMS: Element-specific counting method



- Uses readily available ICPMS instrumentation
- Method development simpler than FFF
- Provides # distributions
- Higher size detection limit than FFF (depends on MS)
- Single element detection
- Rapid analysis allows for high-throughput applications

Principles of Single Particle ICPMS

- Dissolved analyte gives a constant signal
- Dilute NP solution: single nanoparticle in a single dwell time
- Assumption: one pulse = one particle
- Number of pulses = number of nanoparticles (corrected for nebulization efficiency)
- Size of pulse related to NP size

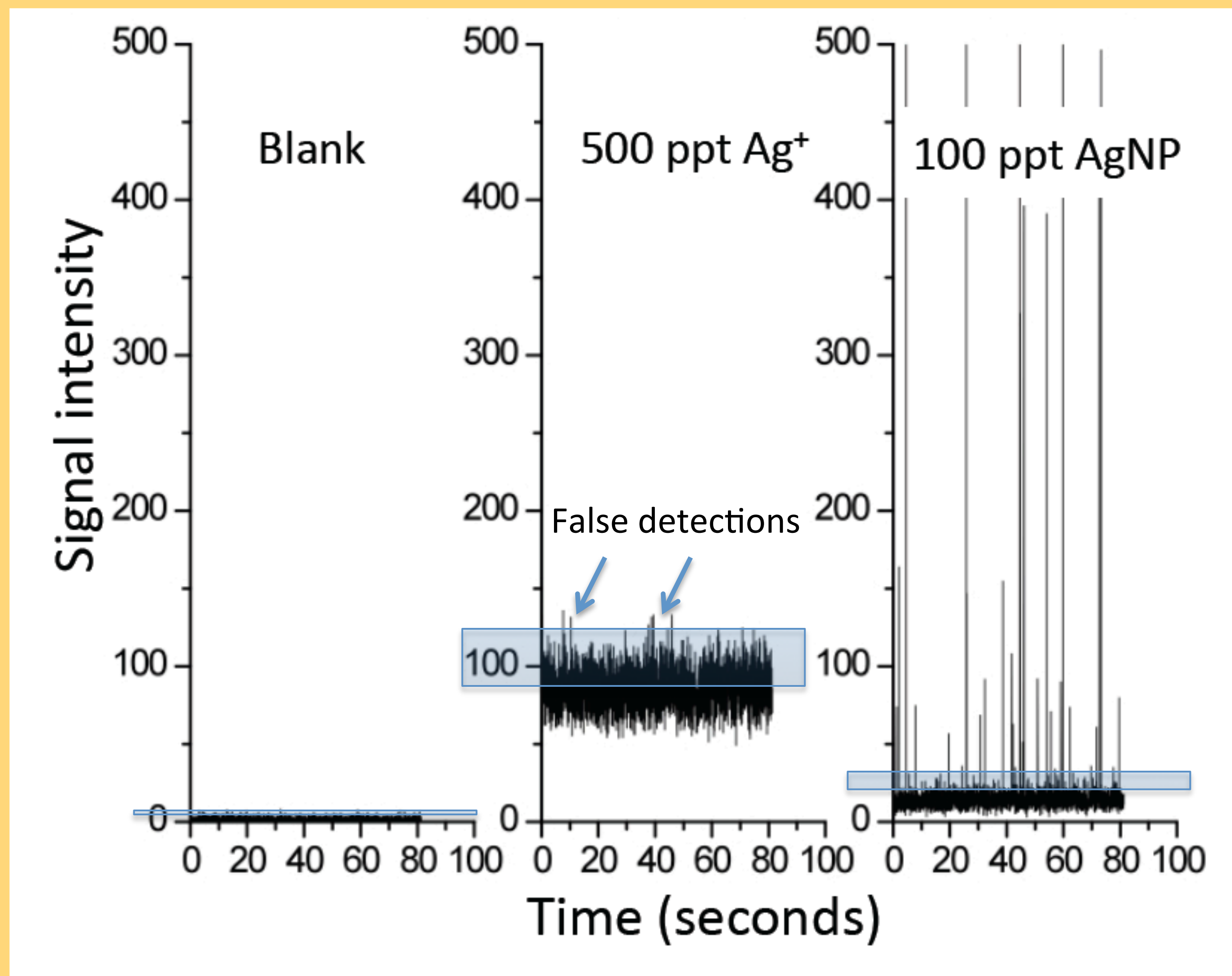


Mitrano, D., **Lesher, E**., Bednar, A. et al. 2012. *Environmental Toxicology and Chemistry*, **31,** 115-121

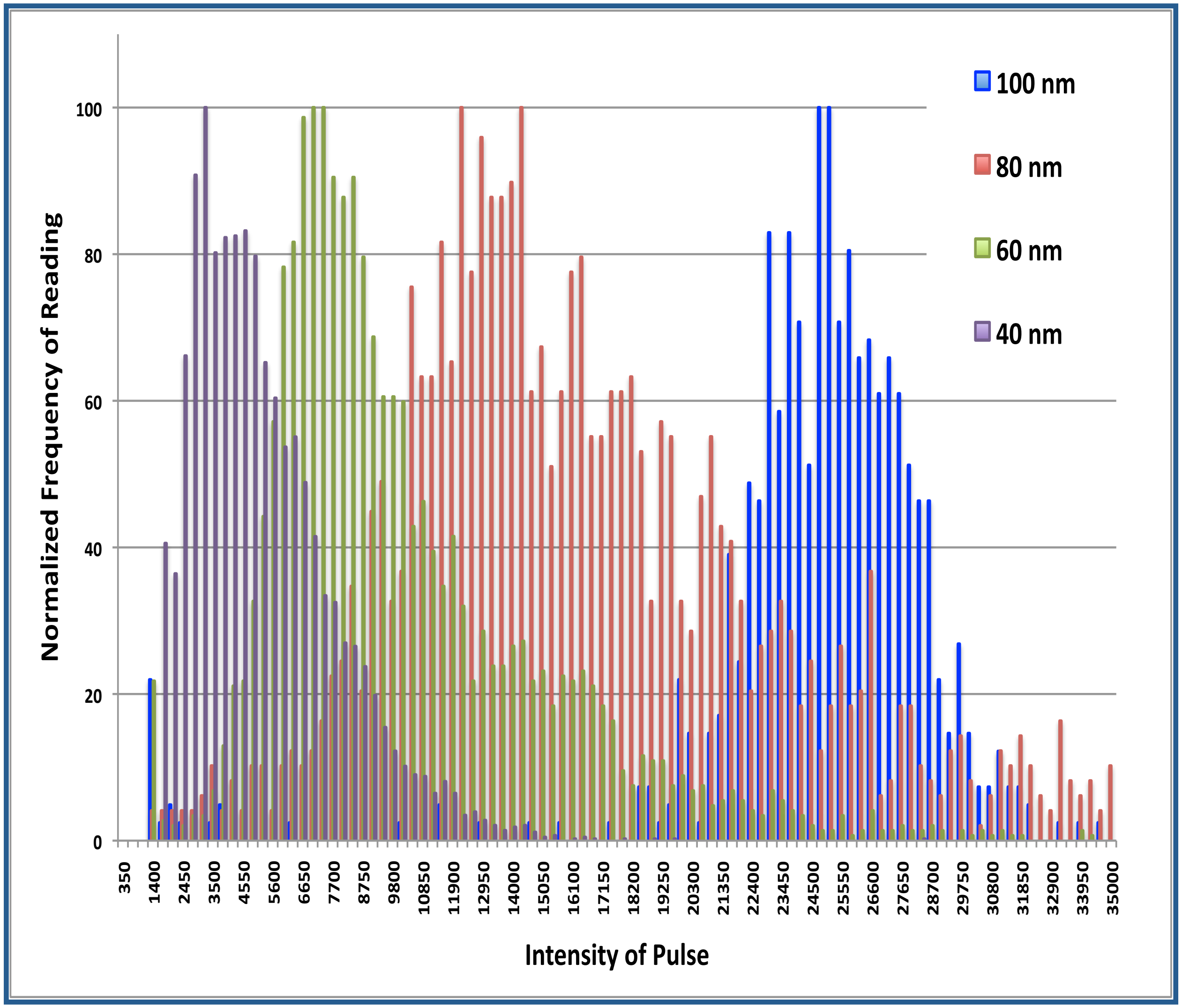
Defining NP size cutoff

Typically choose 3 to 5 σ above background

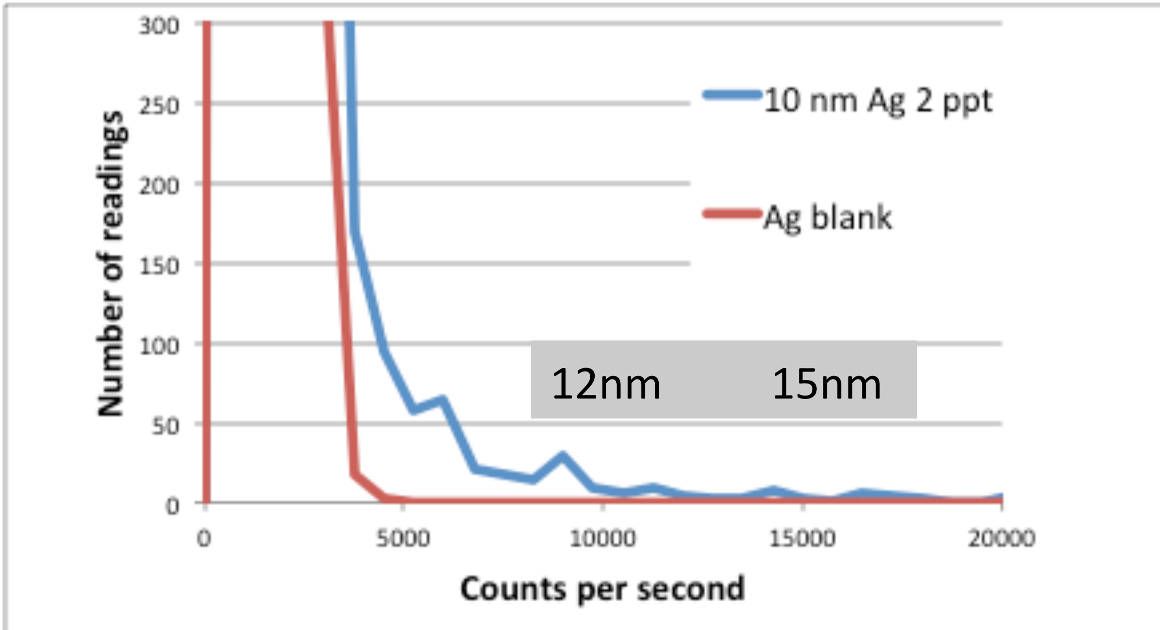
Other statistical approaches examined by ASU team and others

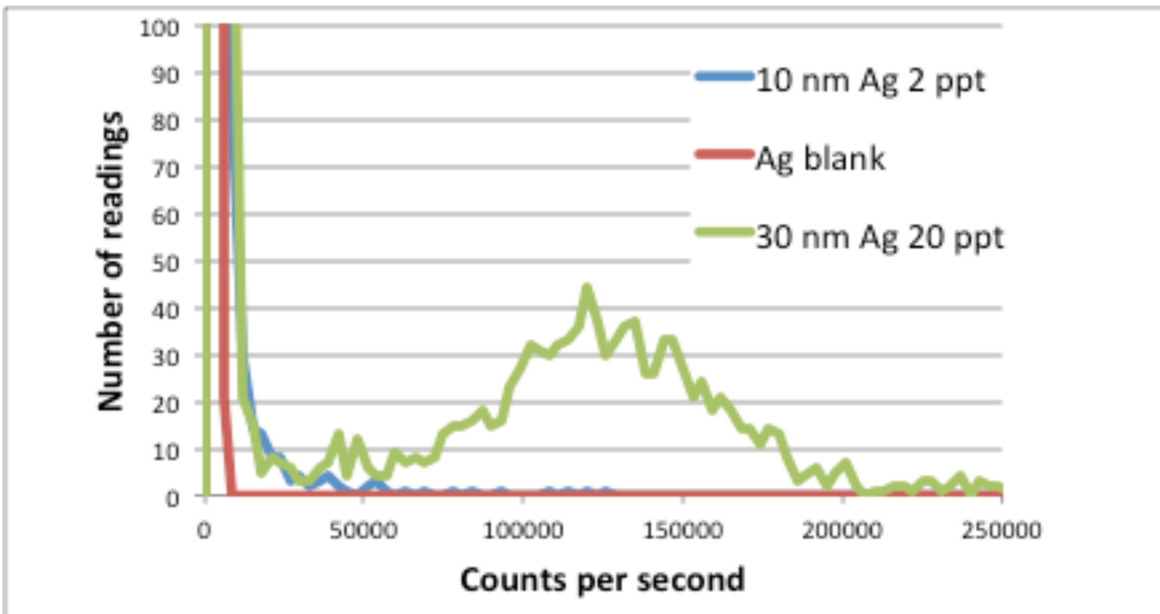


Size Detection Limit



- Normalized frequencies to highest value for each sized particle for clarity
- Background/ dissolved Ag+ omitted from graph (< 1400 cps)
- Smallest detectable particle with Quadrapole ICPMS: 30-40nm for Ag

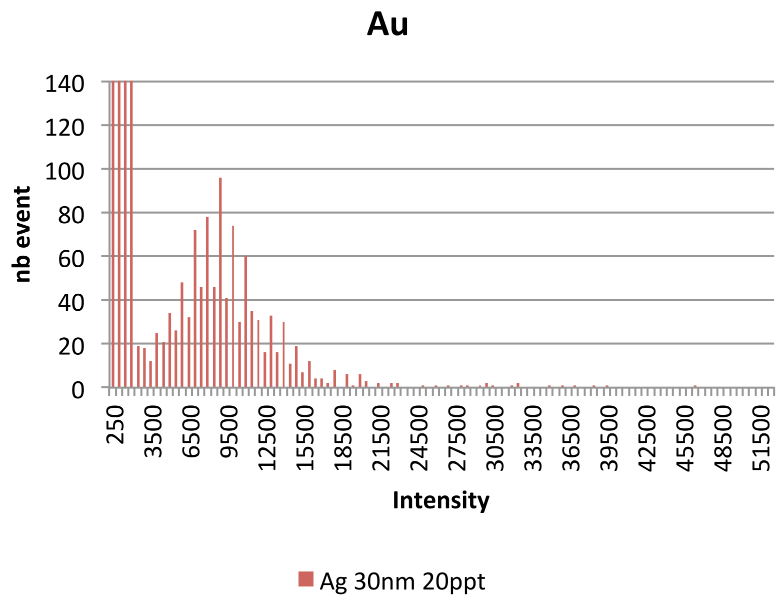




ELEMENT II Size detection limits-Ag

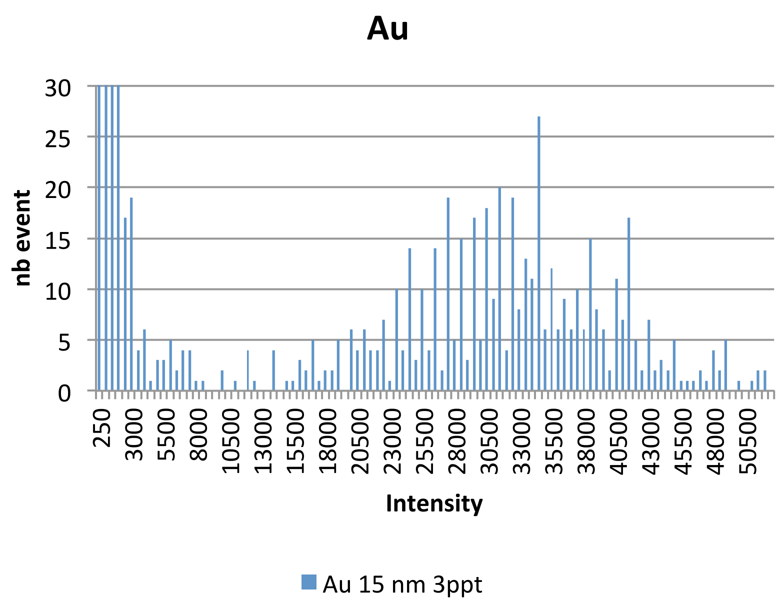
12-15 nm (8000-15000 cps or so) possible?

ELEMENT II Size detection limits-Au



Au seed in 30 nm Ag NP
NanoComposix states the size is 8 nm

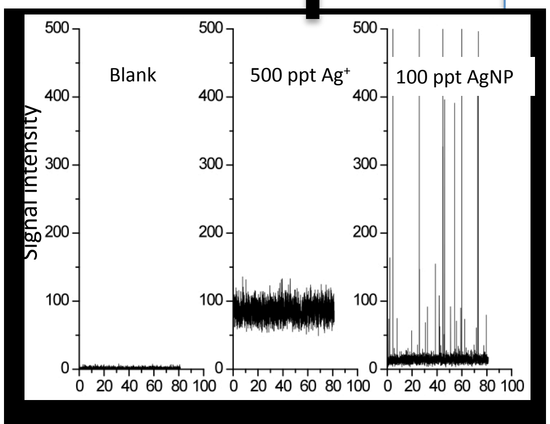
Intensity in cps

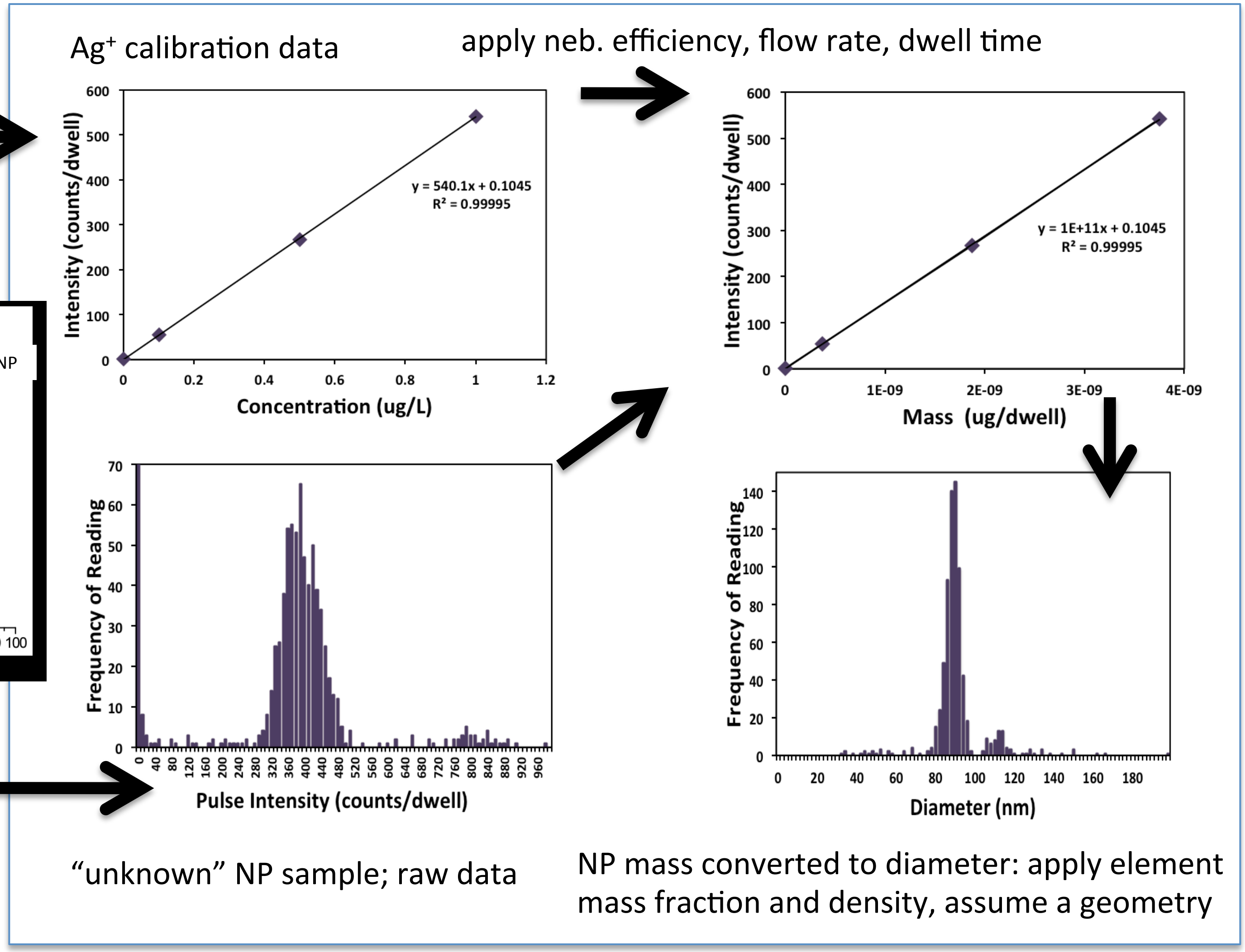


15 nm Au NP

< 7 nm possible?

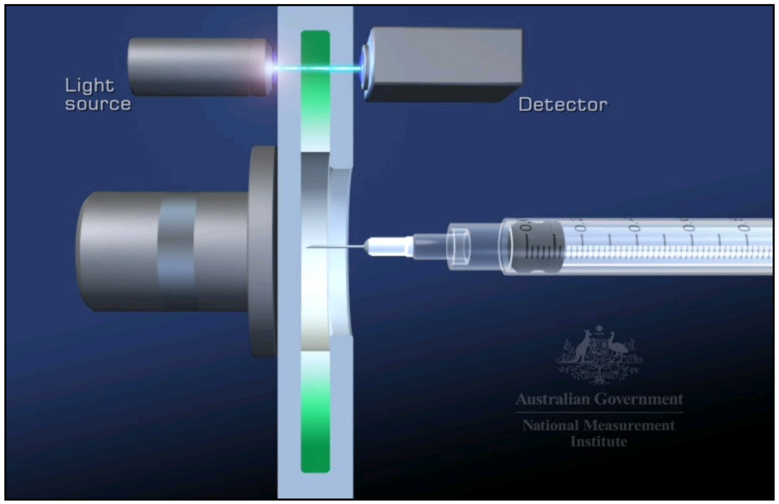
Convert pulse counts to diameter

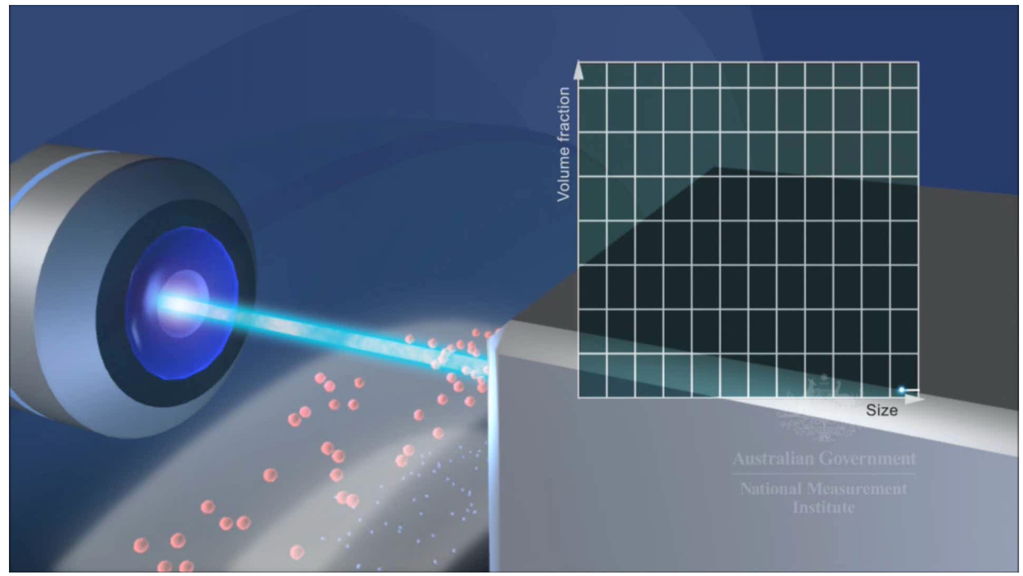


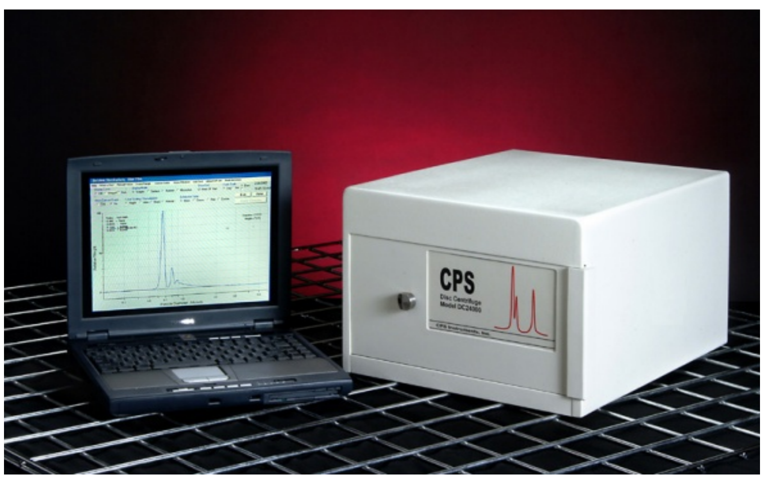


Pace et al. 2011, Anal. Chem, 83, 9361-9369; Pace et al 2012, ES&T, 46, 12272-12280

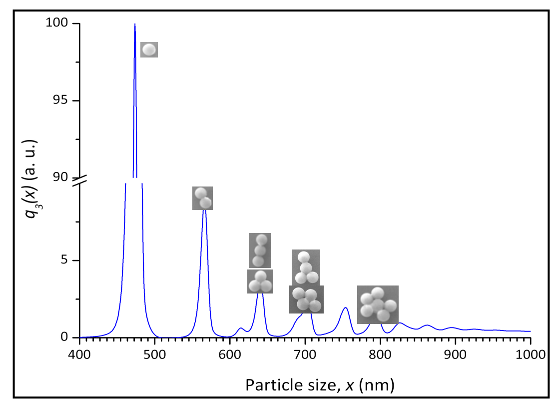
Comparision of spICPMS to Other Methods: Disc Centrifugation







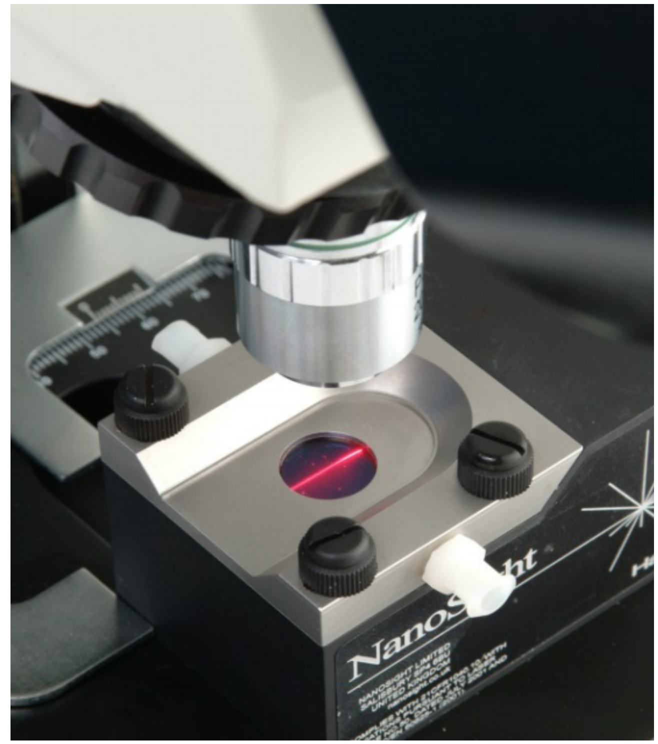
Very high resolution but need to know density



Slide courtesy of NMI, Sydney Australia, Animation by MagiPics

Comparison of spICPMS to Other Methods: Particle Tracking

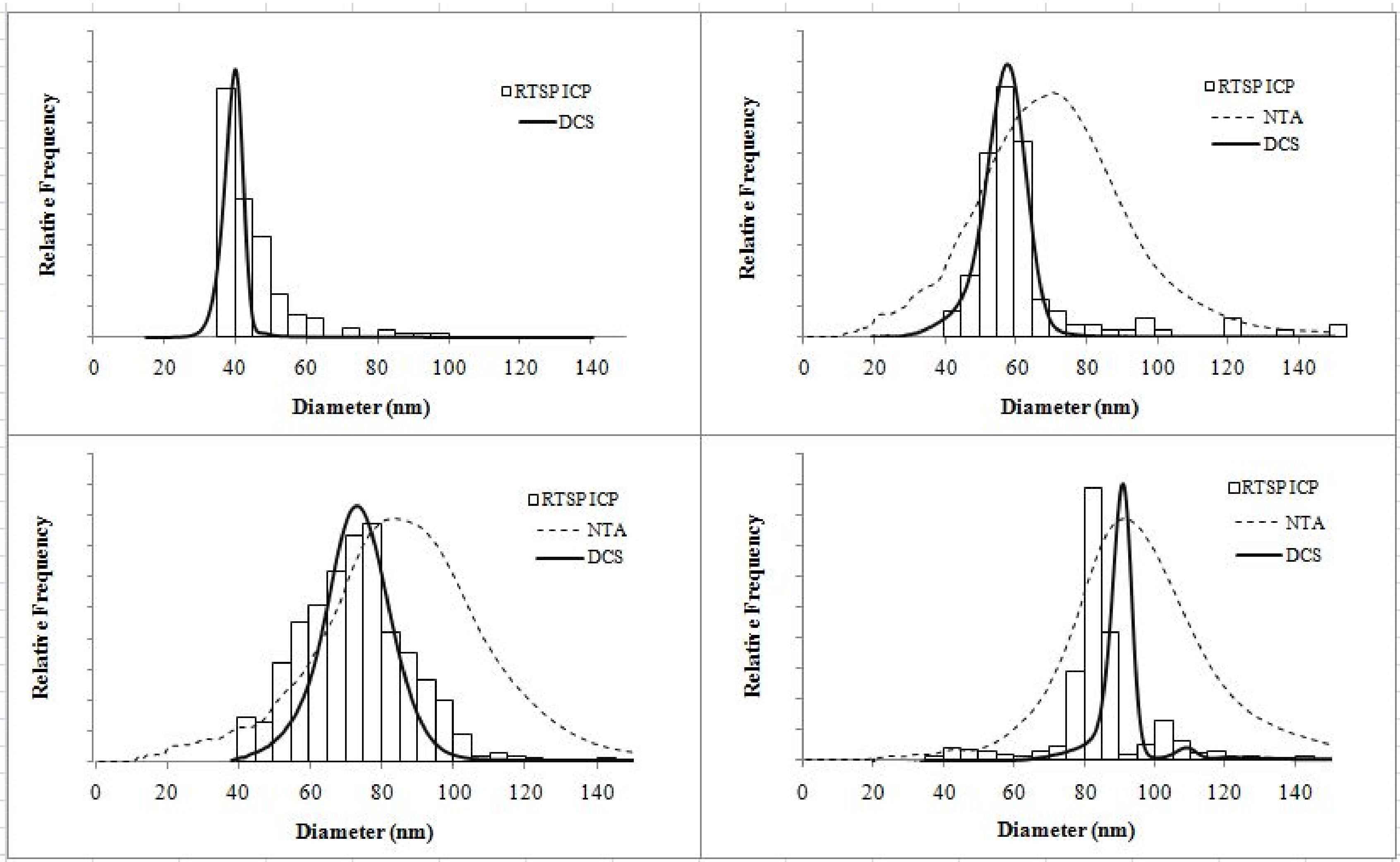
- Visualize particles via laser beam through liquid sample
- Size determined by Brownian motion of visualized particle (hydrodynamic size)
- Able to size polydisperse samples
- Can discriminate particles of different composition via different refractive indices



www.nanosight.com

Method Evaluation

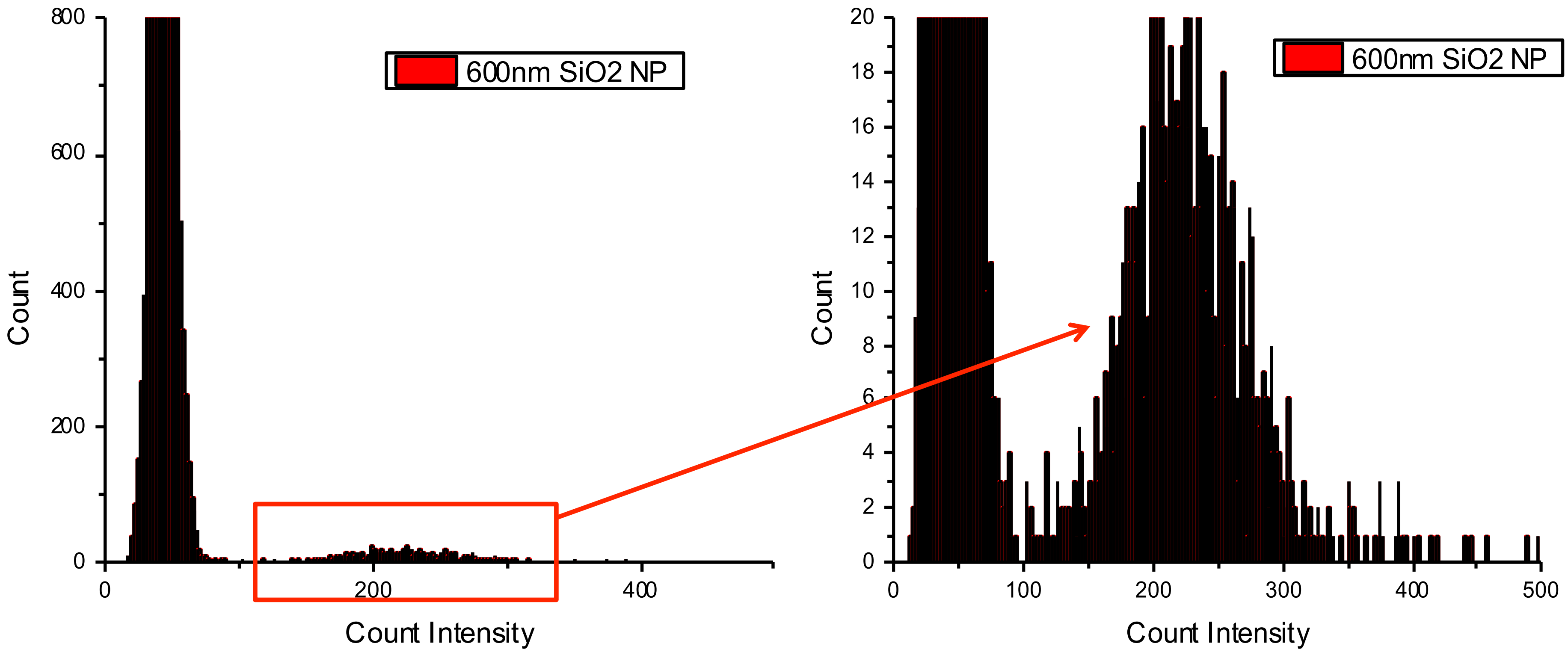
- Comparison ICP-MS to disc centrifuge and particle tacking analysis



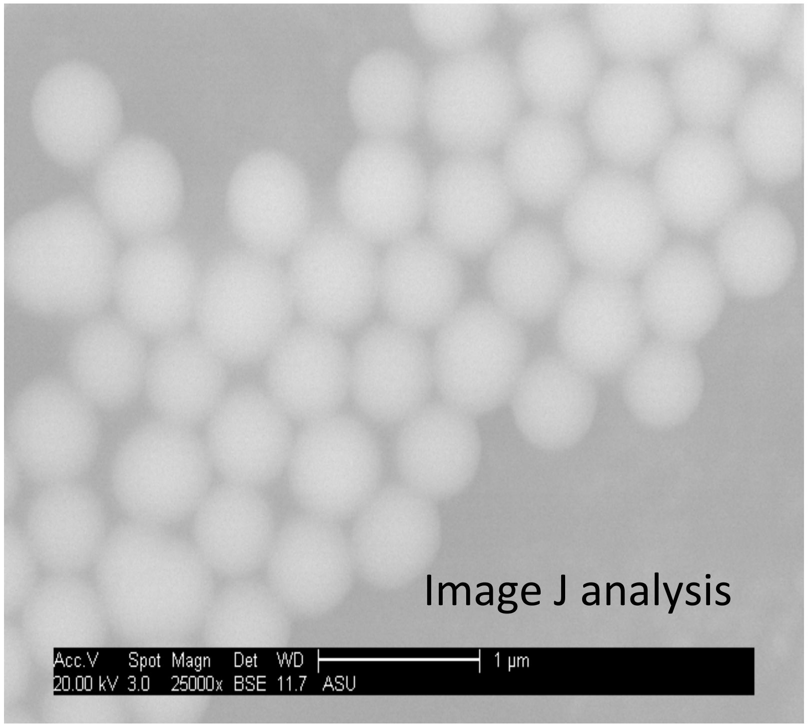
Pace et al 2012, ES&T, 46, 12272-12280

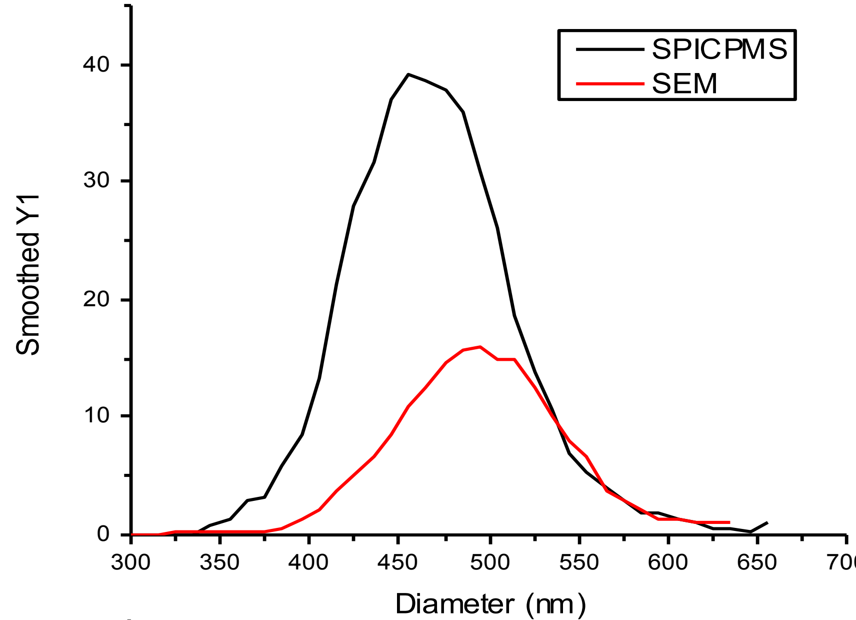
Frequency count of 600nm SiO_2 Data

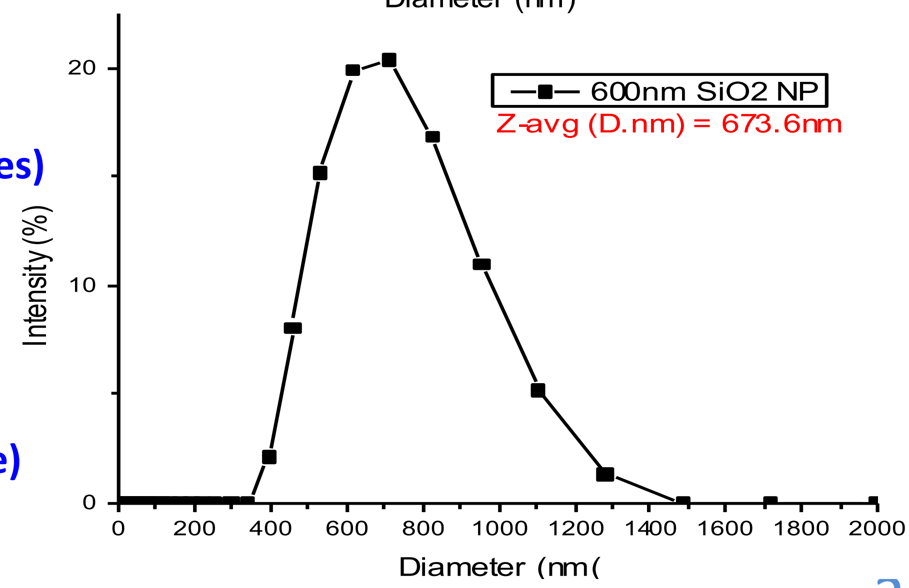
Data collected with an Agilent 7700 using He collision gas (3.5 ml/min)
(Collaboration with University of Denver)



Size Analysis of "600 nm" SiO_2







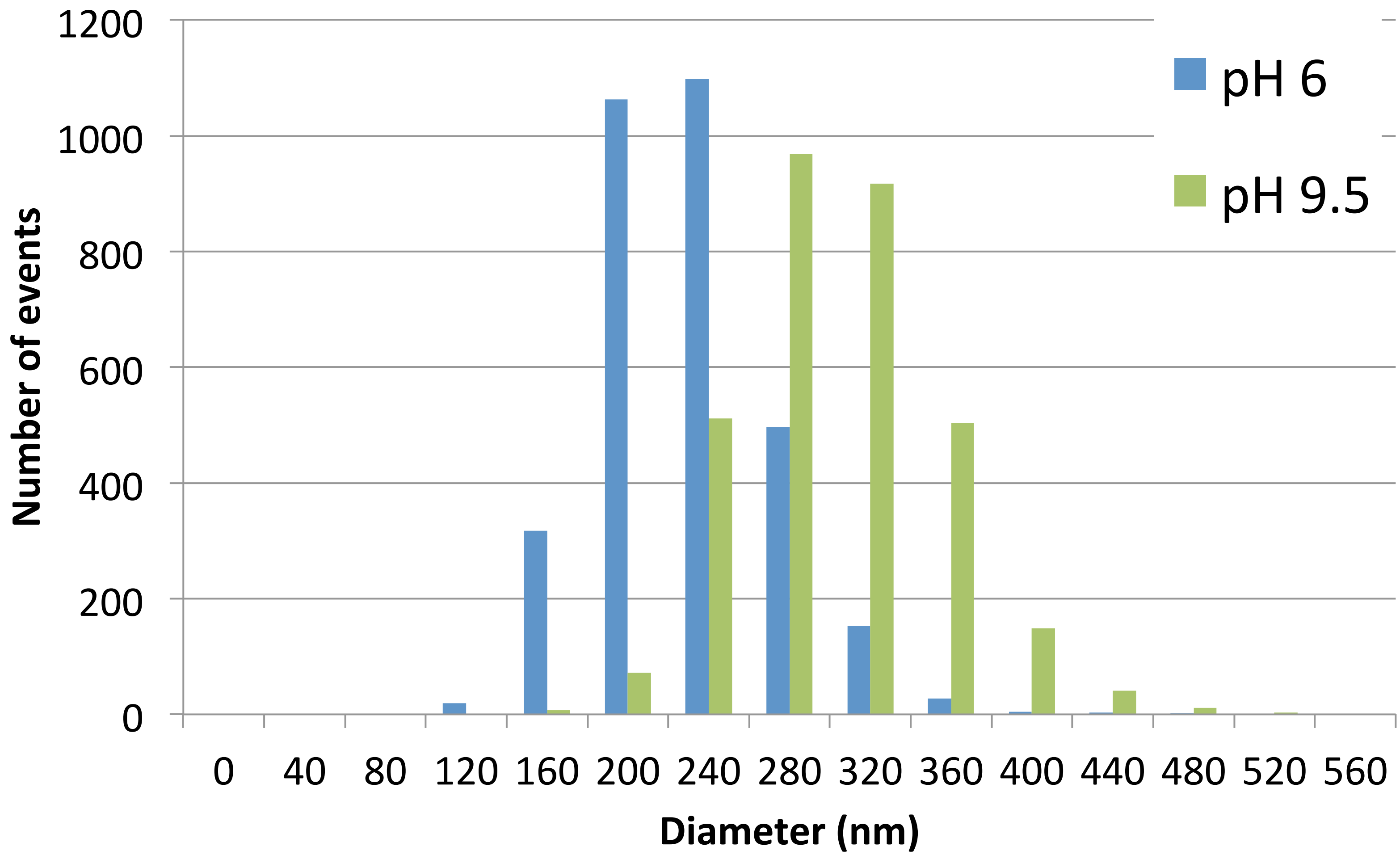
SEM Average size: 495 ± 46 nm (n= 180 particles)
Data collection and analysis: ≈ 60 minutes

spICPMS Mean: 460 nm (n = 430 pulses)
Data collection and analysis: < 10 minutes

DLS Z-average: 674 nm (n = thousands or more)
Data collection and analysis: < 5 minutes

Aggregation of Hematite

Use of spICPMS to study aggregation untested
Preliminary results encouraging



Recent test of spICPMS

Interlaboratory study sp-ICPMS

Thomas P.J.. Linsinger[1], Ruud Peters[2], Stefan Weigel[2]

1 European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Retieseweg 111, 2440 Geel (BE)

2 RIKILT - Institute of Food Safety, Akkermaalsbos 2, 6708 WB Wageningen (NL)

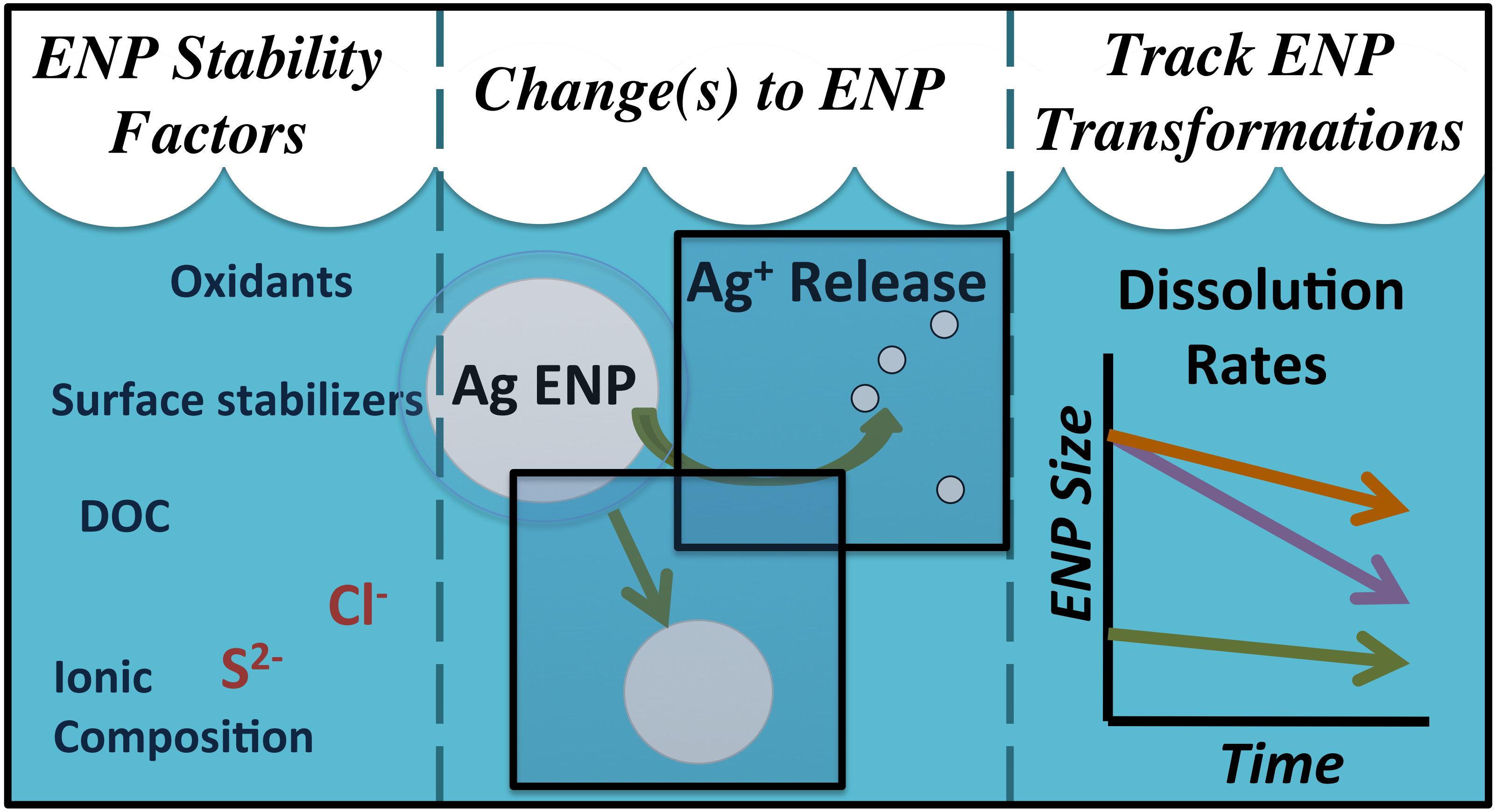
- 21 labs across the globe
- Several Ag nanoparticles mailed out
- ASU and CSM facilities performed excellent – right on measured values
- A few labs showed poor results, but most showed consistent findings
- Validates reproducibility of SP-ICP-MS method

Outline

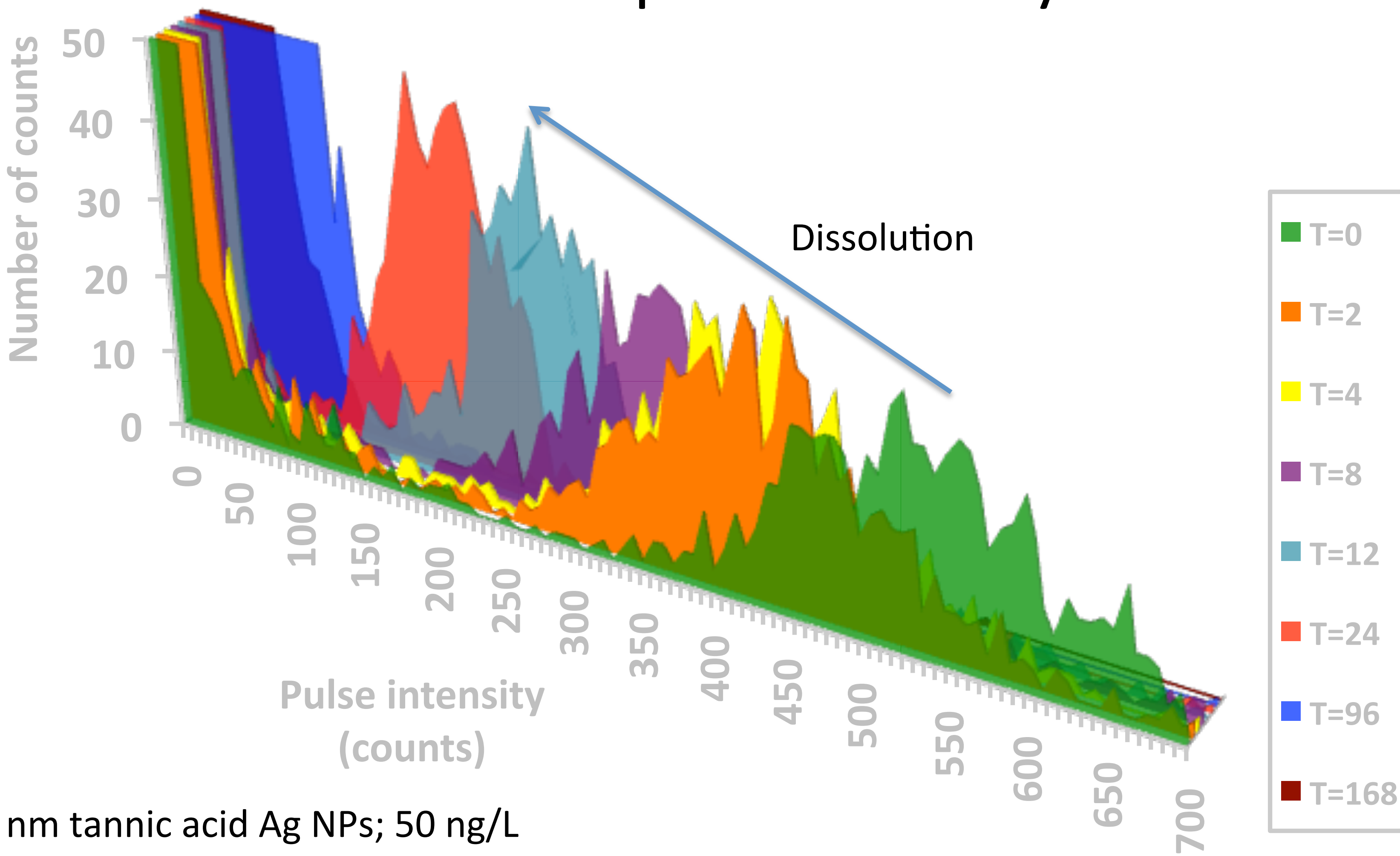
- ∗ Implementation of techniques for “real world” studies
  - ∗ NP stability (nano Ag)
  - ∗ Product release (CNTs)
  - ∗ NP biological uptake (nano Au & Ag)

Implementation

Following NP Transformations



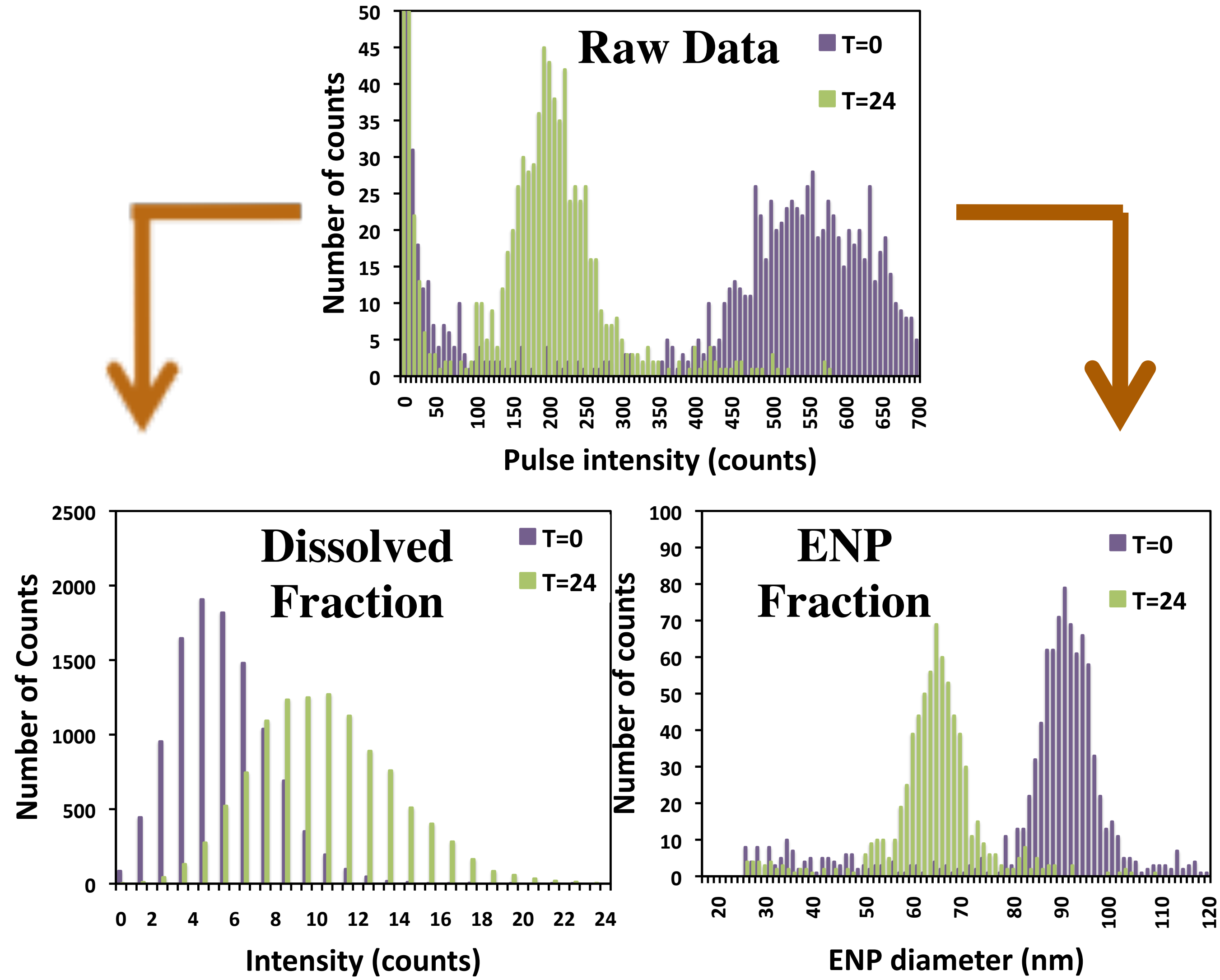
Dissolution vs pulse intensity



100 nm tannic acid Ag NPs; 50 ng/L

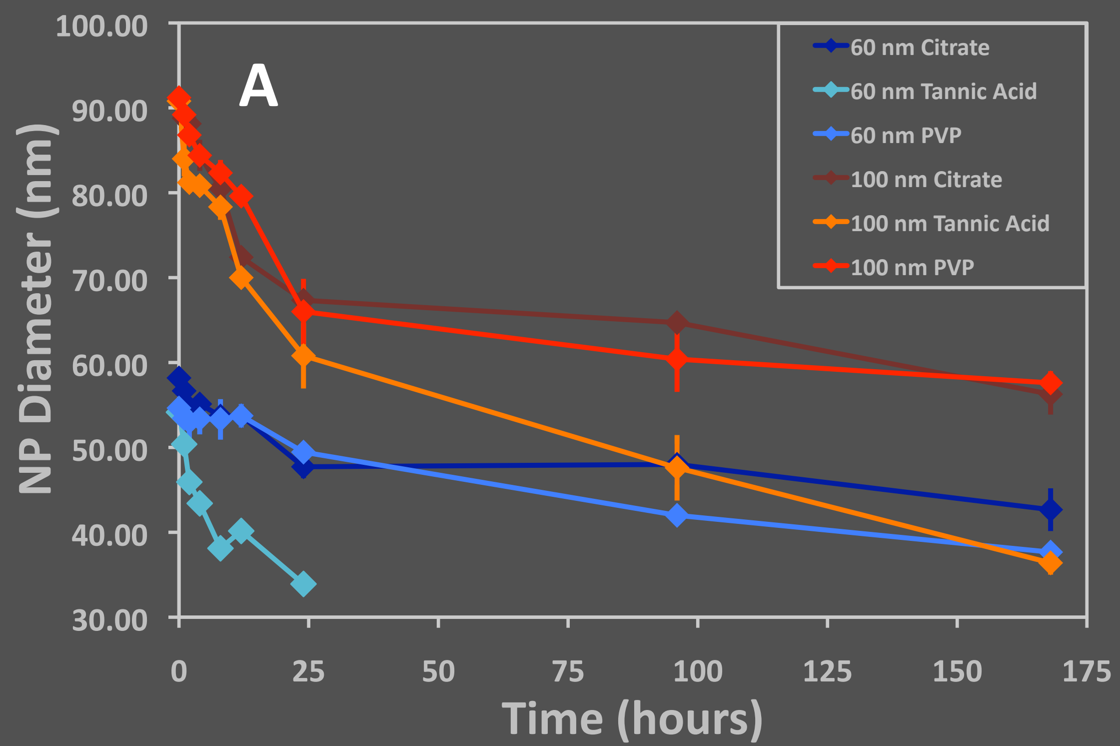
Decrease pulse intensity correlates with decreasing particle diameter

spICPMS: nanoAg dissolution

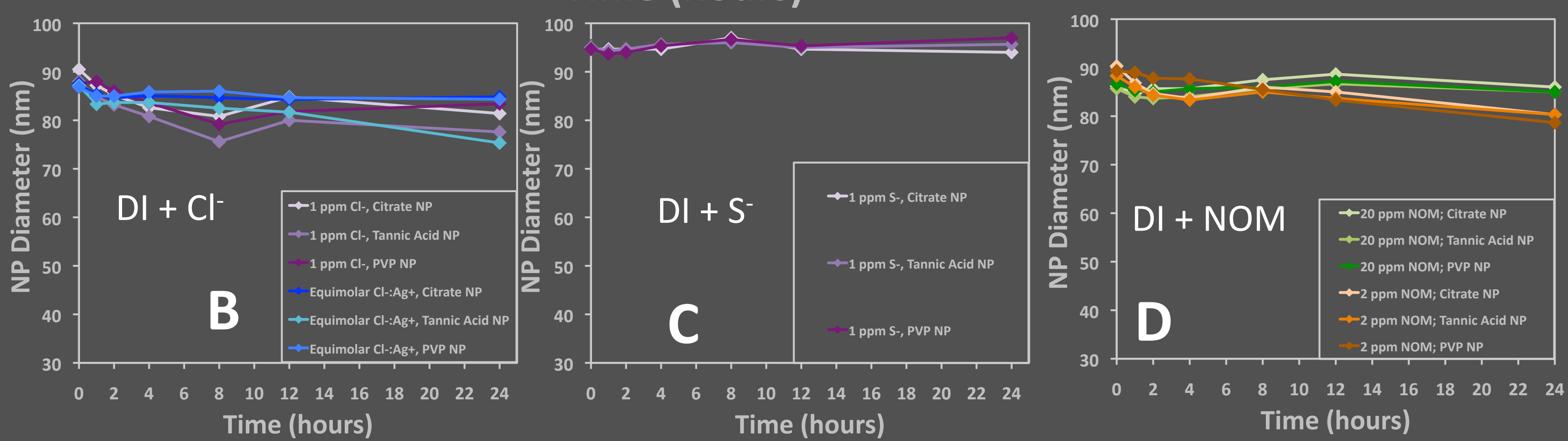


Mitrano et al. JAAS 2012

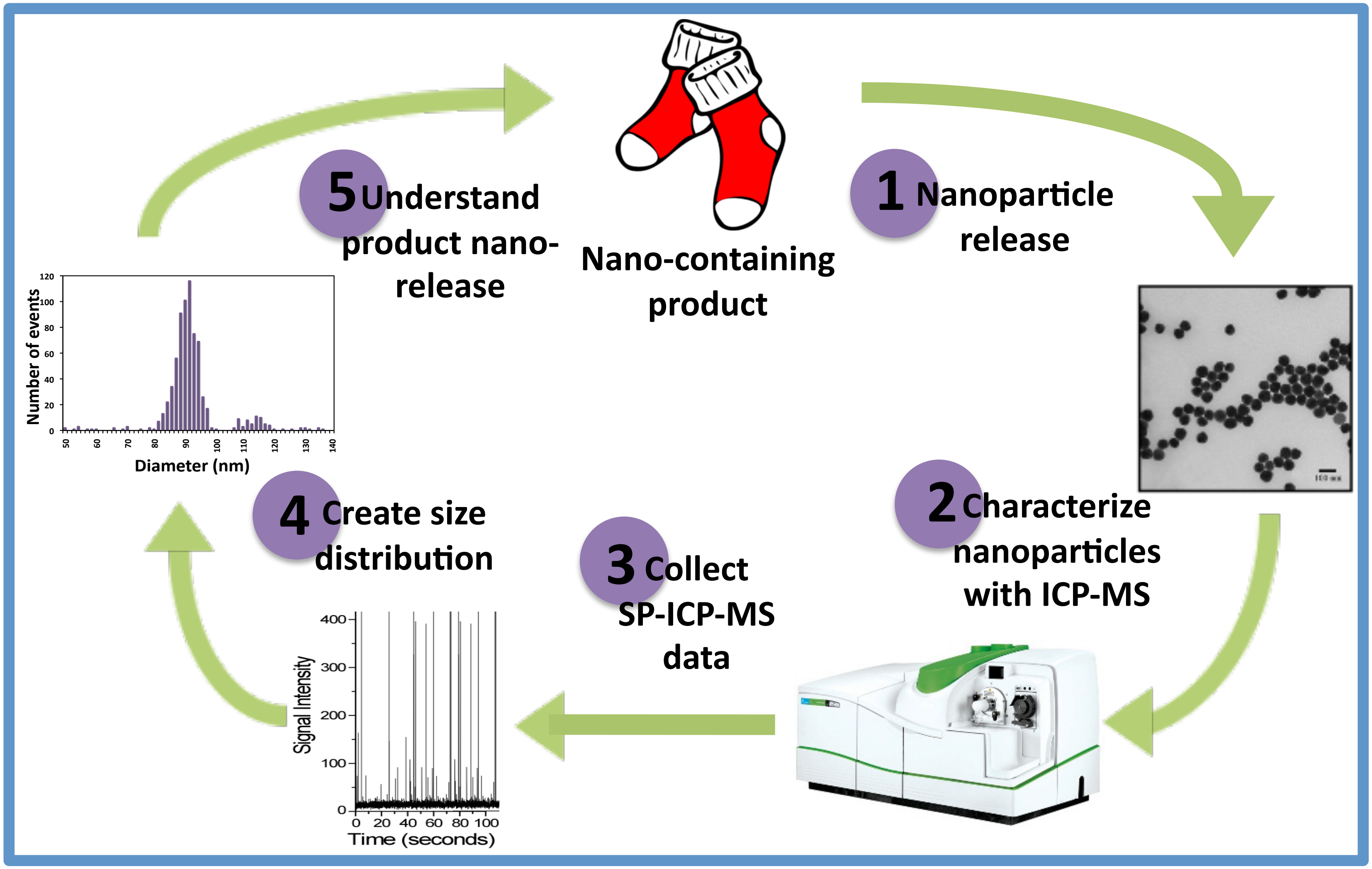
Dissolution in laboratory-prepared waters



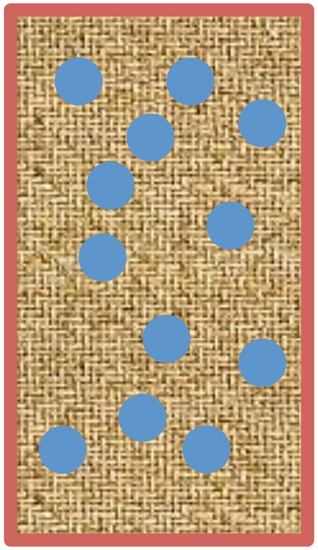
A) Comparison of 60 nm and 100 nm NPs in DI water
B) B) Addition of 1 mg/L and equimolar Cl^-,
C) Addition of 1 mg/L and equimolar S^-
D) Addition of 2 and 20 mg/L NOM



Applying spICPMS to product release studies



spICPMS can be applied to carbon-based NPs



NMs embedded in polymers or other composites

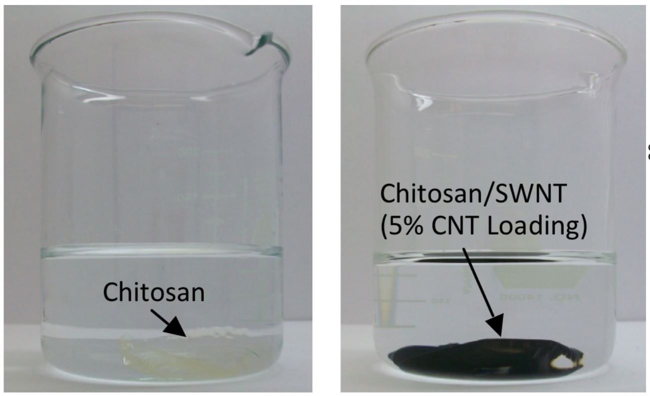
spICPMS detection of CNT metallic impurities

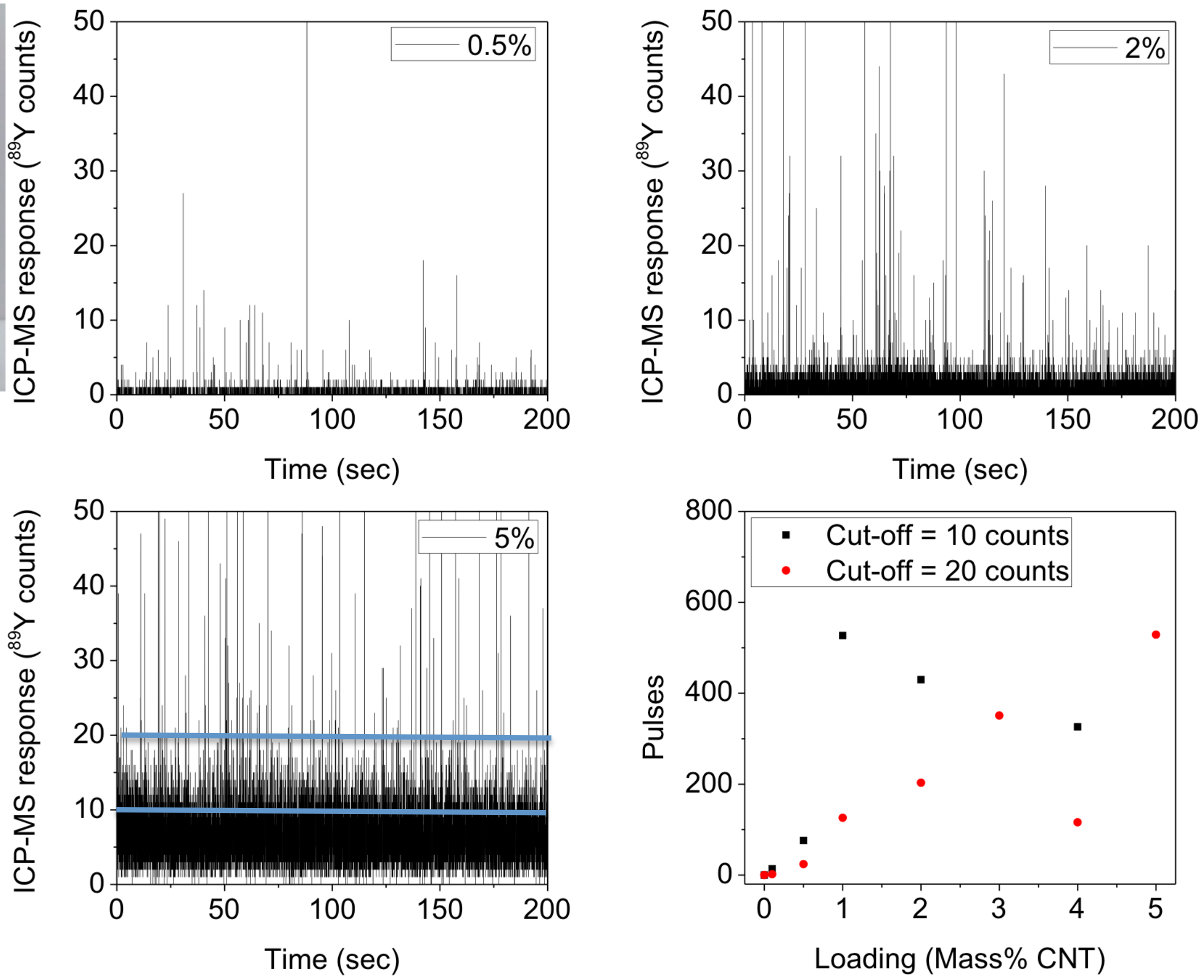
- CNTs can contain residual catalyst metals
- spICPM can detect these as a surrogate for direct detection of CNT
- Variable metal content, polydisperse length and width, and poor dispersion make analysis challenging

CNT brand	Type	Length (nm)	Diameter (nm)	Metal content (manufacturer)	Metal content by EDS
Nanostructured and Amorphous Material (NanoAmor)	SWNT	5000-15000	1.1	Co 0.6%, Mo 0.1 %, Mg 1.2% (at%)	Co 0.5%, Mo 0.1%, Fe 0.1% (at%)
Carbon Solutions	SWNT	1800±1000	3.8±1.8	Ni, Y (1-30 wt%)	Ni 19.4%, Y 6.0% (at%)
Southwest Nanotechnologies	SWNT	578±358	0.8±0.1	Co, Mo (1-15 wt%)	Co 1.1%, Mo 3.7% (at%)

Results of polymer loading

- Prepare chitosan matrix with variable CNT concentration
- DI leach for 7 days
- Collect spICPMS data and analyze with variable background cutoffs

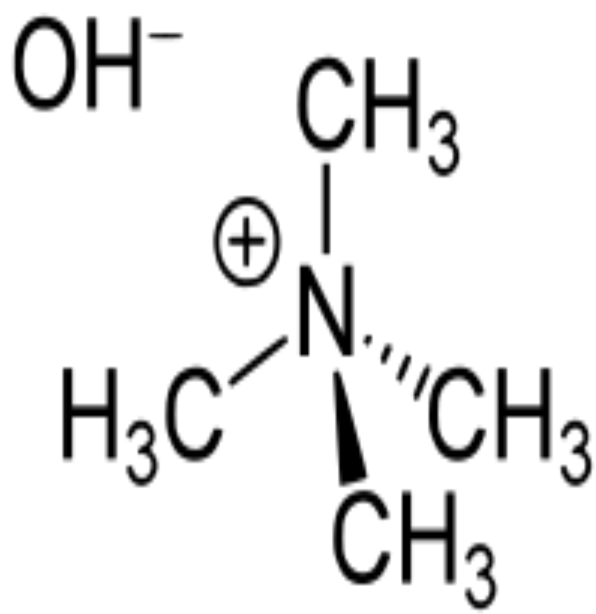




- Both NP size (length) and metal content control pulse intensity
- HIgh polydispersity and lack of clear separation from background are challenges

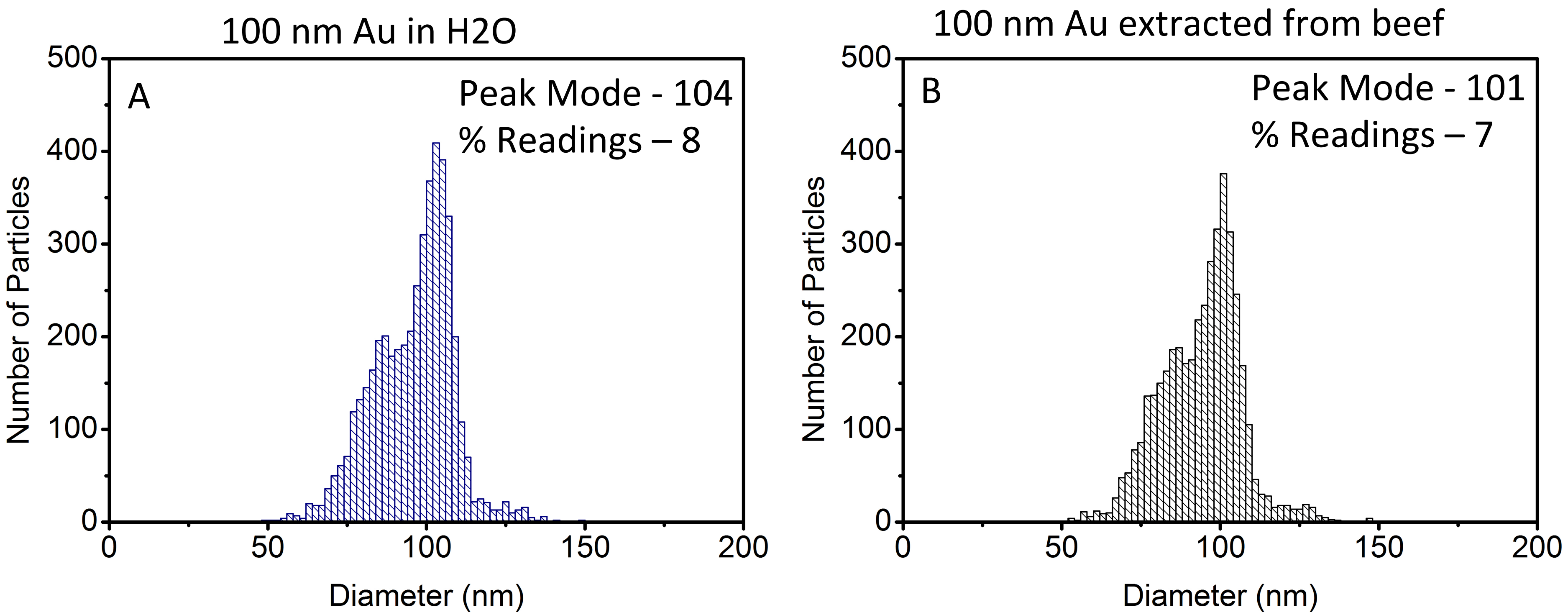
Determining Dose

- What is the external and internal dose in toxicity testing?
- Tissue digestion method development
- Tetramethylammonium Hydroxide
  - 20% solution (w/w)
  - pH 13.5
  - 24 hour digestion
- Cleanup steps
  - Filtration (abandoned)
  - Low G Centrifugation
  - Dilution to ppt levels

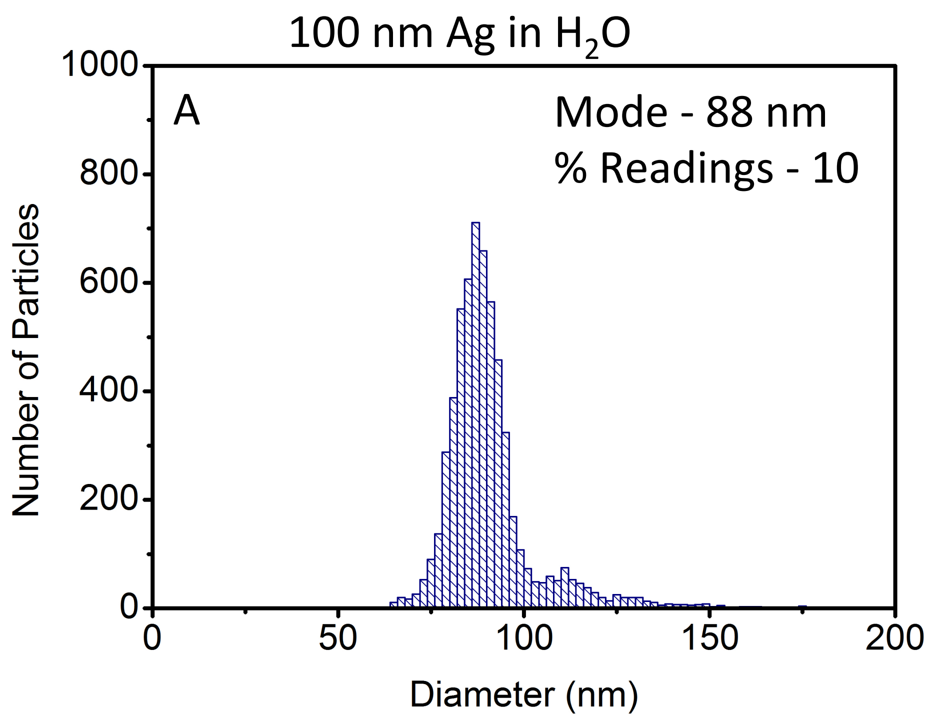


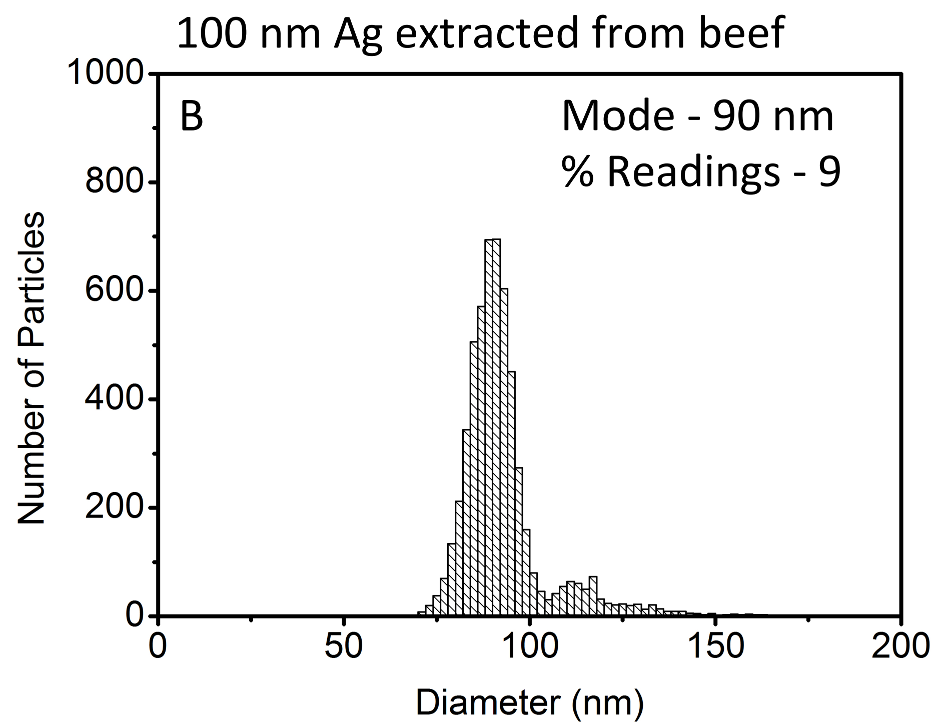
Au NPs extracted from beef:Spiked

Equivalent dilution allows direct comparison of particle number



Ag NPs extracted from beef: Spiked

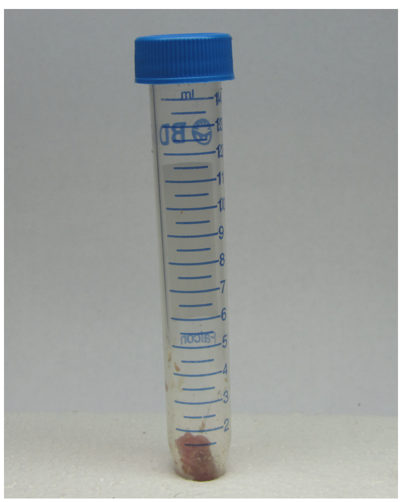




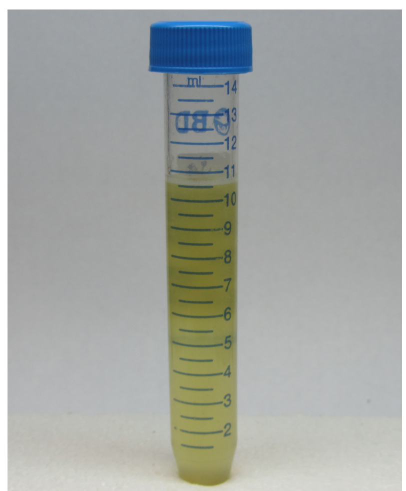
NP Recovery (spiked tissues)

Tissue Matrix	Particle Number Recovery % (±SD)	Particle Mass Recovery % (±SD)
	Au	
Ground Beef	94 (3)	89 (3)
D. magna	95 (2)	109 (4)
L. variegatus	95 (3)	95 (3)
	Ag	
Ground Beef	95 (3)	104 (3)
D. magna	84 (4)	105 (8)
L. variegatus	95 (3)	107 (7)

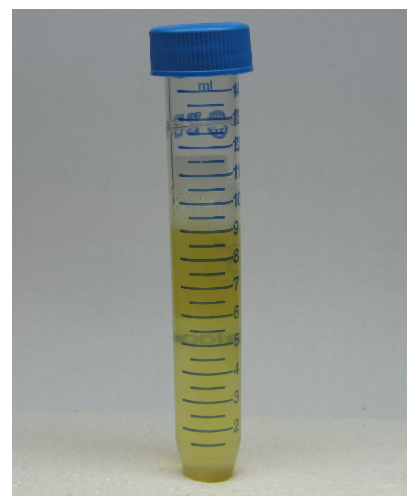
Beef only



Digested beef

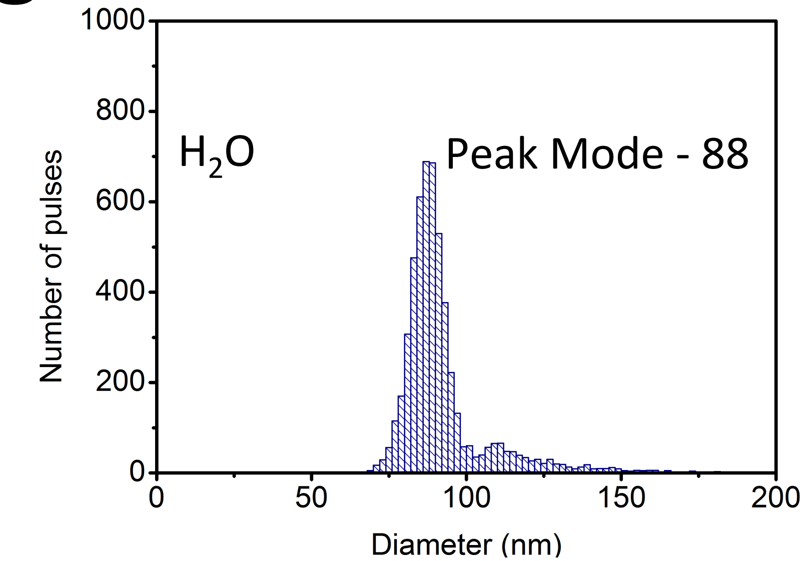


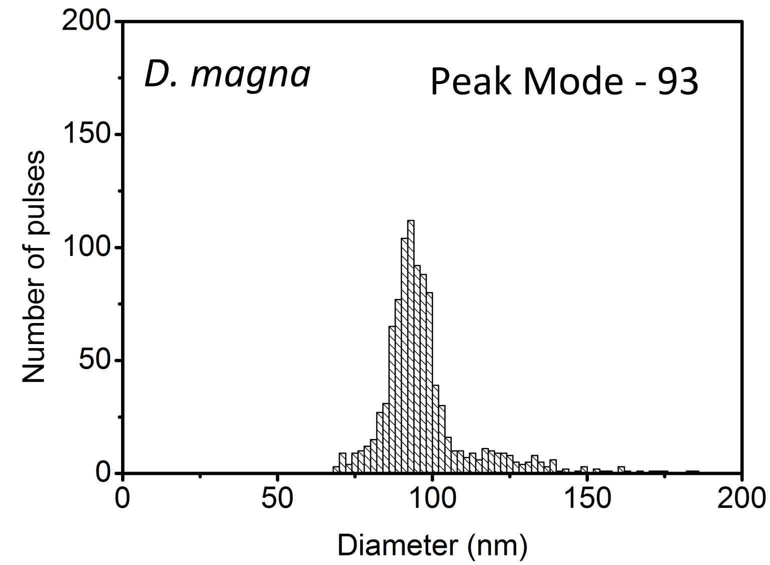
Digested *L. variegatus*



D. magna Whole Organism Extraction

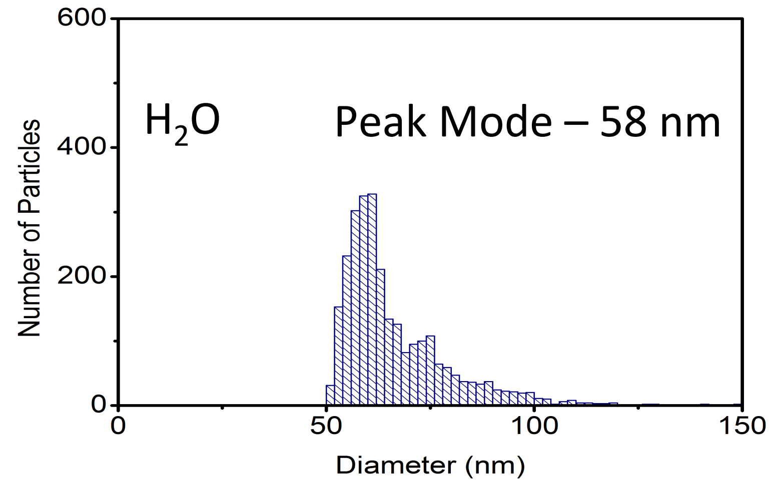
- *D. magna* bioaccumulation test
  - 5 *D. magna* per test chamber, total of 20 *D. magna* per treatment (EPA 2021.0)
  - Exposed at 10 µg/L of 100 nm Ag particles, PVP capped



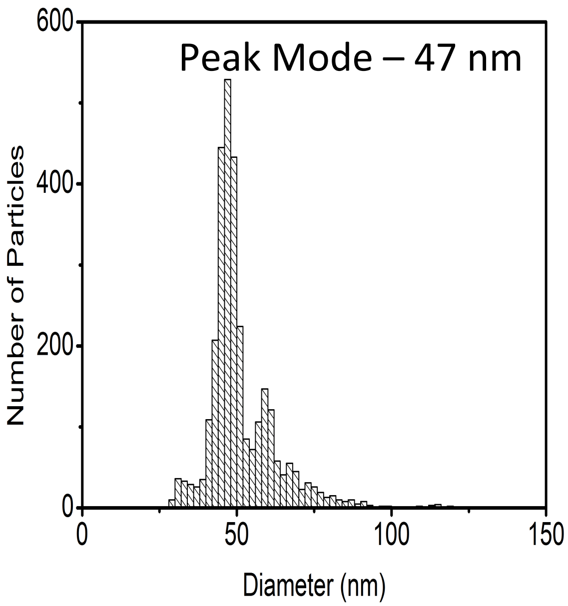


L. variegatus Whole Organism Extraction

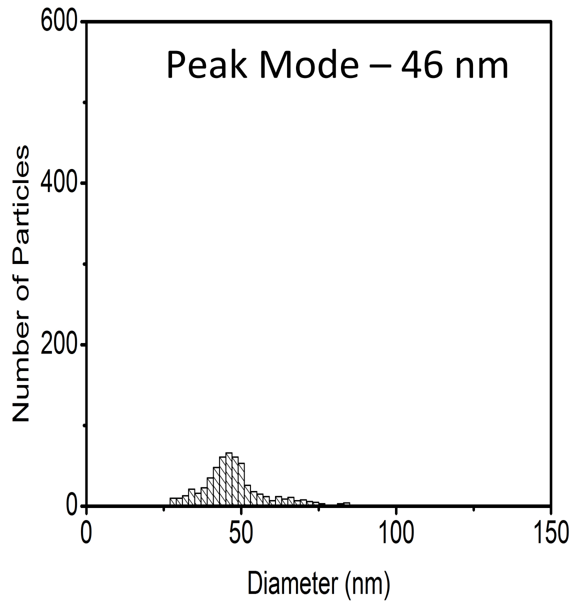
- *L. variegatus* <u>bioaccumulation</u> test
  - Exposed 24 hours at 5 mg/L and depurated for 0, 24, 48 hours in de-chlorinated tap water
  - 0.5 grams of worms analyzed per treatment, n=3 chambers per treatment.
  - 70 nm Ag PVP capped
  - Percent readings all below 10%



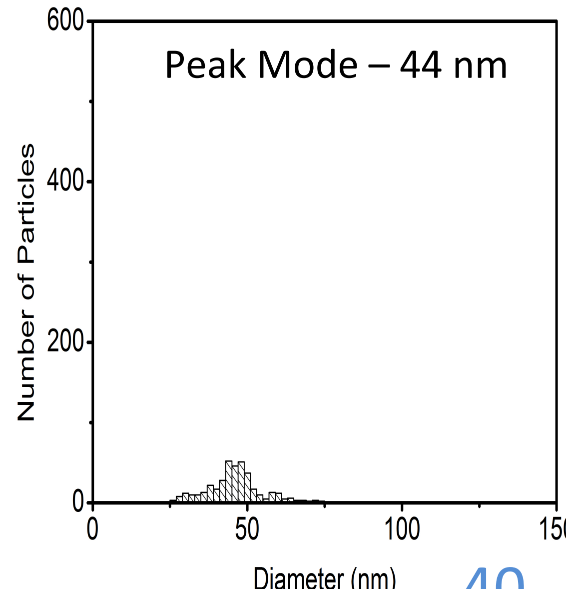
L. Variegatus T=0



L. Variegatus T=24



L. variegatus, T=48

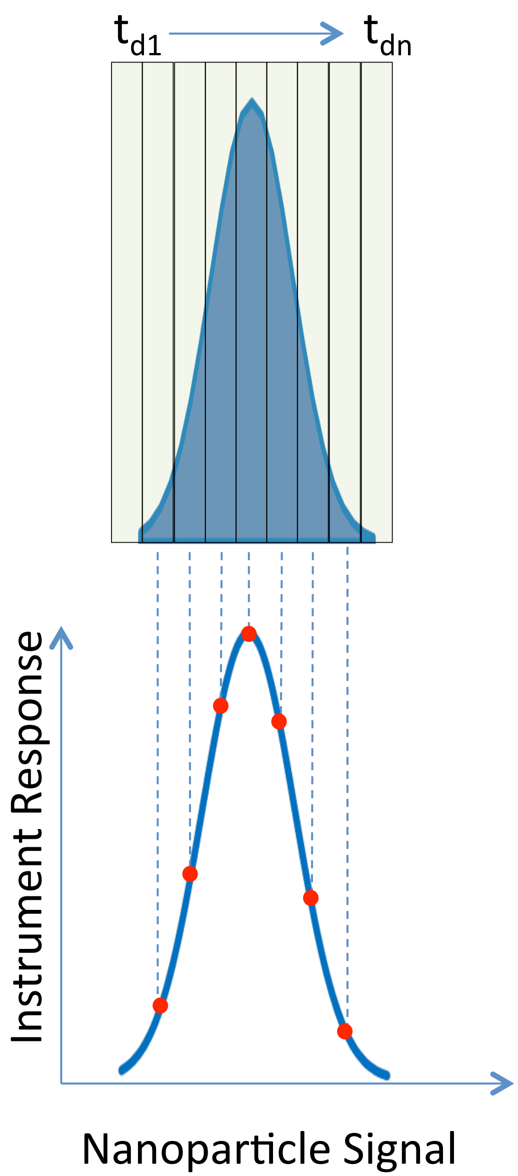


Topics of the talk

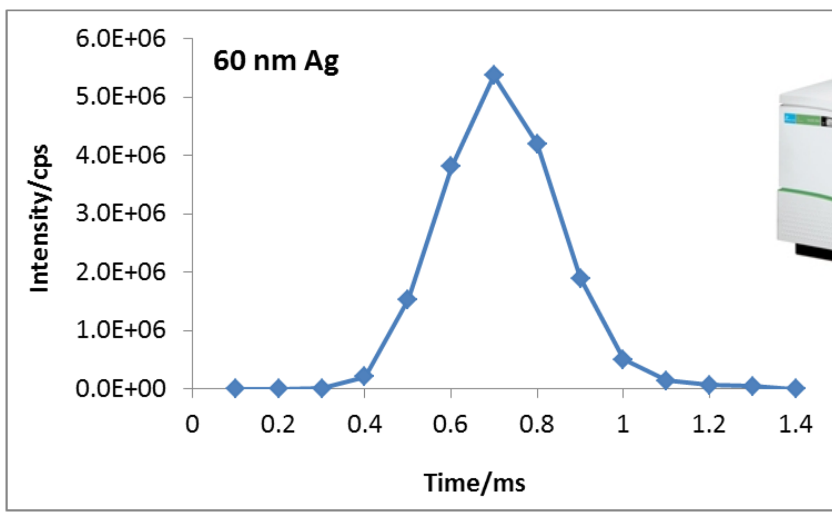
* Collaborations with ICP-MS manufacturers

New Approaches

Collaboration with Perkin Elmer: NexION's Fast Scanning Mode



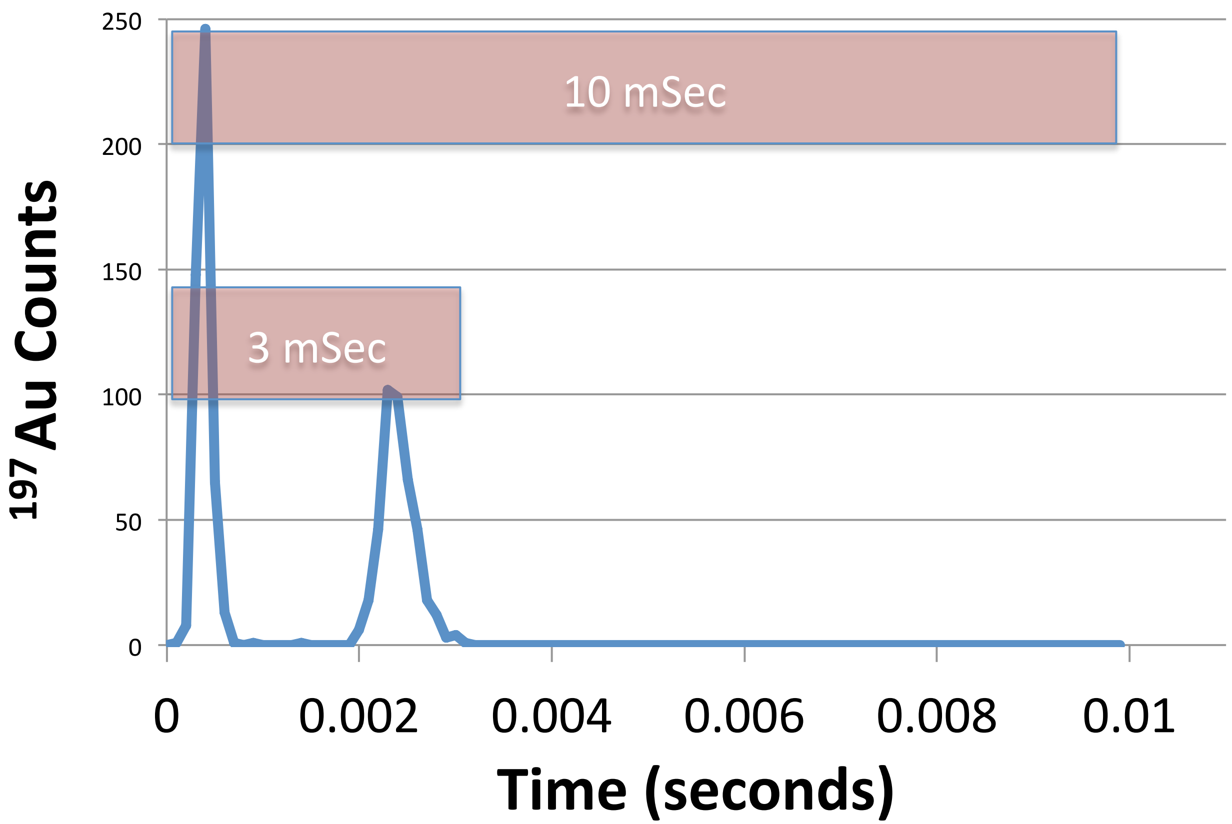
- NexION is only Quad instrument capable of < 3 msec dwell times
- Data shown for 100 µs dwell time
- No settling time for single mass measurements
- Dwell Times as short as 1 µs
- Benefits: reduction in background contribution to signal, reduction in potential particle coincidence, multi-element detection (?)



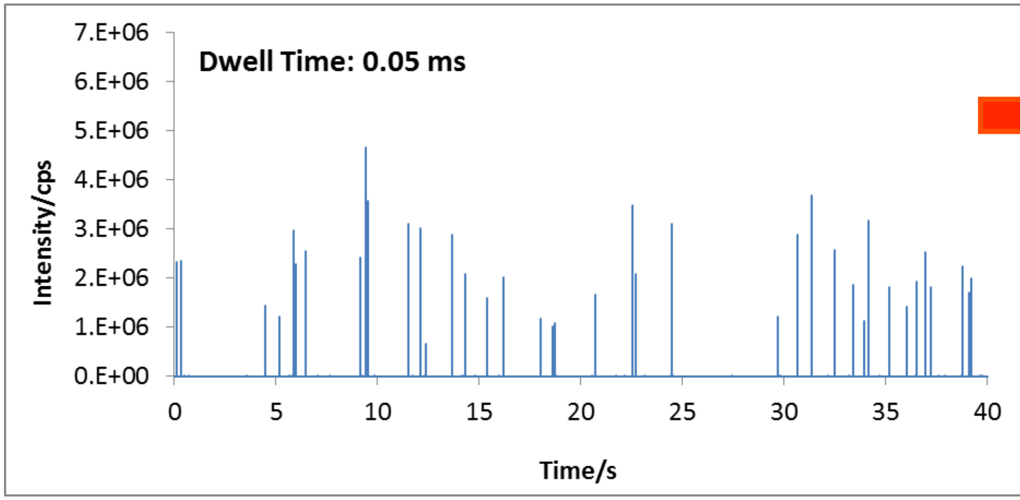
Slide courtesy of Perkin Elmer

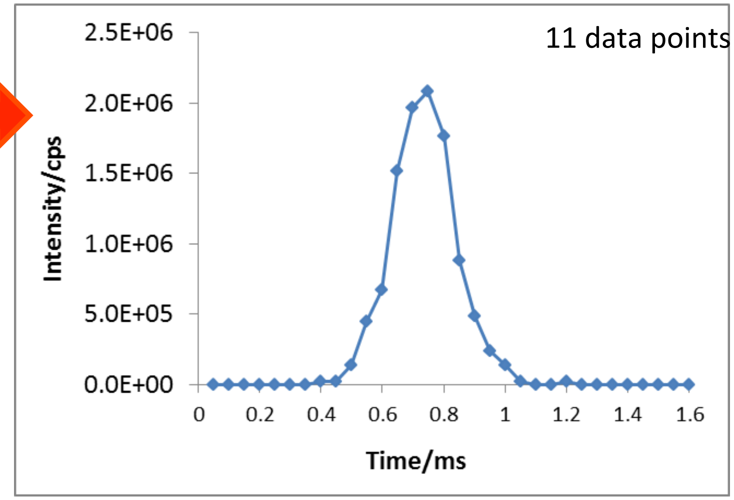
Elimination of Coincidence at short dwell times

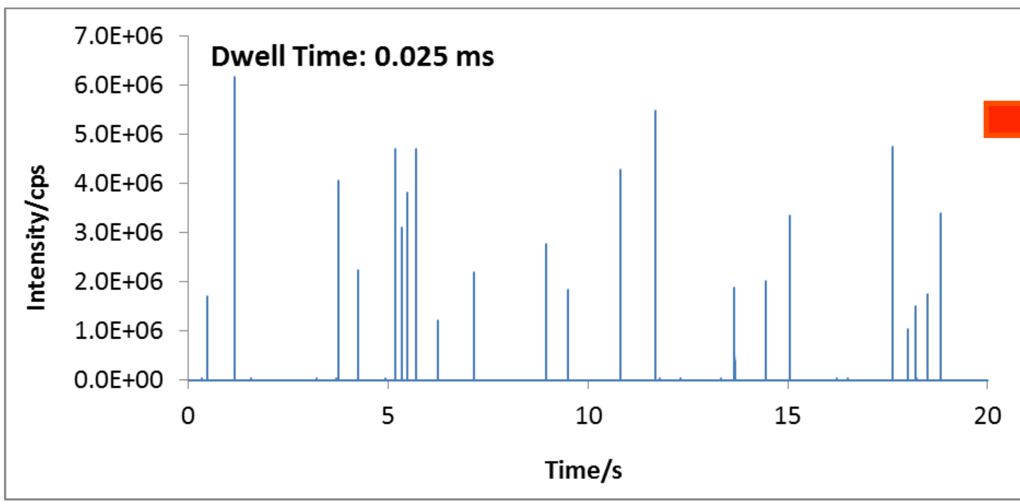
500 ppt Au
0.1 msec dwell times

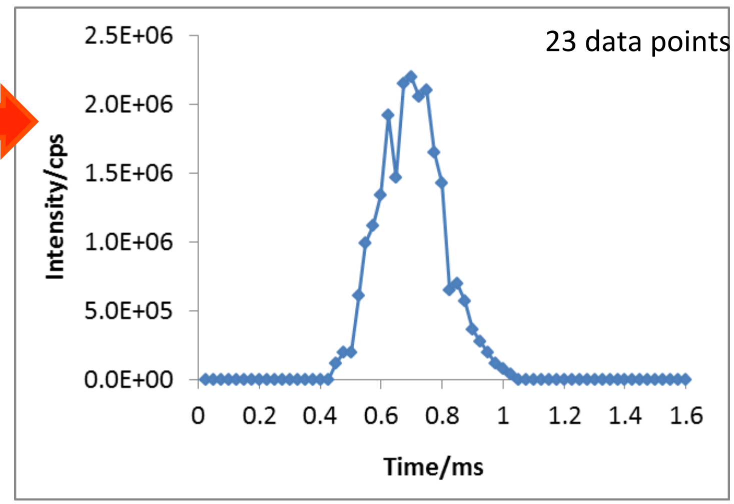


More Fast Scanning Examples

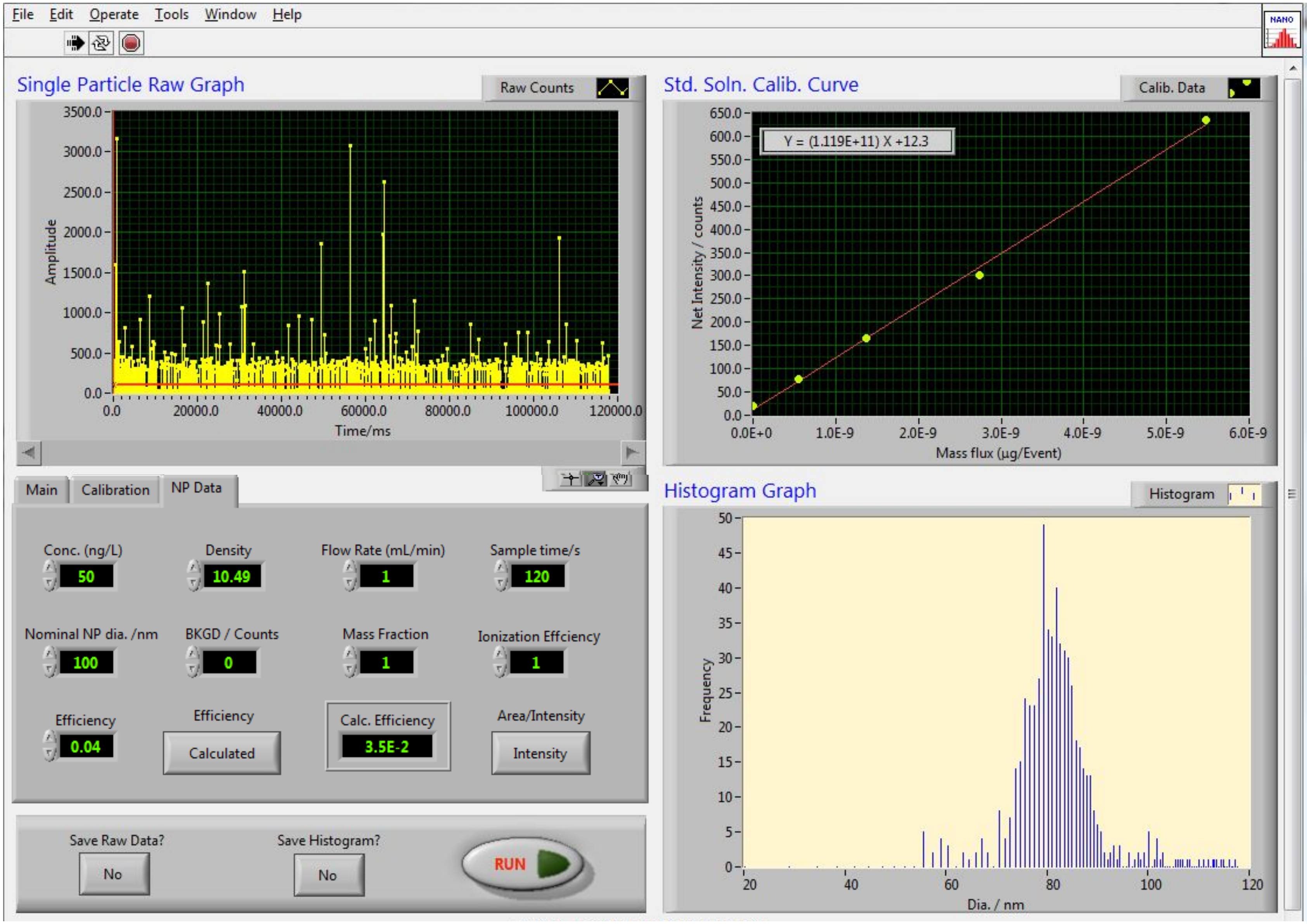








Automating Nano Data Processing



Slide courtesy of Perkin Elmer

Other collaborations

- PE- Wyatt Collaboration: Integrating FFF data collection and analysis into PE Chromera software to improve FFF-ICPMS method optimization.

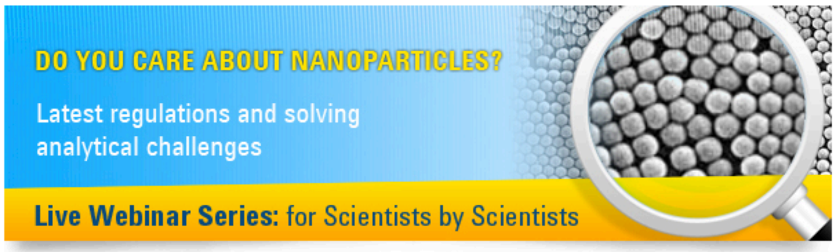
- Coordinating spICPMS method development with NIST (E. Peterson).

Upcoming Webinars

POSTNOVA Leading in FFF

Agilent Technologies

NANOPARTICLES: LIVE WEBINAR SERIES



The ongoing race for nanotechnology development has resulted in a need for analytical methods that can accurately and efficiently detect and characterize nanoparticles.

The hyphenation of Field-Flow Fractionation (FFF) with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) presents a state-of-the-art method for high sensitive nanoparticle analysis.

During these three webinars, leading scientists in the field of nanotechnology will present the latest legislation and regulations that govern nanoparticles and will discuss the analytical challenges and solutions for nanoparticle analysis in **food**, **cosmetics** and **environmental** samples.

REGISTER NOW

4 June 2013
4pm CET (1h)
- Nanoparticles: Definition, regulations and analytical challenges
  Speakers: Dr. Hubert Rauscher (European Commission), Dr. Sebastien Sannac (Agilent Technologies), Dr. Soheyl Tadjiki (Postnova Analytics)

11 June 2013
4pm CET (1h)
- Food and cosmetics application examples for nanoparticle characterization and detection
  Speakers: Dr. Heidi Goenaga-Infante (LGC London), Dr. Frank von der Kammer (University of Vienna)

18 June 2013
4pm CET (1h)
- Environmental application examples for nanoparticle characterization and detection
  Speaker: Prof. James R Ranville (Colorado School of Mines)

Unable to attend on a specific date?
Register now and you will receive the recording after the event.

PerkinElmer For the Better

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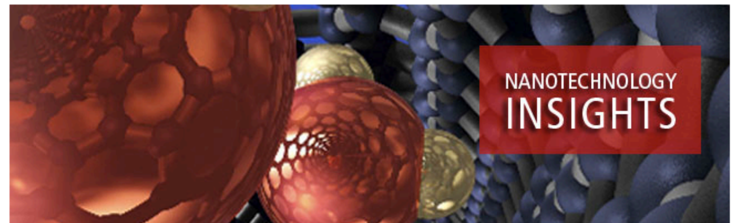


REGISTER NOW

Live Webcast - Breakthrough Technology: Single Particle ICP-MS for Characterizing Five Attributes of Metallic Nanomaterials

Date and time:
June 25, 2013 at 9:00-10:00pm EDST

In recent years, there has been ever-increasing activity and interest within the scientific and engineering fields about engineered nanoparticles (ENP). With the advancement of nanomaterials used in products, new regulations requiring the characterization of nanomaterials, and the unknowns of the hazards of these materials, researchers and manufacturers will have an increased need to quantitate nanomaterials.
PerkinElmer offers a breadth of solutions that enable engineers and scientists to measure, characterize and better understand nanomaterials for industrial and academic nanotechnology research. One such technology is Single Particle ICP-MS, which allows the quantitation of nanoparticles for particle size, particle size distribution, agglomeration, concentration and composition, delivering accurate, fast and reliable results. Attend this free webcast to learn how this revolutionizing technology will change the way you can measure nanoparticles.

In this webcast you will learn:

- What is Single Particle ICP-MS (SP-ICP-MS) and what types of information it provides
- The ability to screen for nanoparticles in real-world samples with SP-ICP-MS
- Who will benefit the most from SP-ICP-MS technology to analyze nanoparticles
- Examples of key applications for SP-ICP-MS

The webcast will be followed by a live question & answer session.

>> Click here to register for the webcast and download our nanotechnology applications

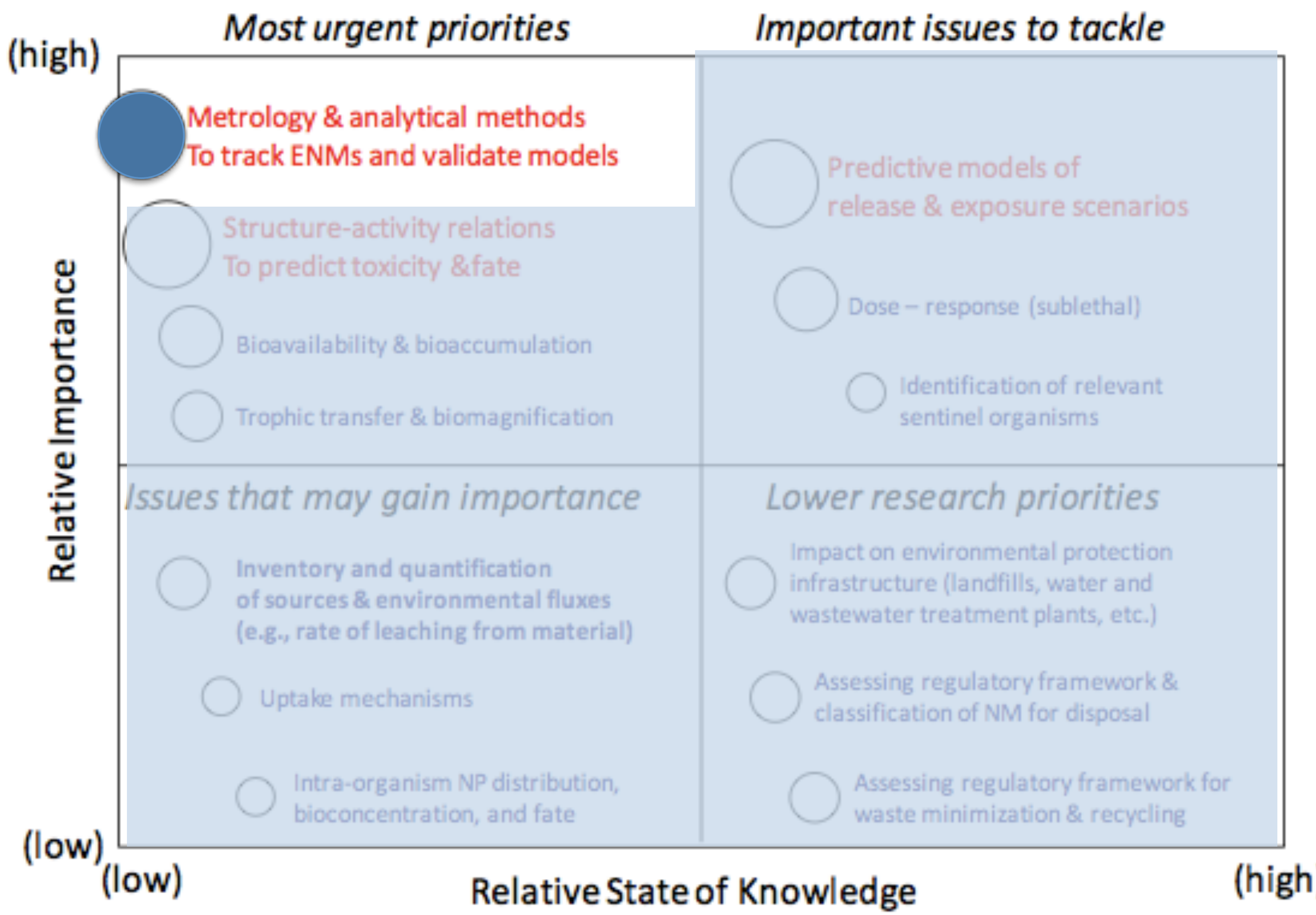
Presenters:

Chady Stephan
PerkinElmer

Dr. James Ranville
Professor Colorado School of Mines

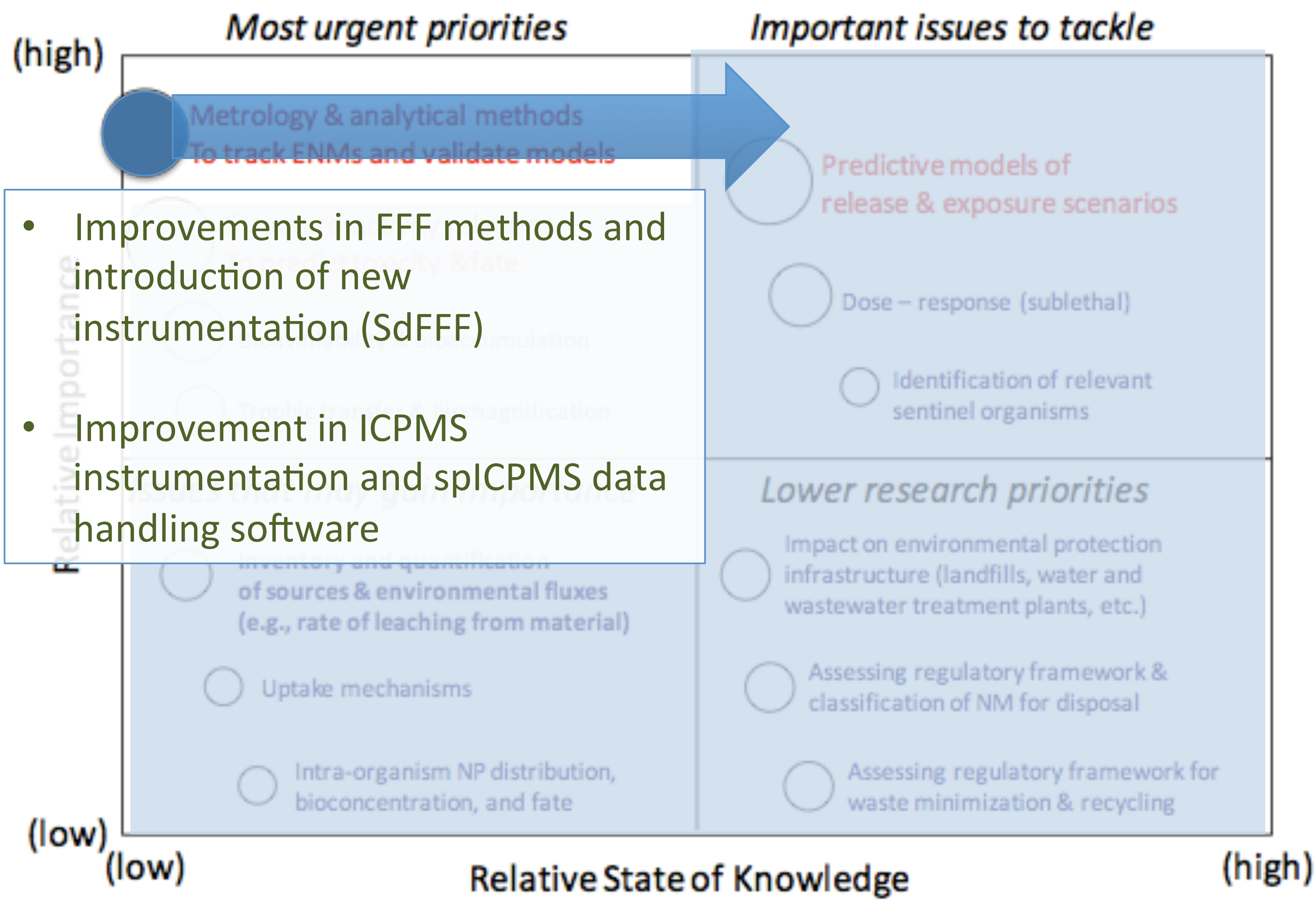
HUMAN HEALTH | ENVIRONMENTAL HEALTH

Summary



National Nanotechnology Initiative Workshop, Arlington VA, 2009

Summary



- Improvements in FFF methods and introduction of new instrumentation (SdFFF)

- Improvement in ICPMS instrumentation and spICPMS data handling software

National Nanotechnology Initiative Workshop, Arlington VA, 2009

Thank You