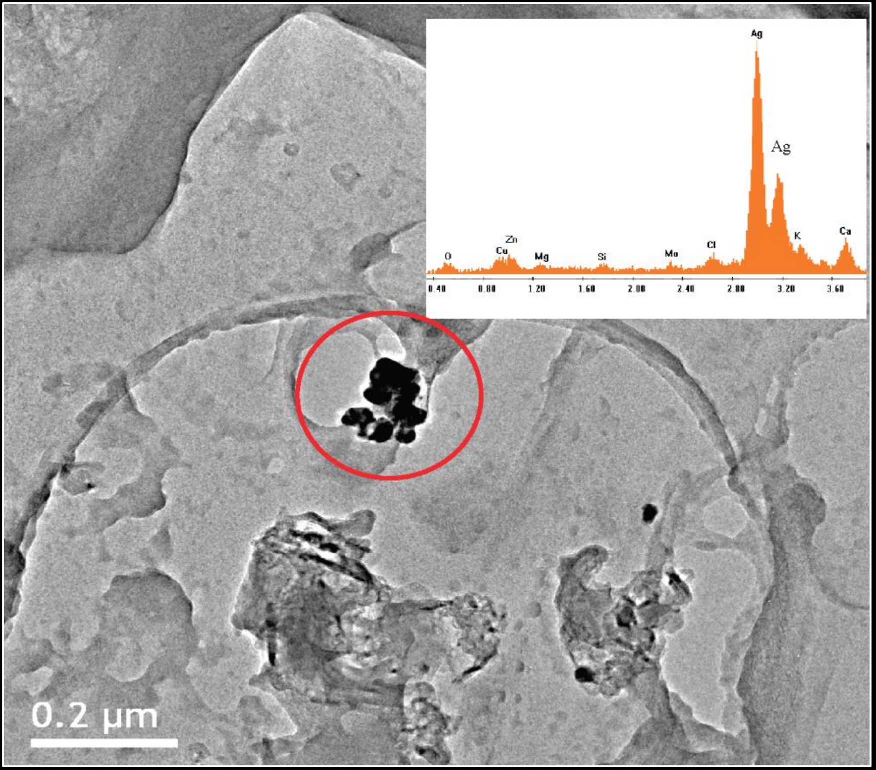
Microsecond spICP-MS for dual-element detection: Environmental and Analytical Applications

Manuel David Montaño

ERC Teleconference Seminar
Colorado School of Mines
July 10th, 2014

spICP-MS dual-element detection

- Entry of ENMs into the environment
- Principles and operation of spICP-MS
- <u>Particle-by-particle dual-element analysis</u>
  - ➢ Isotopic ratio determination (Ag NPs)
  - ➢ Core-shell nanomaterials
    - o Sed-FFF fraction collection
    - o Particle size and number determination
  - ➢ Natural vs. engineered NPs
    - o Bulk elemental ratios
    - o Cerium dioxide ENPs in stream water



Benn, T.; Westerhoff, P. *Environmental Science and Technology*, **2008**

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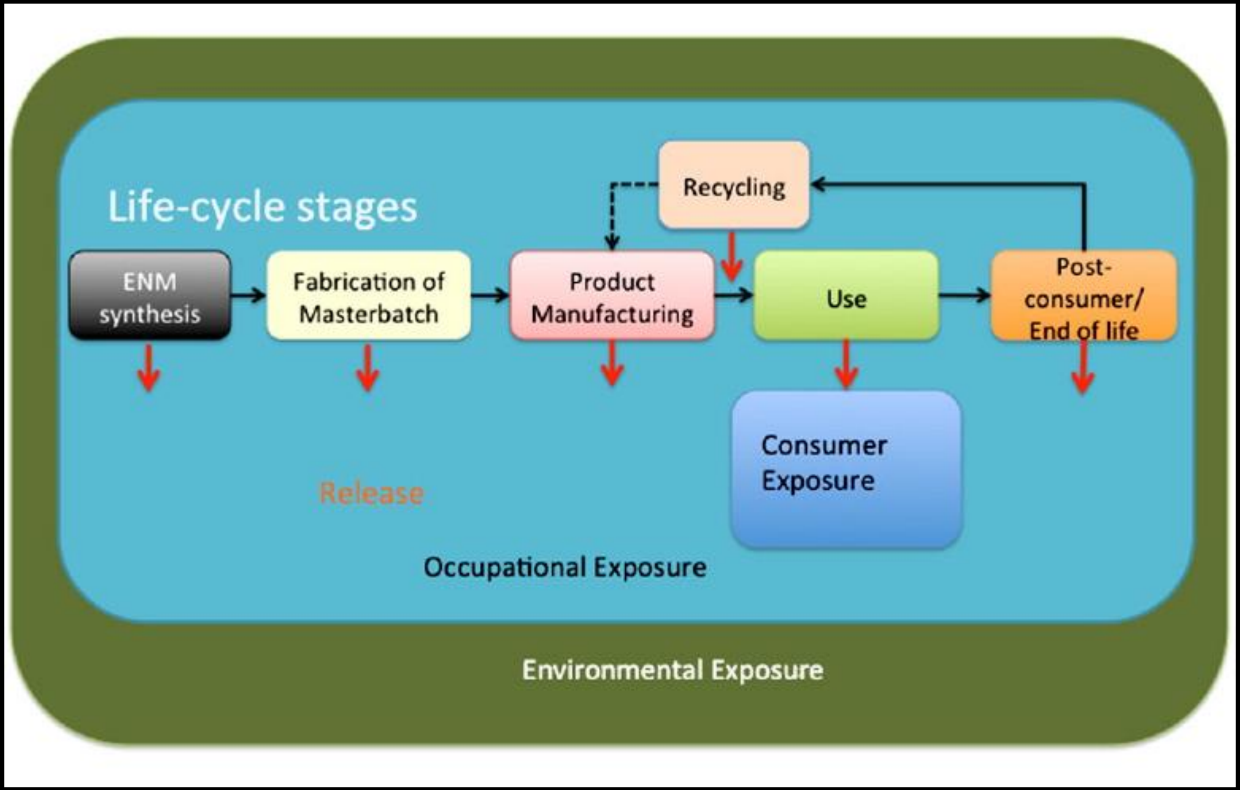
ENM Environmental Release

• Increasing production of ENPs will lead to inevitable environmental release and exposure

• Release of nanomaterials can come at any point during fabrication and use

• Little information regarding quantity, fate, and behavior of ENPs in environment



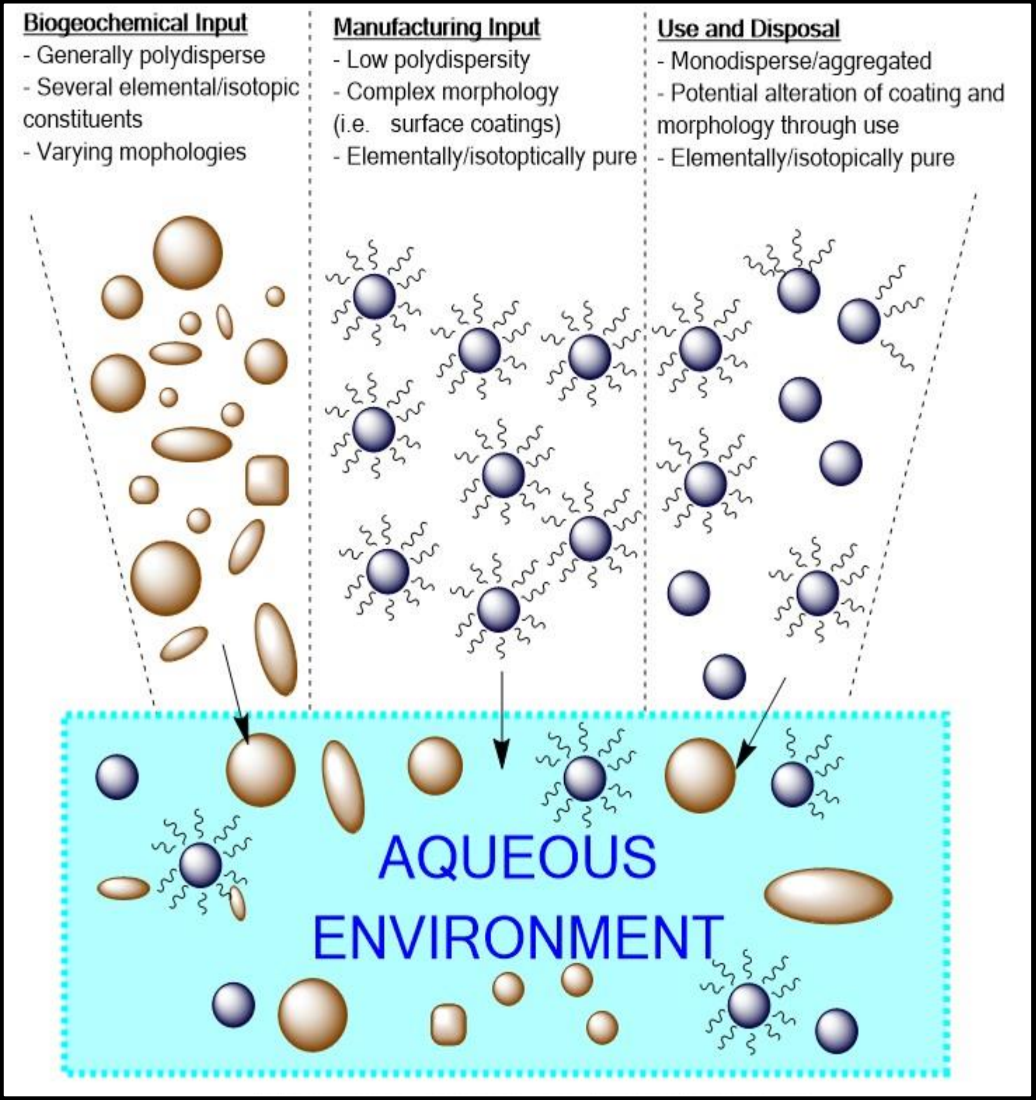
Nowack, B. et al. *Environment International,* **2013**.

ENM Environmental Release

- Aqueous environment will contain varied assortment of nanomaterials

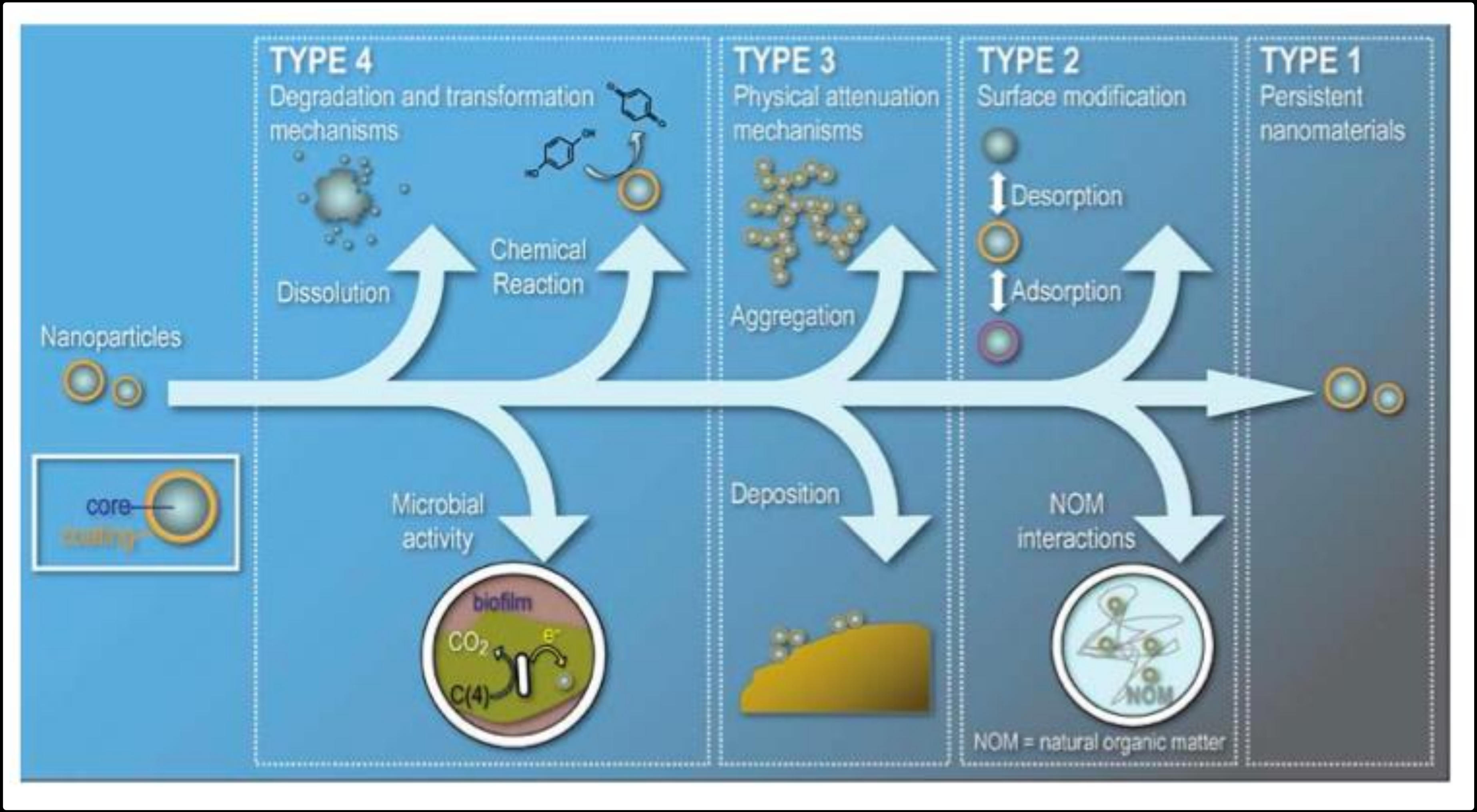
- <u>Important properties to characterize</u>
  - Particle size
  - Aggregation state
  - Particle number concentration
  - Surface groups / chemistry

- <u>Challenges for environmental analysis</u>
  - Low expected release concentrations (ng L^{-1})
  - Changes to surface chemistry / dispersity by environmental molecules (i.e. humic acid)
  - High background of naturally occurring nanomaterials



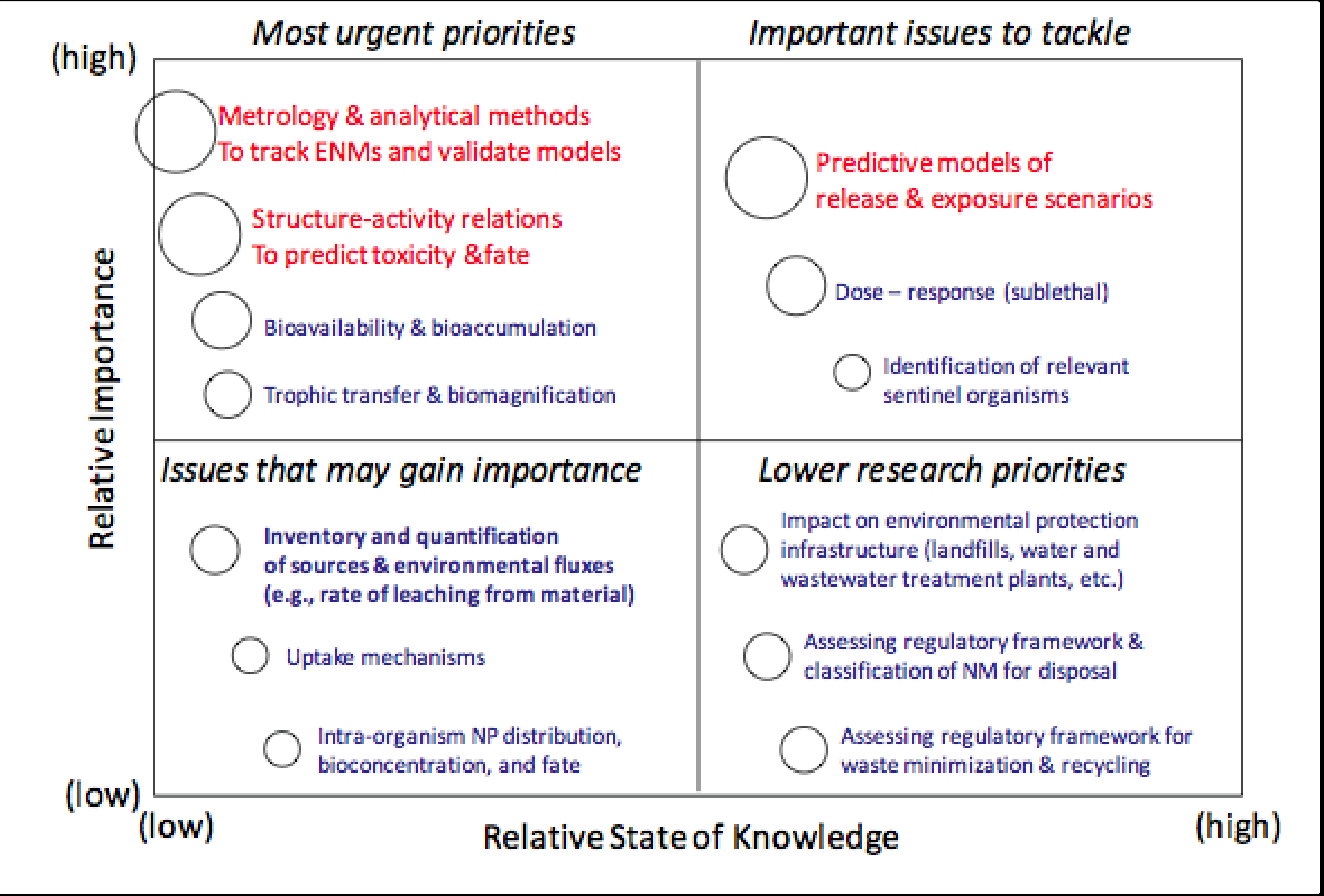
Montaño, M. et al. *Environmental Chemistry*, **Accepted**

Environmental Transformation of ENMs



Alvarez, *ACS Nano*, **2009**

Need for Advanced Nanometrology



National Nanotechnology Initiative Workshop, Arlington VA, **2009**

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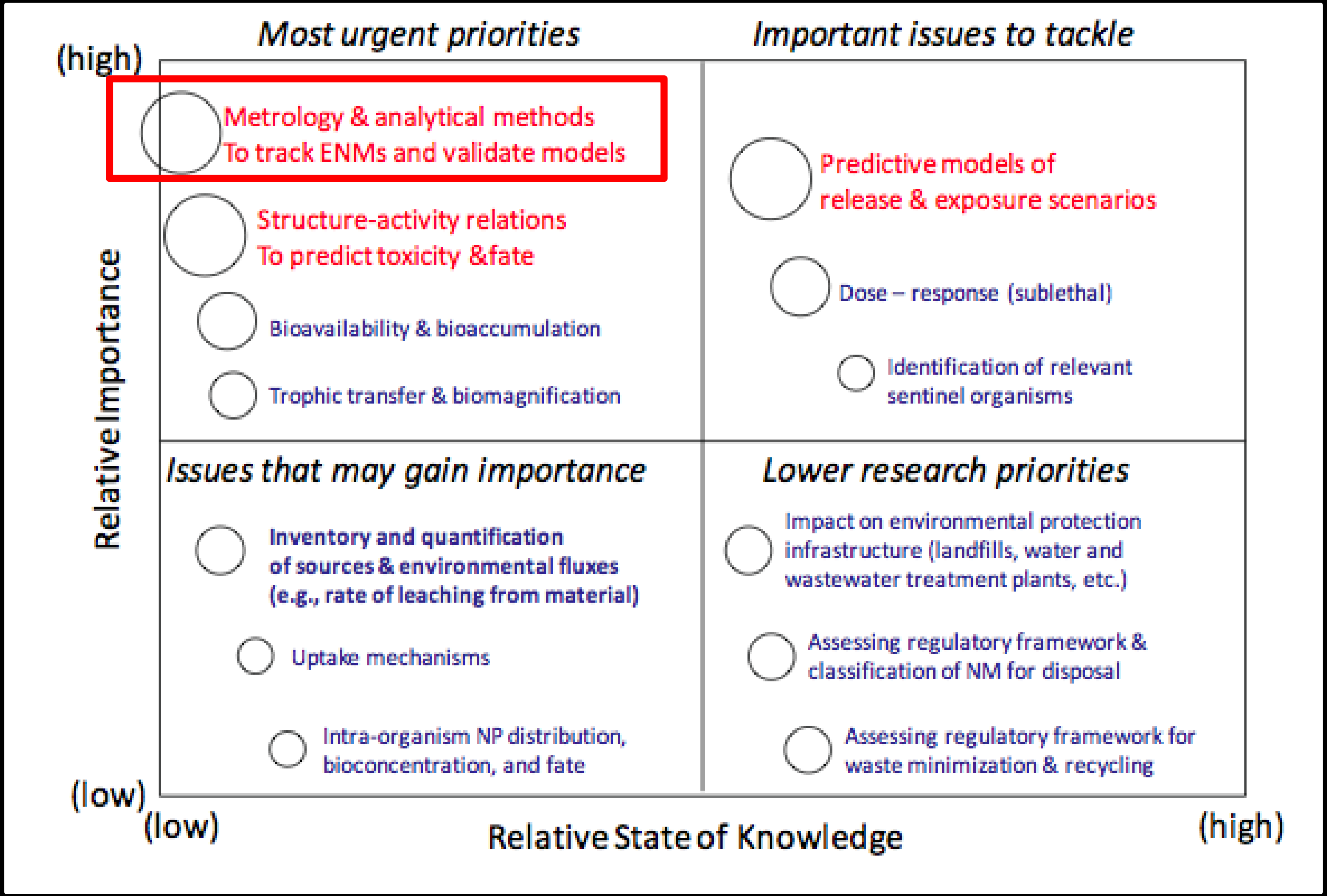
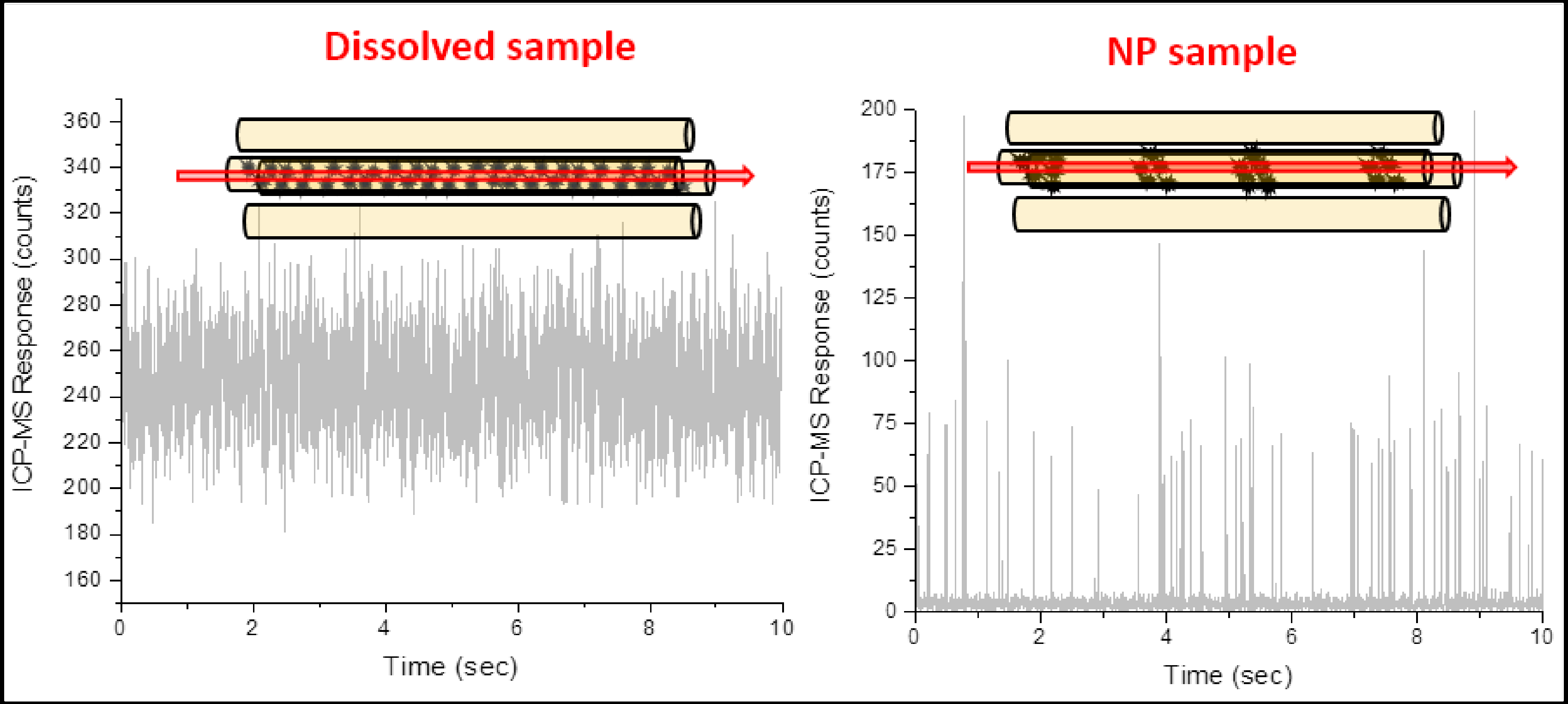


National Nanotechnology Initiative Workshop, Arlington VA, **2009**

Single Particle ICP-MS

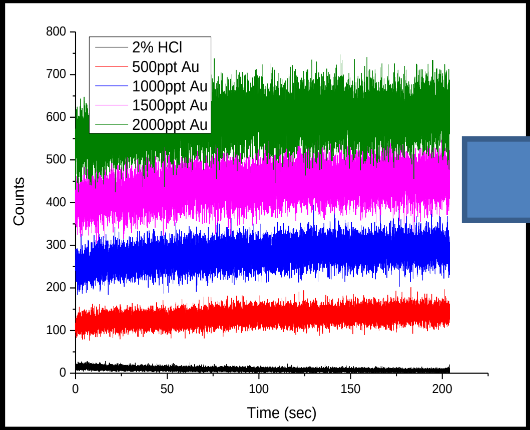
- Utilizes short dwell times (ms) to detect discrete particle events
- Environmentally relevant detection limit (ng/L)
- Need particles of sufficient mass to be detected
- Can distinguish particle and dissolved



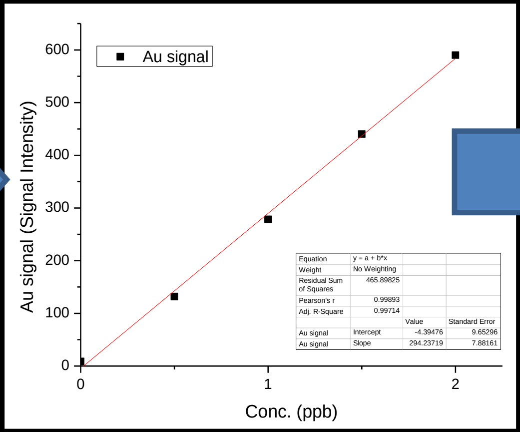
Montaño, M. et al. *Environmental Chemistry*, **2014**

Principles of spICP-MS Operation

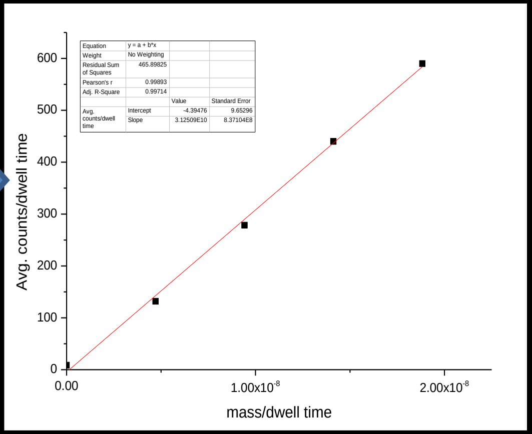
Dissolved standards



Calibration curve



Mass flux curve



Montaño, M. *Unpublished Data*

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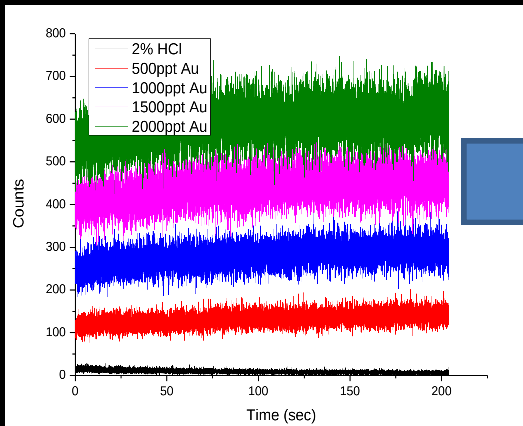

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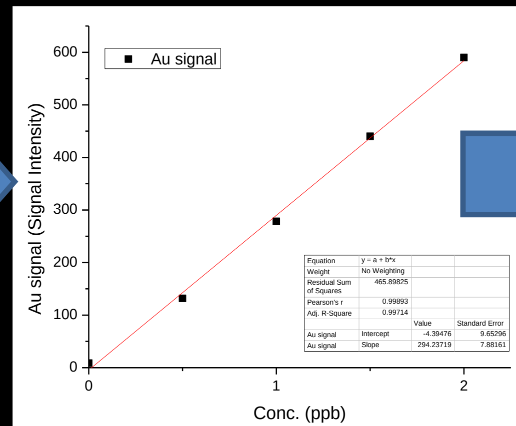

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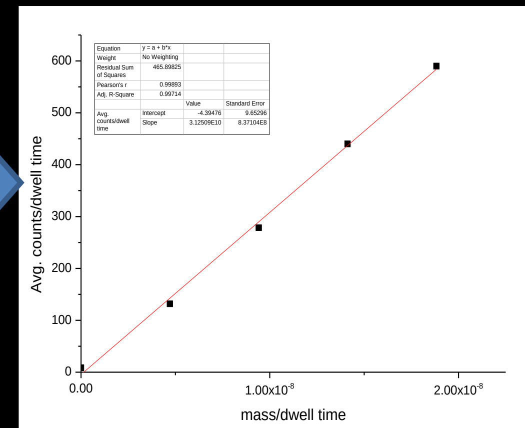
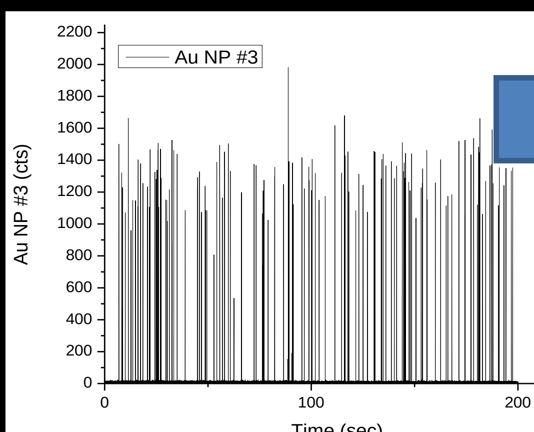
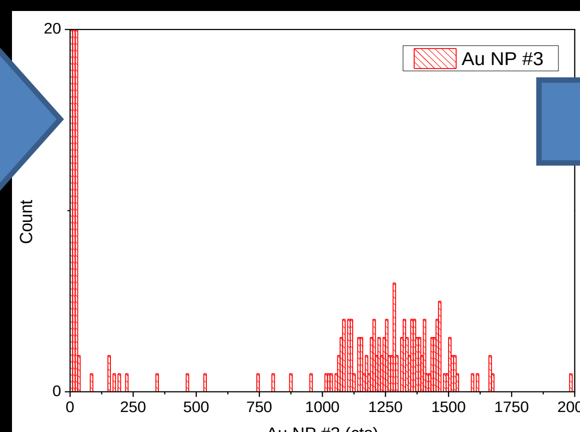


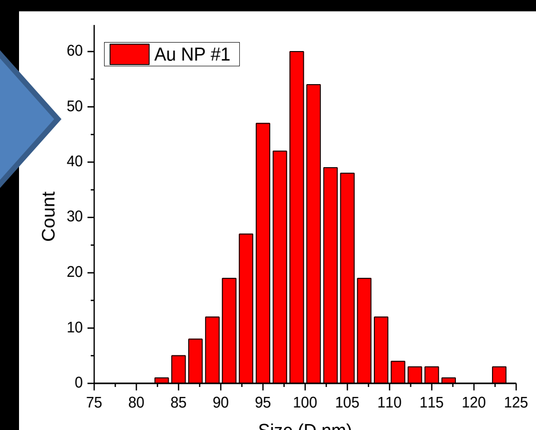
Raw particle counts



Frequency of particle counts



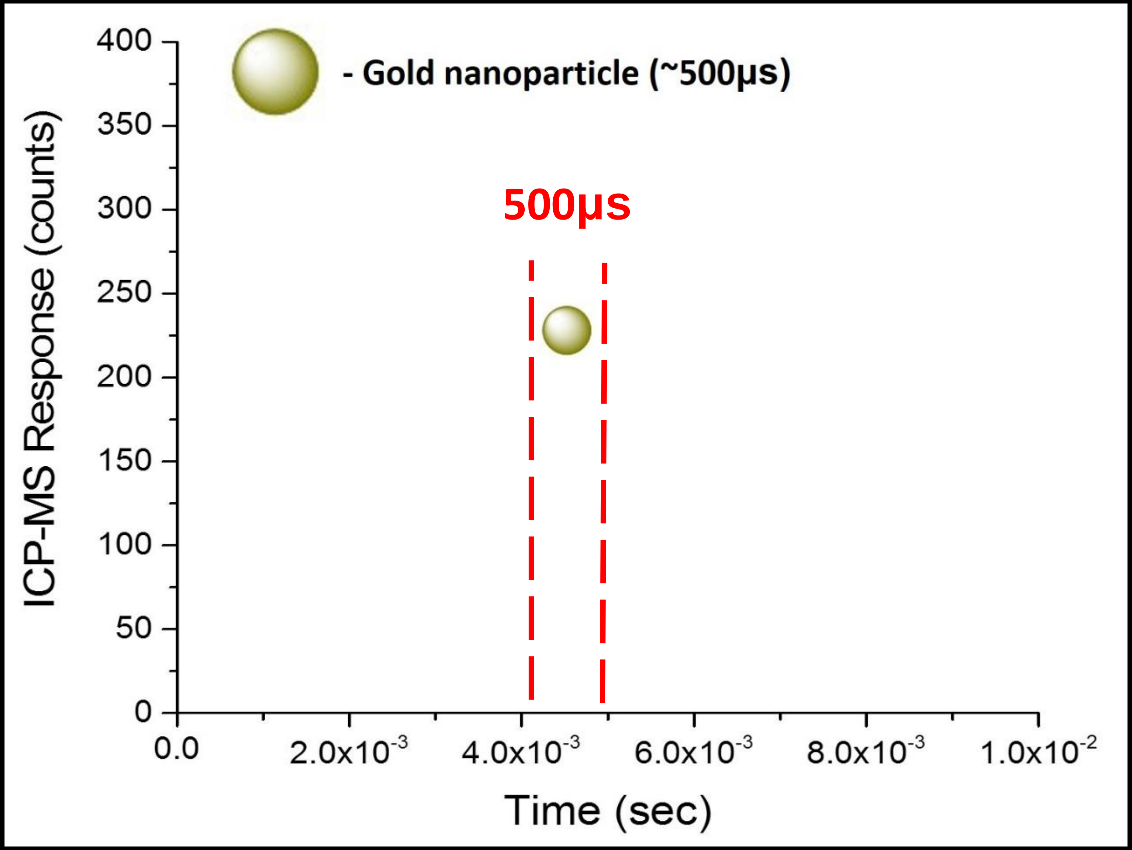
Particle size / number



Montaño, M. *Unpublished Data*

Analytical Challenges – High particle no. conc.

- Nanoparticle events occur over a few hundred microseconds
- Millisecond dwell times may be too large, resulting in coincidence
- This can lead to:
  - Underestimation of particle number
  - Inaccurate sizing of particles



Montaño, M. et al. *Environmental Chemistry*, **In Press**

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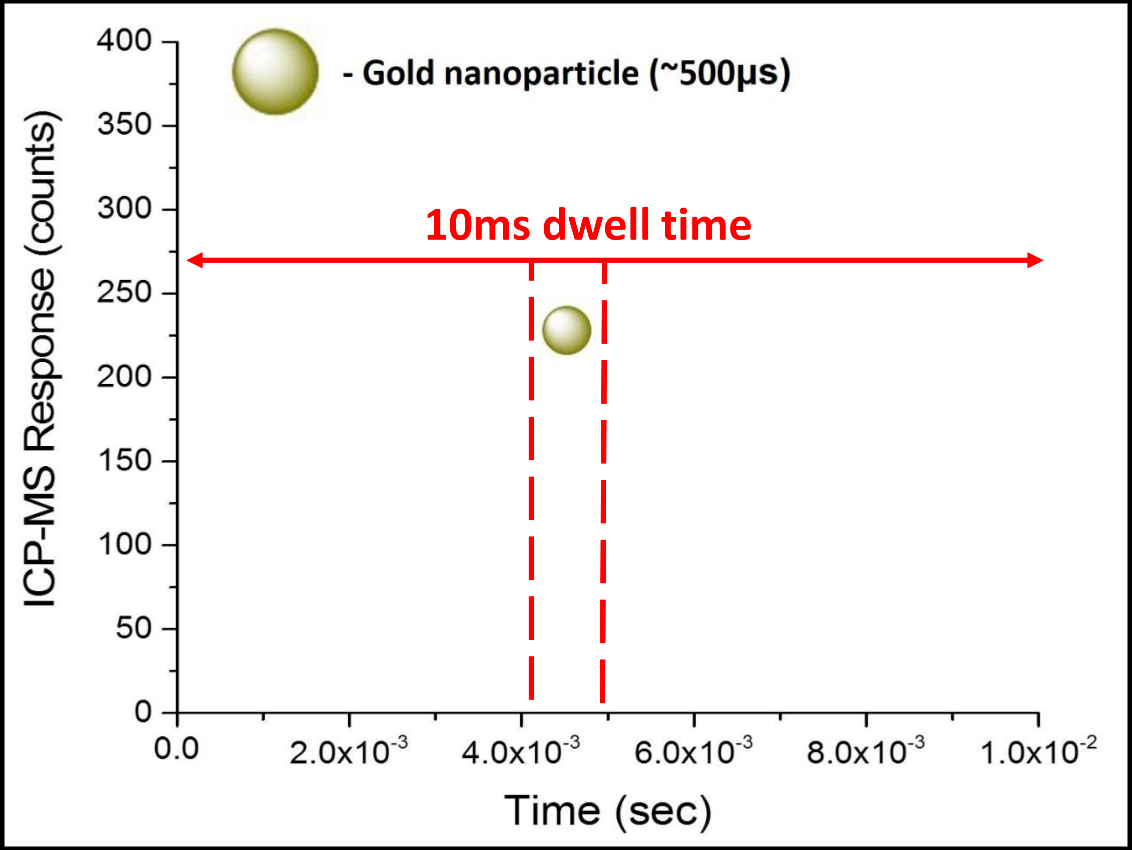

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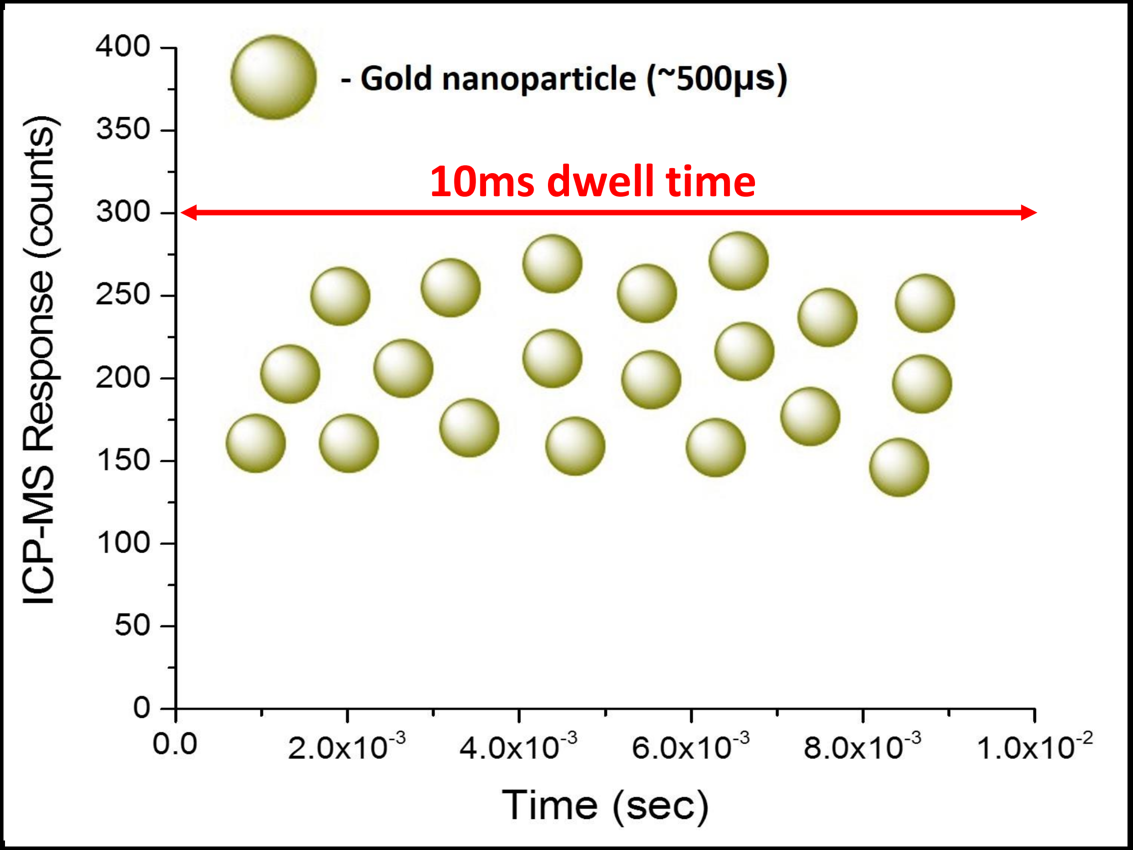

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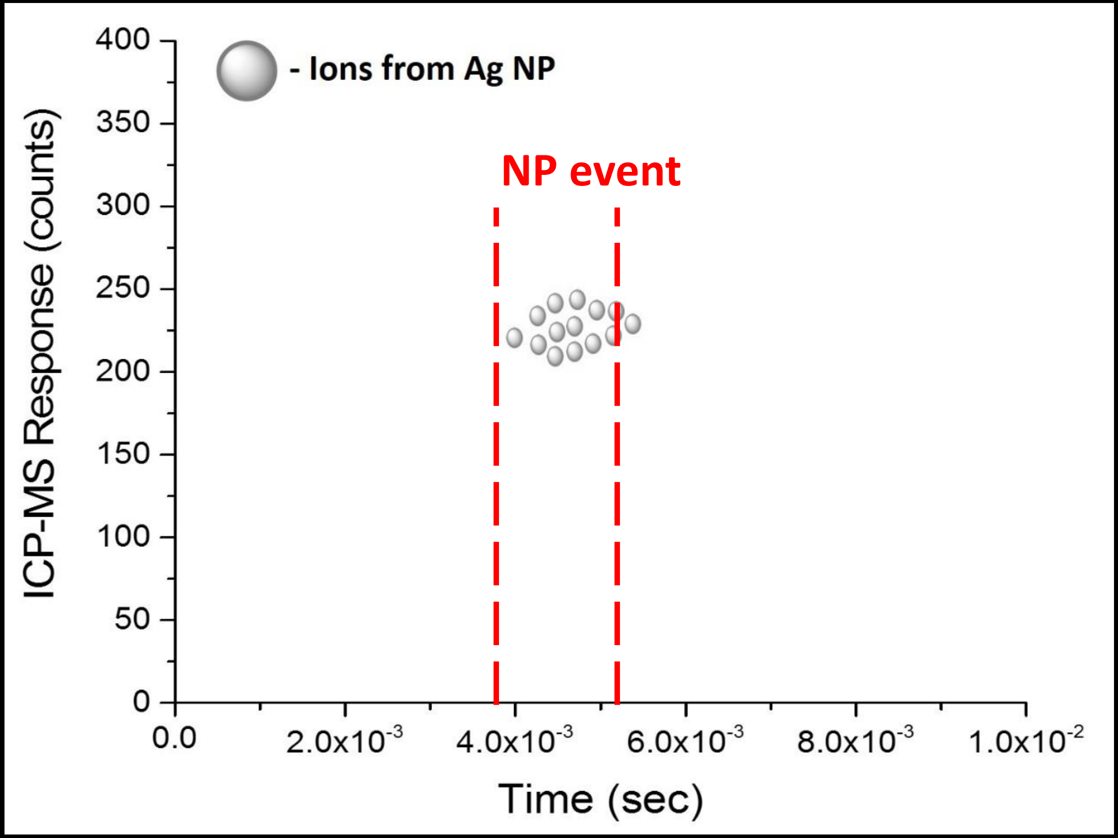
Analytical Challenges – High dissolved background

- Nanoparticles entering the plasma are ionized and detected
- The occurrence of background ions is shown as an elevated background
- If the concentration is high enough, it can mask the presence of a nanoparticle event



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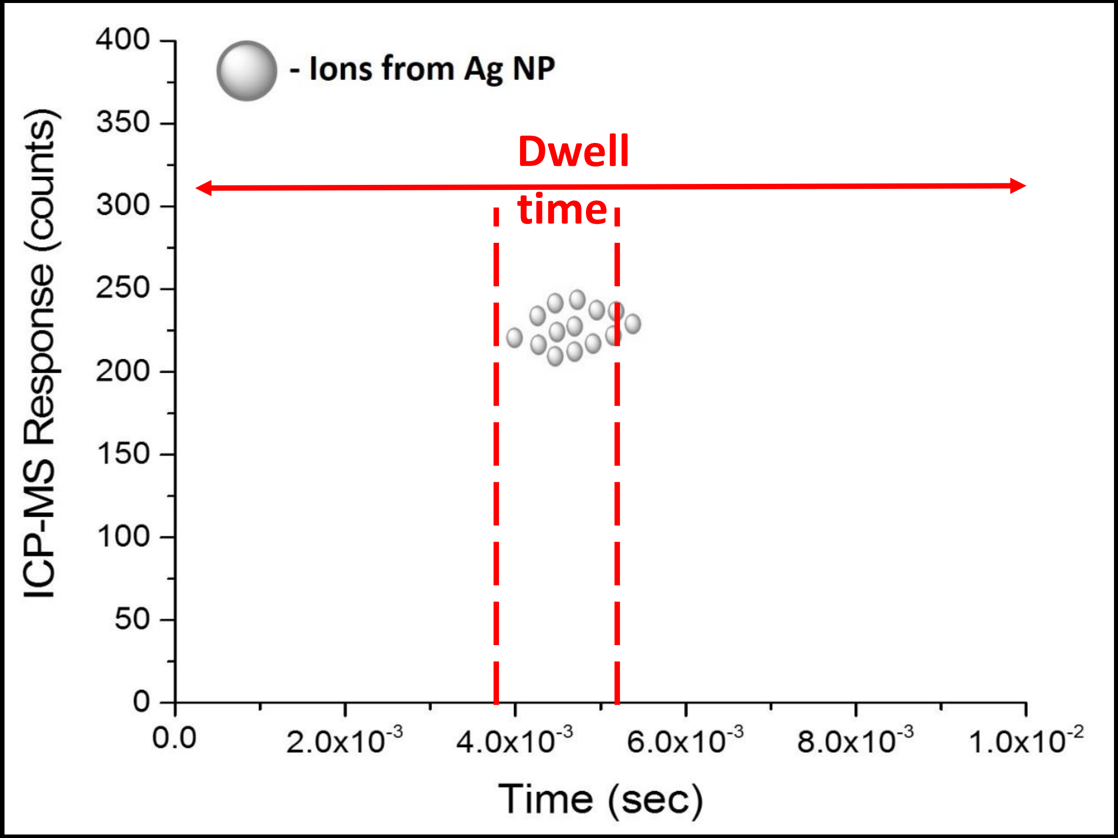

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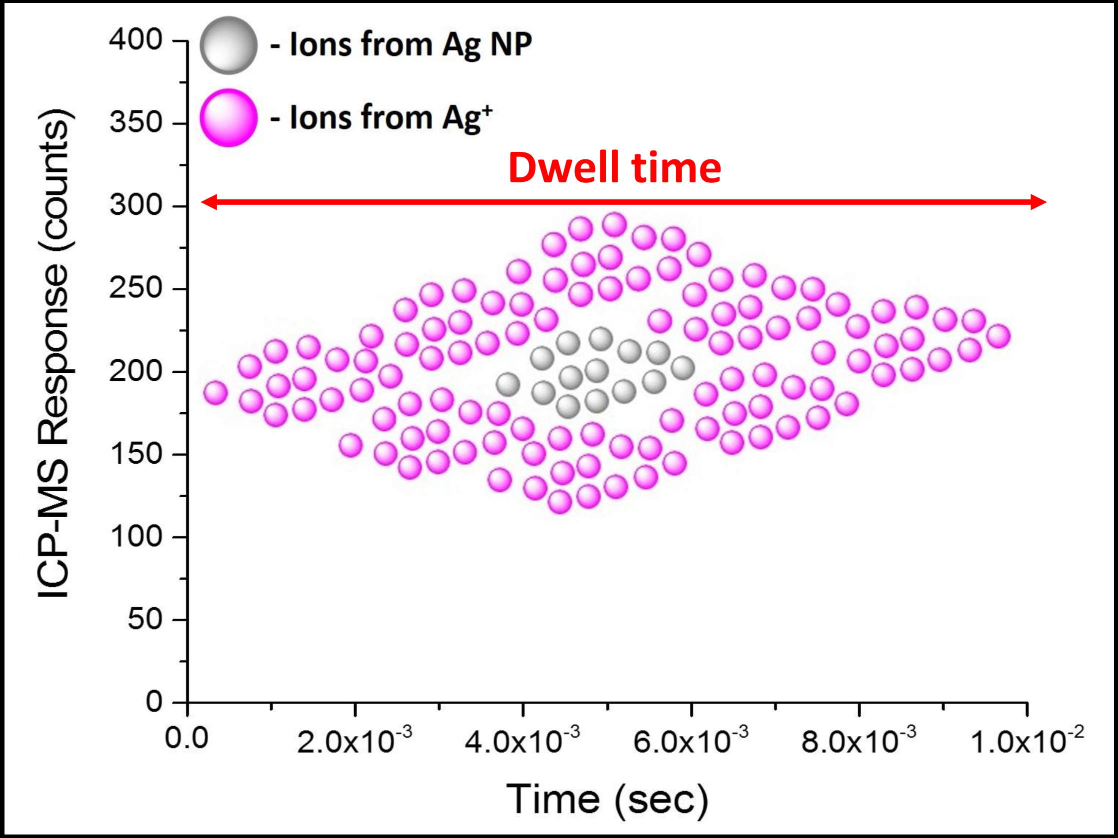

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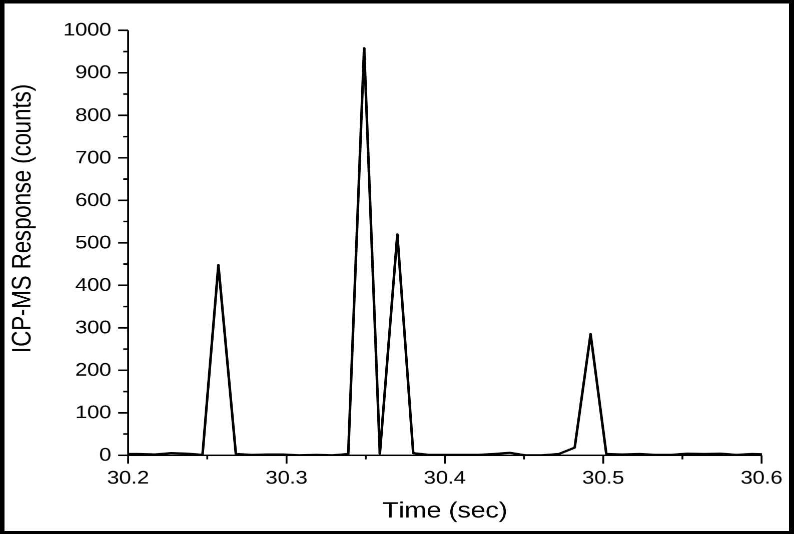
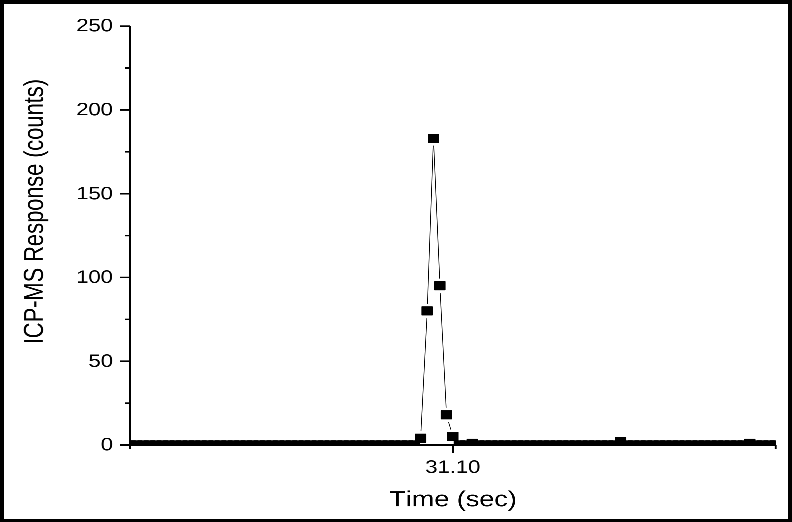
Microsecond-single particle ICP-MS

- Conventional single particle ICP-MS analyzes dilute concentration of nanoparticles at short dwell times (~10ms)
- Nanoparticles events occur over span of hundreds of microseconds (10ms too long)
- Microsecond dwell times parse nanoparticle events into a distribution of intensity
- Improves ability to analyze high particle number concentrations and high dissolved backgrounds
- Opens the door for multi-element analysis on a particle-by-particle basis

Conventional (10ms)



100µs dwell times



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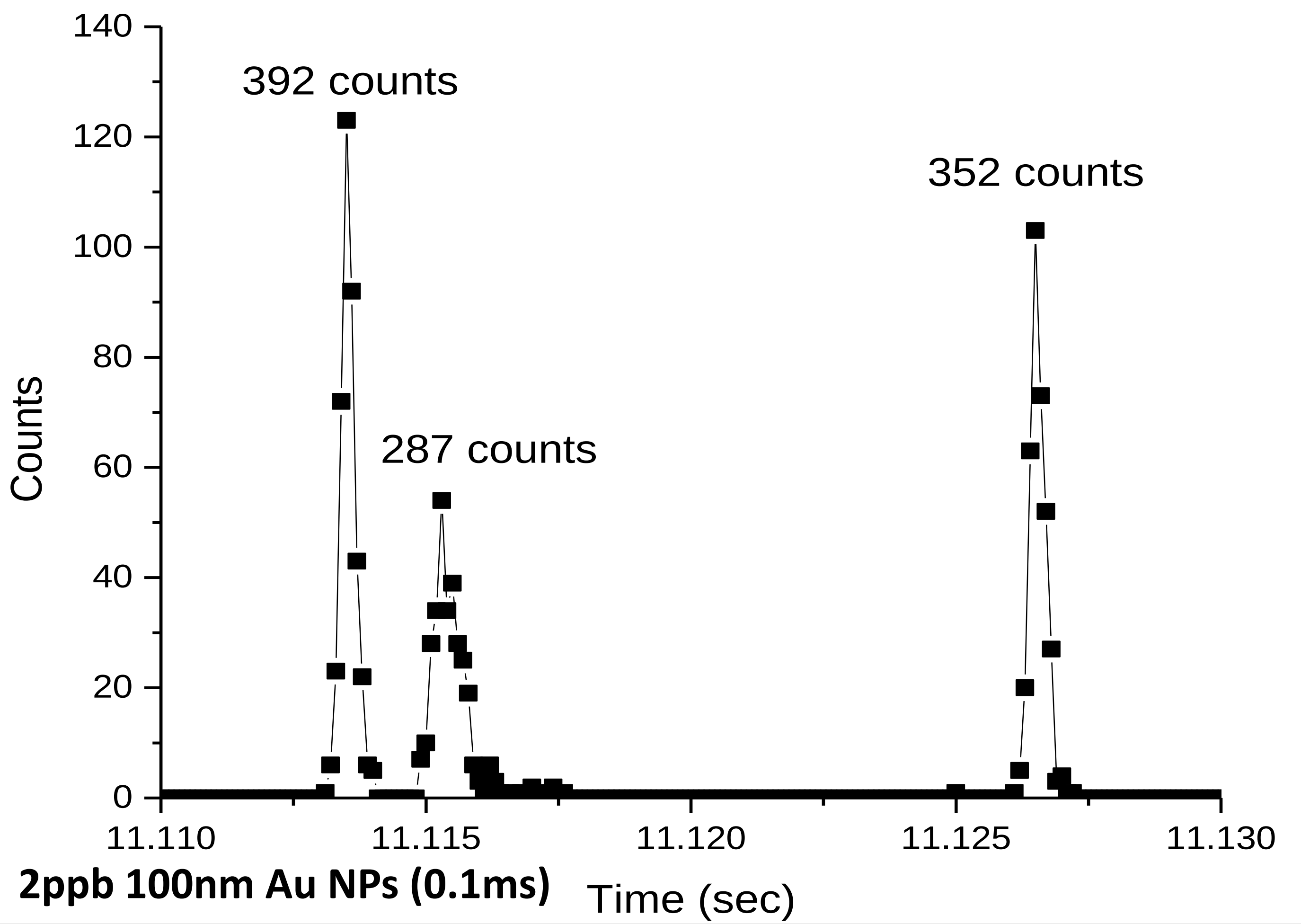
Improving Particle Resolution: Overcoming coincidence



2ppb 100nm Au NPs (0.1ms)

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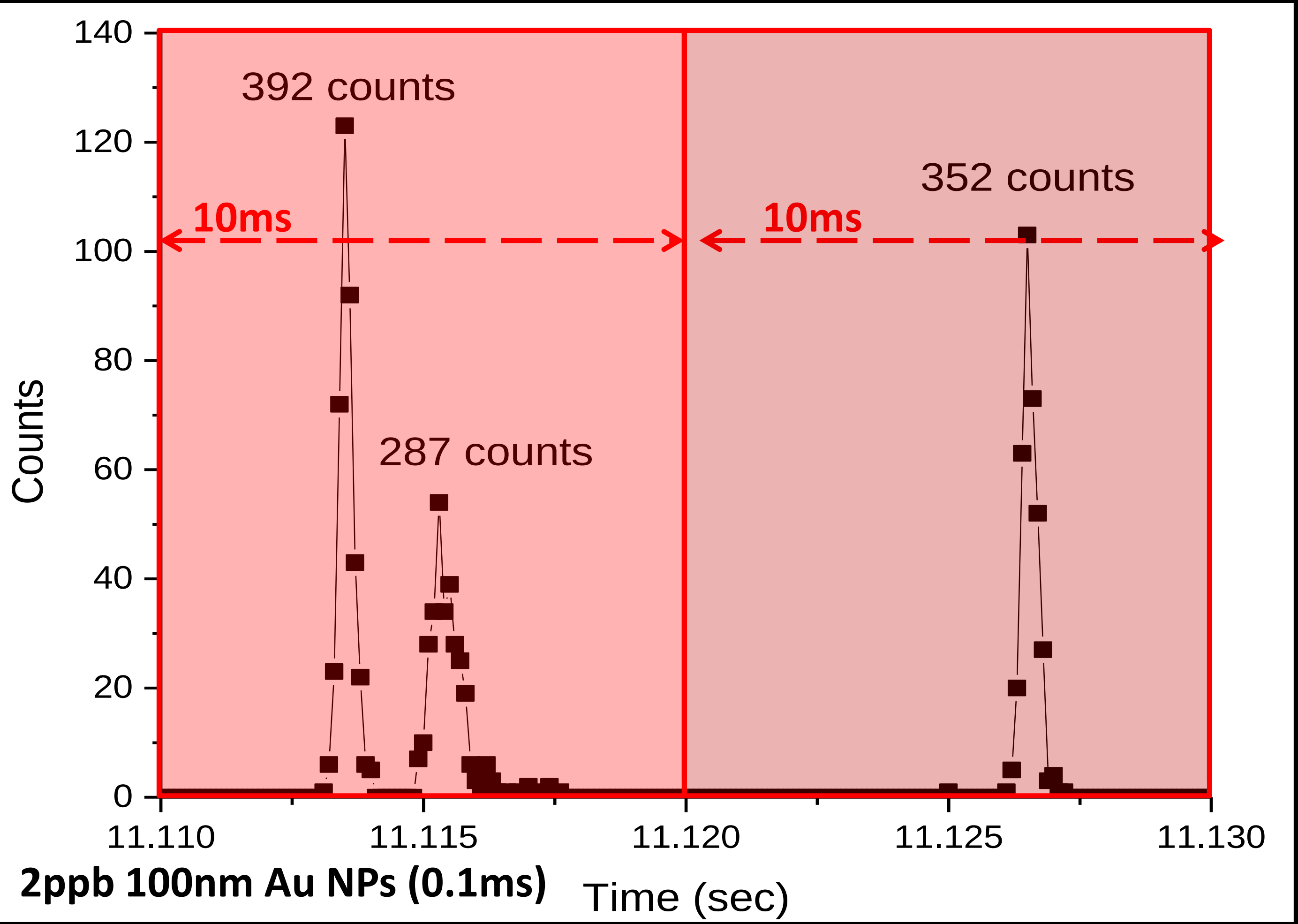
Improving Particle Resolution: Overcoming coincidence



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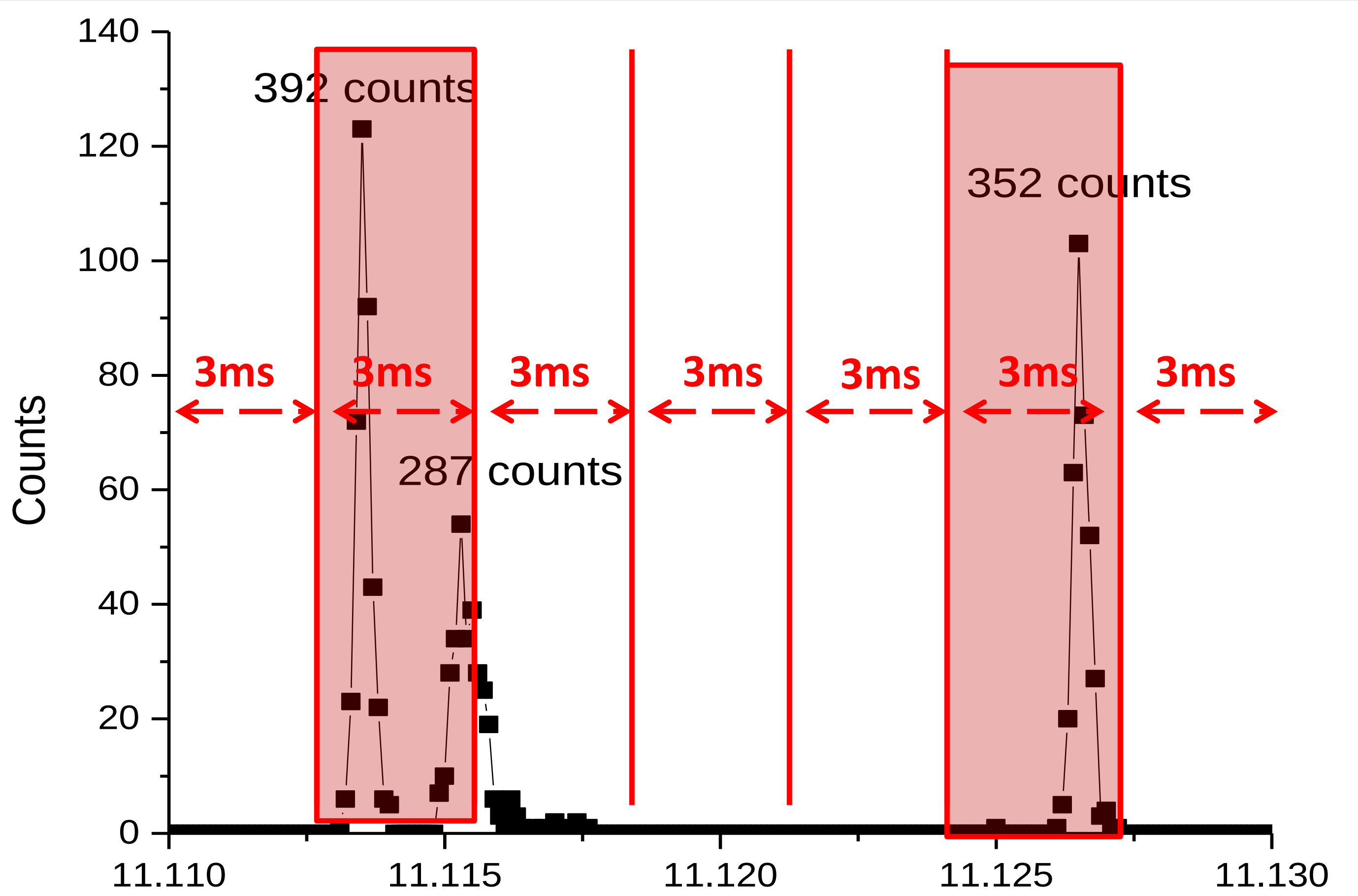

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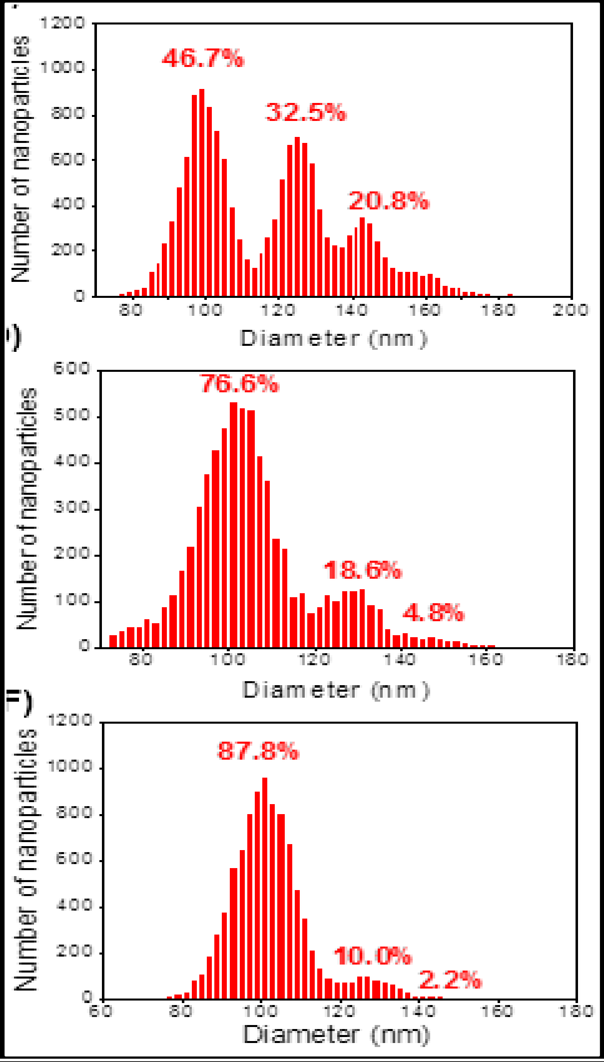
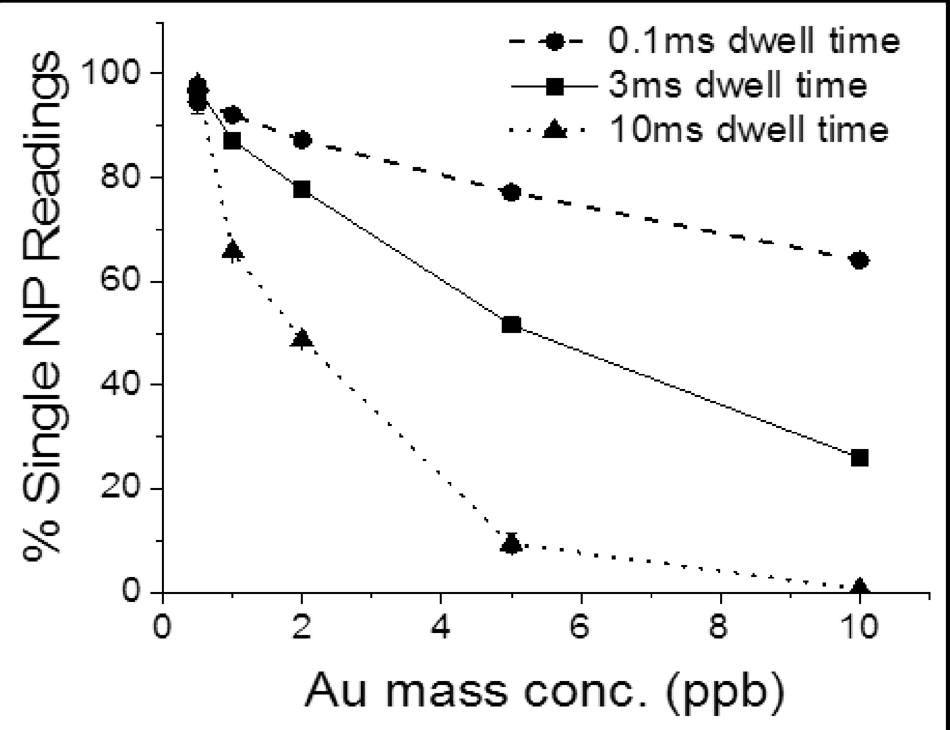


Montaño, M. et al. *Environmental Science: Nano*, **2014**

- Microsecond spICP-MS vastly improves particle resolution
- Particle number concentrations and sizing can be better determined

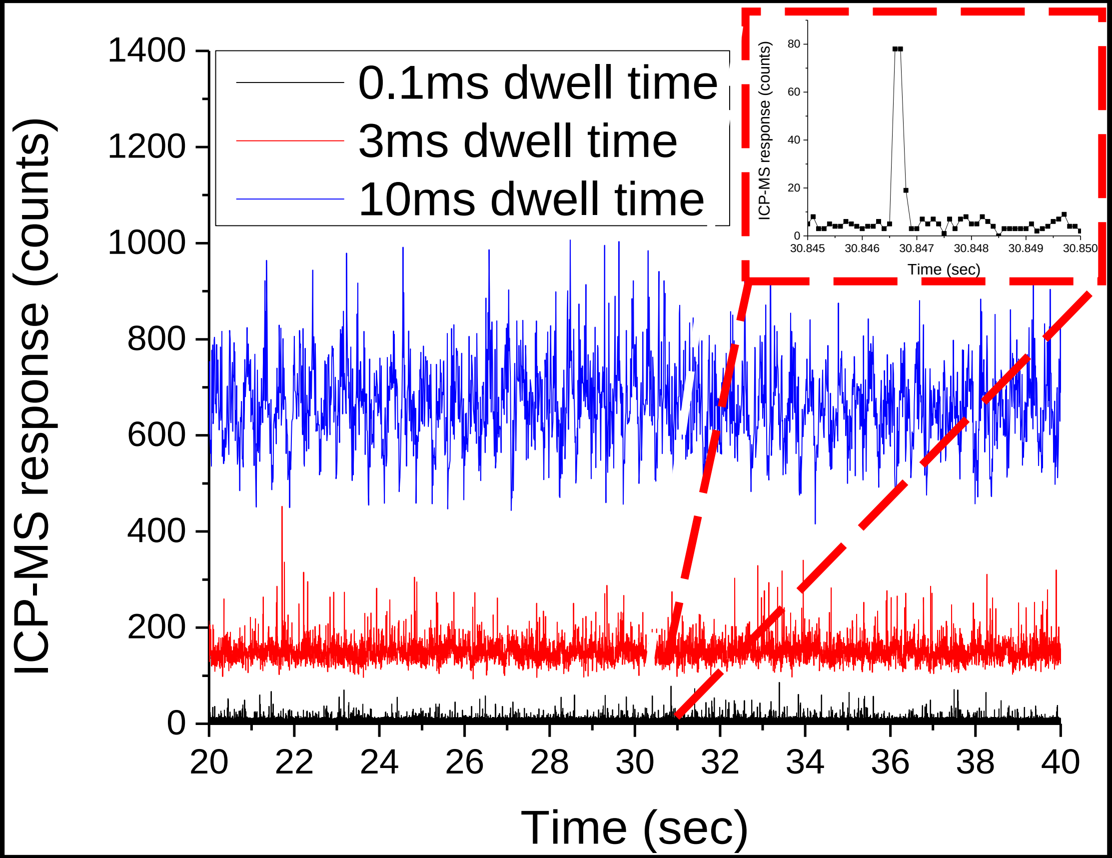


Reducing Background Interference

500ppt Ag^{+} + 50ppt Ag NPs

- Reducing dwell time results in a reduction of counts from dissolved analyte

- Lower dwell times allow for better resolution between background and analyte signals



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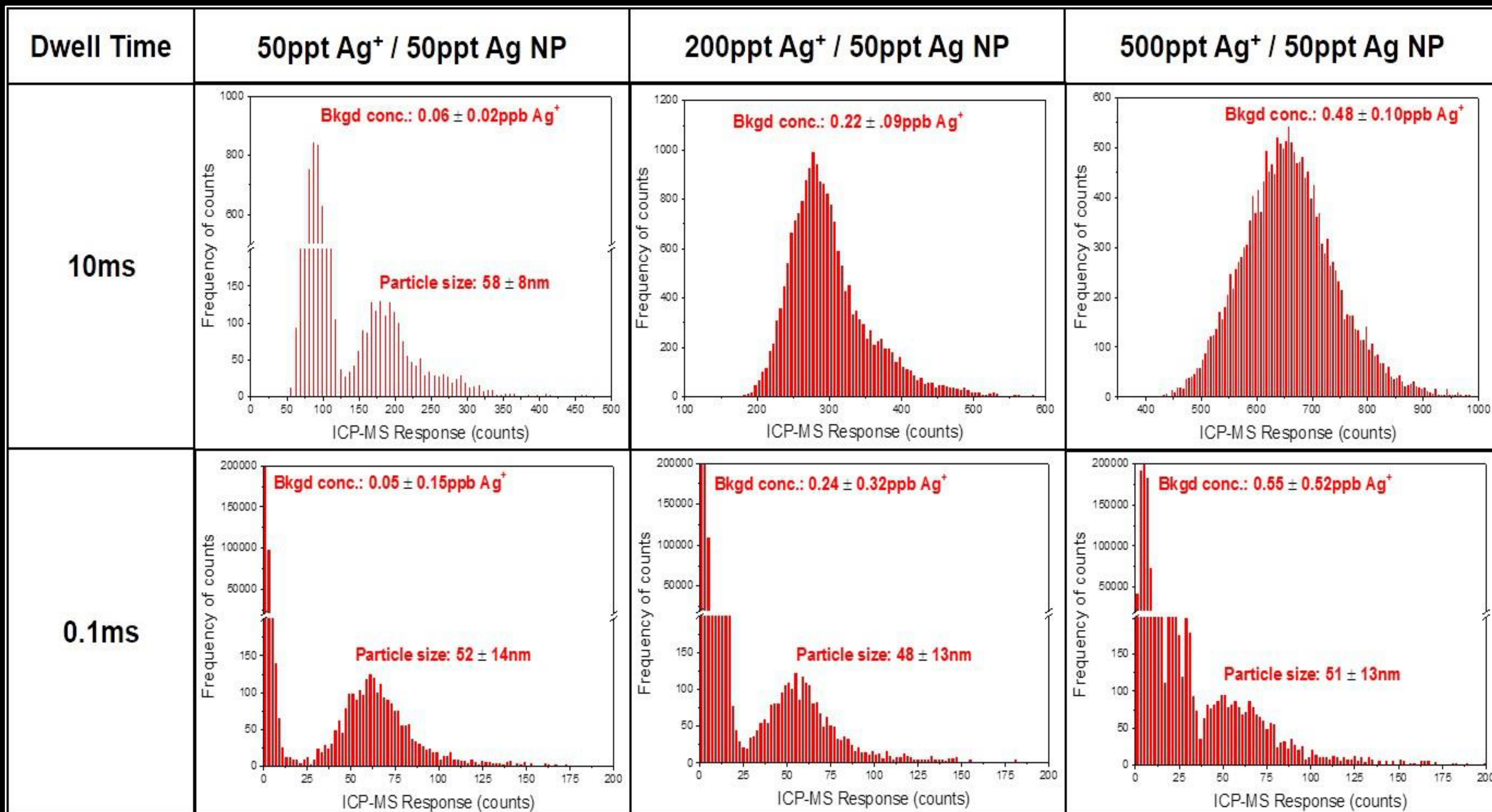
Reducing Background Interference

Increasing Dissolved Ag^+ Concentration →

Decreasing dwell time ↓



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Dual-element Detection in spICP-MS

- New microsecond dwell times allow for the analysis of two elements within a single particle
- Applied to the analysis of complex (core-shell) nanomaterials
- Possible method for differentiating between naturally occurring and engineered nanomaterials

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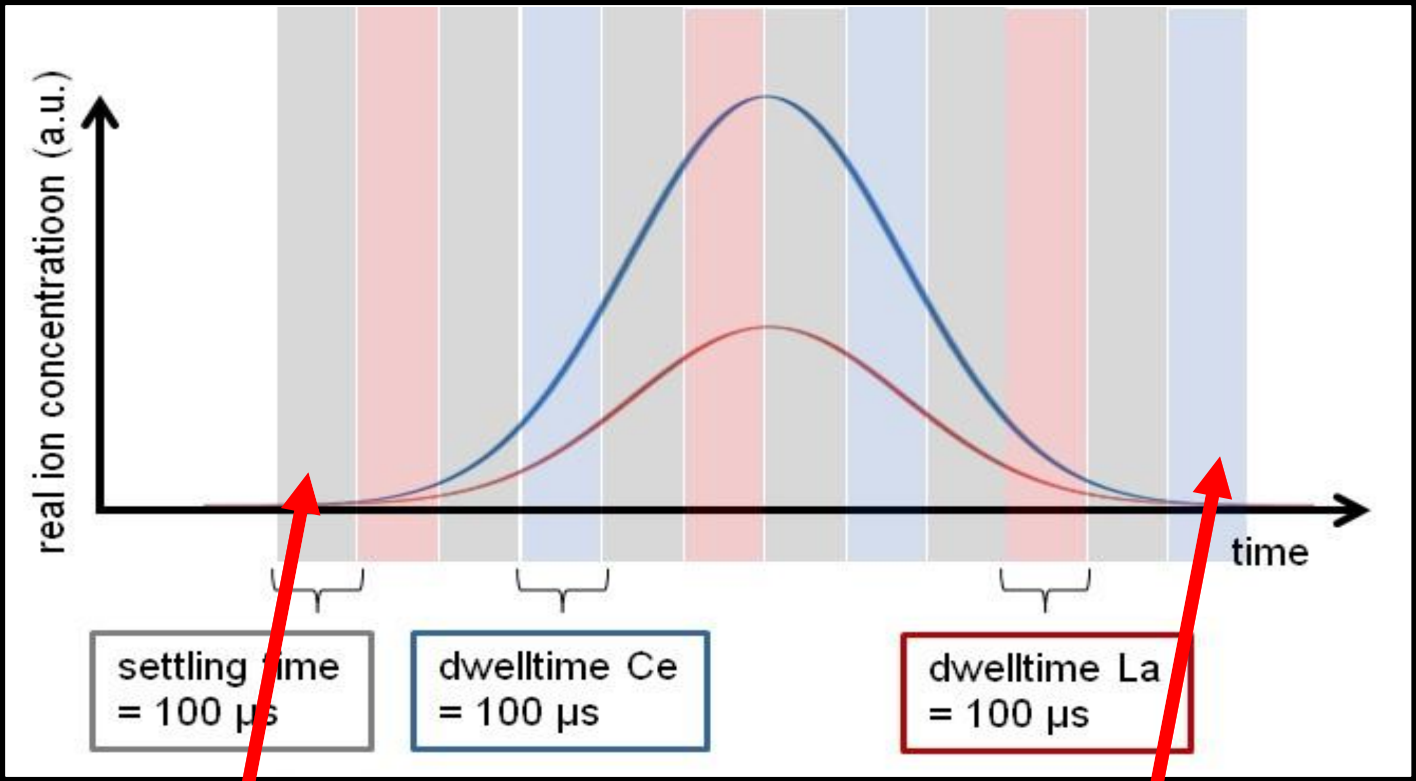
Principles of Dual-element Analysis



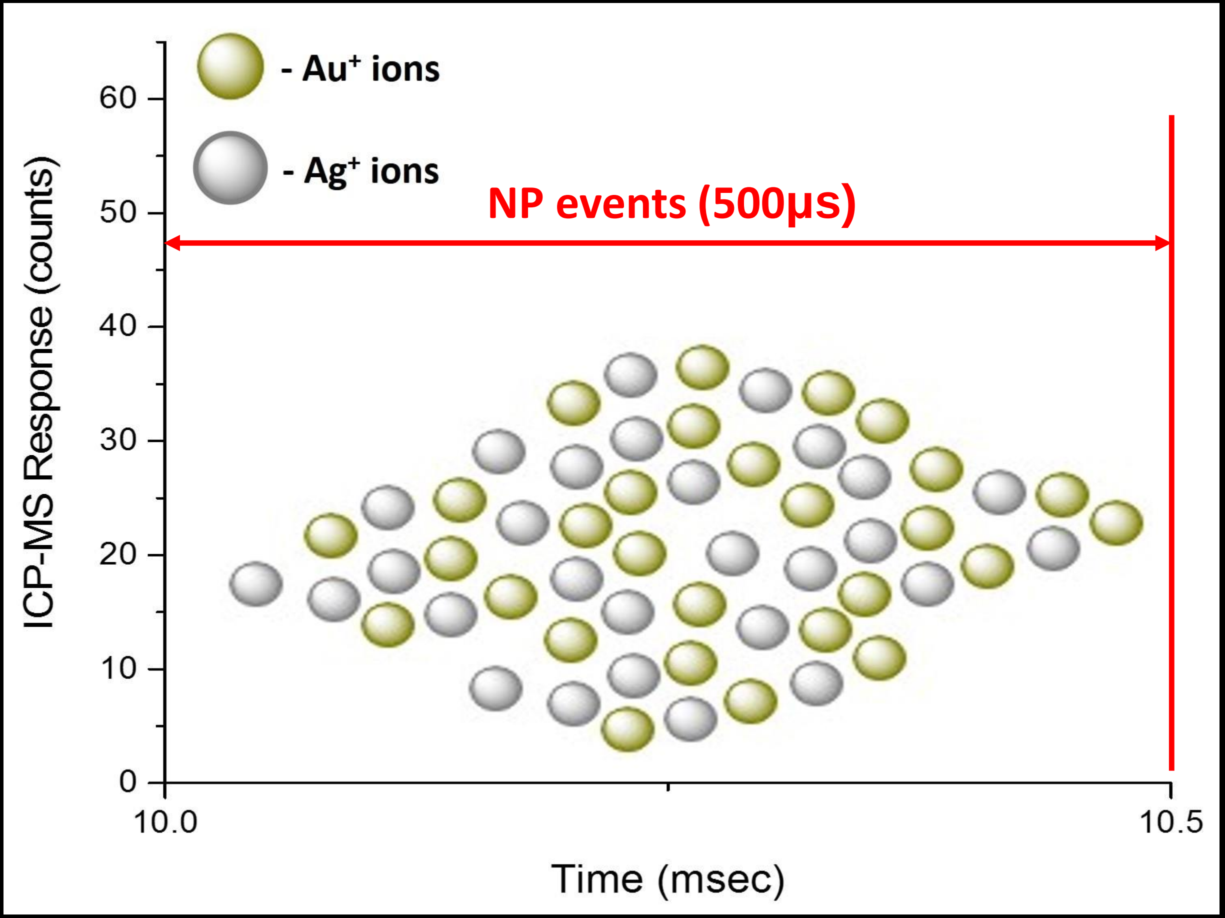
Time required for the quadrupole to switch between the two masses

Dwell time of a given mass analyte

Montaño, M. et al. *Environmental Chemistry*, **In Press**

Limitations of dual-element ICP-MS

- The length of the settling time results in "lost" analyte signal
- Analysis is not simultaneous, and will result in variable signal of the two analytes
- Currently qualitative on a particle by particle basis, but can be quantitative with the overall average of signal intensity



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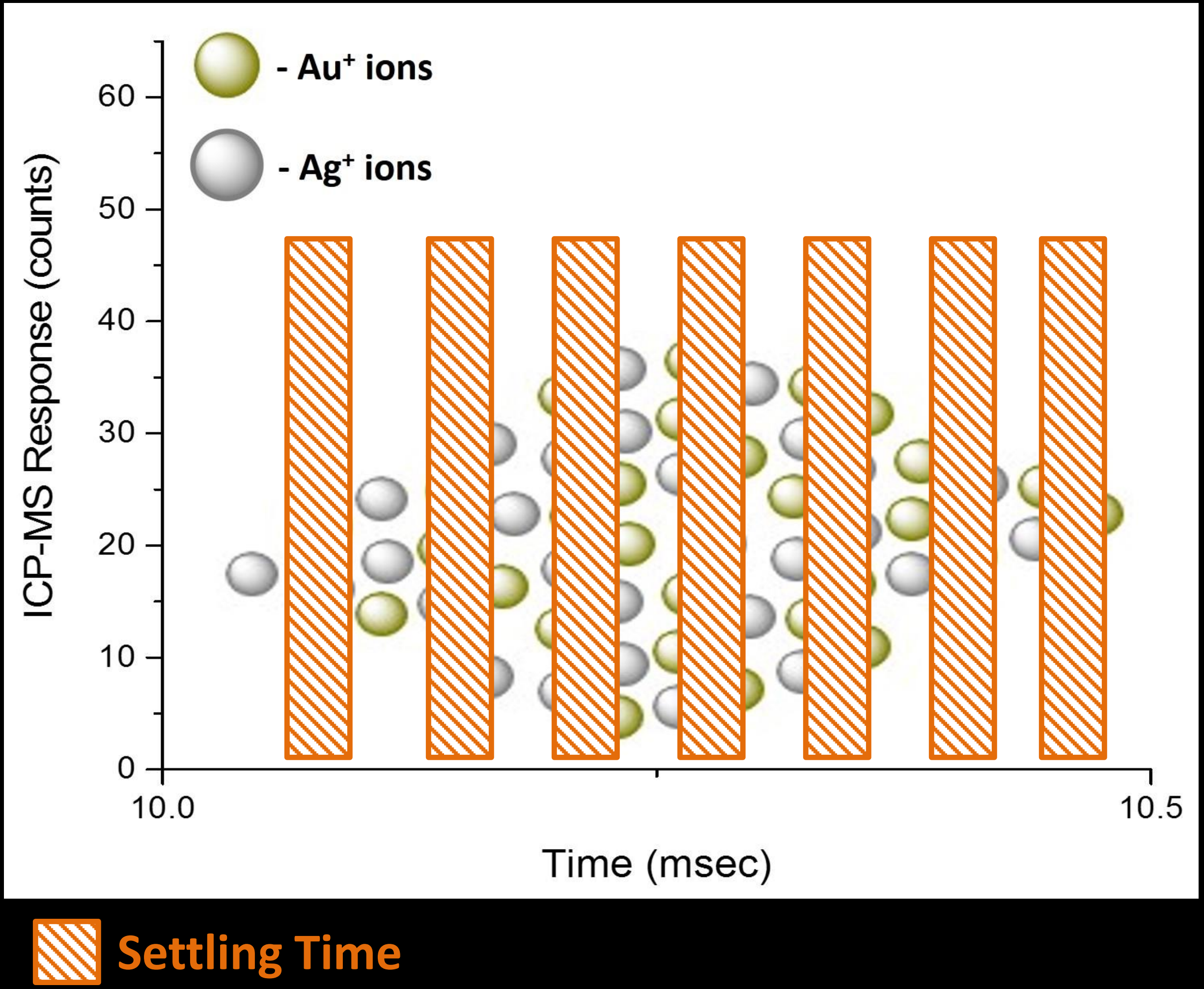

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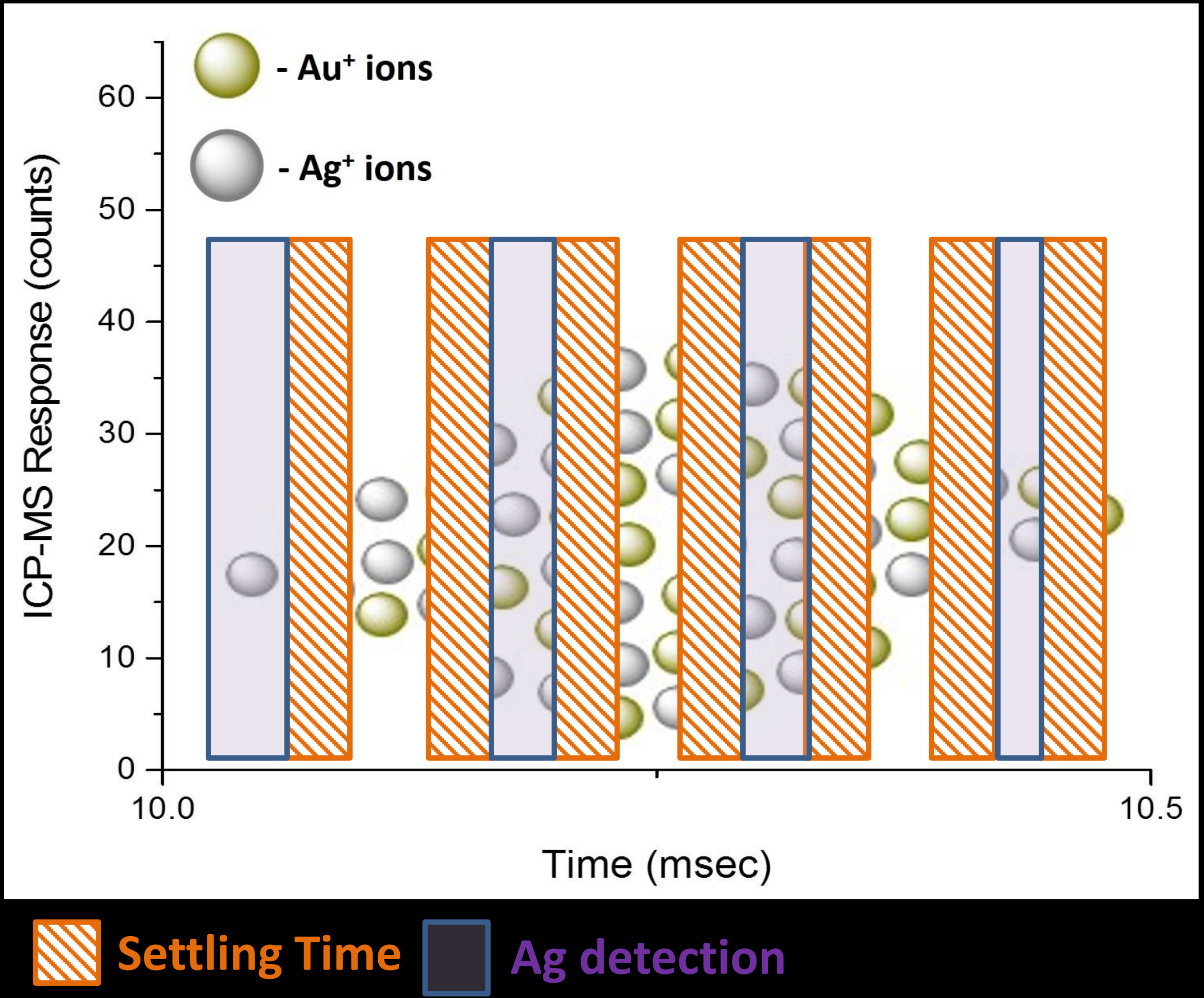

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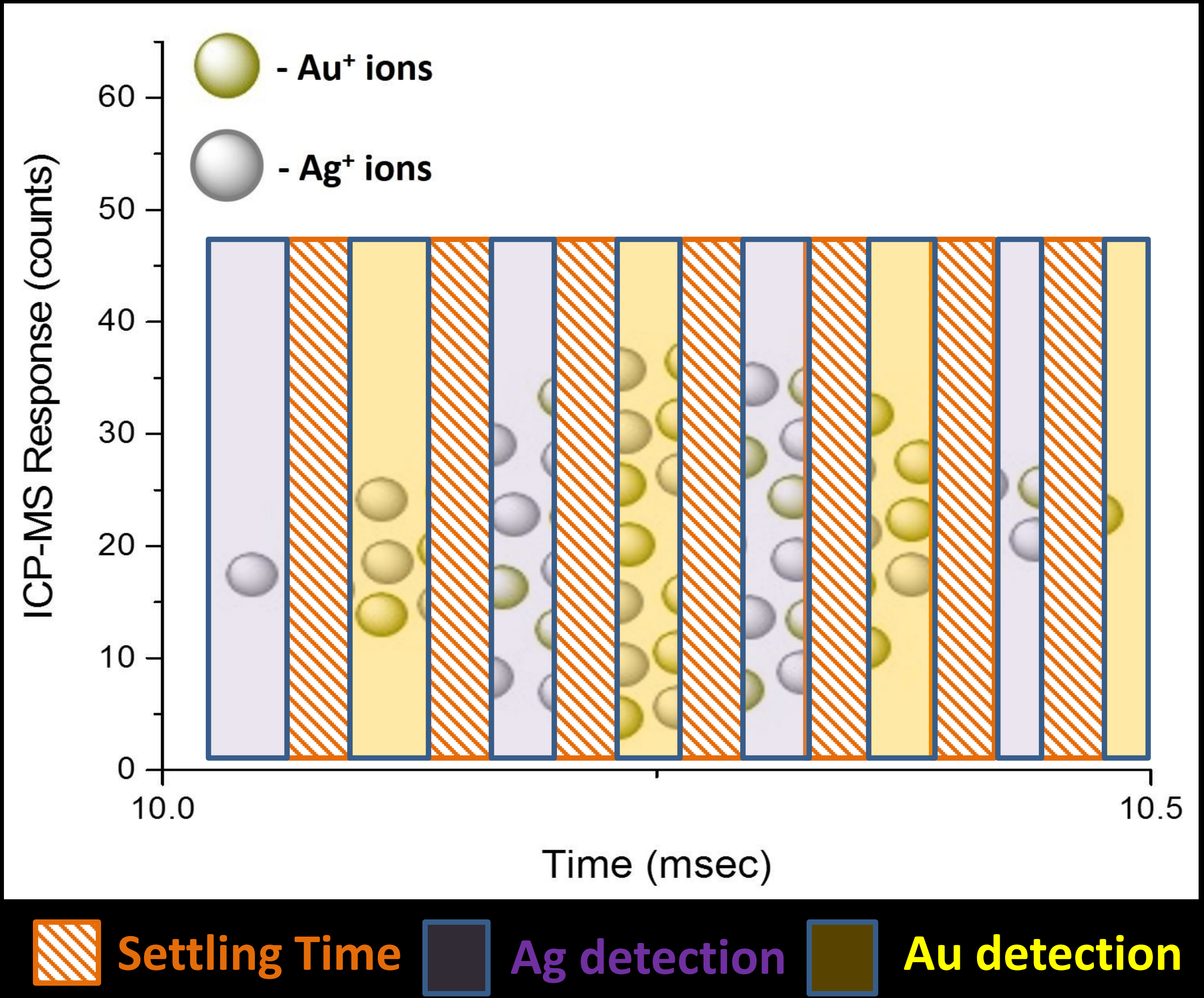
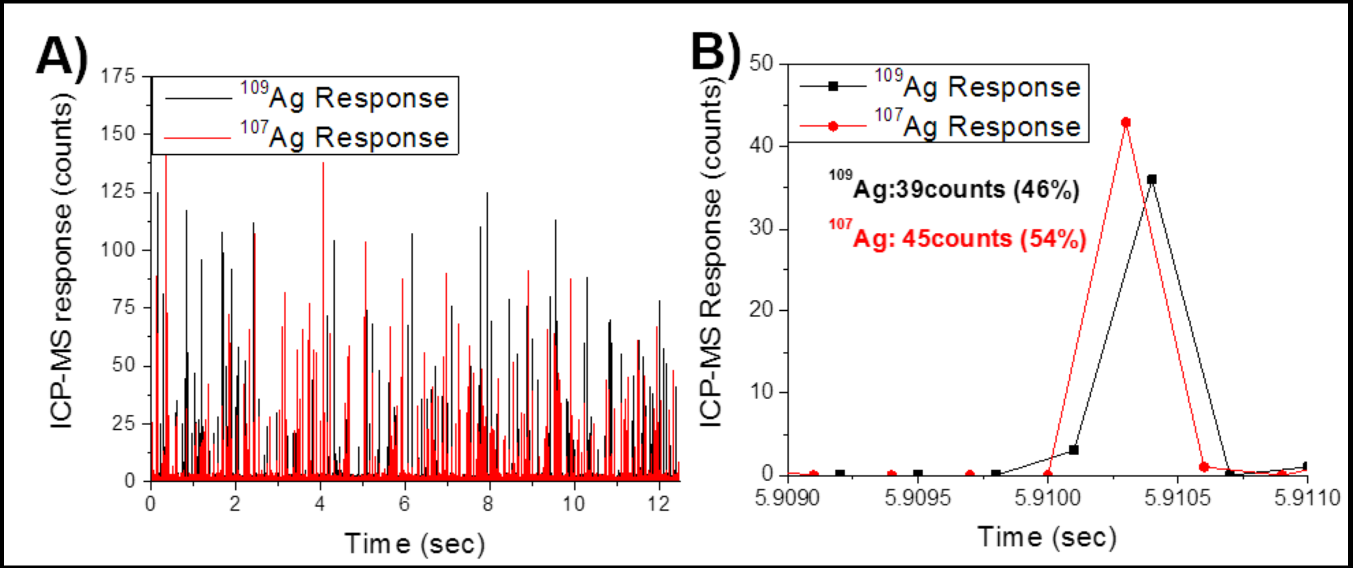


Proof of Concept – Isotopic Ratios

- 60nm silver nanoparticles were analyzed for isotopes ^{107}Ag and ^{109}Ag
- These two isotopes occur in early equal ratios naturally
  (^{107}Ag: 51.35% and ^{109}Ag: 48.65%)
- Some individual peaks show ratios similar to natural isotopic abundance
- Average of overall intensities match closely with natural abundance:
  (^{107}Ag: 50.7% and ^{109}Ag: 49.2%)
  (n= 125000)



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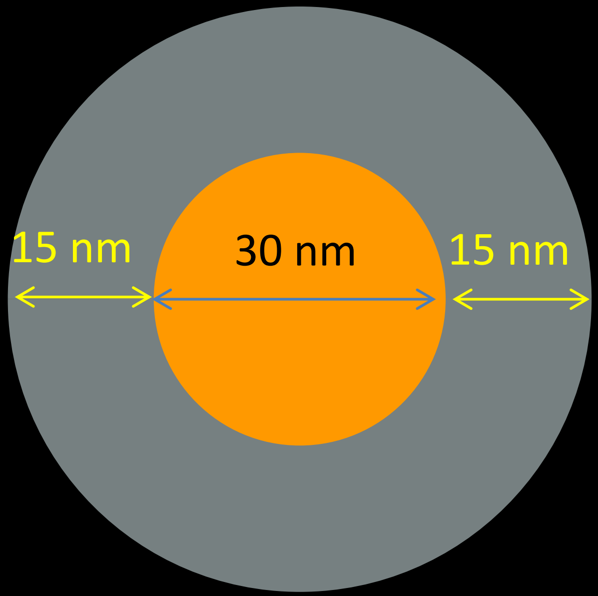
Core-shell Nanomaterials

- Some nanomaterials have complex morphologies such as a core-shell structure

- Examples of core-shell nanomaterials include
  - Carbon-coated metal oxides for catalysis
  - Metal sulfide capped semiconducting quantum dots

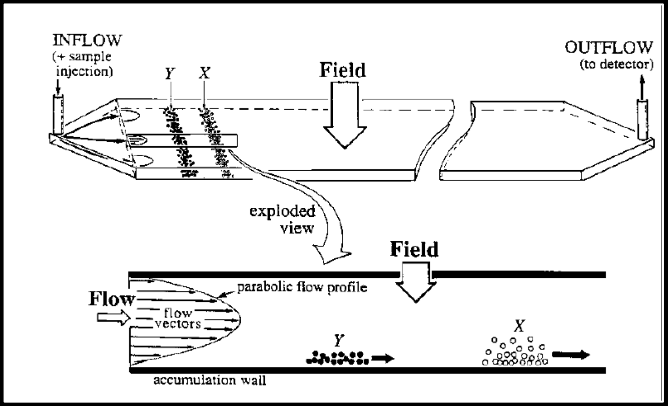
- Both the core and shell must contain an detectable amount of mass to be analyzed by dual-element spICP-MS



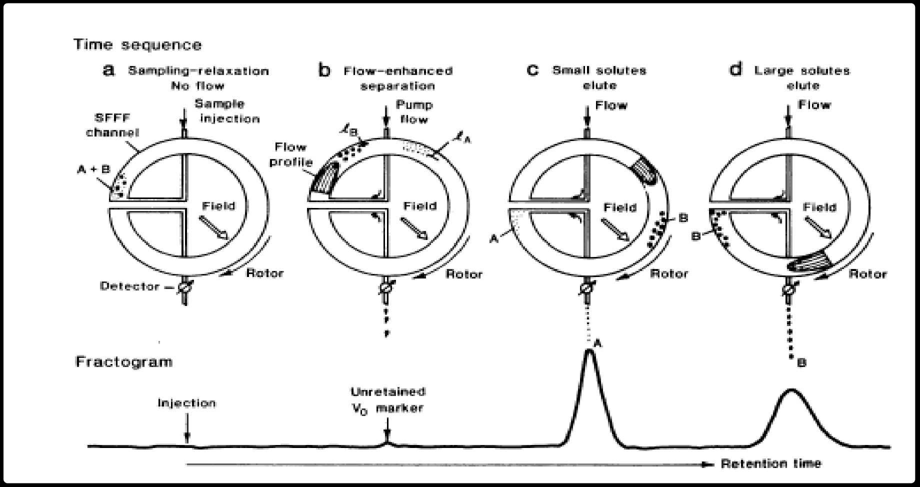
Experimental Set-up

- Gold core (30nm) – Silver shell (15nm) nanoparticles were analyzed by single particle ICP-MS
- Fractions were collected from both Flow field flow fractionation (AF4) and Centrifugal-FFF (Sed-FFF)
- AF4 is a separation technique based off of hydrodynamic diameter
- Centrifugal-FFF separates according to a particles buoyant mass

Asymmetrical Flow Field Flow Fractionation (AF4)



Centrifugal Field Flow Fractionation (Sed-FFF)



Suwanpetch, R.; Montaño, M.; Tadjiki, S.; Ranville, J. *In preparation*, **2014**

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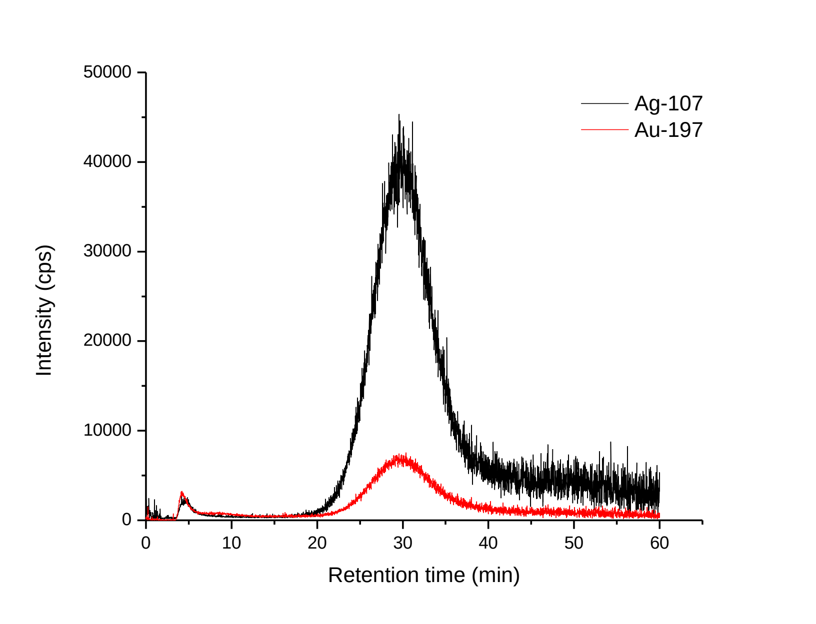
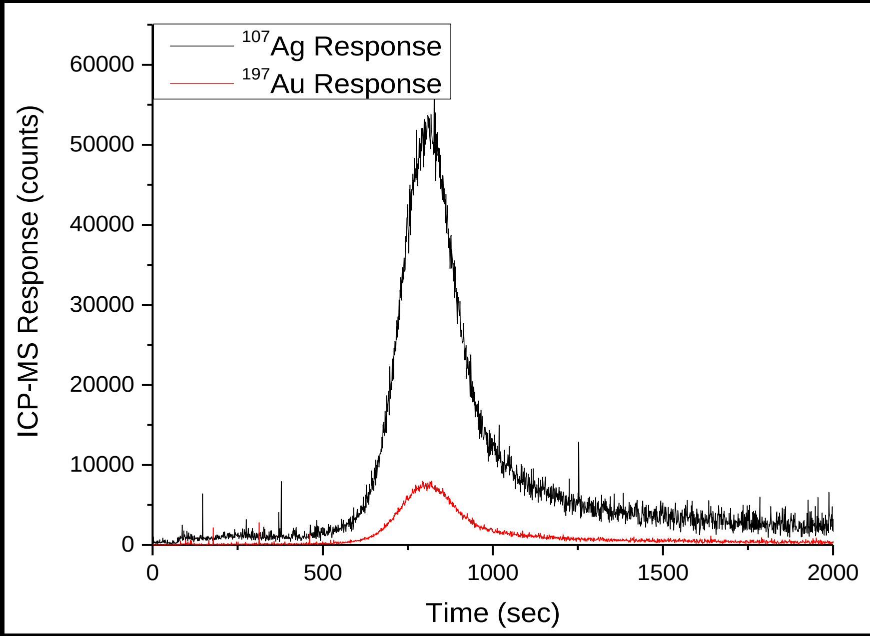
Flow Field Flow Fractionation Chromatograms

- Both fractograms show co-eluting of gold and silver peaks
- Evidence for one single particles, instead of individual gold and silver particles in solution

AF4 coupled to ICP-MS



Sed-FFF coupled to ICP-MS



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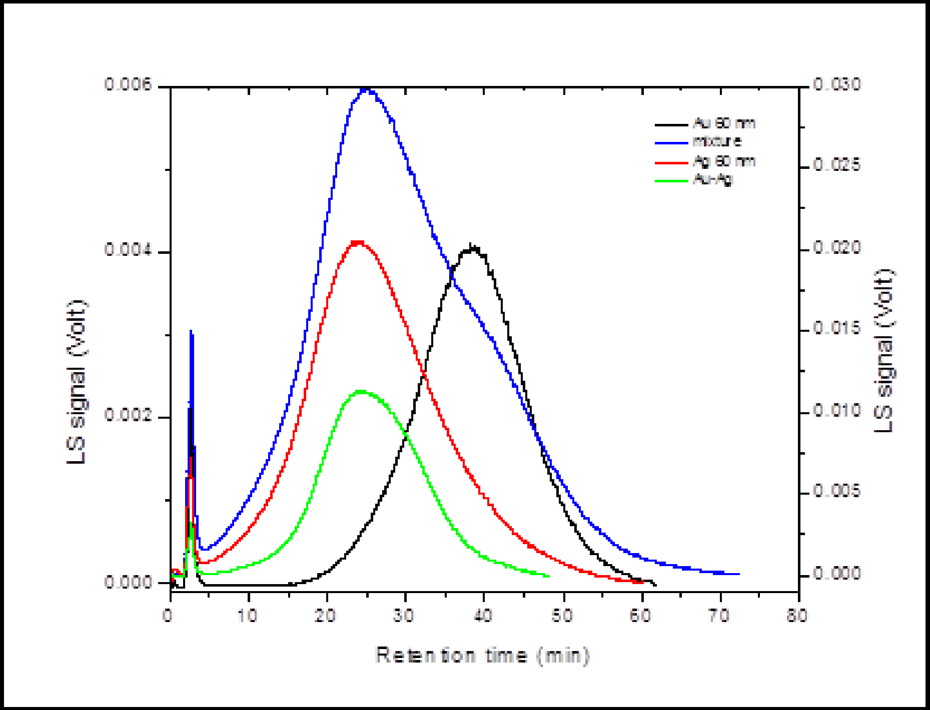
Flow Field Flow Fractionation Chromatograms - Mixtures

- Separation of a mixture by AF4 would show just one particle type at 60nm
- Separation of particles by Sed-FFF would show particle of similar mass
- Analysis by spICP-MS can differentiate between core-shell (bi-metallic) and single metal nanomaterials



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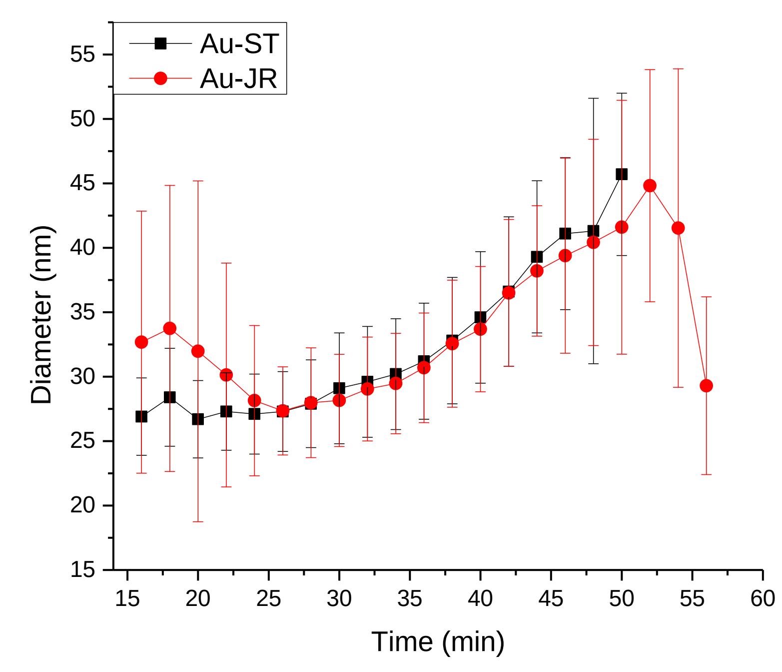
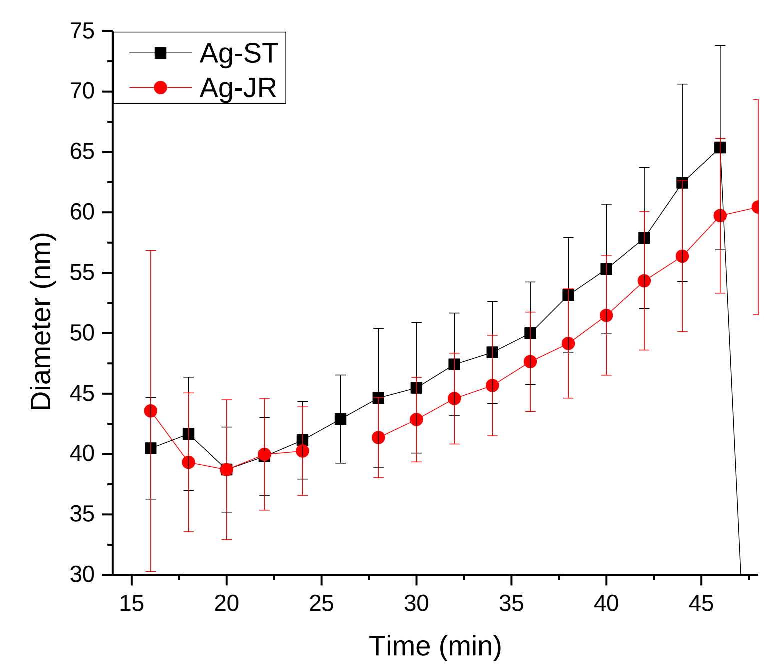
Particle size of Core-shell NMs by spICP-MS

- Particle sizes are consistent with distribution of intensity by FFF-ICP-MS
- Gold core at peak maxima (30min) is 30nm
- Total diameter at peak maxima (assuming 30nm core) is ~45nm

Gold Core Diameter Comparison



Total Diameter Comparison (Based on silver mass)



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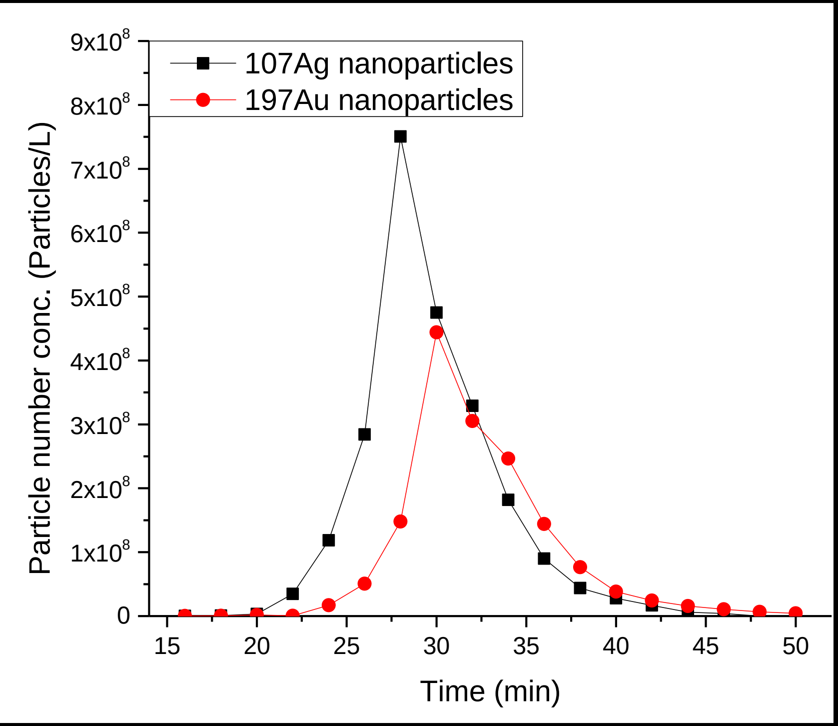
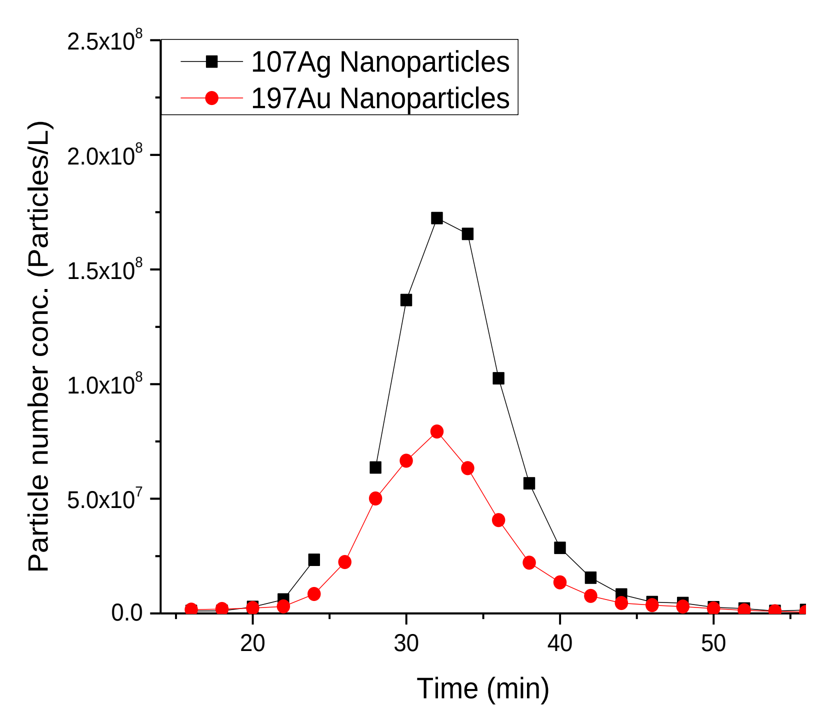
Particle Number Concentration Comparison

- Discrepancy in particle number concentration (# of events detected)
- Possible loss of gold analyte signal to background due to small size

Replicate 1



Replicate 2



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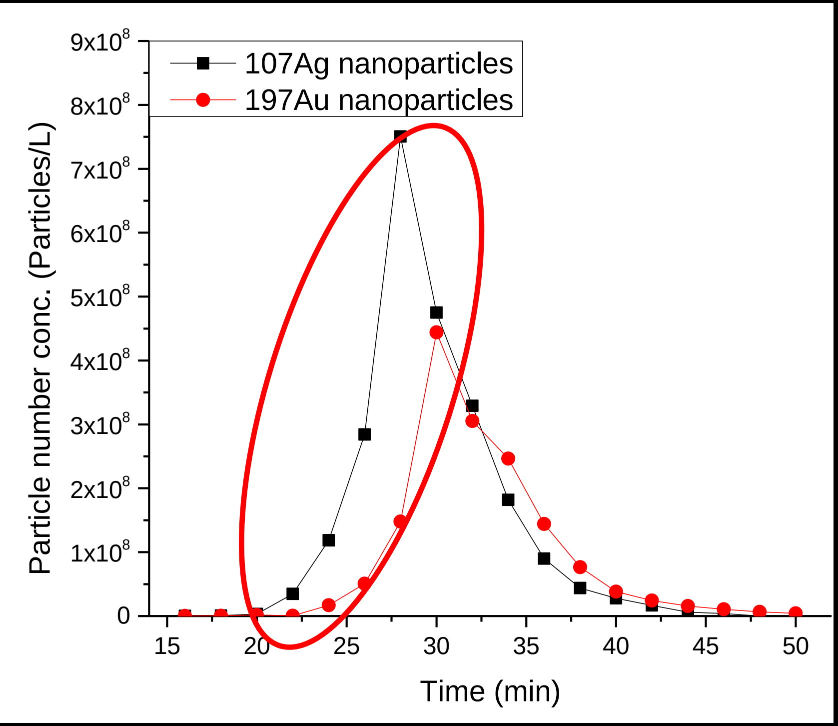

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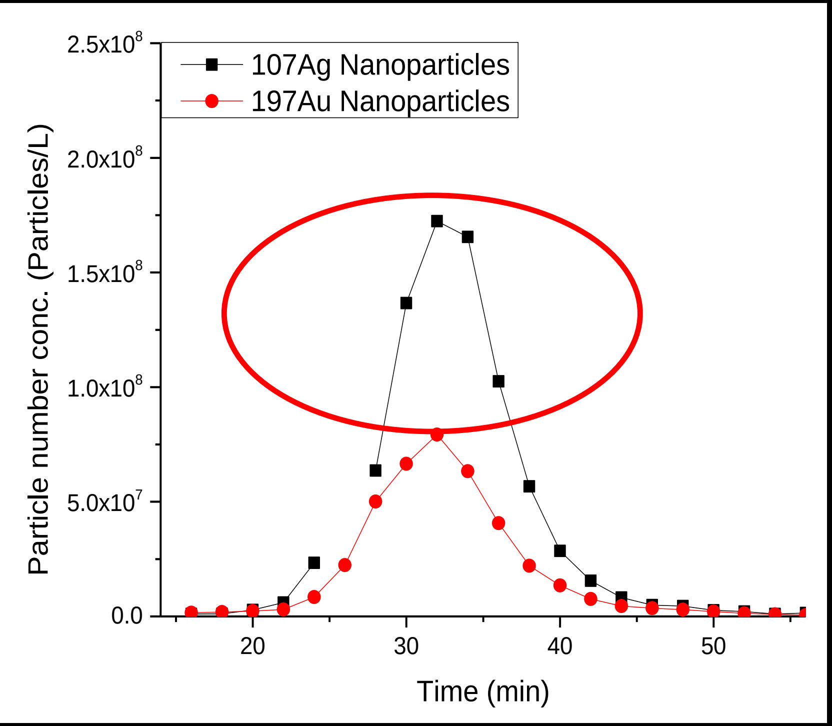

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Dual-element Analysis of Core-shell NPs

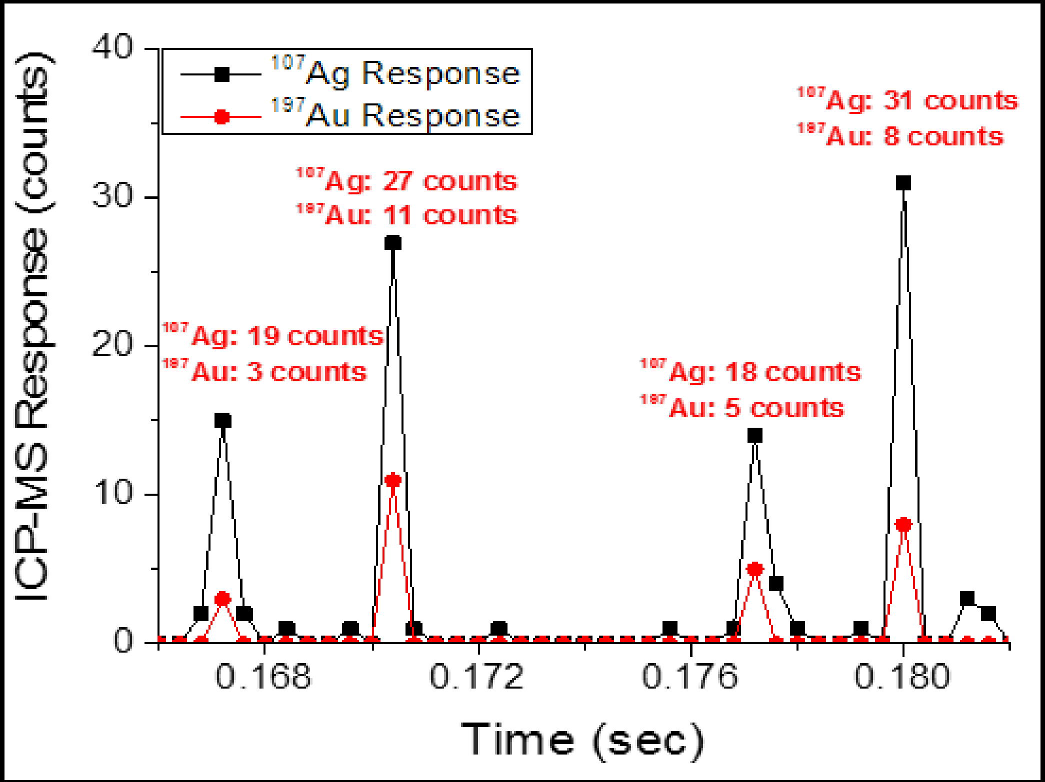
- Dual-element analysis of NPs show presence of both gold and silver
- Some gold signal may be lost to the background
- Dual element analysis and individual particle analysis shows consistent elemental intensity ratios:

  Dual element analysis

  ^{107}Ag: 77.7% /^{197}Au: 22.3%

  Individual particle analysis

  ^{107}Ag: 71.2%/ ^{197}Au: 28.8%



Montaño, M. et al. *Environmental Science: Nano*, **2014**

Environmental Analytical Challenges – Natural Nanomaterials

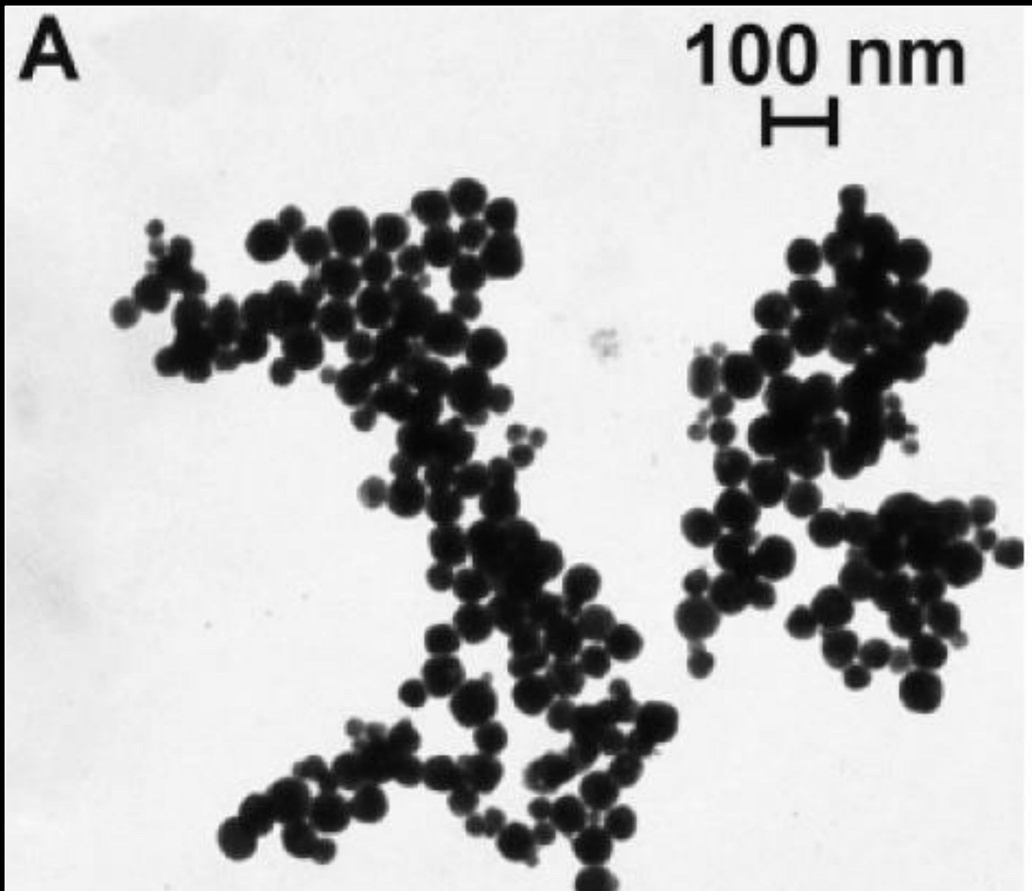
- ENPs will be released into an environment containing several naturally occurring nanomaterials
- Natural nanomaterials are present in concentrations much higher than expected release concentrations
- Many of these nanomaterials will be of similar chemical composition to their engineered analogues

Ti-containing mineral in biosolid (Kiser)

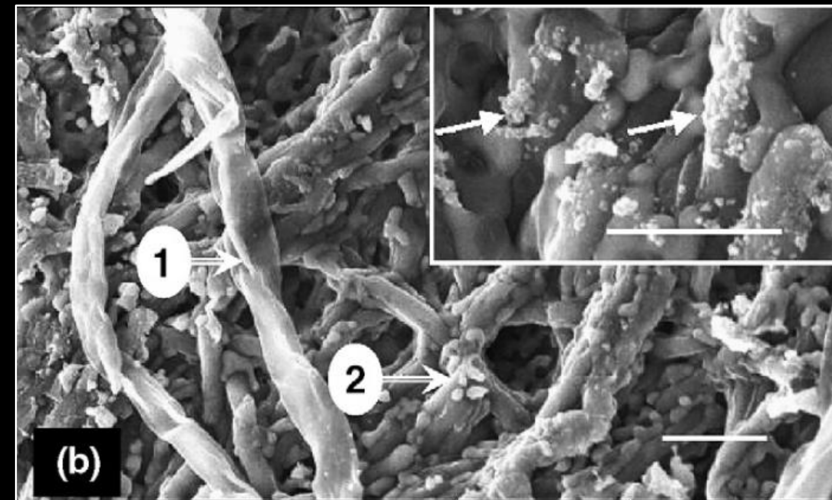
TiO_2 nanoparticles in toothpaste

Kiser, M. et al. *Environmental Science and Technology*, **2008**

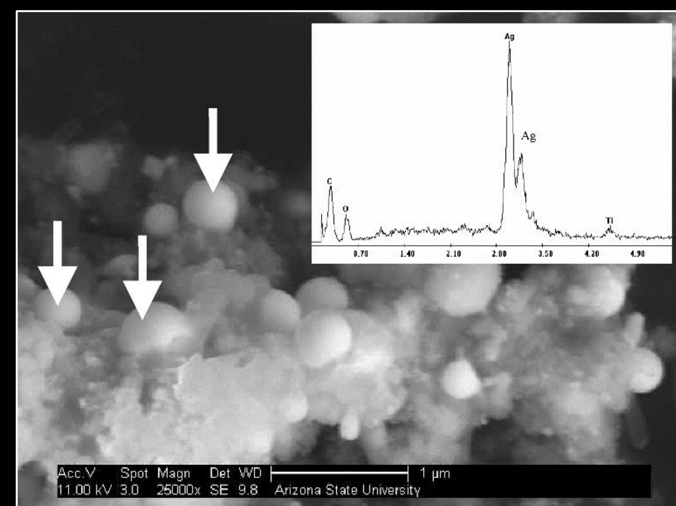
Environmental Analytical Challenges – Natural Nanomaterials



Ag nanoparticles prepared by silver ammonia reduction (Panacek)



Ag nanoparticles synthesized by *Aspergillus flavus* (Vigneshwaran)



Ag nanoparticles found in sock fabric (Benn)

Kiser, M. et al. *Environmental Science and Technology*, **2008**

Manuel David Montaño
Colorado School of Mines
July 10th, 2014

ENM vs. NNP Properties

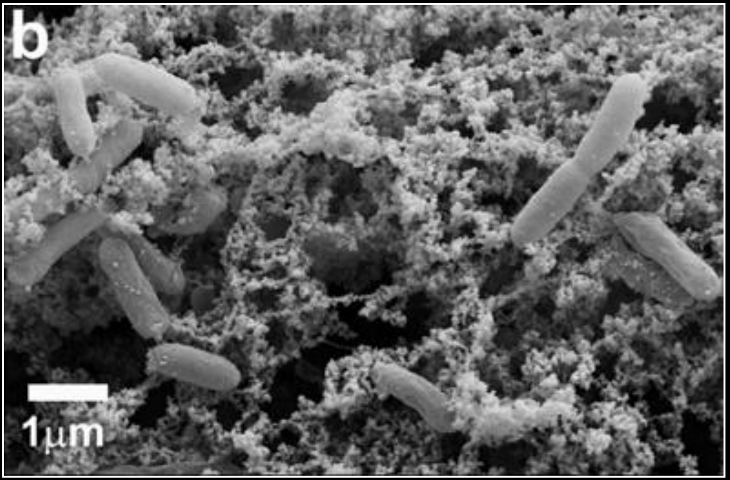
POTENTIAL DISCRIMINATING PROPERTIES	
Size distribution	- Natural particles may have broader size distributions than manufactured ENMs
Morphology	- ENMs can have complex shapes and highly engineered surface coatings to distinguish them from naturally occuring particles
Elemental compostition	- Natural particles can have elemental/isotopic impurities where ENMs tend to be pure

- Most engineered nanomaterials have naturally occurring analogues
- Some key differences can be used to differentiate natural and engineering NMs
- Environmental processes may drastically affect some of these properties (i.e. surface coatings, aggregation state, size distribution)
- Elemental composition may remain the most unchanged property in the environment

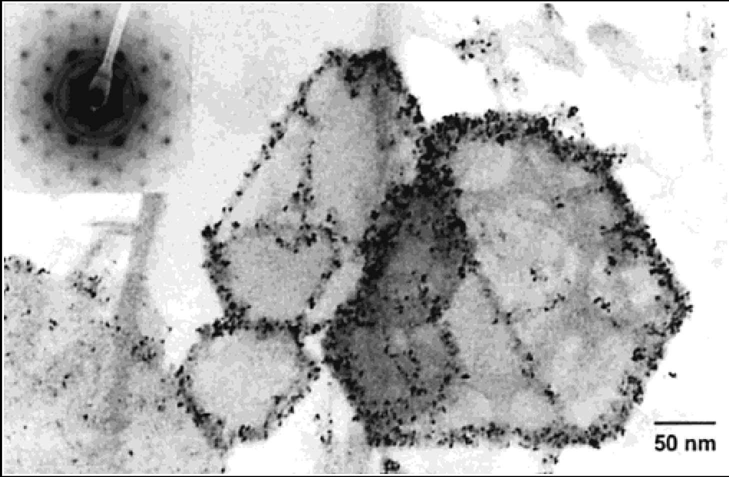
Montaño, M. et al. *Environmental Chemistry*, **In Press**

Elemental Ratio Analysis

- Elemental ratios may be used to differentiate engineered and naturally occurring nanomaterials
- Natural nanomaterials may have broader size distribution than more tightly controlled ENMs
- Particle-by-particle analysis of elemental ratios (µsec-spICP-MS) can be used to differentiate between naturally occurring and engineered nanomaterials



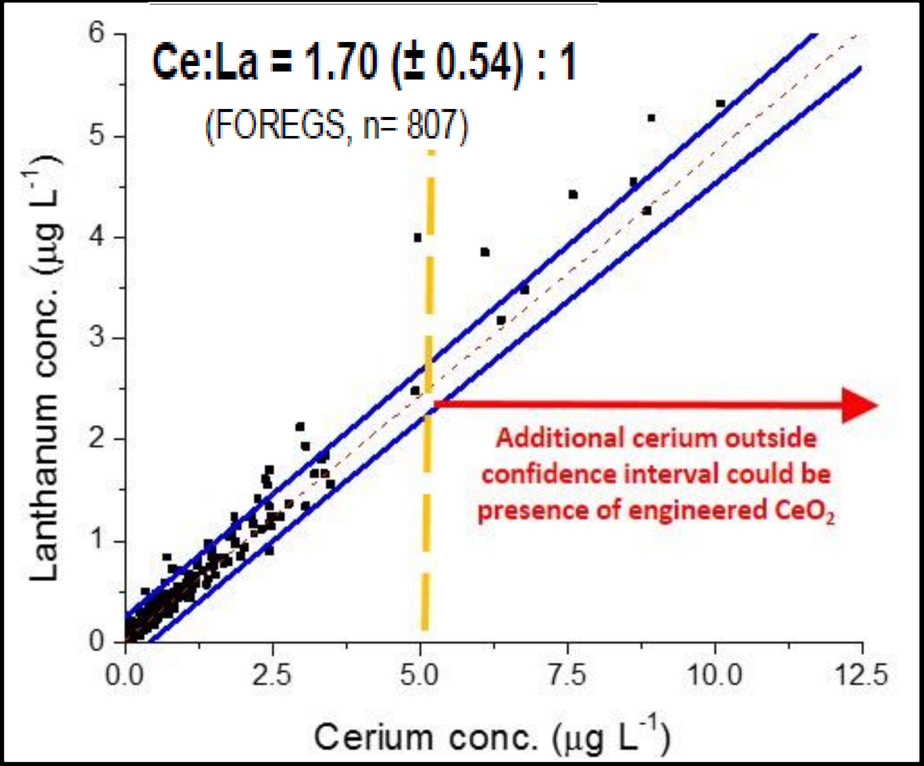
Uraninite nanoparticles precipitated from soluble U(VI) by *Shewanella oneidensis* MR-1 strain



Uraninite nanoparticles precipitated on mixed Fe(II)/Fe(III) hydroxides

1) Montaño, M. et al. *Environmental Chemistry*, **In Press**
2) O'Loughling, E. et al. *Environ Sci. and Tech.* **2003**
3) Burgos, W. et al. *Geochimica et Cosmochimica Acta.* **2008**

Elemental Ratio Analysis



- Natural elemental ratios show a trend with a natural variation
- Statistically significant deviations outside confidence interval of trend may be presence of engineered nanomaterials
- May require significant amounts of engineered nanomaterial

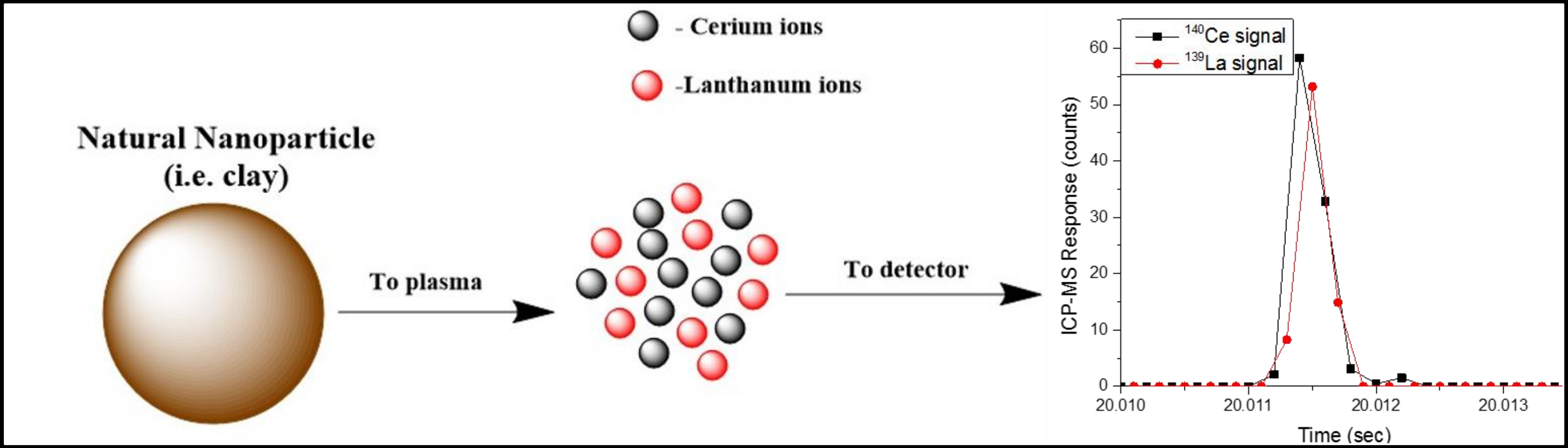
$$\frac{\text{Ce } concentration\ \left(\frac{\mu g}{L}\right)}{\text{La } concentration\ \left(\frac{\mu g}{L}\right)} = \frac{\frac{1.7\mu g}{L}\,Ce}{\frac{1\mu g}{L}\,La} = 1.7$$

$$\frac{\frac{1.7\mu g}{L}\text{Ce} + \frac{170ng}{L}\,CeO_2\ NPs}{\frac{1\mu g}{L}\,La} = 1.87$$

- Limited information about physical/chemical state of nanomaterials (i.e. aggregation)

Montaño, M. et al. *Environmental Chemistry*, **In Press**

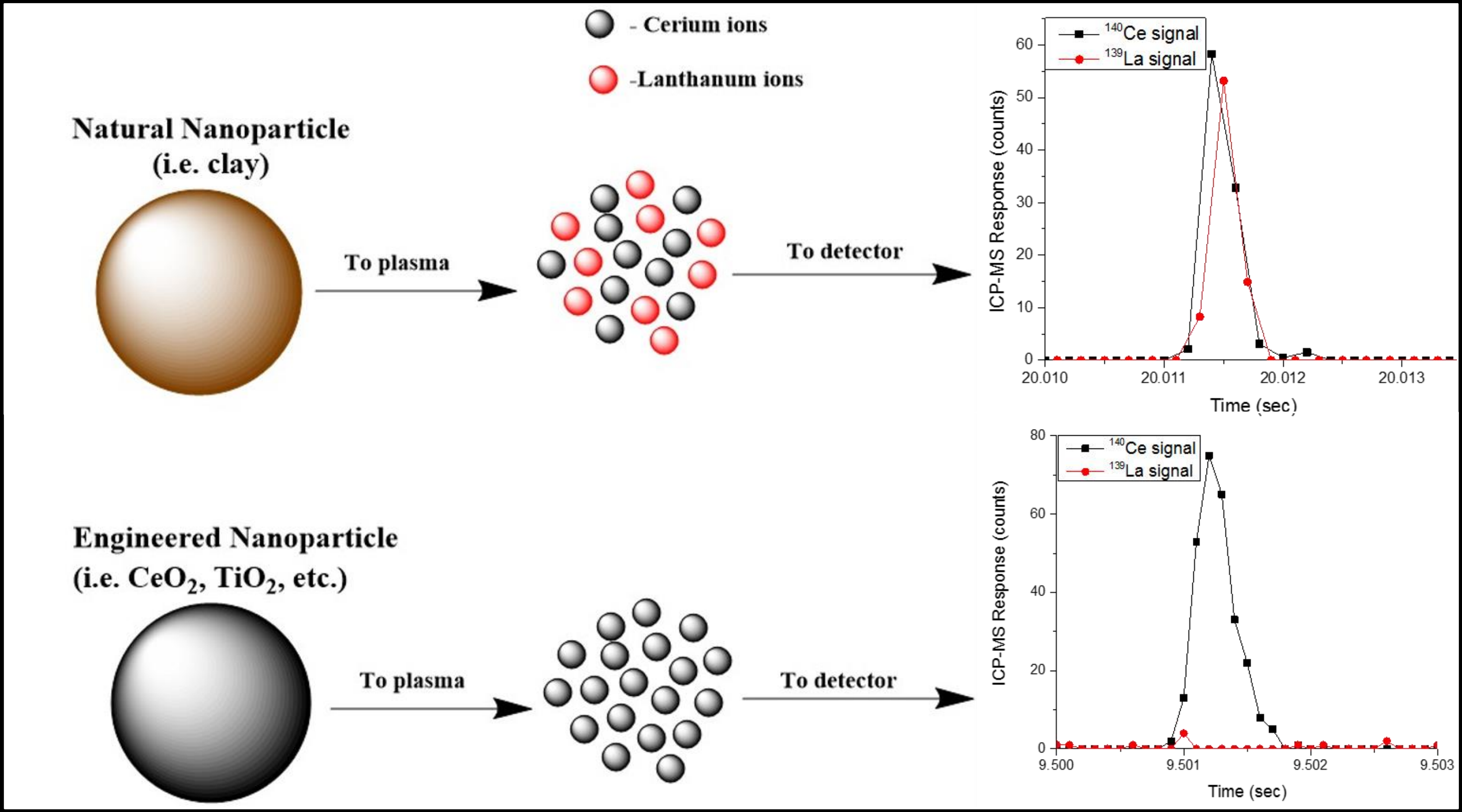
Particle-by-particle Elemental Analysis



- Analysis of a natural nanoparticle will show presence of many elements
- Summation of elemental signal can be used to give elemental ratio on a particle basis

Montaño, M. et al. *Environmental Chemistry*, **In Press**

Particle-by-particle Elemental Analysis

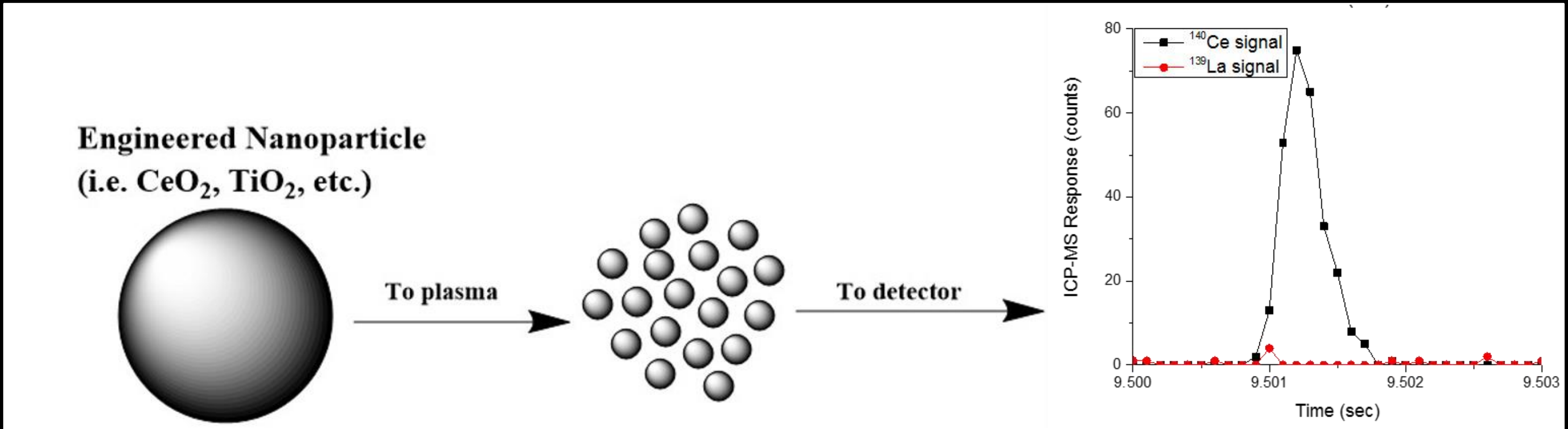


Montaño, M. et al. *Environmental Chemistry*, **In Press**

Particle-by-particle Elemental Analysis

- Engineered nanomaterial will show the presence of only one element, or have a different elemental ratio

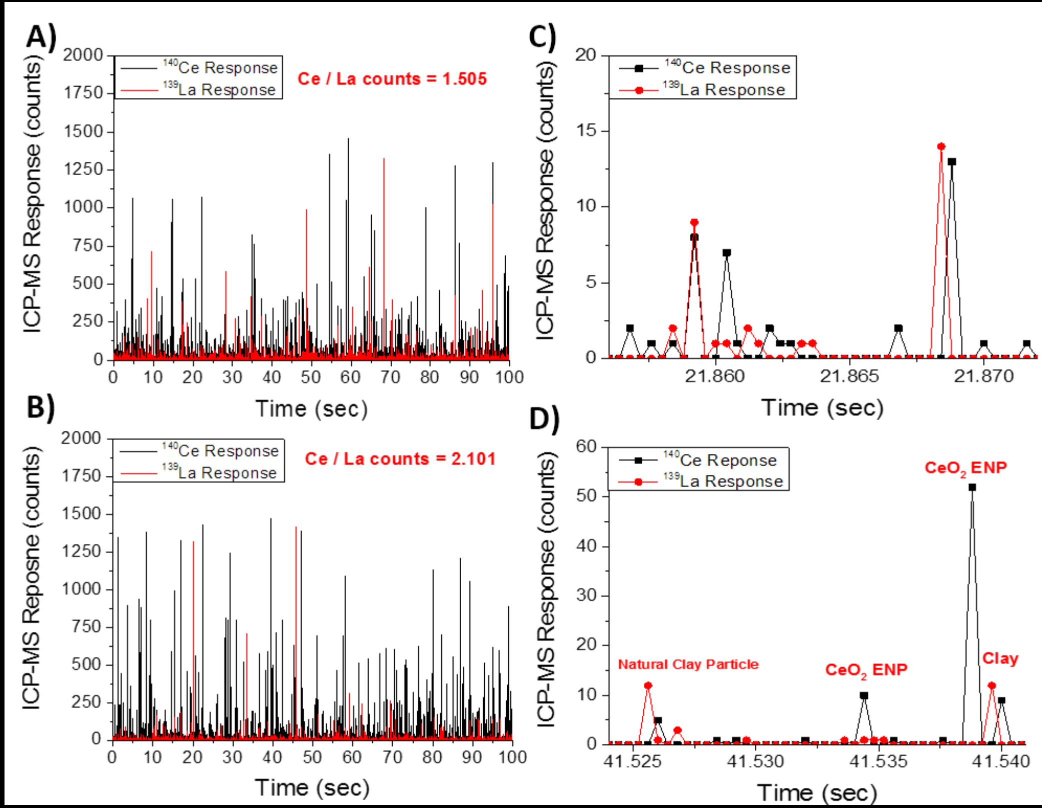
- Requires sufficient mass to produce an appreciable, detectable signal



Montaño, M. et al. *Environmental Chemistry*, **In Press**

Analysis of an Impacted Natural System

- Analysis of a nearby natural stream (Clear Creek, Golden, CO, USA) showed presence of particles containing Ce and La (**fig. A and C**)
- Ratio was consistent with literature values
- 80-100nm engineered cerium dioxide was spiked into natural water
- Elemental ratio shifted toward cerium. Presence of cerium-only particles persisted (**fig. B and D**)



Montaño, M. et al. *Environmental Science: Nano*, **2014**

Conclusions and Future Outlook

Conclusions

- Conventional single particle ICP-MS uses dwell times too large for accurate particle sizing and counting
- The presence of natural nanomaterials will impede the detection and characterization of engineered nanomaterials
- Microsecond dwell times off the ability to improve particle resolution, reduce background signal and introduce particle-by-particle elemental ratios

Future Research

- More work is required to improve sensitivity of single particle ICP-MS to detect smaller particle sizes
- New TOF-ICP-MS may be used to detect several elements within a single particle*
- Develop methods to identify aggregation state of nanomaterials in the environment

Borovinskaya, O. et al. *JAAS*, **2013**.

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Pictured from left to right: Jacob Williamson, Rabiab Suwanpetch, Jingjing Wang, Dr. James Ranville, Angela Barber, Evan Gray, Manuel Montaño, Elizabeth Traudt

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  - Soheyl Tadjiki (PostNova Analytics)
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QUESTIONS?