Developing Methods for Examining NP Transformations using Single Particle ICP-MS & Field Flow Fractionation

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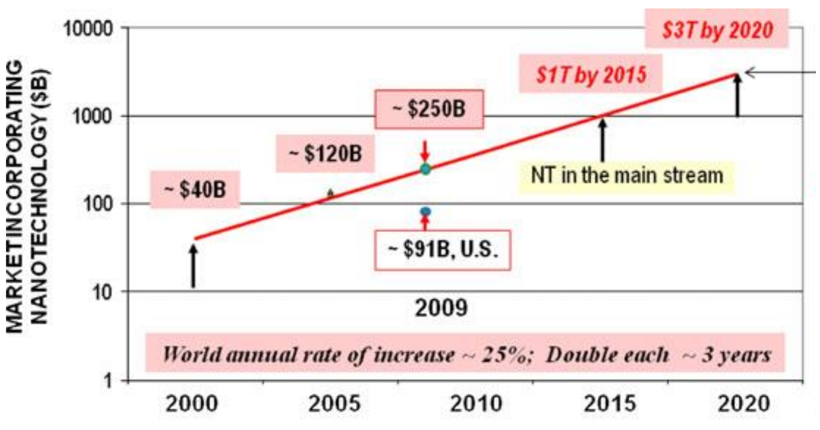
Motivation

Applications

Nanotechnology industry continues to grow[1]

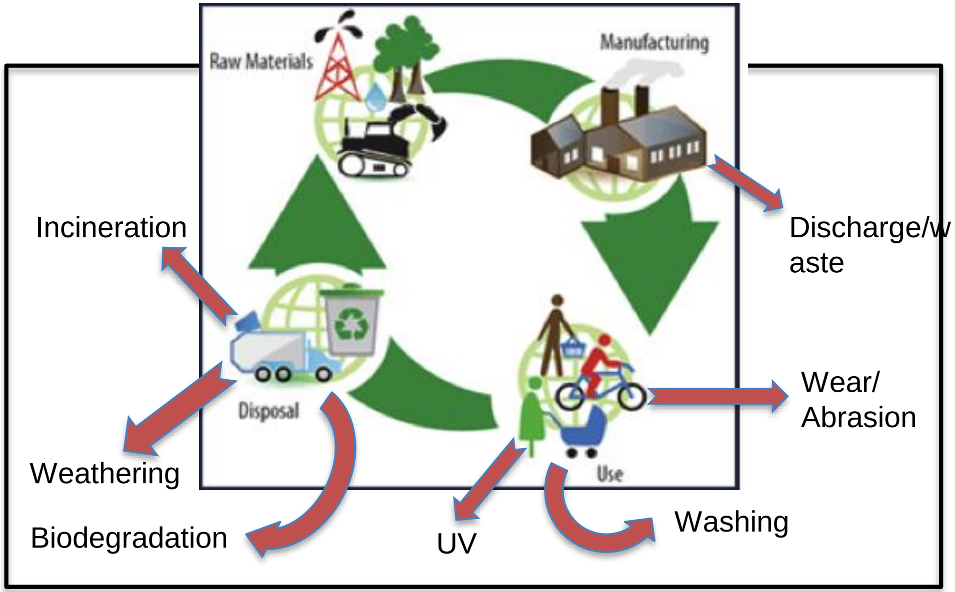
- From 2010 to 2013 worldwide revenue from NEPs grew from $339 billion to > $1 trillion[1]
- Multitude of nano-enabled products (NEPs)[2] that incorporate engineered nanomaterials (ENMs) to improve desired functionality



Source: Roco, M.C. *Journal of Nanoparticle Research*, **2011**

Implications

Release of ENMs into the environment during product lifecycle is inevitable



Source: www.epa.gov

- The risks posed to human health and the environment due to ENM release are difficult to predict as a result of <u>limited information regarding: quantity, release rates, stability, transport, and fate</u>

[1] www.nsf.gov
[2] Progress Review on the Coordinated Implementation of the NNI 2011 Research Strategy, **2014**

Analytical Challenges

Development of nano-metrology to enable accurate and reproducible measurements of ENMs[1] is essential

We expect:	We need analytical methodology that is:
Low environmental concentrations	Sensitive down to ng/L range
Potentially high background of dissolved (i.e., ionic) species	Capable of element-specific quantification of both ions and nanoparticles
Complex environmental matrices	Capable of dealing with matrix effects
Complex particle structures in part due to NP transformations upon release	Capable of element-specific characterization and quantification of "composite" particles
Interfering naturally occurring NPs (NNPs)	Able to distinguish between ENPs and NNPs

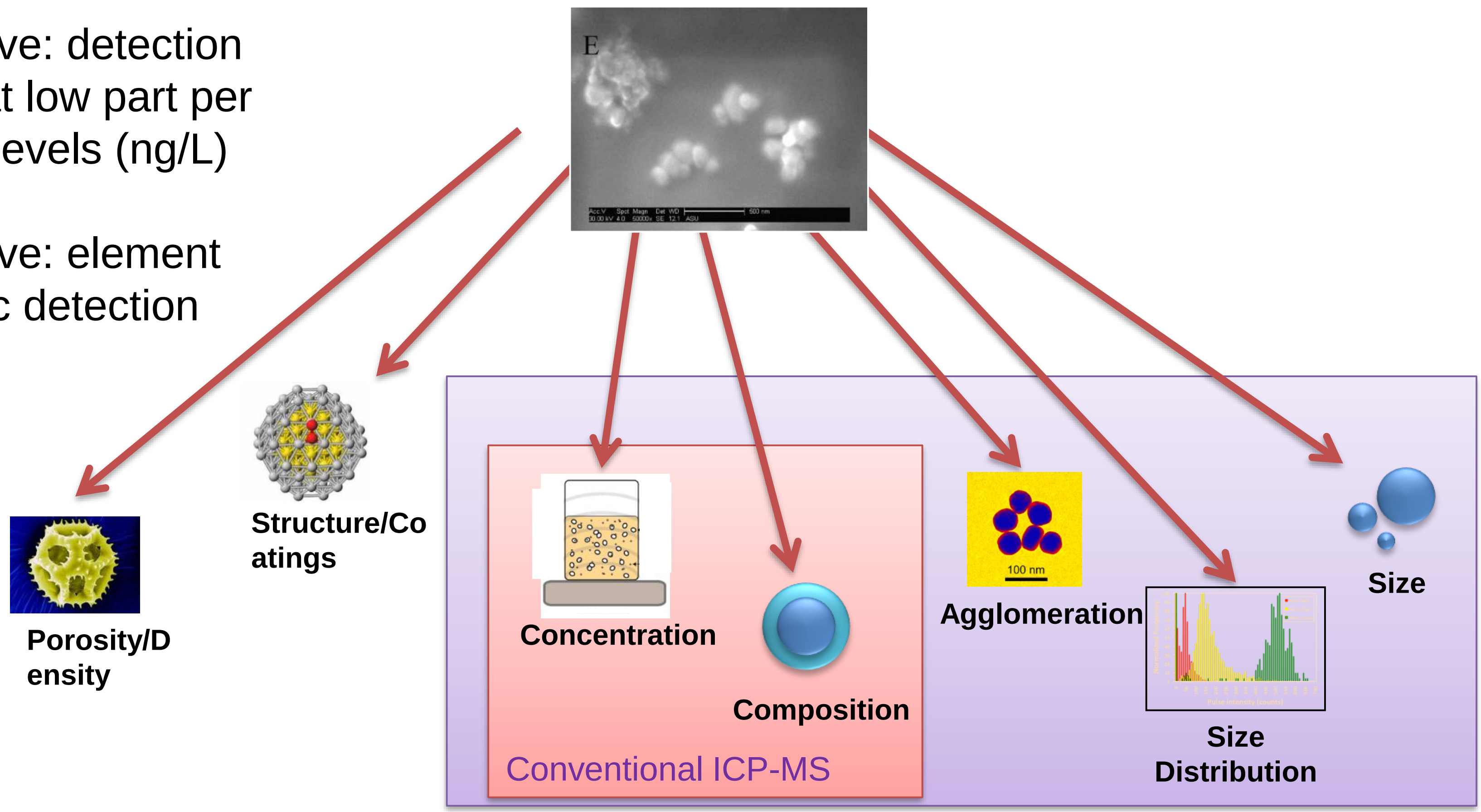
Single particle ICP-MS + Field-Flow Fractionation

[1] Progress Review on the Coordinated Implementation of the NNI 2011 Research Strategy, **2014**

ICP-MS Analysis for Nanoparticle Characterization

Sensitive: detection limits at low part per trillion levels (ng/L)

Selective: element specific detection

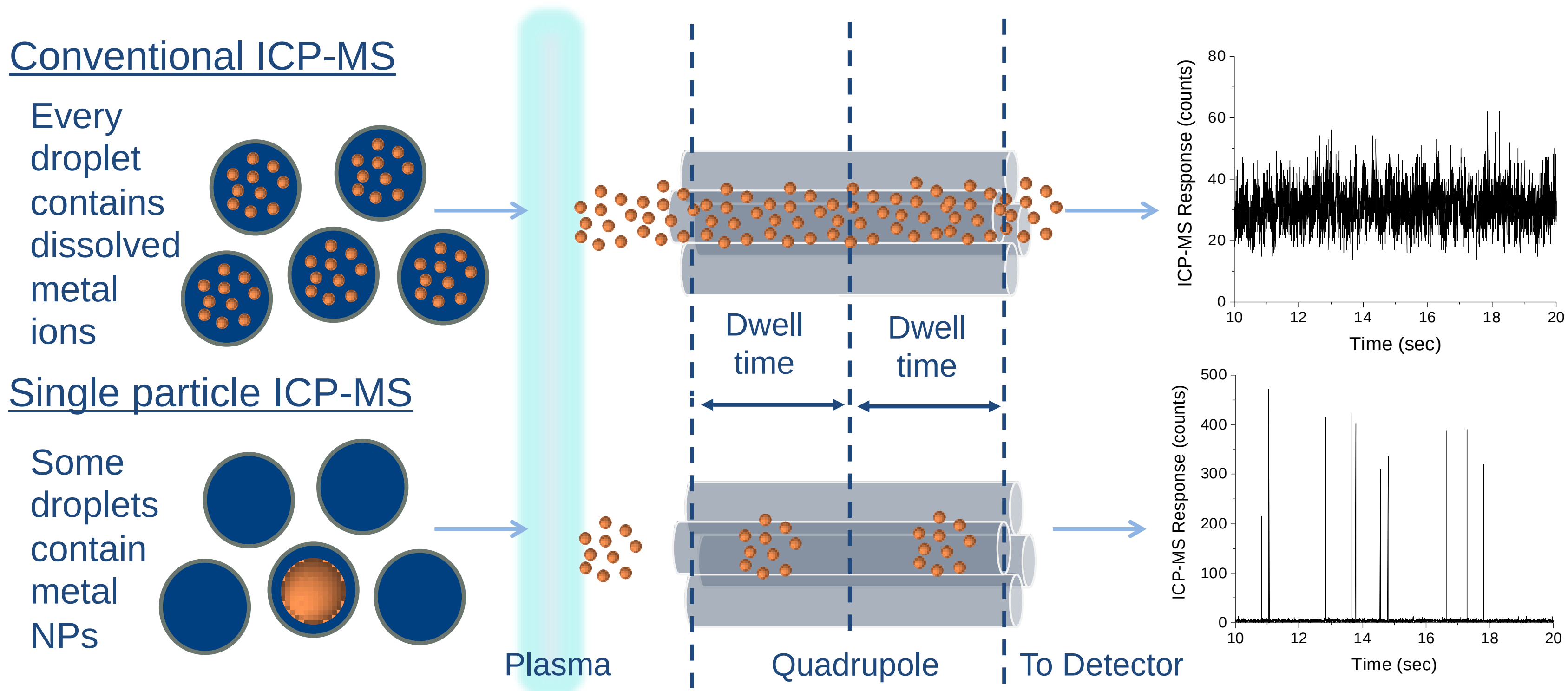


FFF-ICPMS and spICP-MS

spICP-MS

single particle Inductively Coupled Plasma Mass Spectrometry

uses the inherent sensitivity and elemental specificity of ICP-MS to detect pulses of ions that result from the sequential introduction of NPs into the instrument

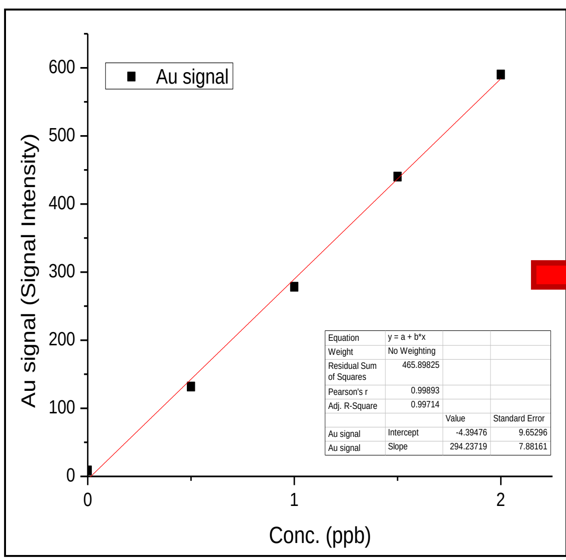


Overview of spICP-MS Data Processing

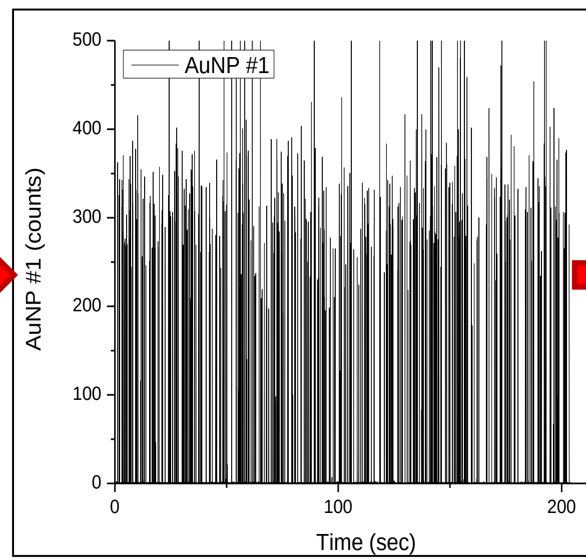
- Calibration curve of dissolved concentration vs. intensity
- Use transport efficiency to relate intensity to mass

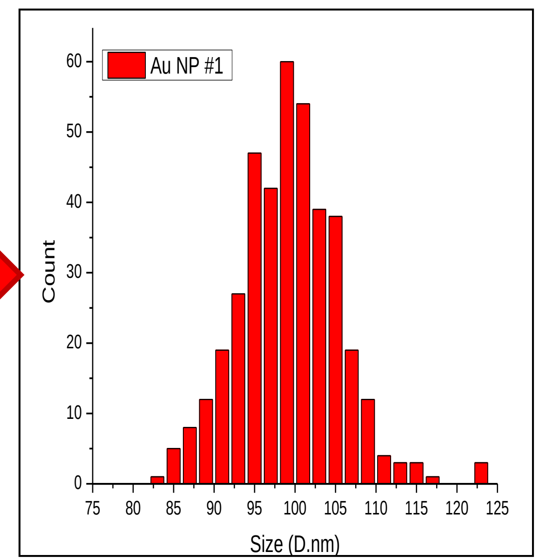
- Nanoparticle gives pulse of intensity above background

- Convert pulse intensity to mass, then to diameter



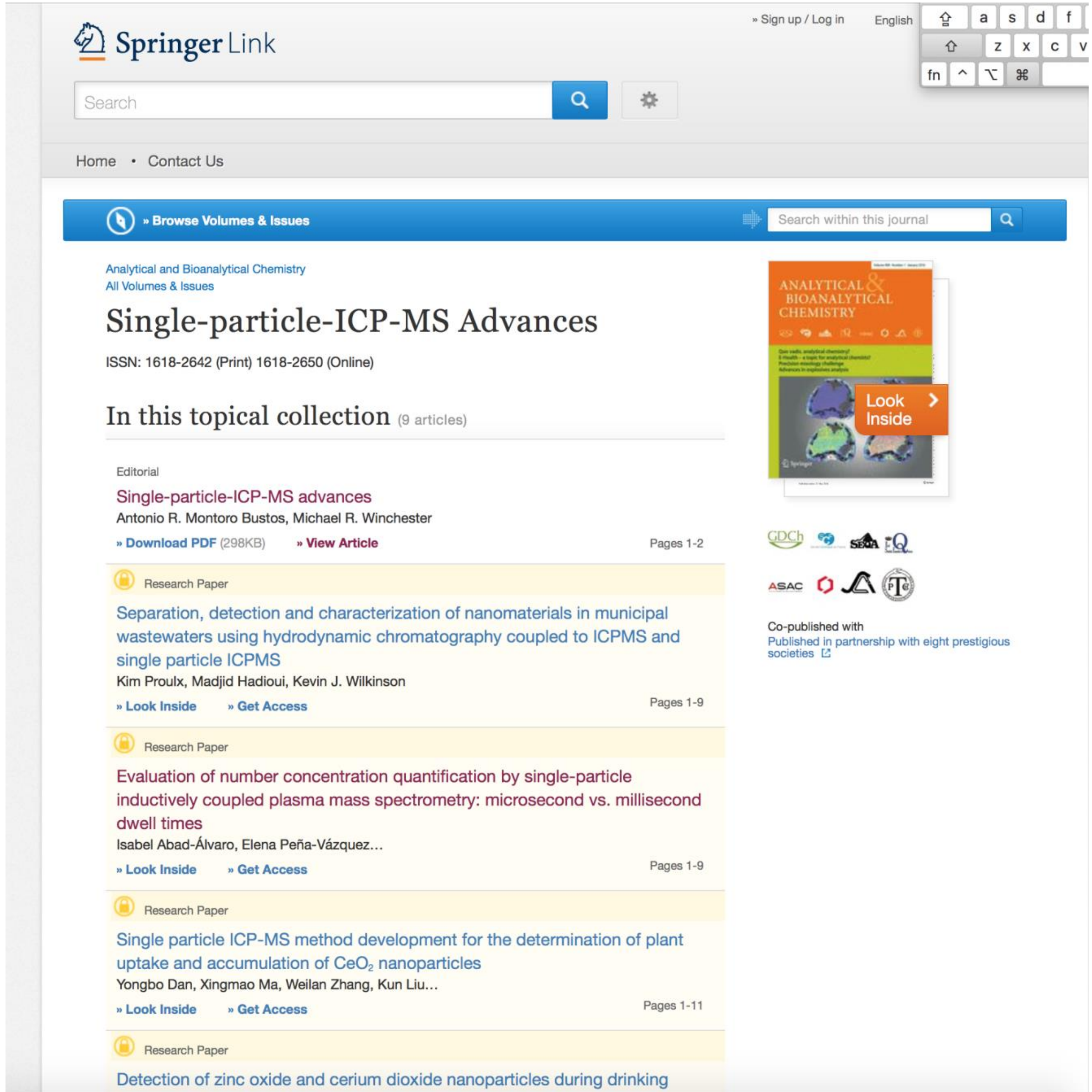
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	465.89825		
Pearson's r	0.99893		
Adj. R-Square	0.99714		
		Value	Standard Error
Au signal	Intercept	-4.39476	9.65296
Au signal	Slope	294.23719	7.88161





Collection of Single Particle ICP-MS papers

ABC, June 2016



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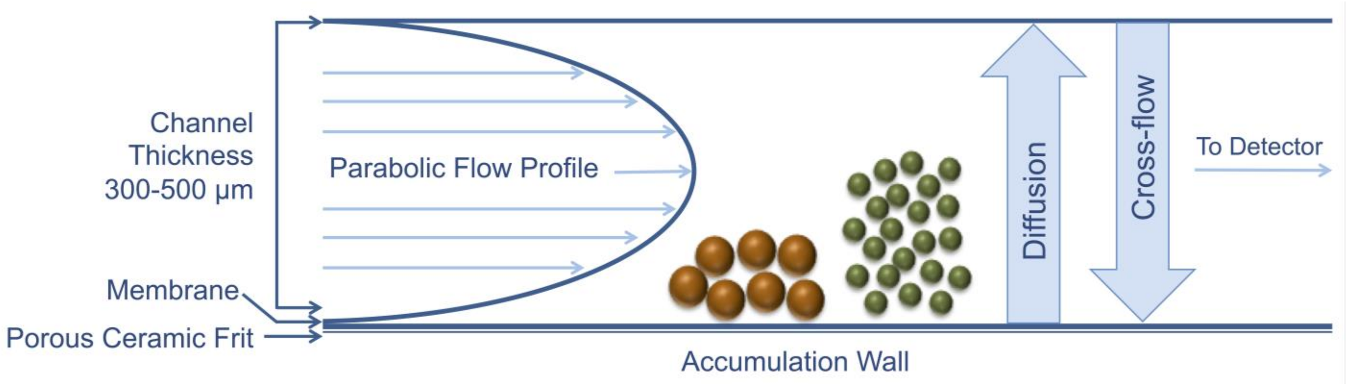
FFF

Field Flow Fractionation
uses an applied field (i.e., force) to separate particles based on particle mass, hydrodynamic size, and/or density, depending on the type of field applied

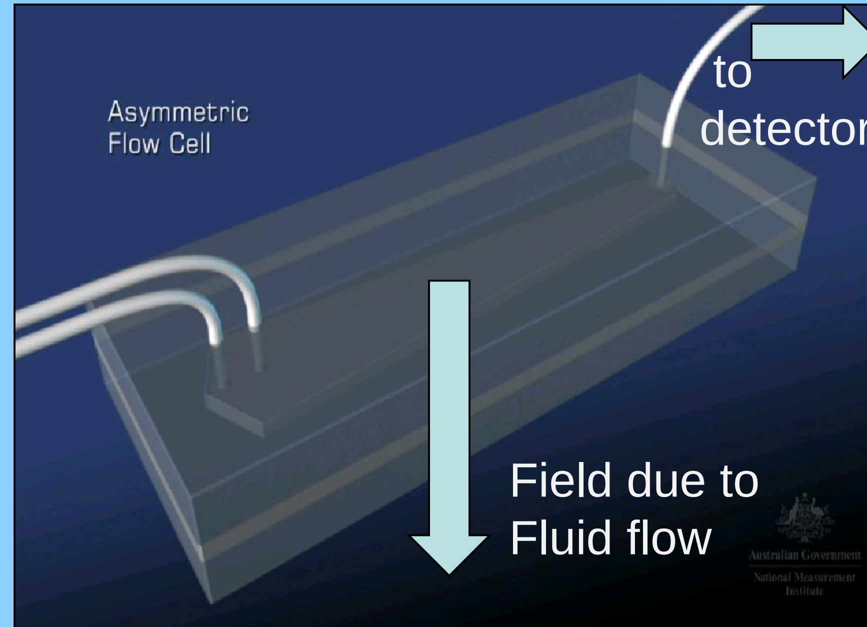
Asymmetric Flow FFF (AF4) separates based on **hydrodynamic size**



Centrifugal FFF (CFFF) separates based on **buoyant mass**

Source: www.postnova.com

ASYMMETRICAL FLOW FFF

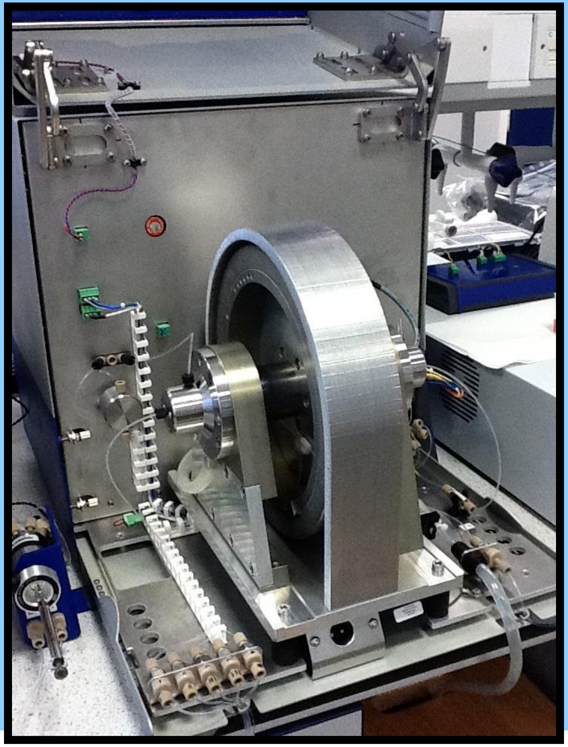


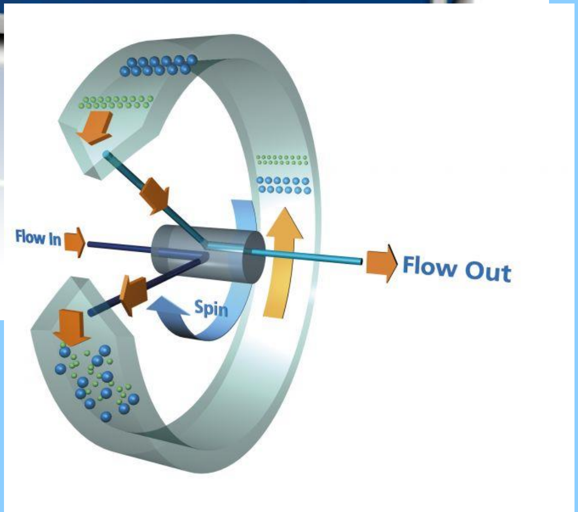
$$d_h = \frac{2kT}{\pi \eta w^2 \ln\left(1 + \alpha \frac{\overset{\circ}{V}_c}{\overset{\circ}{V}}\right)} t_r$$

$$\alpha = 1 - \frac{b_0 z' - \frac{(b_0 - b_L) z'^2}{2 L_{Eff}} - y}{A_{Eff}}$$

Where:
b_0 is the channel breadth at the inlet triangle
b_L is the channel breadth at the outlet triangle
z' is the position of the focusing band
L_{eff} is the effective channel length
A_{eff} is the effective channel cross section area
y is the tapered area

CENTRIFUGAL FFF

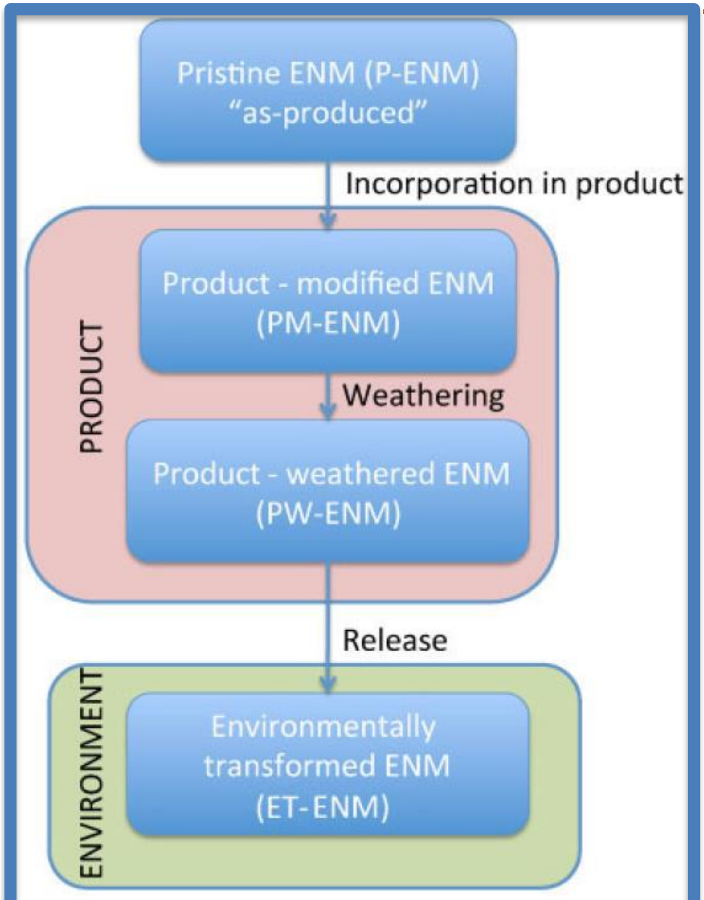




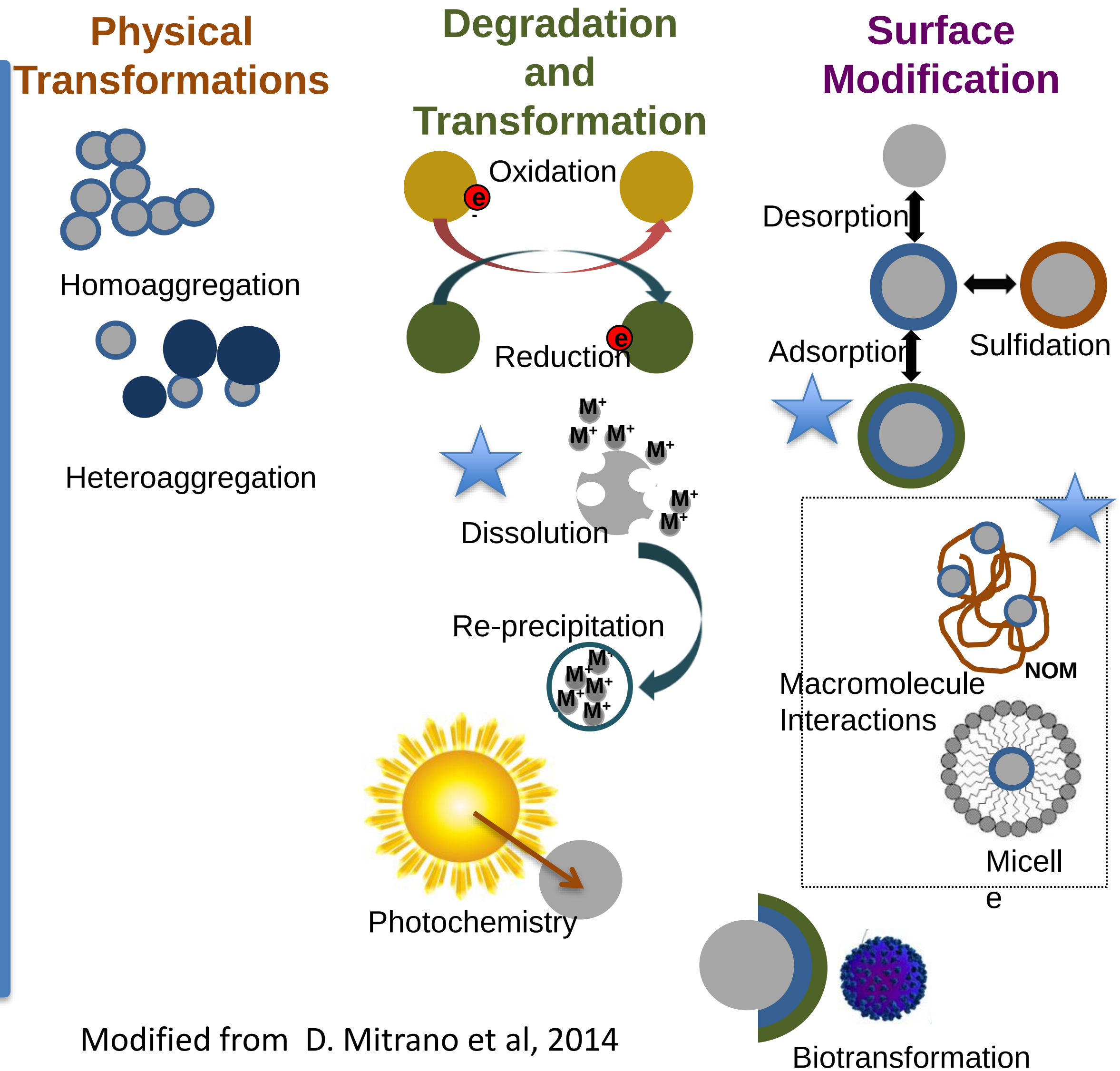
$$d^3 = \frac{36kT\,V^0 t_r}{\pi|\Delta\rho|wGV^0}$$

Challenge: We are not analyzing pristine NPs

NPs will likely be **transformed** from their **pristine state**



Nowack et al, 2012



Modified from D. Mitrano et al, 2014

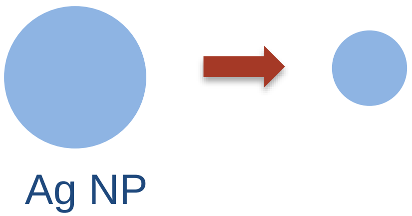
Method Development with Model Particles

Environmentally Transformed NPs

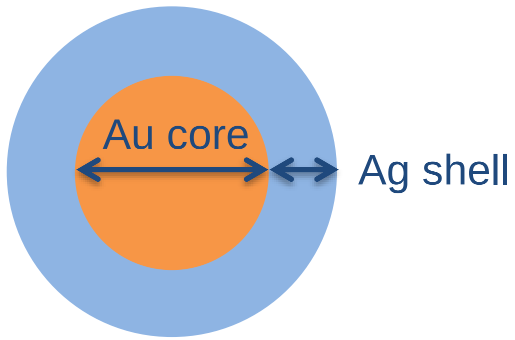
Model Particles

NP Dissolution

A

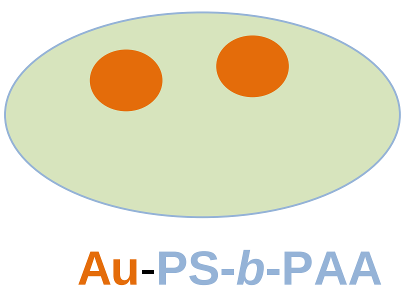


Surface modified NPs



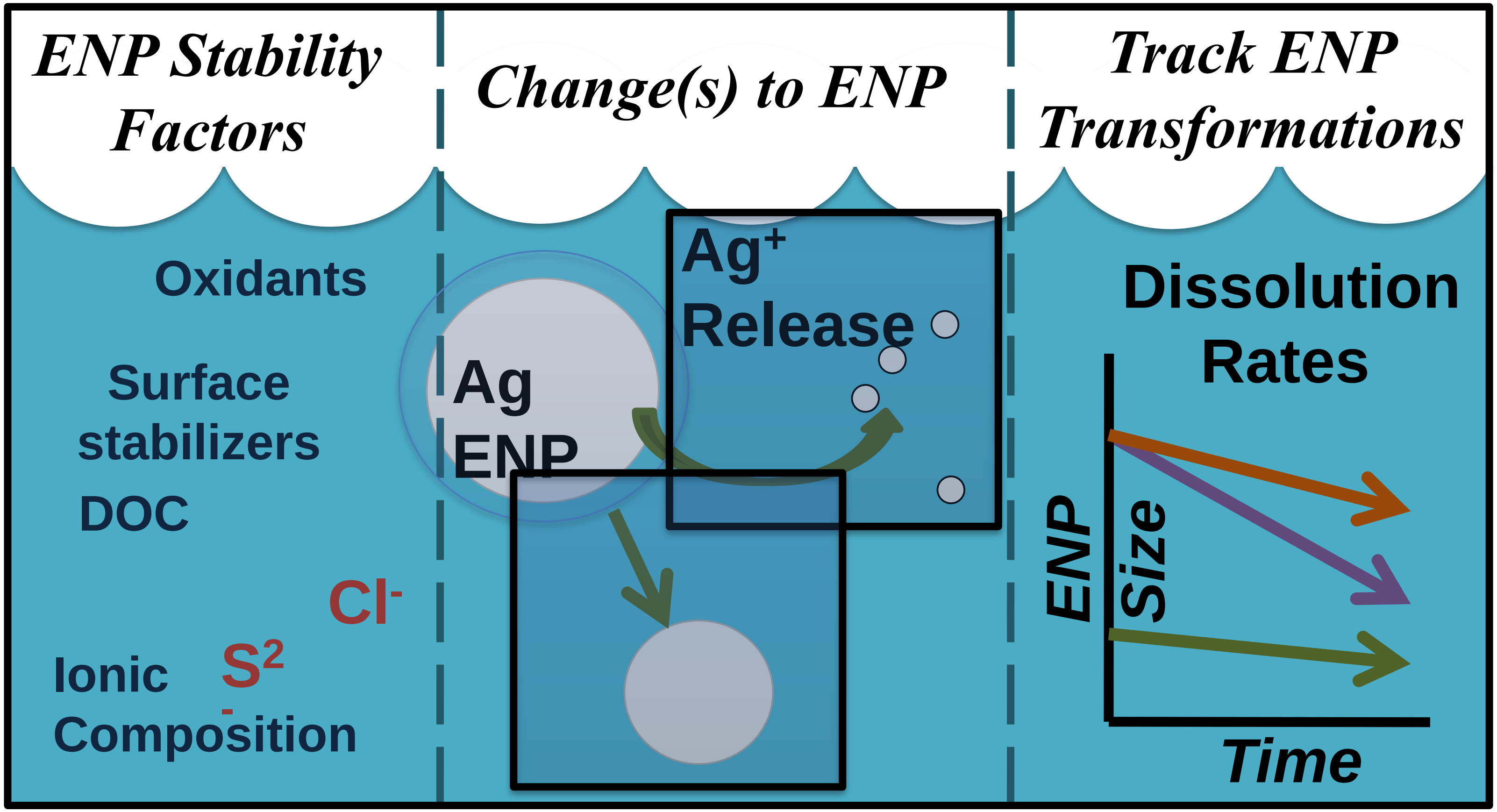
B

NP-Organic Coatings/Heteroaggregates



C

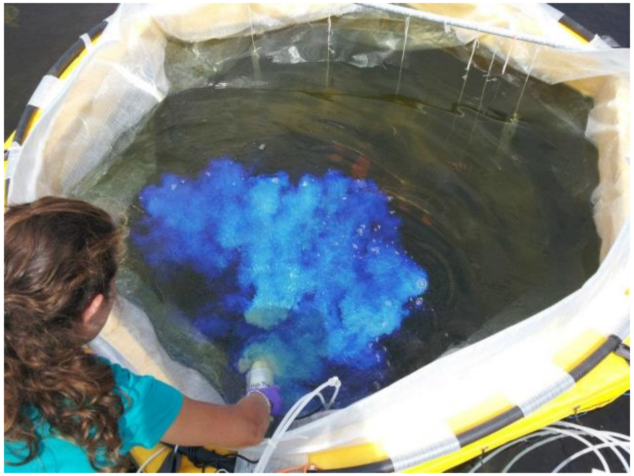
Transformation: Dissolution



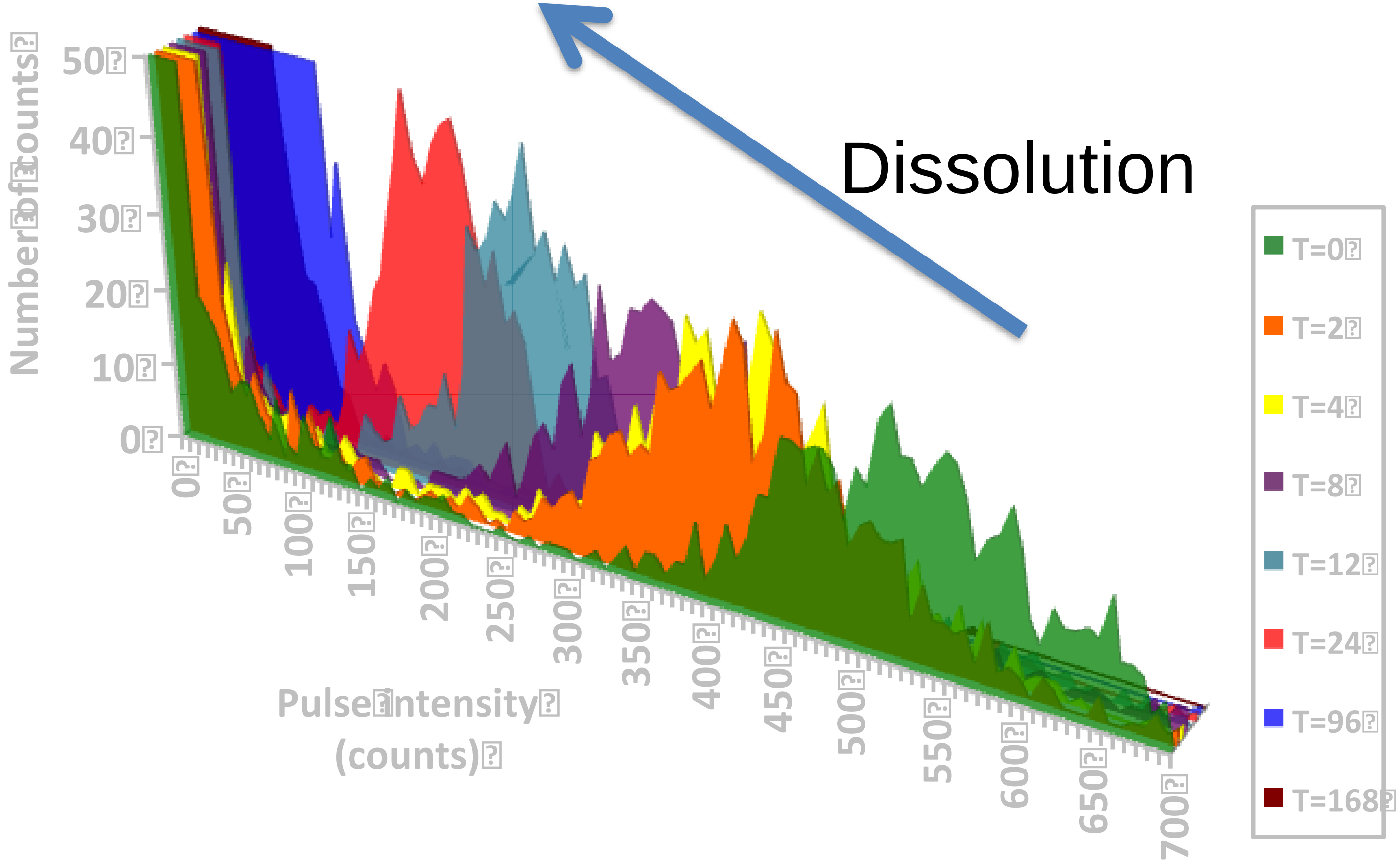
Mitrano et al., Environ Sci:Nano, 1, 248-259, 2014

Transformation in natural waters

- Trent University Lens Project (Chris Metcalf & Lindsay Furtado)
- Lake 239 at the Experimental Lakes Area (ELA) in Ontario, Canada
- Single addition of 80 mg/L, 50 nm PVP capped Ag ENP
- Mesocosms (2 m diameter x 2m depth). Two used for in study.
- Samples analyzed by AF4-ICPMS and spICPMS
- Furtado et al 2014, *Environmental Chemistry* **11**, 419-430



Dissolution vs pulse intensity (spICP-MS)



100 nm tannic acid Ag NPs; 50 ng/L

Decrease pulse intensity correlates with decreasing particle diameter

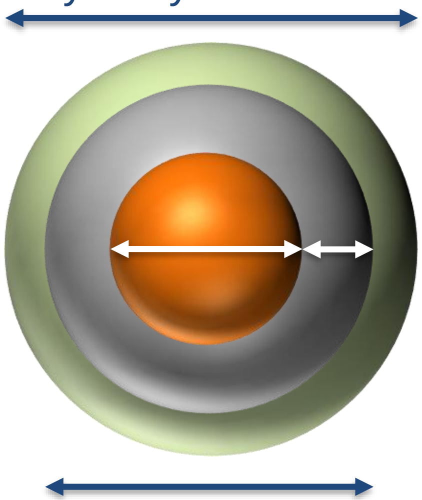
Mitrano et al., Environ Sci:Nano, 1, 248-259, 2014

Surface Transformations: Investigation of NP Structure

<u>Manufacturer-reported characteristics</u>

Size by TEM. Concentrations by ICP-MS.

100.2 nm
hydrodynamic size

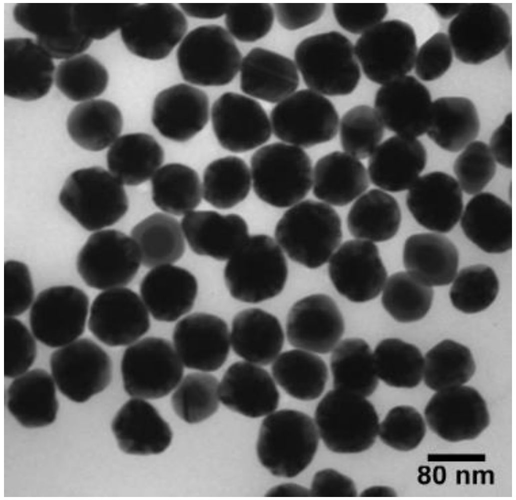


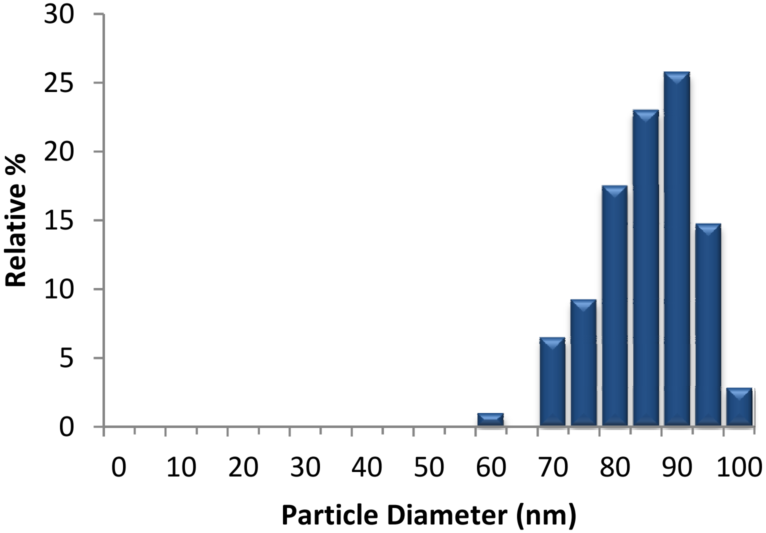
8.8 nm thick
PVP-shell

48.2 nm
Au-core

17.2 nm Ag-shell
(**76.8 nm** equivalent spherical diameter)

82.7 nm NP

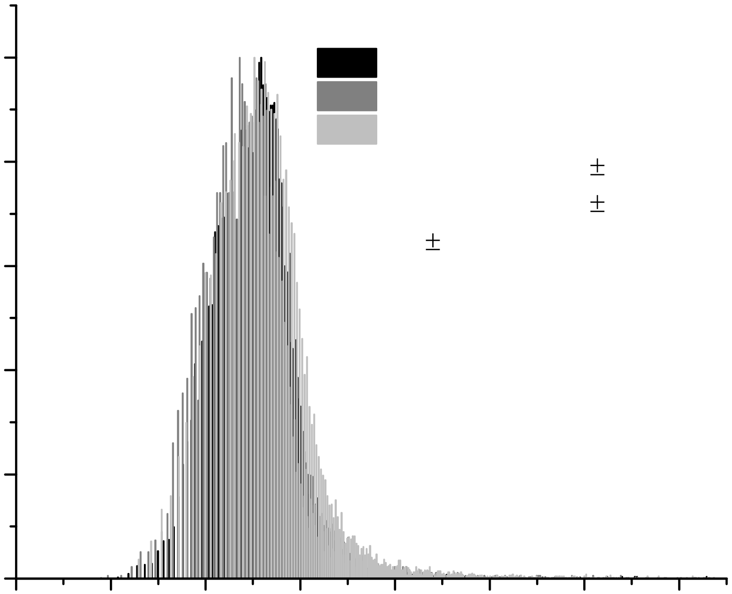




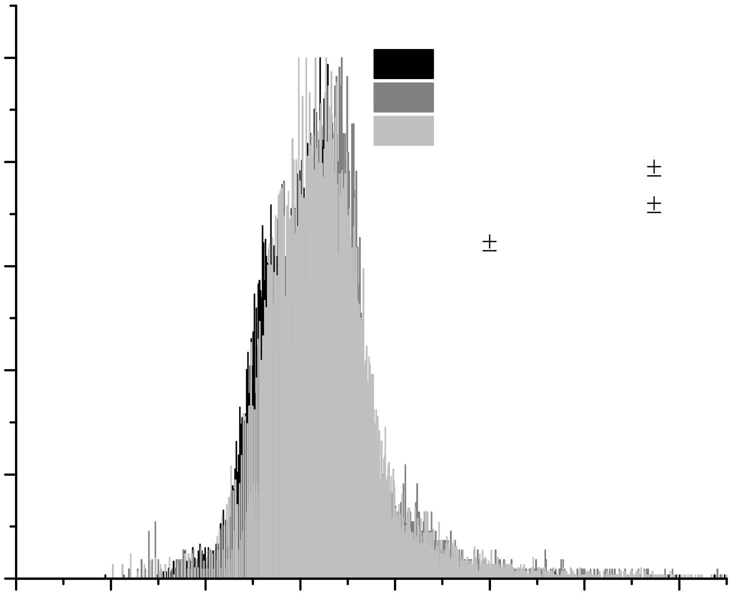
What if this was an unknown particle?
Can we determine composition and structure?

spICP-MS analysis

spICP-MS: ^{197}Au



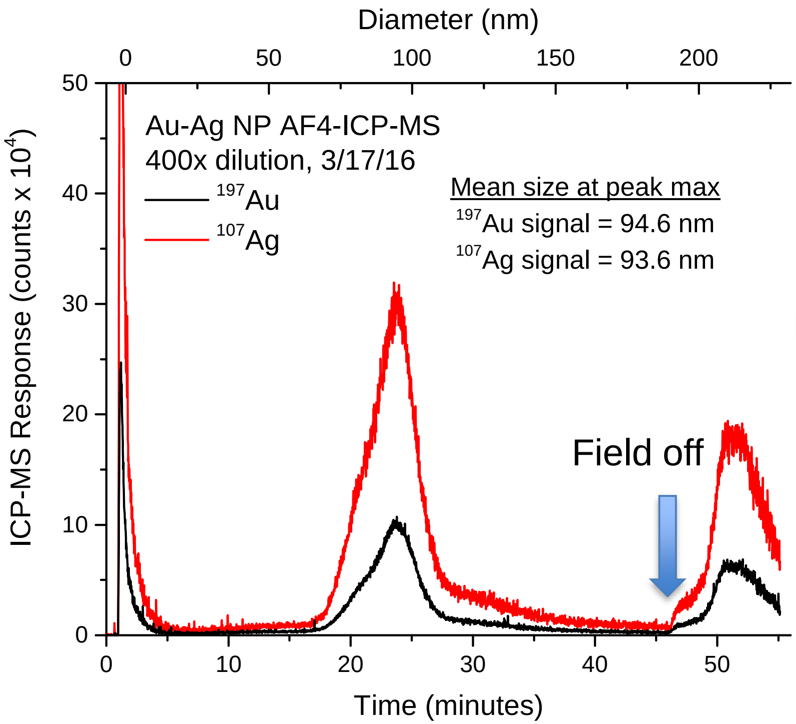
spICP-MS: ^{107}Ag

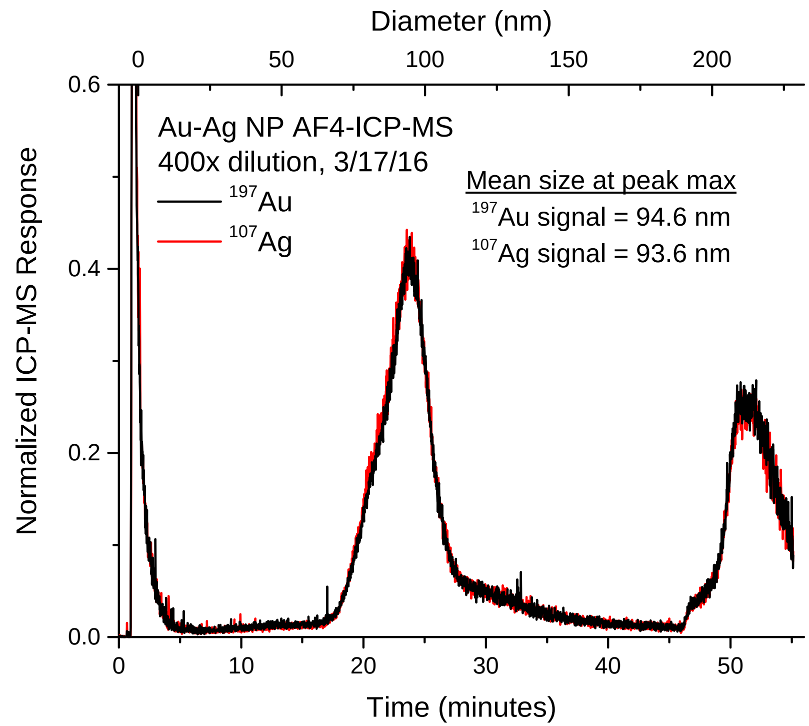


2.0x10^{11} NPs/mL = 2.0x10^{11} NPs/mL

Suggests but does not confirm bimetallic NP

AF4-ICP-MS analysis



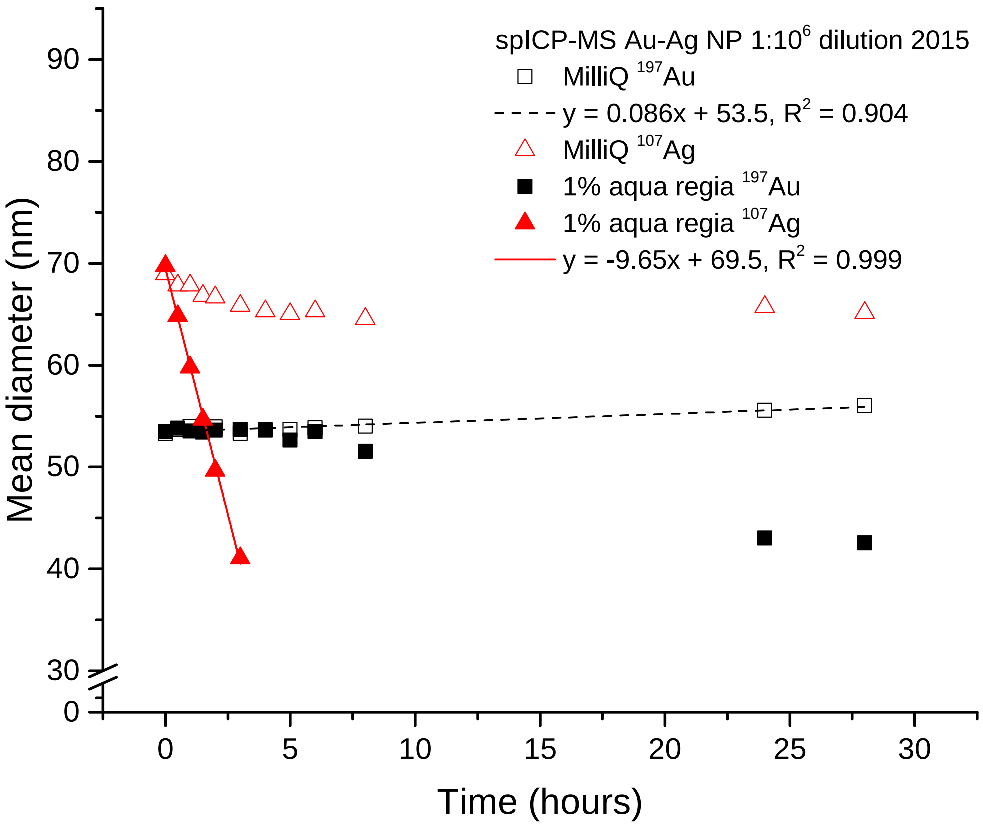


$^{197}Au_{norm.signal} \sim {}^{107}Ag_{norm.signal}$

Bimetallic particle is highly likely

Investigation of NP Structure: Dissolution

Au-Ag NP dissolution in Milli-Q water and 1% (v/v) aqua regia was observed using spICP-MS over 28 hours.



In Milli-Q water, NP sizes are relatively constant.

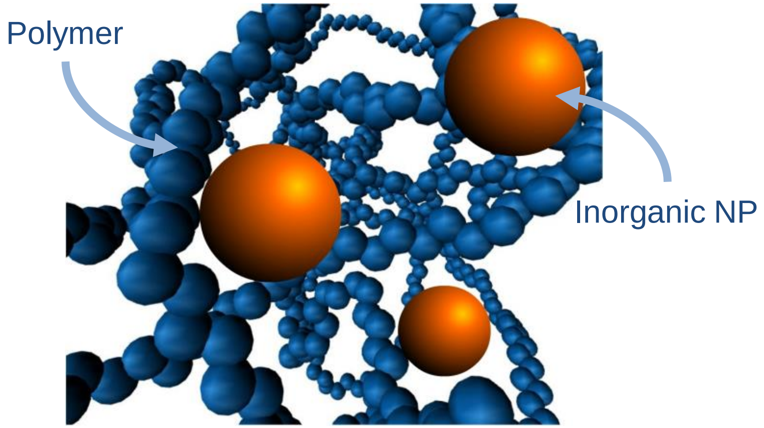
In 1% aqua regia, Ag NP size decreases from 0-3 hours, until below size detection limit.
Au NP size is constant until 8 hours.

Core-shell structure is revealed.

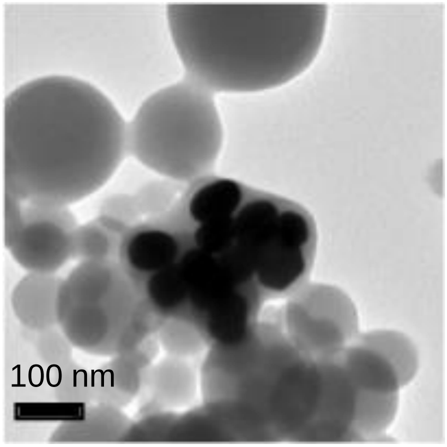
Heteroaggregation/Organic matter coatings

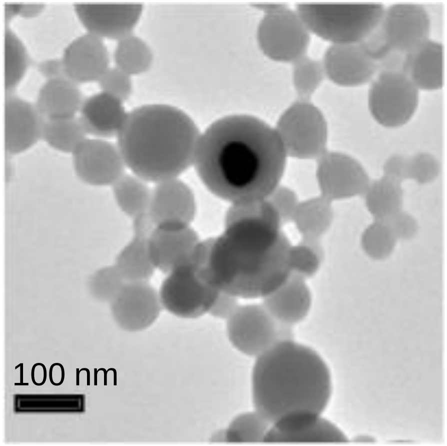
Model particle

Polymer nanocomposite (PNC) is a material with NPs dispersed in a polymer (or copolymer) matrix.



Source: www.fch.vutbr.cz/cs/laboratore/kompozity/nanocomposites.html



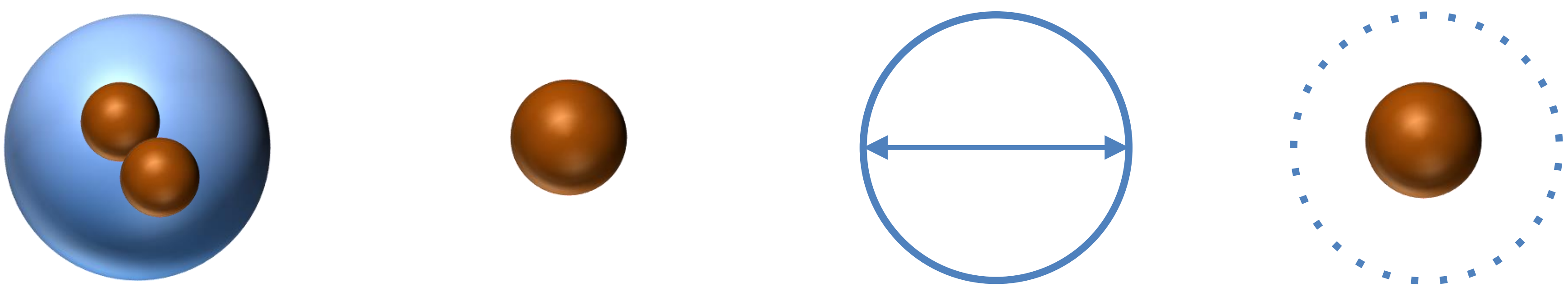


Au-PS-*b*-PAA Compsite NP: Use as a model for heteroaggregates and coated NPs

One or more gold NPs (40-50 nm) surrounded by a thick polystyrene-polyacrylic acid block copolymer shell (~10-175 nm)

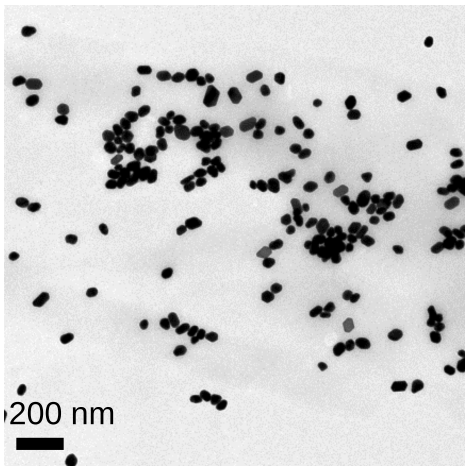
Methodology

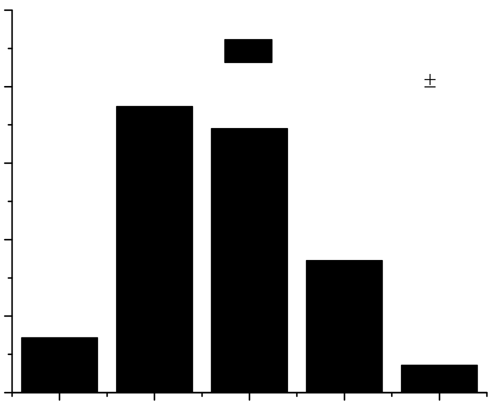
TEM	spICP-MS	AF4	CFFF
structure and size	*mass and number conc.*	*hydrodynamic size*	*buoyant mass*



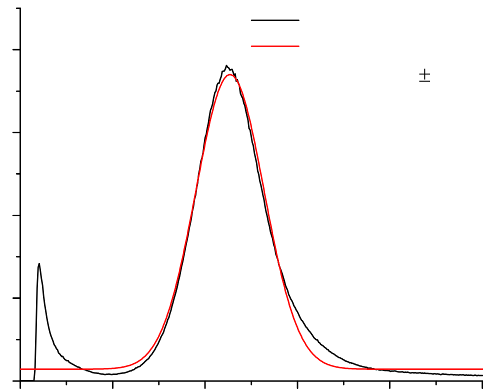
Characterize Au-citrate Precursor NP

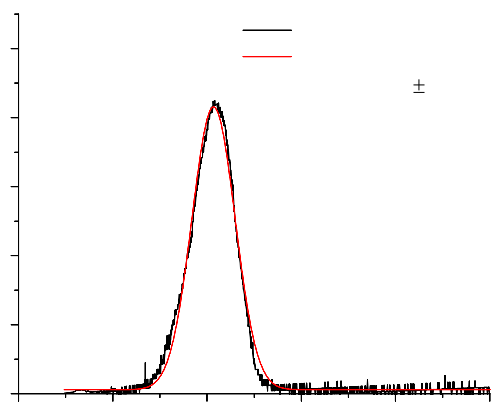
TEM



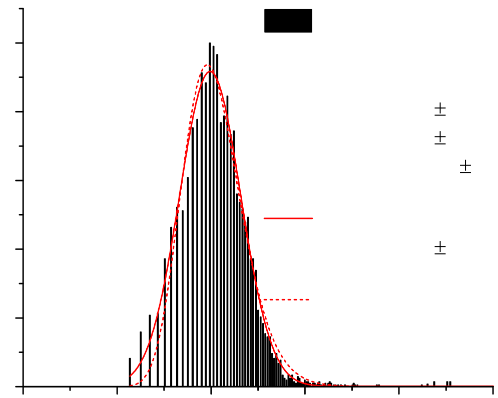


AF4 and CFFF





spICP-MS

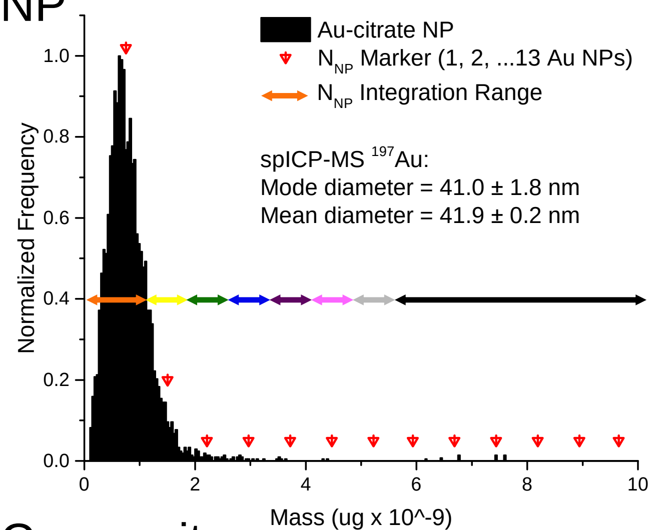


Mean size (nm)

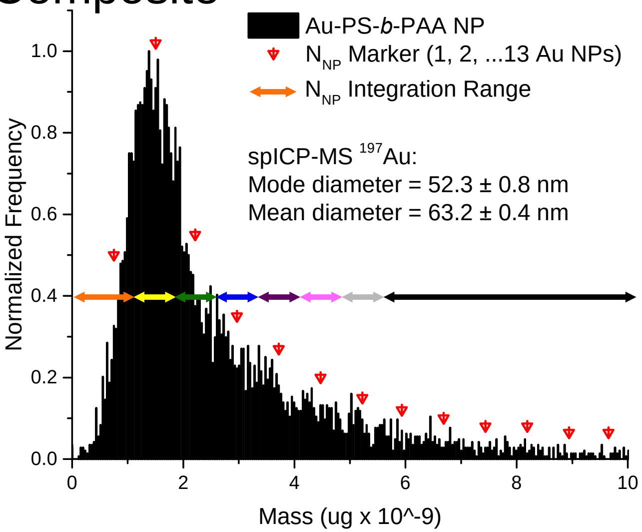
TEM = 51
AF4 = 45.9 ± 1.2
CFFF = 41.4
spICP-MS = 41.9 ± 0.2

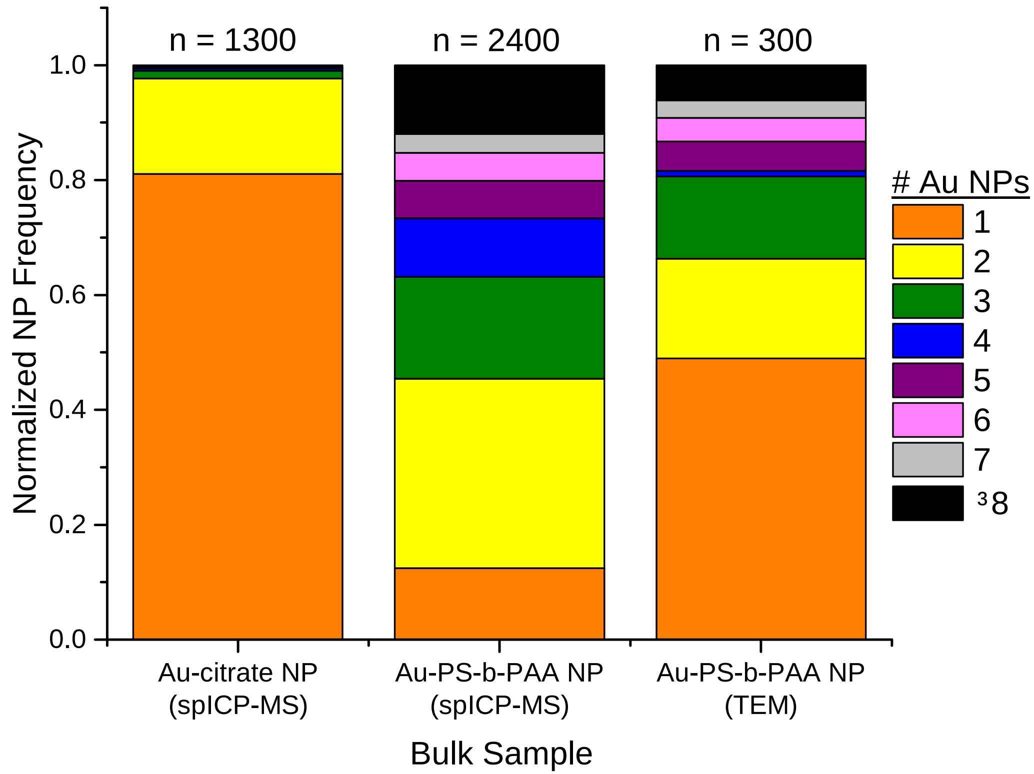
Au-PS-*b*-PAA NP: spICP-MS

NP



Composite

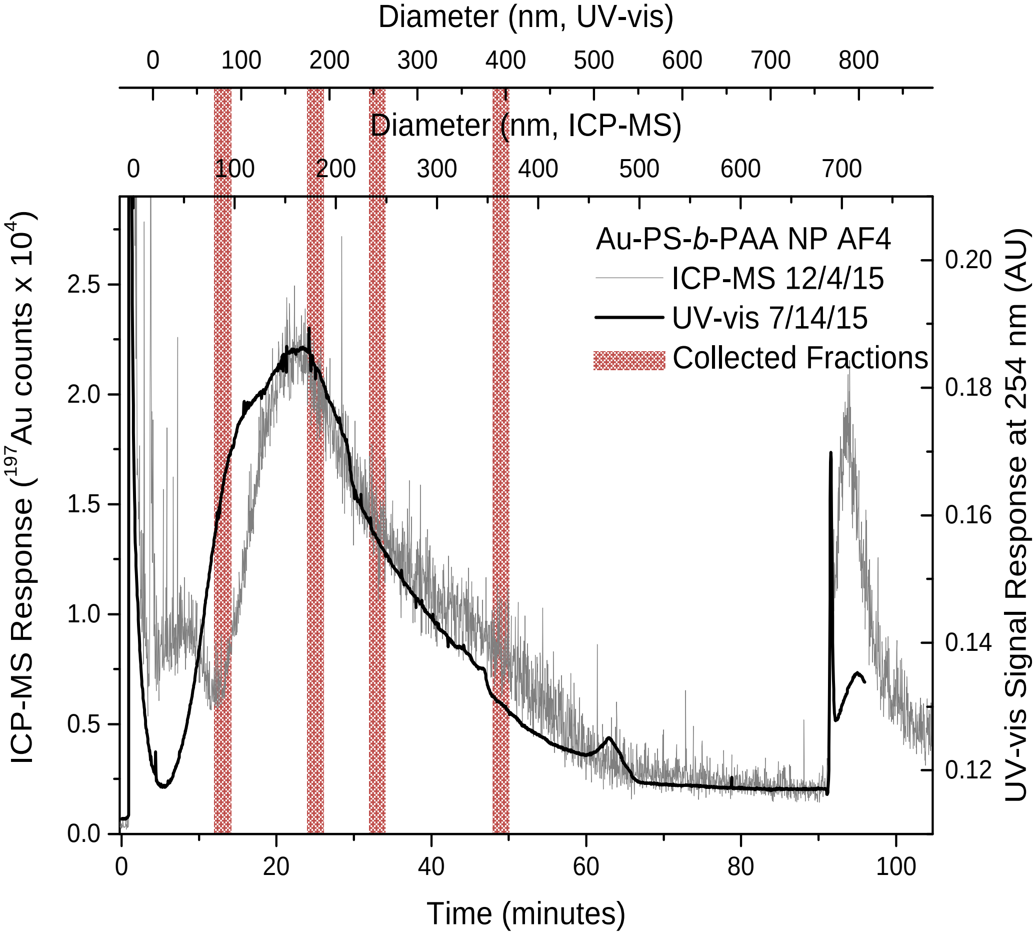




The increase in mean Au size for the Au-PS-*b*-PAA NP is due to incorporation of multiple Au-cit NPs.

Au-PS-*b*-PAA NP AF4 Separation

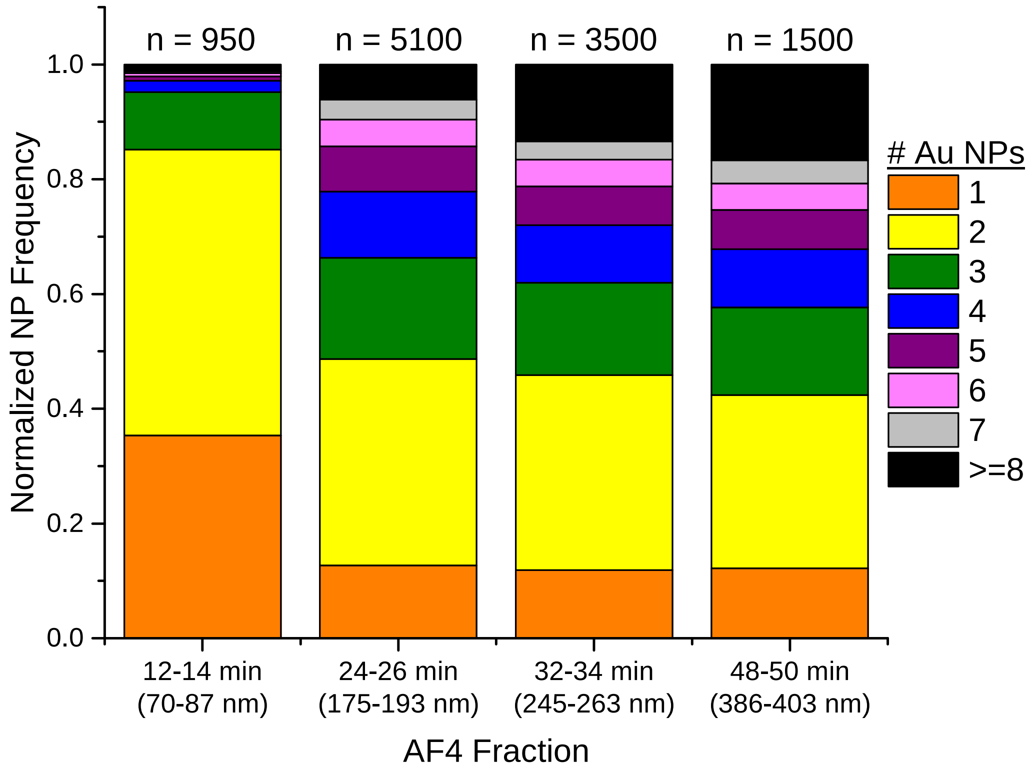
AF4 separates by hydrodynamic size

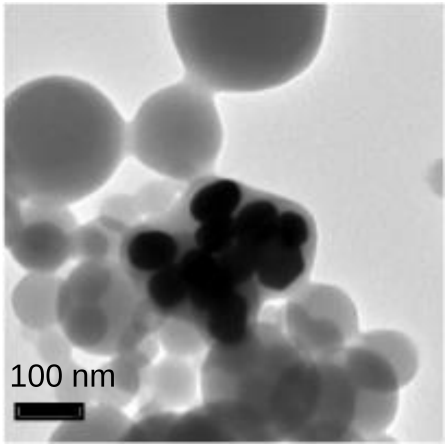


Fractions were collected and analyzed by spICP-MS to provide the mass distribution of incorporated Au NPs as the hydrodynamic size increases

A particle with a small hydrodynamic size has a limit on the maximum possible incorporated Au mass.

AF4 Fractions by spICP-MS





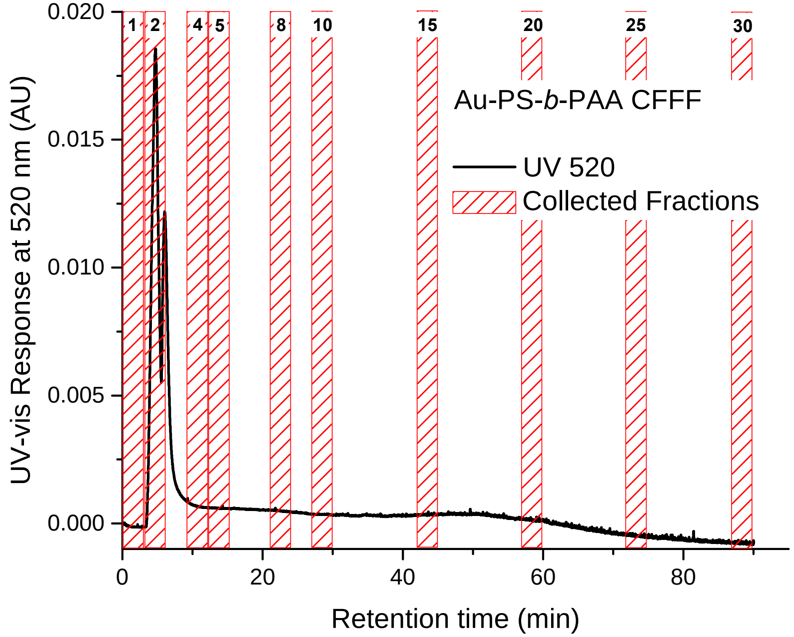
As the hydrodynamic size increases:

- Frequency of larger Au mass increases
- % containing 1-2 Au NPs decreases
- % containing ≥ 8 NPs NPs increases

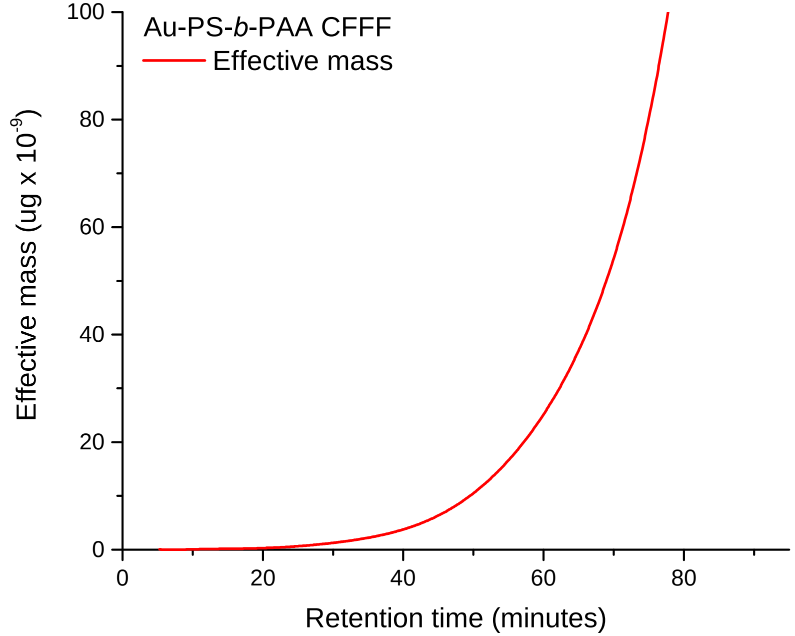
Au-PS-*b*-PAA NP CFFF Separation

AF4 separates by buoyant mass

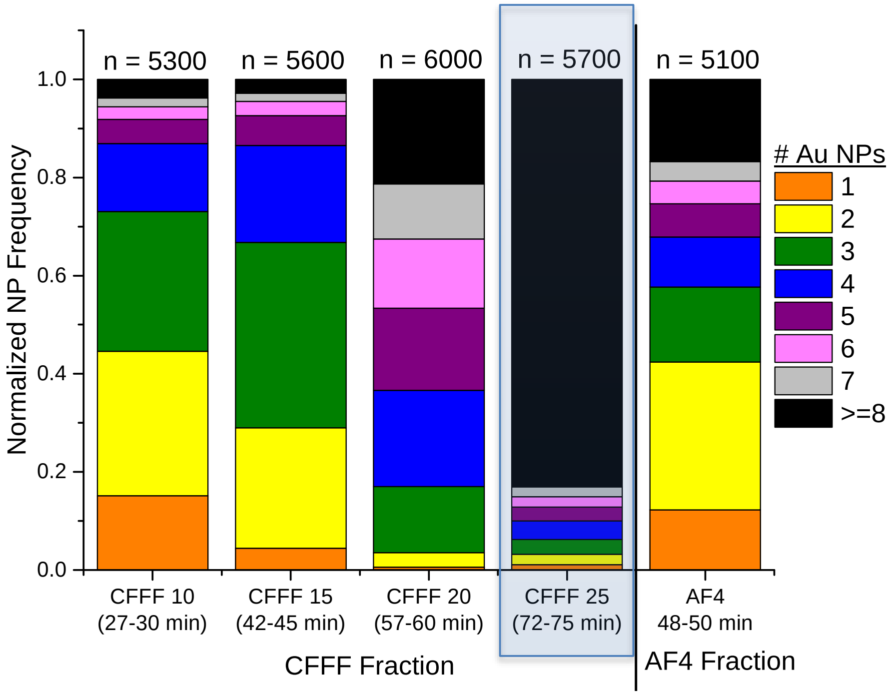
By matching the density of the CFFF carrier fluid with the PS-*b*-PAA density, the buoyant mass is only the incorporated Au NP mass



Calculated from FFF data

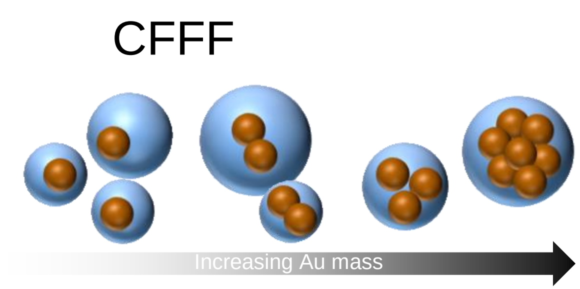


CFFF Fractions by spICP-MS

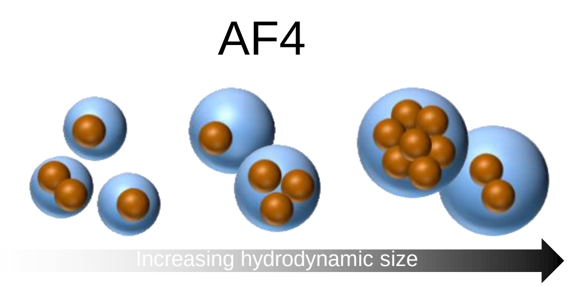


The Au mass distribution shifts to larger Au masses with increased retention time.

Little or no detection of single Au NPs at longer retention time



Increasing FFF retention time



Increasing FFF retention time

Information gained from various methods

TEM	spICP-MS	AF4	CFFF
structure and size	*mass and number conc.*	*hydrodynamic size*	*buoyant mass*
Composite particles containing ≥ 1 Au NPs are present.	Multiple Au-cit NPs are incorporated into the composite NPs.	The maximum number of incorporated Au-cit NPs increases as hydrodynamic size increases.	The Au mass distribution shifts to higher masses as CFFF retention time increases.

Summary

- Combining spICP-MS with FFF provides a detailed characterization of complex nanomaterials and NP mixtures

- Combined with dissolution methods they can reveal structure

- The methods can provide insight into the transformations and fate of NPs introduced into the environment

- Further work on method development is needed to fully investigate NPs in environmental samples

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LC nano