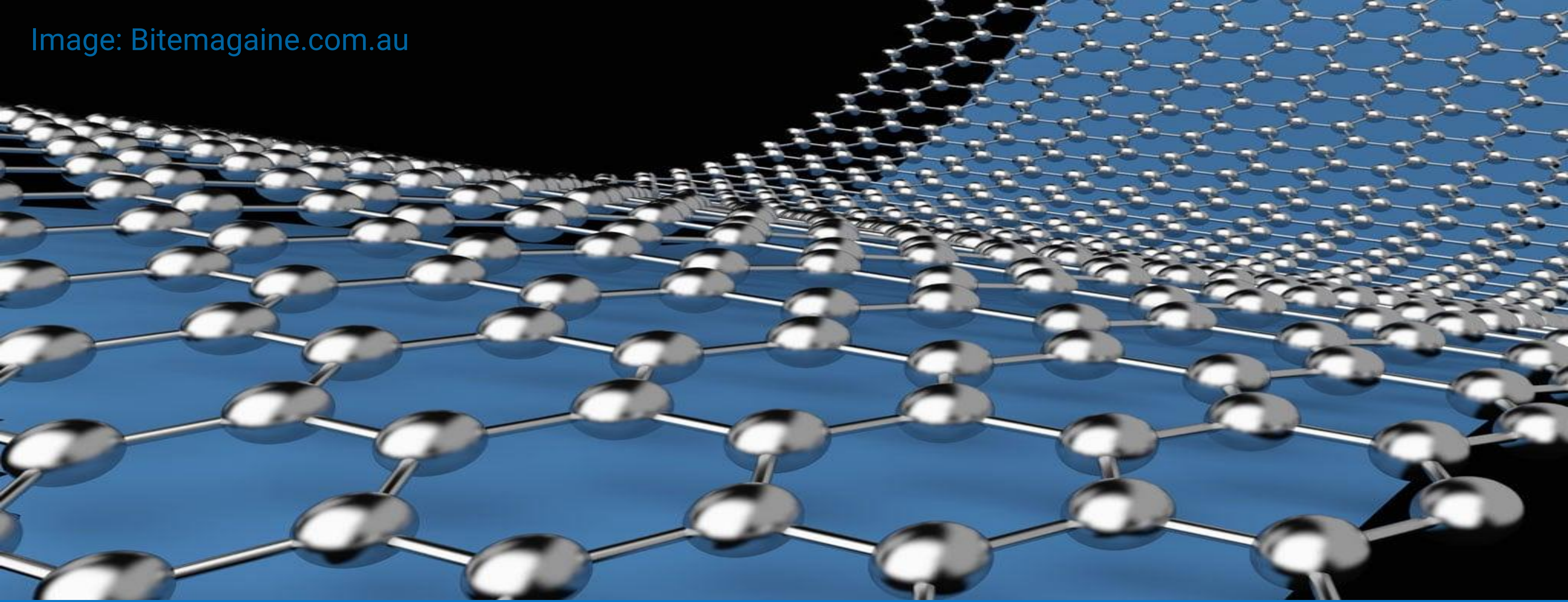

Fast multi-element quantification of nanoparticles in water supplies and wastewater treatment using single particle ICP-MS

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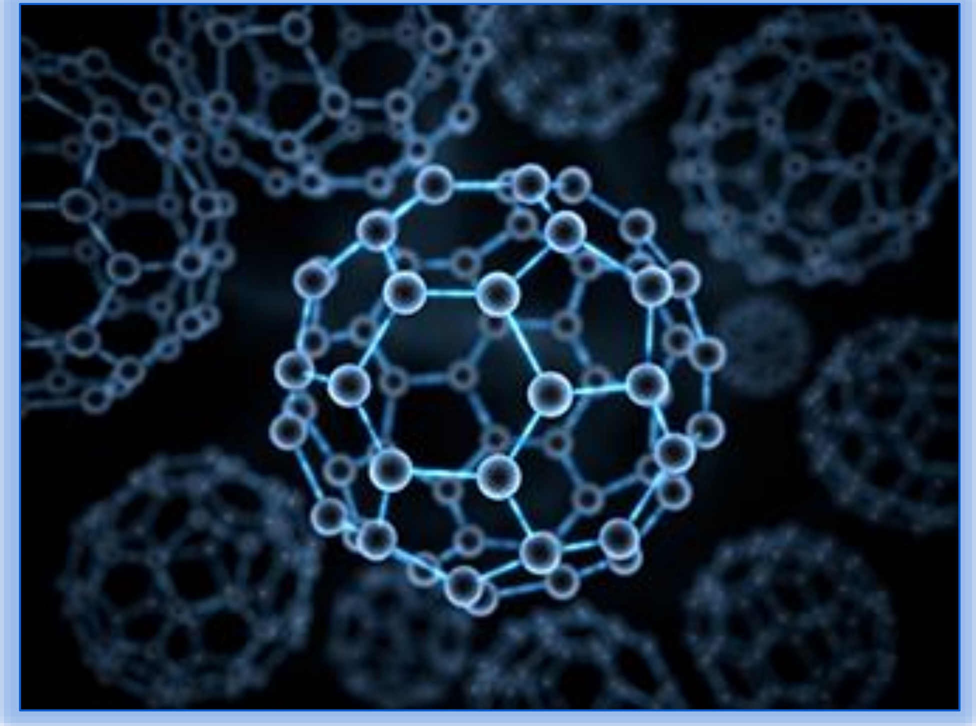
This material is in part supported by the National Science Foundation and Environmental Protection Agency under Cooperative Agreement # NSF-EF0830117. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation or the US Environmental Protection Agency.

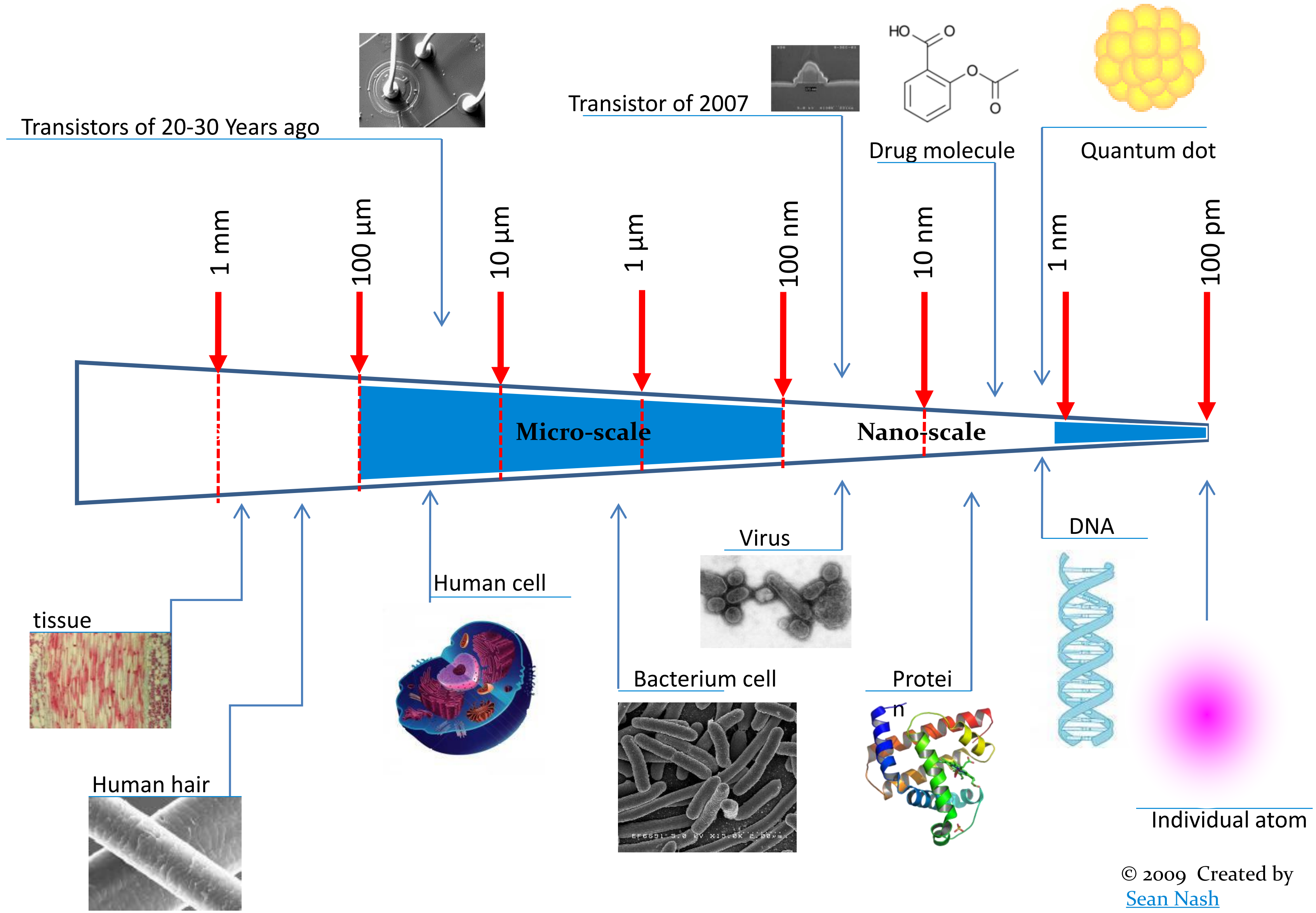
Outline

- What are nanoparticles and where can we find them?
- Nanoparticle (NP) characterization
- NP analysis by ICP-MS:
  - Important concepts
  - Instrumentation
  - NP workflow
- Application:
  - Analysis in water samples
  - Analysis in biological tissues



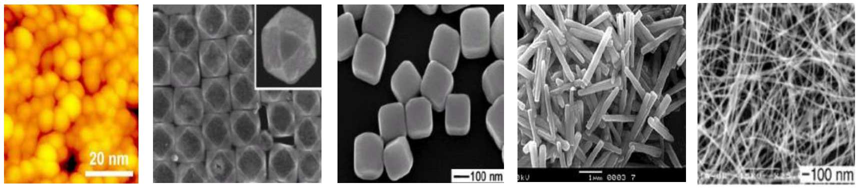
starmans.net

What is a nanomaterial?



Where do they come from?

Particles with at least one dimension in the nano-scale (1~100 nm); 1 nm $=10^{-9}$ m

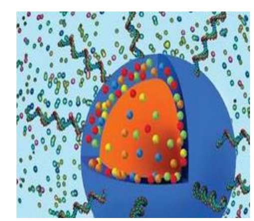


Natural Sources

Produced by redox reactions, weathering, mining, volcanos, dust storms

Unintentionally produced NPs

Emitted to air, water and soil from combustion, wear, metal polishing and metal working, electric motors etc.

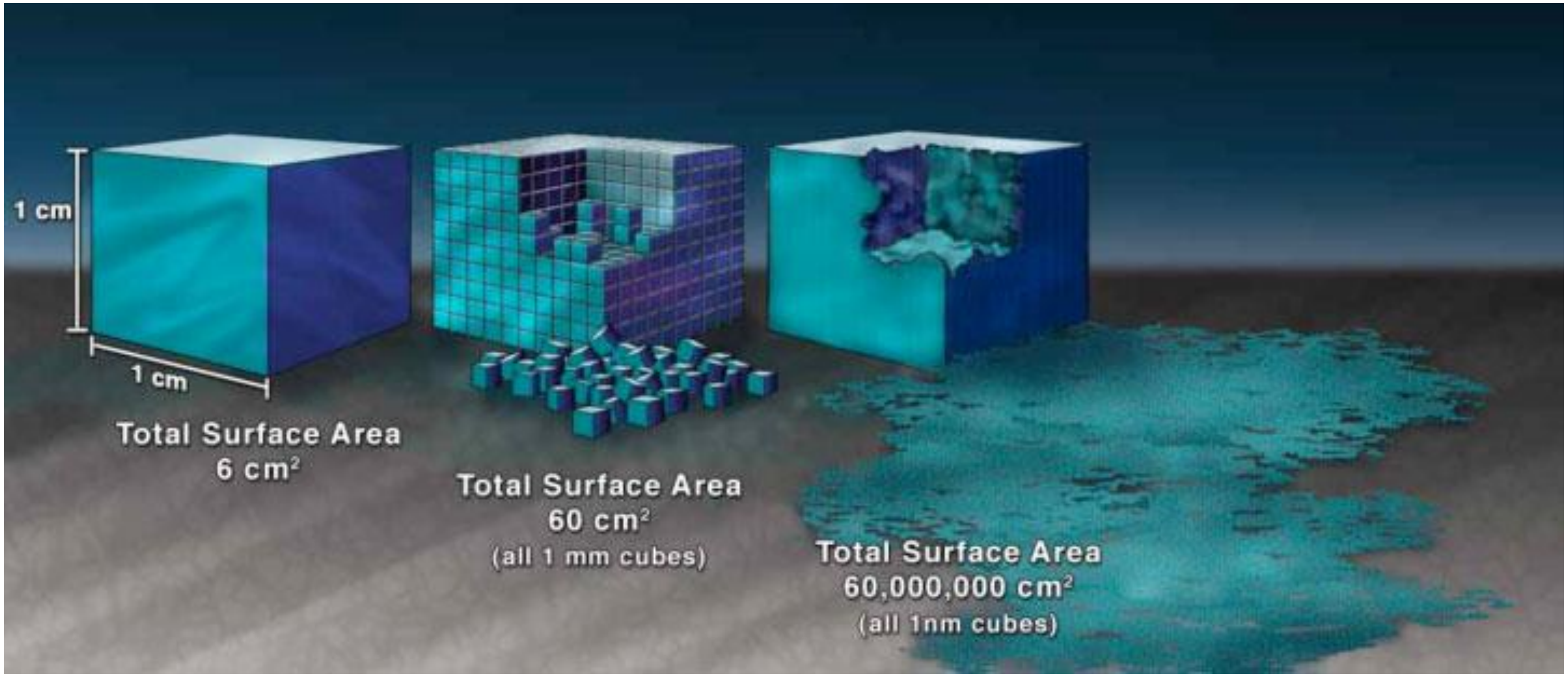


Engineered NPs

Synthesized for a specific purpose. Usually embedded in other products

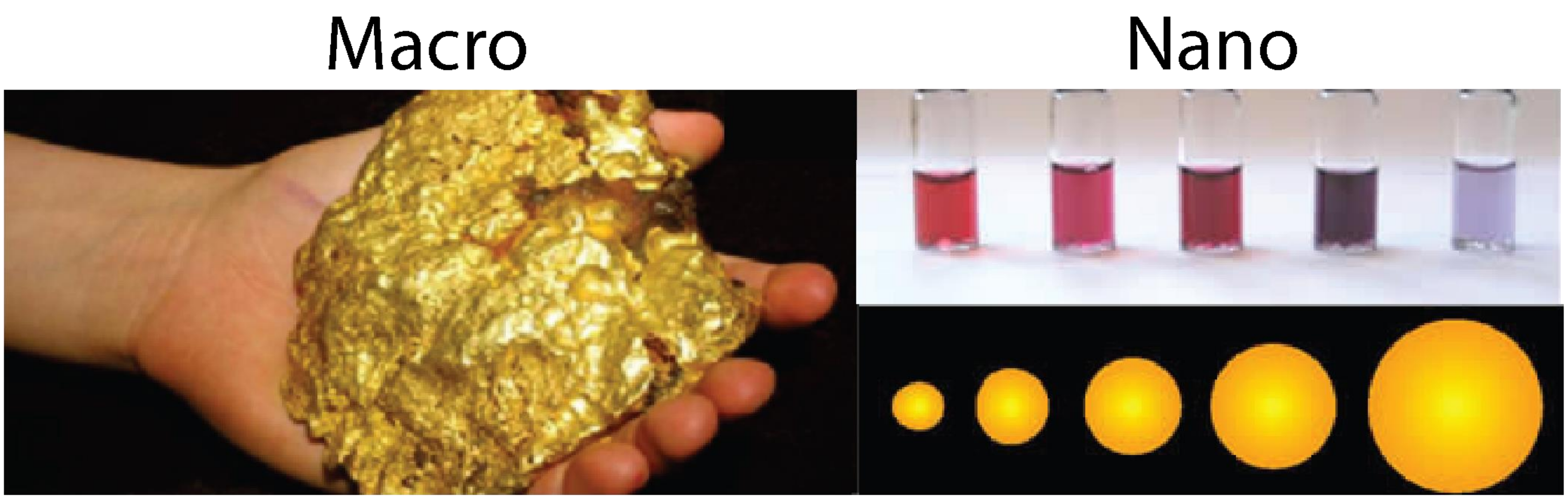
Unique Properties of ENMs

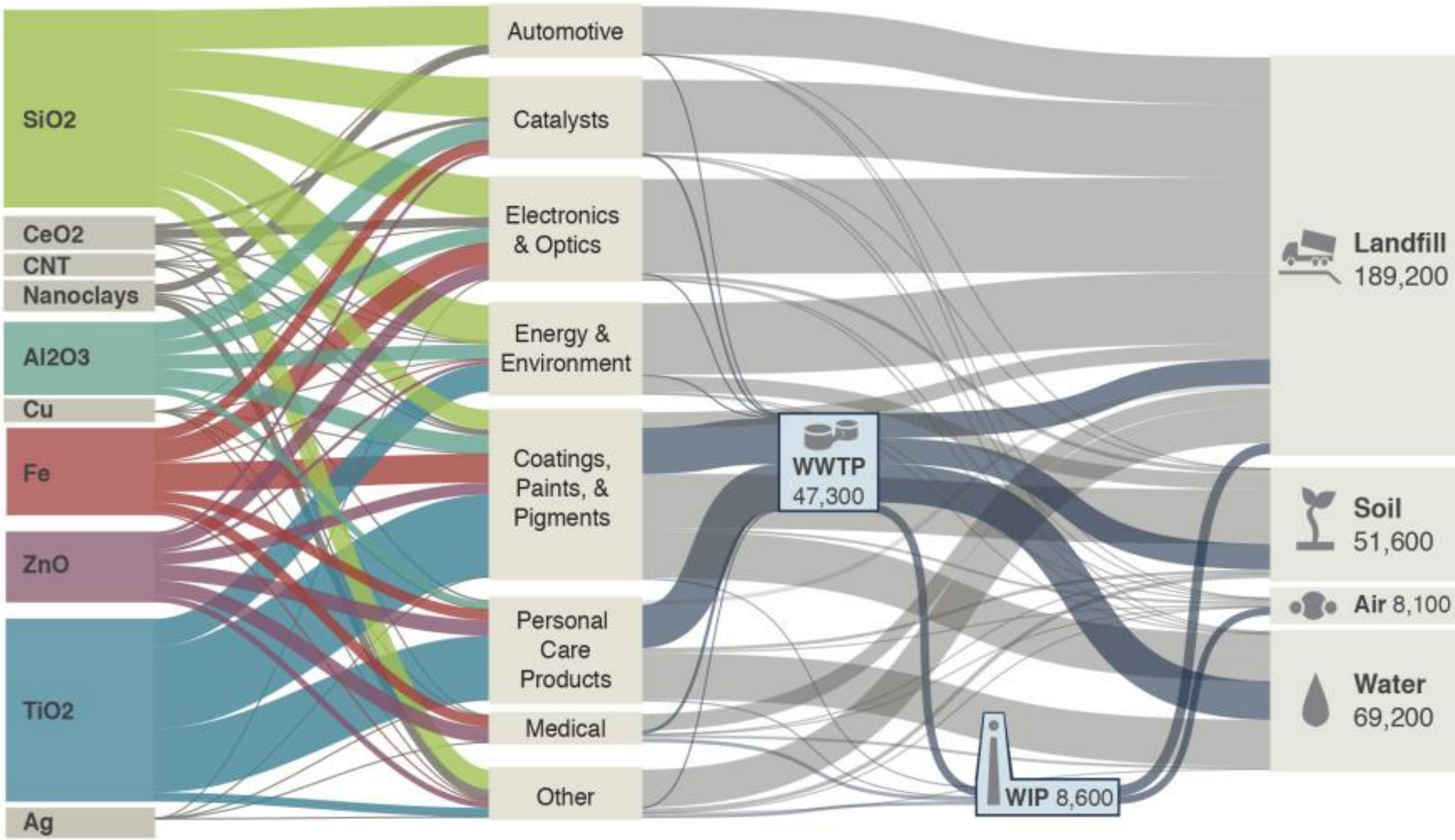
- Huge surface area, with most atoms exposed to surrounding environment
- High surface energy
- Quantum effects



Why does it matter?

- Enhanced reactivity
- Enhanced interaction with photons
- Easily interact with biomolecules
- Can enter cell membranes





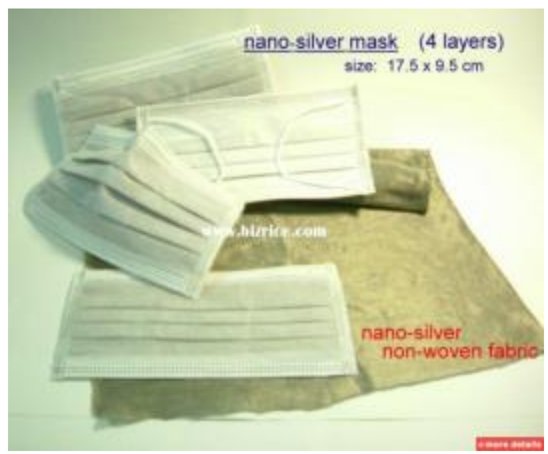
(all flows in metric tons/yr, 2010 estimates from Future Markets, Inc.)

Keller et al., JNR 2013

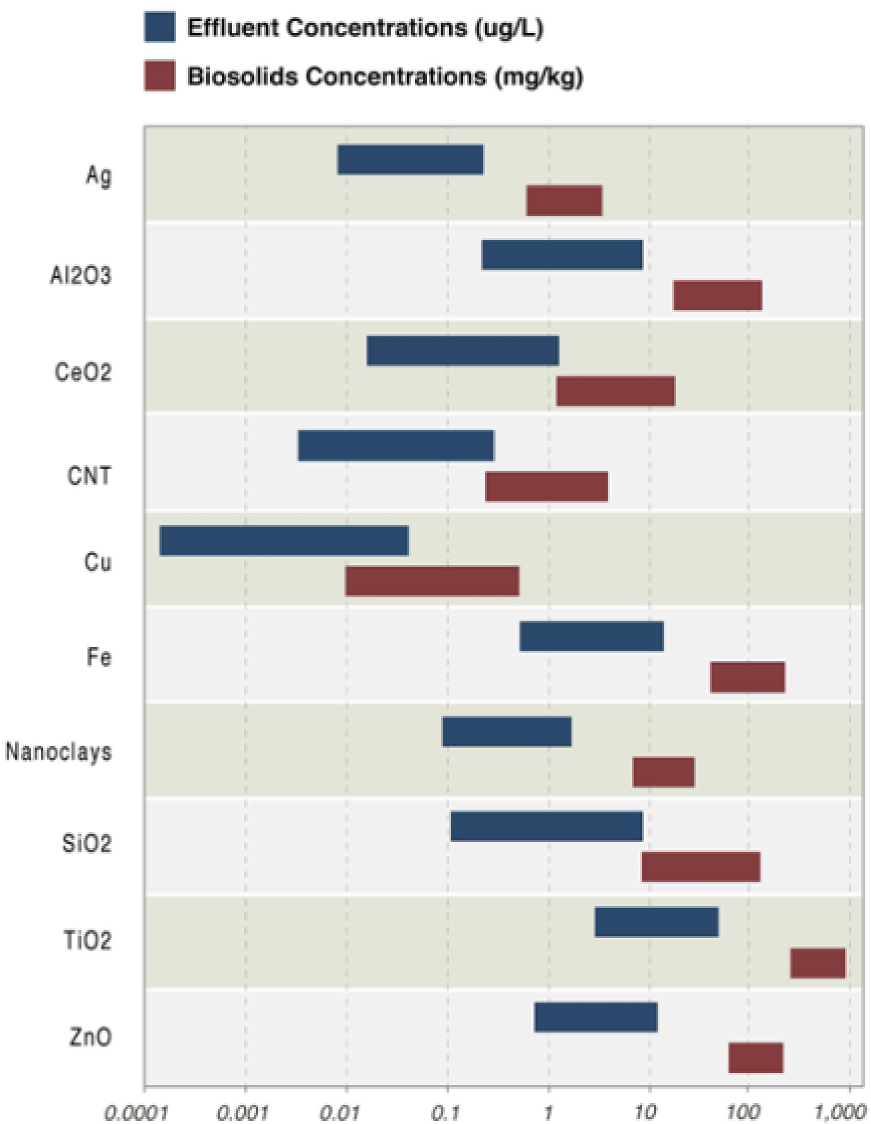
Keller and Lazareva, ES&TL, 2014

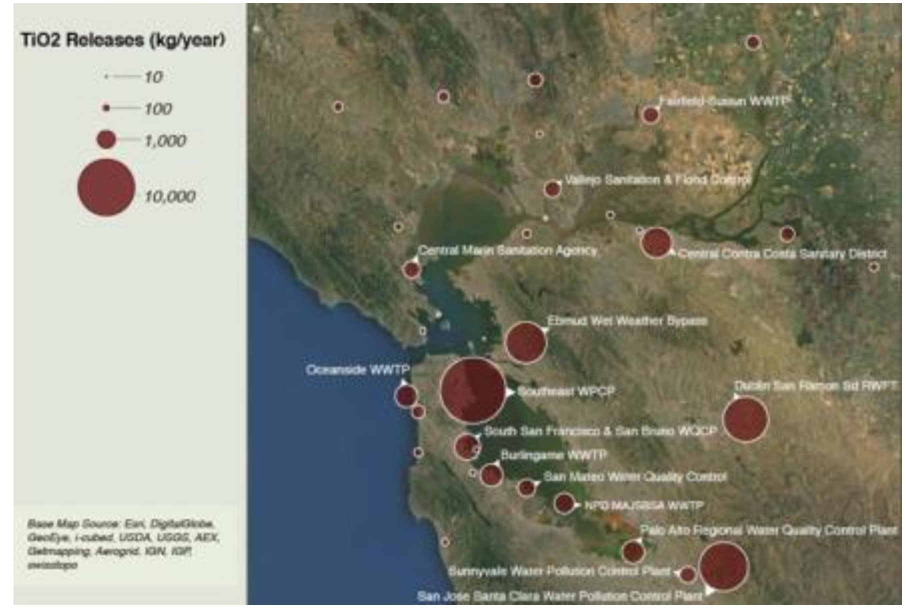
Personal Care Products

- Large application for many ENMs
- Direct human contact
- ENMs go into wastewater
- Small amount to landfill



Predicted Initial [ENM] in SF Bay





ENM concentrations expected to be at ng/L to ug/L levels at point of release

Lazareva and Keller, ACS Sus Chem, 2014

Analytical challenge

- Can we detect ENMs in water and other environmental matrices?
- Composition?
- Size?
- Quantity?
- Other characteristics?

- No EPA methods available to date…

Methods for NP characterization

- **Imaging** methods (TEM, SEM, AFM) are often definitive for detection, shape and size determination. Not quantitative or representative. Labor-intensive.

- **Spectroscopic/optical** methods (UV-Vis, dynamic light scattering) simple, but subject to interferences. No elemental information. DLS needs sharp size distribution.

- **Hyphenated techniques** (Chromatographic (or other online) separation coupled with ICP-MS detection). Allow representative samples, provide good particle size resolution, high elemental sensitivity but no information on individual particles

FFF-ICP-MS

CE -ICP-MS

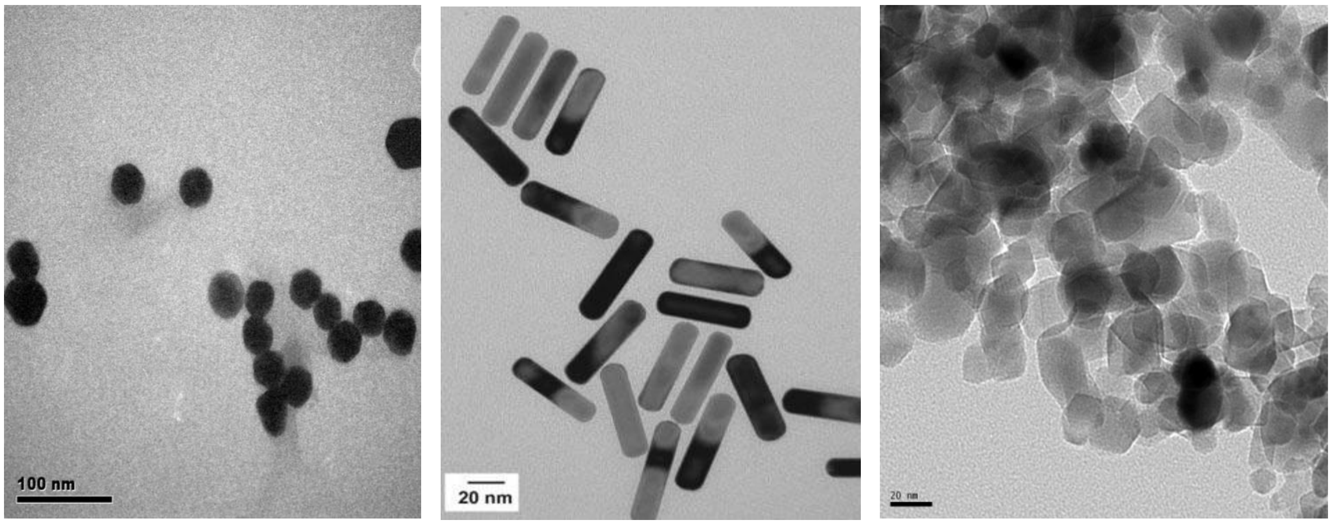
HPLC-ICP-MS

- **Single particle ICP-MS**

Methods for NP characterization

- **Imaging** methods (TEM, SEM, AFM) are often definitive for detection, shape and size determination. Not quantitative or representative. Labor-intensive.

Transmission Electron Microscopy (TEM)

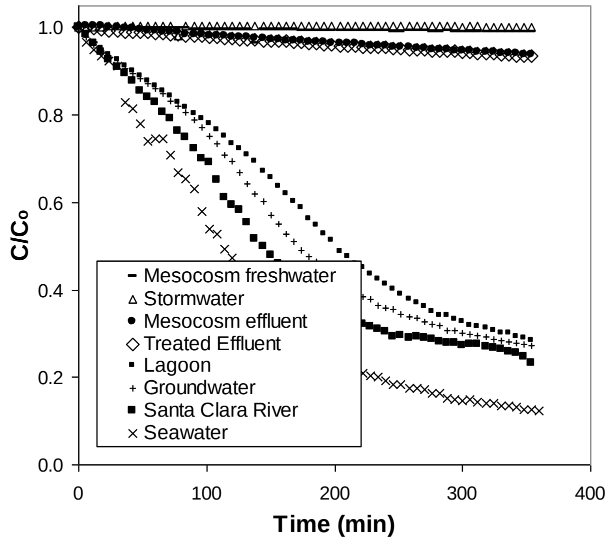


Benefits	Limitations
Excellent size and shape characterization for individual particles	Time consuming preparation
Capability to detect very small particles	Subject to preparation artifacts
	Limited elemental information (hard to be quantitative)

Methods for NP characterization

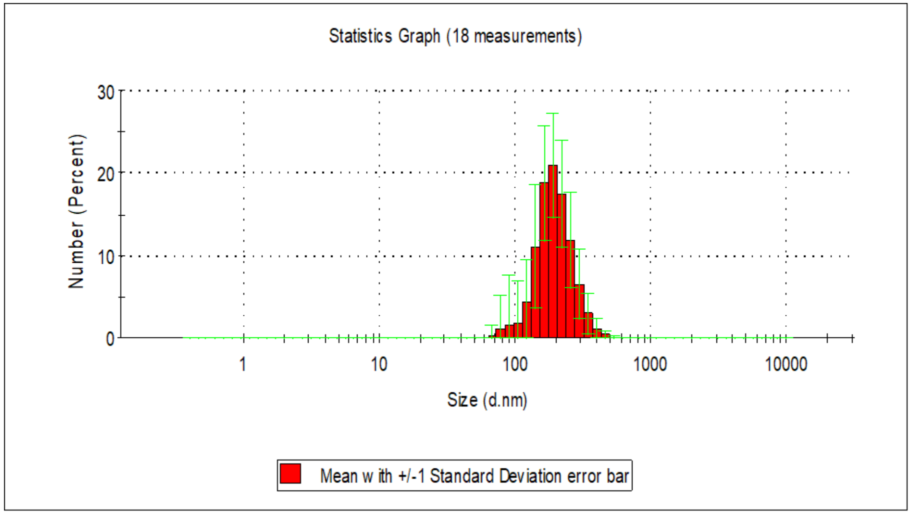
- **Spectroscopic/optical** methods (UV-Vis, dynamic light scattering) simple, but subject to interferences. No elemental information. DLS needs sharp size distribution.

UV-Vis spectroscopy



Keller et al., ES&T 2010

Dynamic Light Scattering



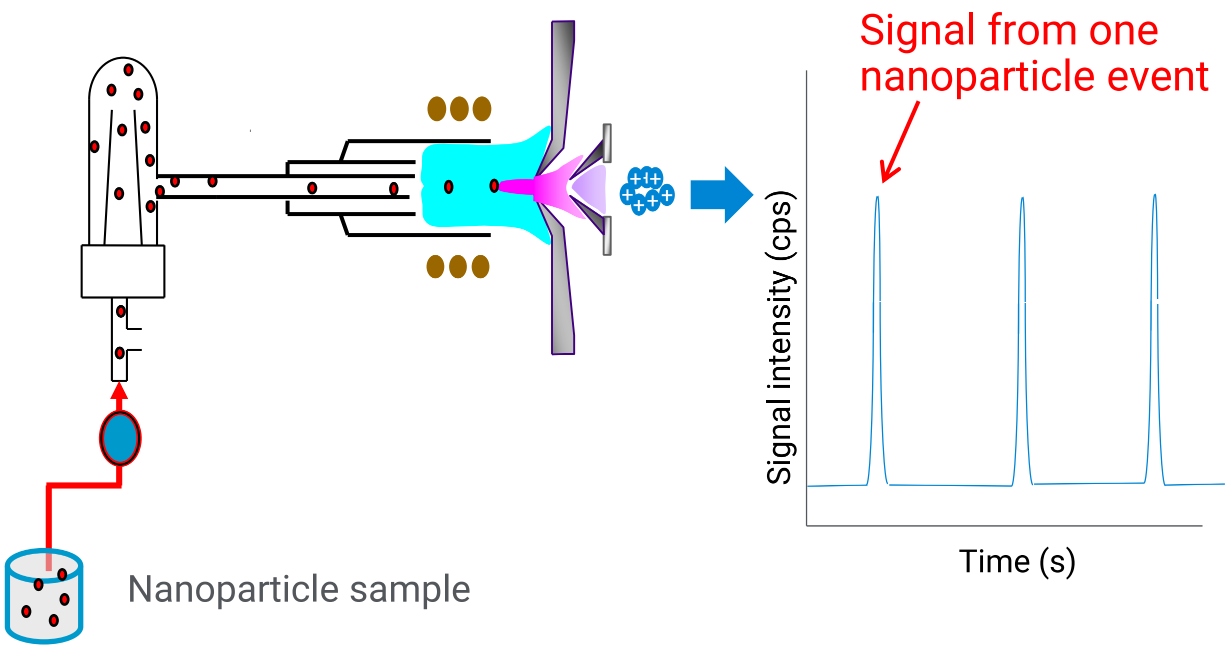
Adeyemi, Keller et al., ES&T 2015

Benefits	Limitations
Low cost	Suspension stability
Capability to detect very small particles	Subject to preparation artifacts & interferences
Several water matrices	No elemental information
	> 1-10 ppm in sample

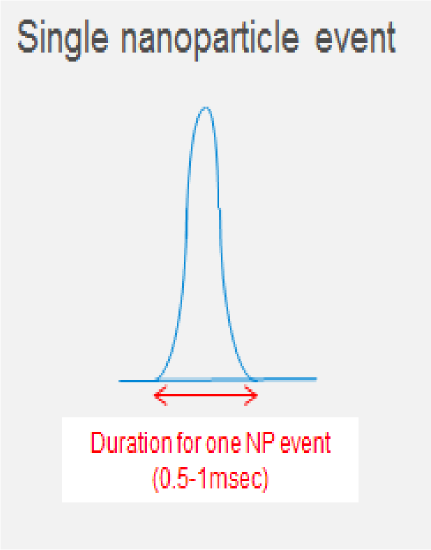
Methods for NP characterization

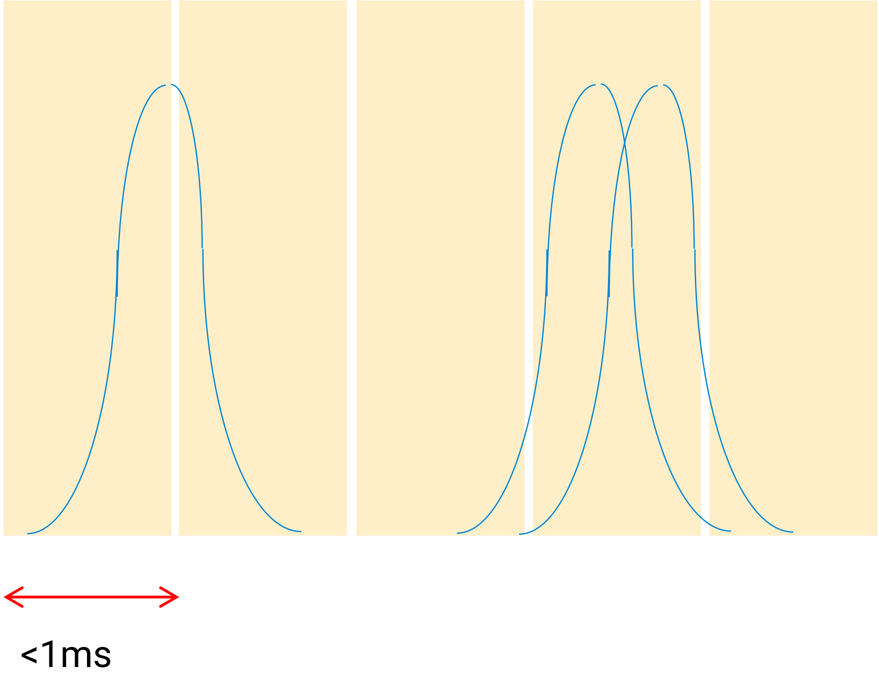
Single Particle ICP-MS (spICP-MS)

- Each nanoparticle gives a transient signal (a plume of ions generated from the particle)
- Use time resolved data acquisition and analysis
- Measure particle concentration, particle size & size distribution, and composition



Important points for single nanoparticle analysis



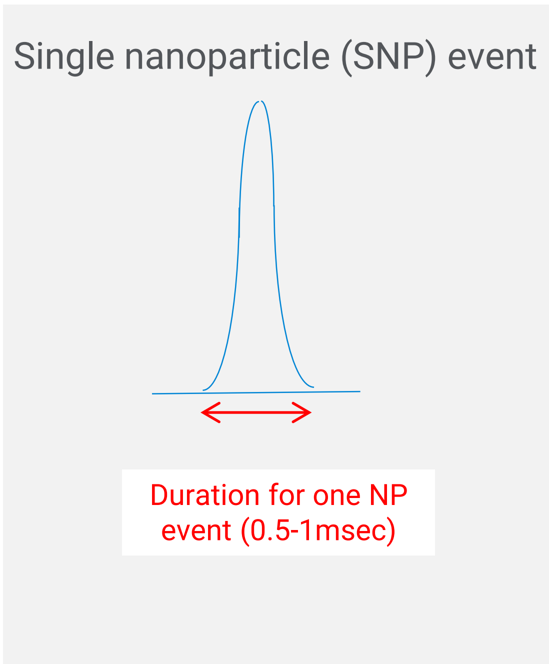


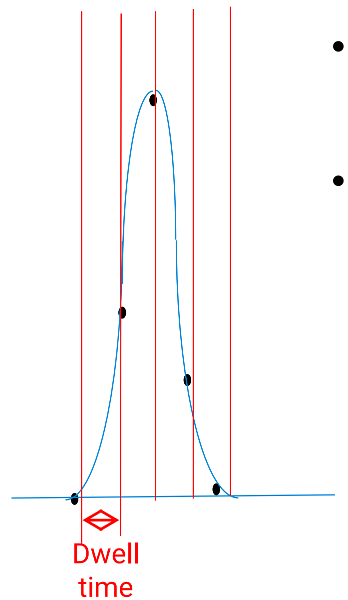
- Need fast acquisition (short dwell time) to capture each NP
- Just shortening the dwell time alone does not solve problem
- Need to integrate signal over multiple scans to:
  - Accurately quantify signal from single particle
  - Help identify overlapping peaks

Microsecond Scanning with no Settling Time

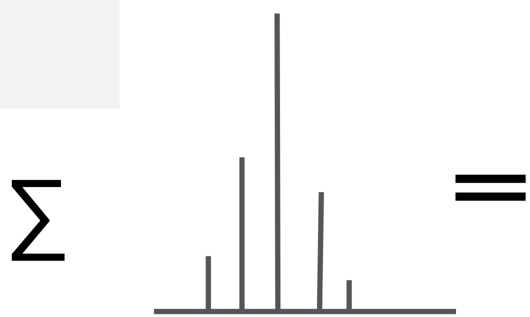
- Short Dwell Time (0.1ms)

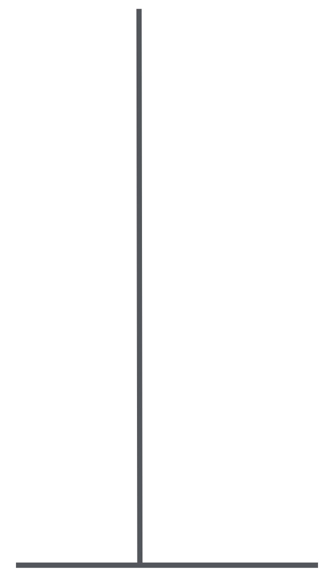
- Peak Integration Mode





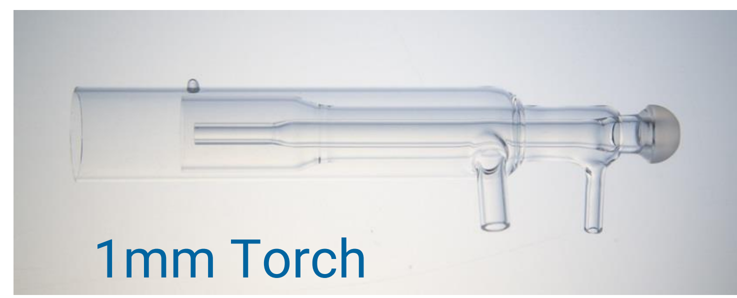
- "Peak Integration Mode" is automatically enabled for SNP
- Data Analysis software employed when dwell time is <1 ms





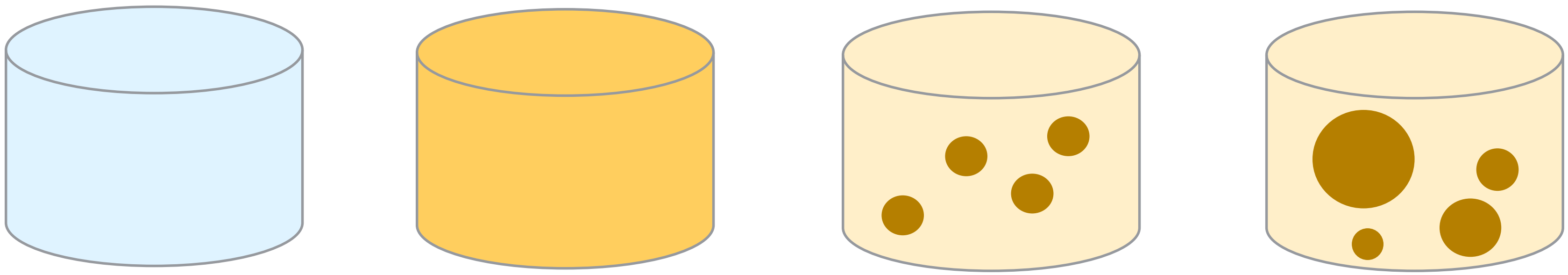
Mass Spectrometer used in our studies

- 7900 quadrupole ICP-MS – ultra-sensitive, ultra-fast 0.1 ms dwell
- Fully automated acquisition and data analysis configuration within MassHunter 4.3 software guided by Method Wizard
  - Supports single particle mode



What is sNP analysis?

➢ Sample Types for single nanoparticle analysis

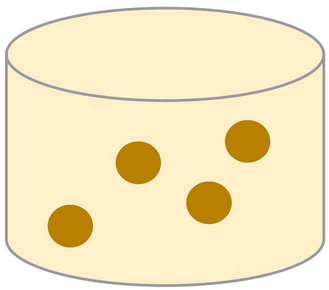


Ionic Blank	Ionic Standard	Reference Material	Unknown Sample
➢ Blank sample	➢ Dissolved metal solution	➢ Metal suspension liquid. ➢ Known particle size ➢ Known conc. ➢ Used to calibrate nebulizer efficiency (η_n).	➢ Metal suspension liquid ➢ To be analyzed ➢ Unknown particle size and conc.

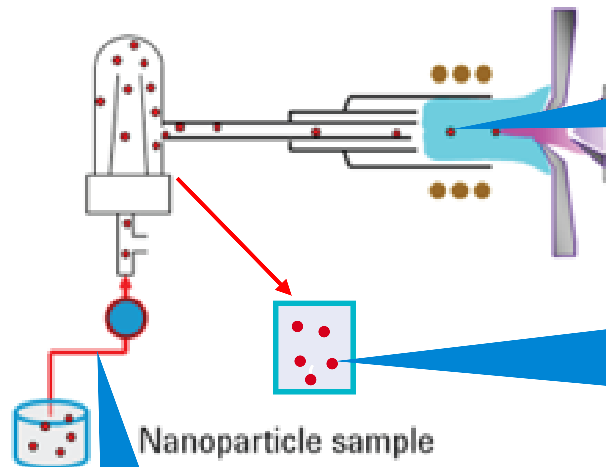
➢ Used to calibrate response factor(s).

What is Nebulizer Efficiency?

- Calibration - Nebulizer Efficiency (η_n)



Reference Material



85
particles
(Detected)

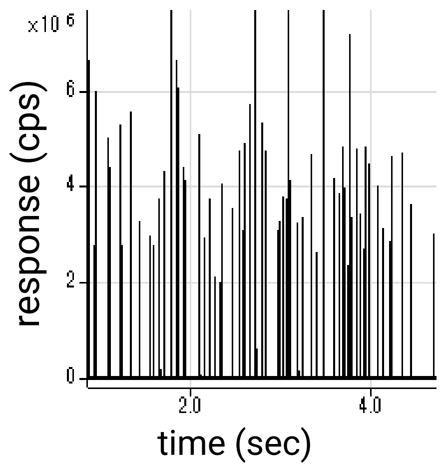
915
particles
(Went to drain)

1000
particles
(Introduced)

η_n = 85 / 1000
= 0.085 or 8.5%

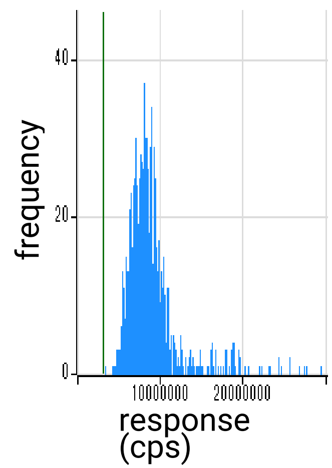
Workflow for NP characterization

ICP-MS TRA data



convert

Response vs frequency

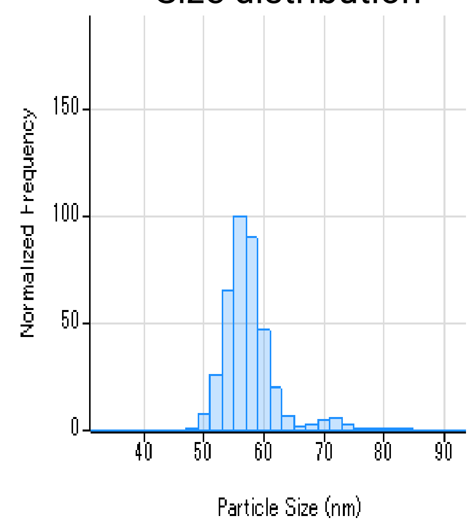


input

- Analyte response factor -> Mass of analyte in particle
- Nebulization efficiency (calculated from reference material)
- Analyte density
- Analyte mass fraction in sample particle

calculate

Size distribution



Tabulate and Report

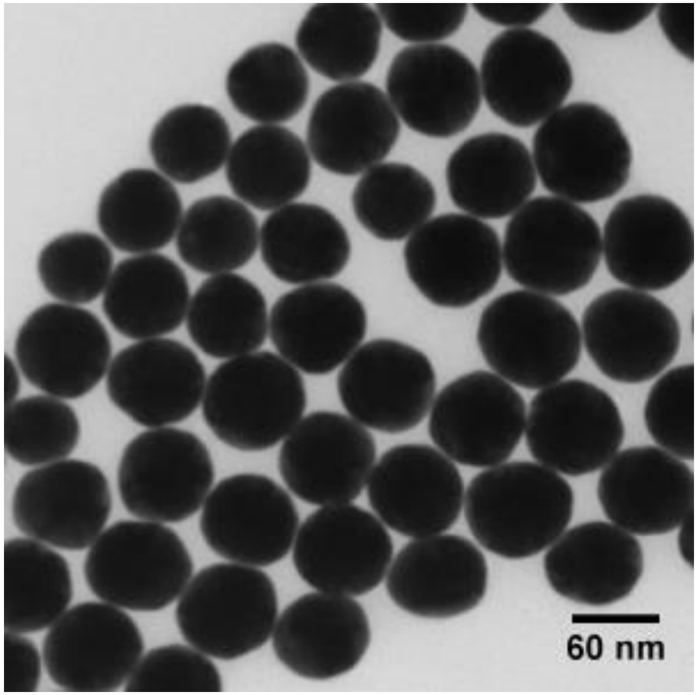
Sample				197 Au						
Data File	Acq. Date-Time	Type	Sample Name	Nebulization Efficiency	# of Particles	Conc. (particles/l)	Conc. (ng/l)	Ionic Conc. (ppb)	BED (nm)	Particle Size (nm)
001IONB.d	5/13/2015 3:10:19 AM	IonicBlk	blank							
002IONS.d	5/13/2015 3:13:07 AM	IonicStd	1ppb							
003_RM.d	5/13/2015 3:15:21 AM	RM	30nm 5ppt	0.071	619	2.5E+7	5.0	0.0178	4.21	27
004SMPL.d	5/13/2015 3:18:20 AM	Sample	60nm 50ppt	0.071	617	2.5E+7	48.6	0.0260	4.73	55
005SMPL.d	5/13/2015 3:20:27 AM	Sample	60nm 50ppt	0.071	681	2.8E+7	51.8	0.0266	4.76	55
006SMPL.d	5/13/2015 3:22:35 AM	Sample	60nm 50ppt	0.071	635	2.6E+7	48.8	0.0258	4.72	55
007SMPL.d	5/13/2015 3:24:26 AM	Sample	60nm 50ppt	0.071	656	2.7E+7	50.4	0.0272	4.80	55
008SMPL.d	5/13/2015 3:28:22 AM	Sample	60nm 50ppt	0.071	649	2.6E+7	48.9	0.0240	4.60	55
009SMPL.d	5/13/2015 3:30:54 AM	Sample	30nm 5ppt	0.071	579	2.3E+7	4.5	0.0083	3.23	26
010SMPL.d	5/13/2015 3:33:29 AM	Sample	30nm 5ppt	0.071	589	2.4E+7	4.8	0.0078	3.16	26
011SMPL.d	5/13/2015 3:37:10 AM	Sample	30nm 5ppt	0.071	568	2.3E+7	4.5	0.0078	3.16	26
012SMPL.d	5/13/2015 3:39:03 AM	Sample	30nm 5ppt	0.071	558	2.3E+7	4.5	0.0076	3.13	26
013SMPL.d	5/13/2015 3:43:05 AM	Sample	30nm 5ppt	0.071	600	2.4E+7	4.7	0.0075	3.12	26

Reference Material

60 nm Gold Nanospheres

•Unagglomerated and monodisperse

•Mean diameter: 60 nm ± 4 nm

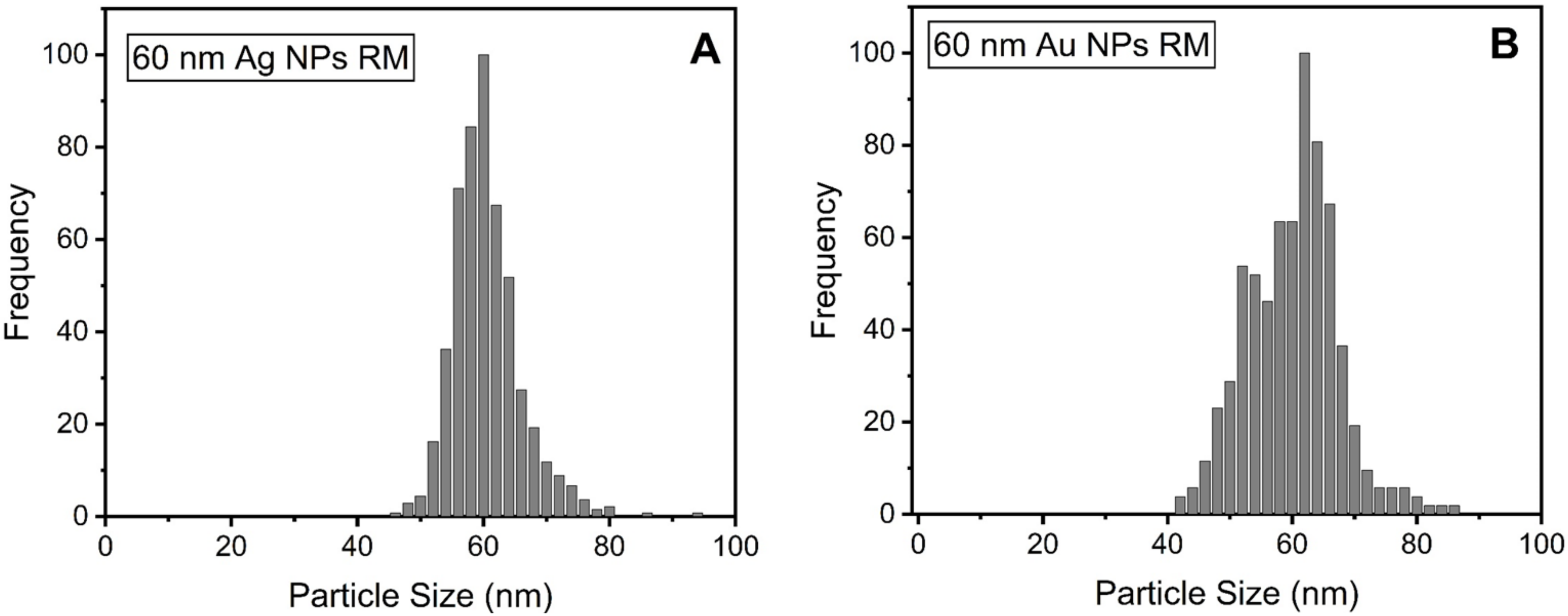


nanoComposix

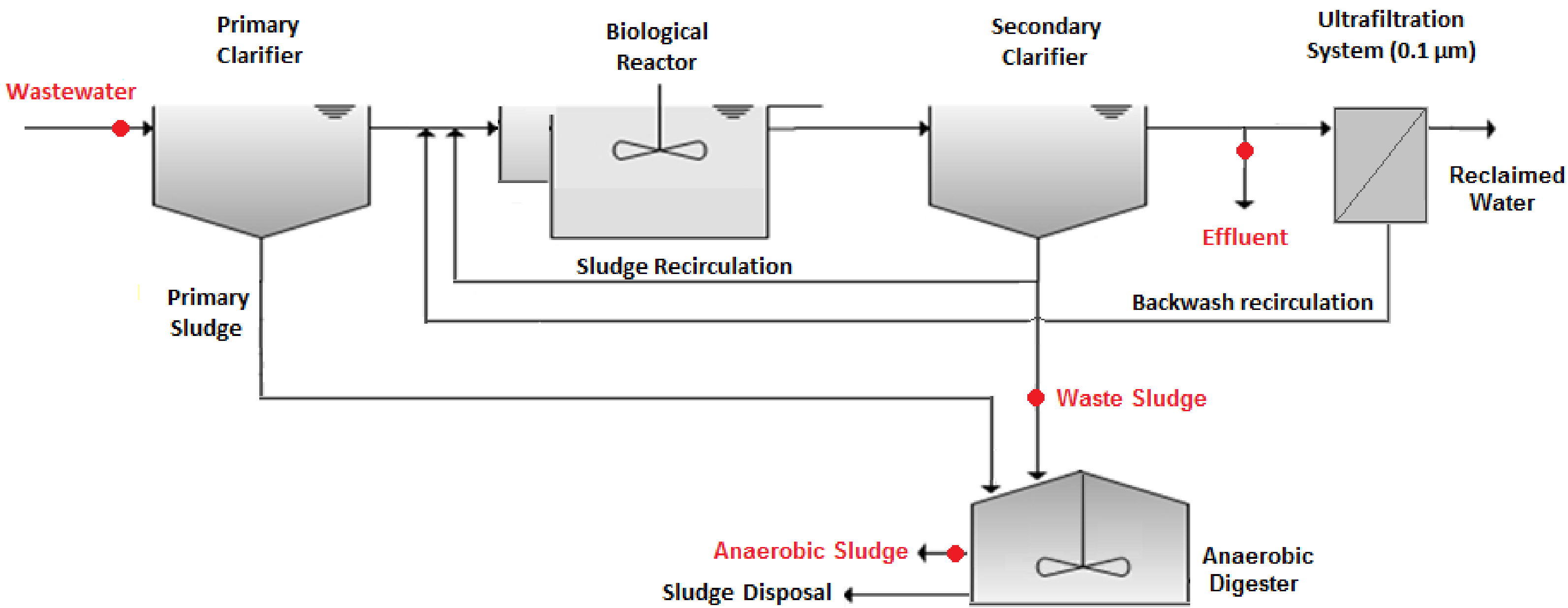
Precision and Accuracy (NIST 8012 and 8013)

Sample (Prepared concentration)	Observed Concentration (particles/L)	Observed Concentration (ng/L)	Observed Particle Size (nm)	Reference Particle Size obtained by TEM (nm)
NIST 8013 Nominal 60nm (100 ng/L)	5.59×10^7	103	55	56.0 ± 0.5
NIST 8012 Nominal 30nm (10 ng/L)	4.27×10^7	10.5	28	27.6 ± 2.1

Size distribution of Reference Materials



Collecting NP samples in WWTP process

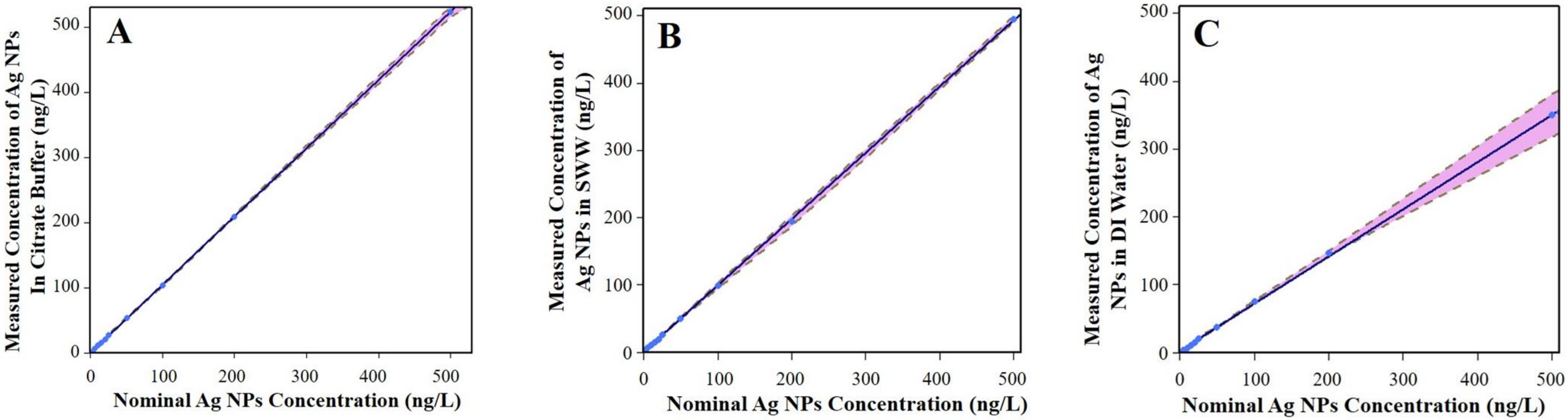


Samples were collected at:

- Raw water before primary clarifier
- Effluent of secondary clarifier
- Reclaimed water after UF
- Waste sludge from the activated sludge basin
- Anaerobic sludge from the sludge digester

Cervantes et al., Water Research 2019

Calibration of Ag NP concentrations

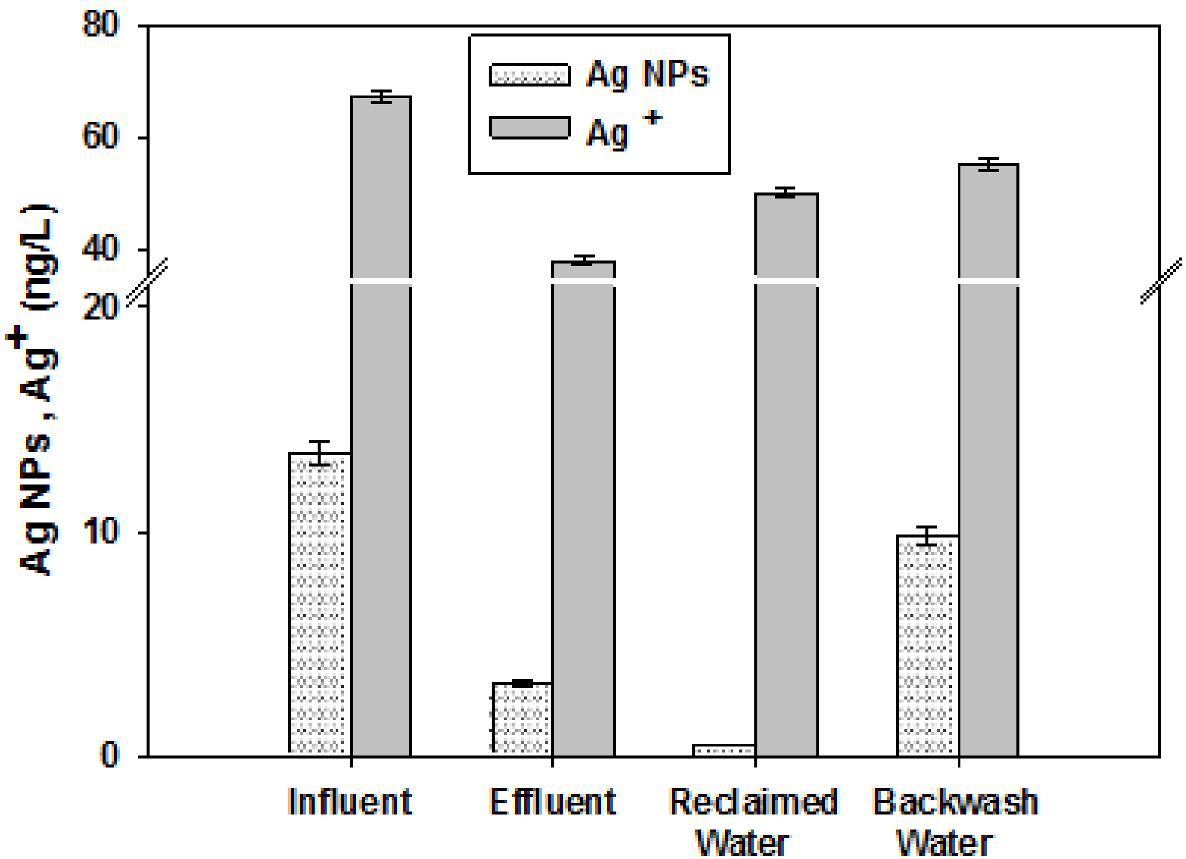


Calibration curves of silver (Ag) nanoparticles in:

- 1 mM citrate buffer solution
- synthetic waste water (SWW)
- DI water

Cervantes et al., Water Research 2019

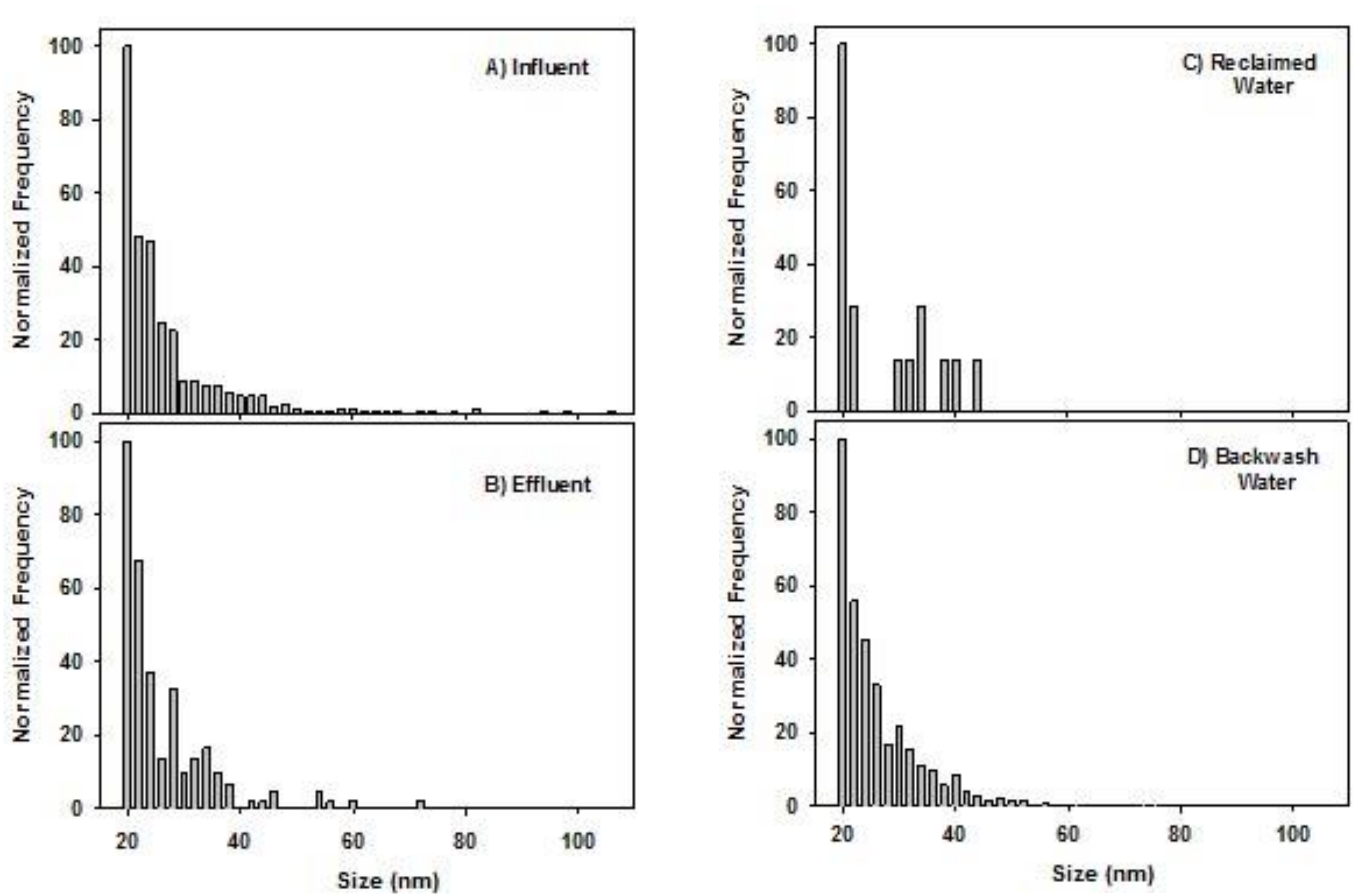
Ag NPs in WWTP process: Concentrations



- Found Ag NPs and Ag^+ in all steps
- Concentrations within range predicted by Material Flow Analysis (Keller et al., 2014)
- Majority of mass as Ag^+
- Backwash water concentrates NPs that recirculate

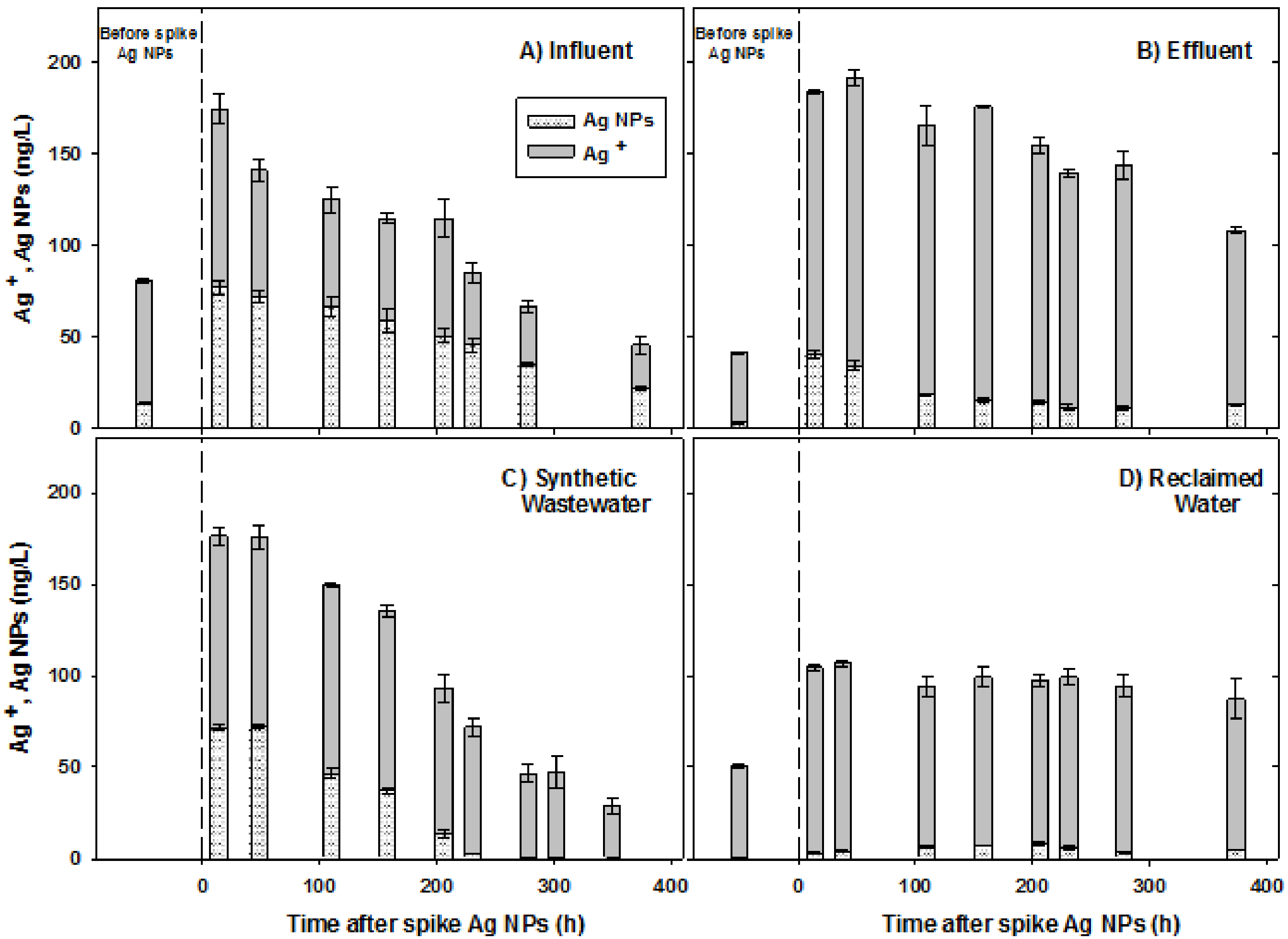
Cervantes et al., Water Research 2019

Ag NPs in WWTP process: Size distributions



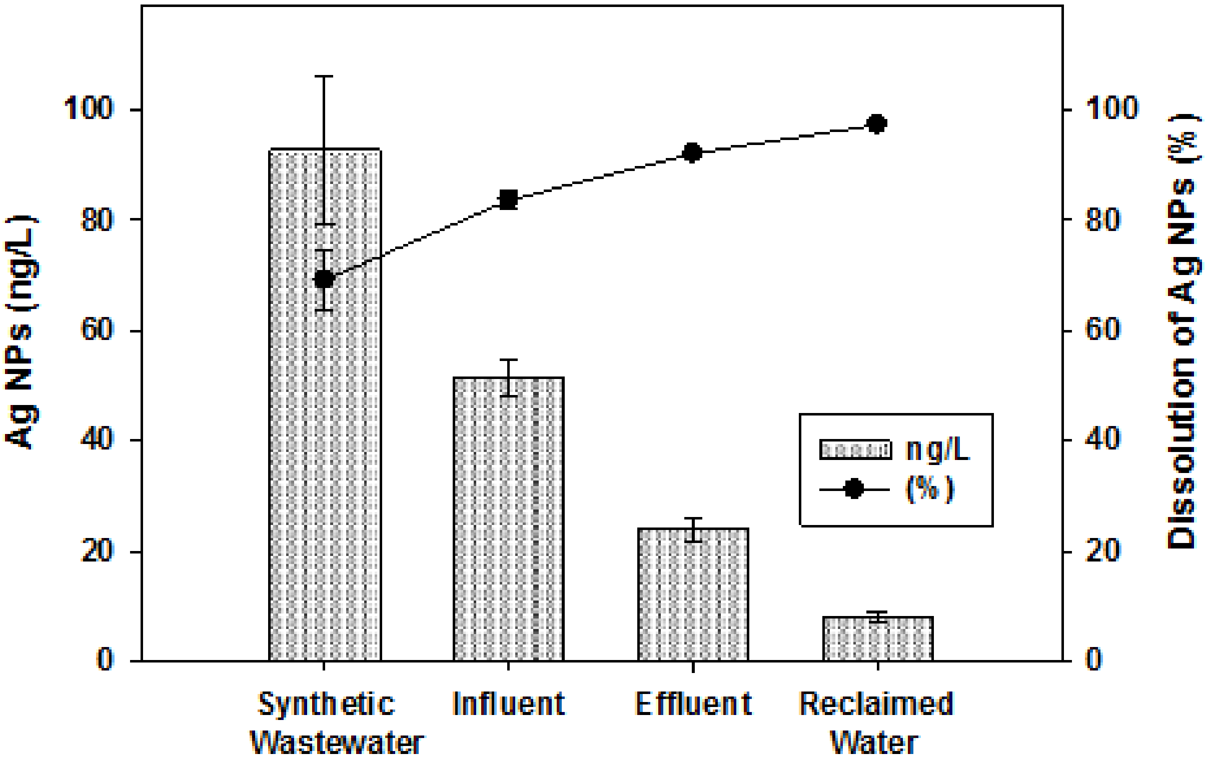
Cervantes et al., Water Research 2019

Ag NPs in WWTP process: Persistence



Cervantes et al., Water Research 2019

Ag NPs in WWTP process: Transformation



- Spiked 300 µg/L as NPs
- After 15 days, Ag NPs are still present in synthetic wastewater mostly as NPs
- More transformation to Ag^+ as the NPs pass through the various processes

Cervantes et al., Water Research 2019

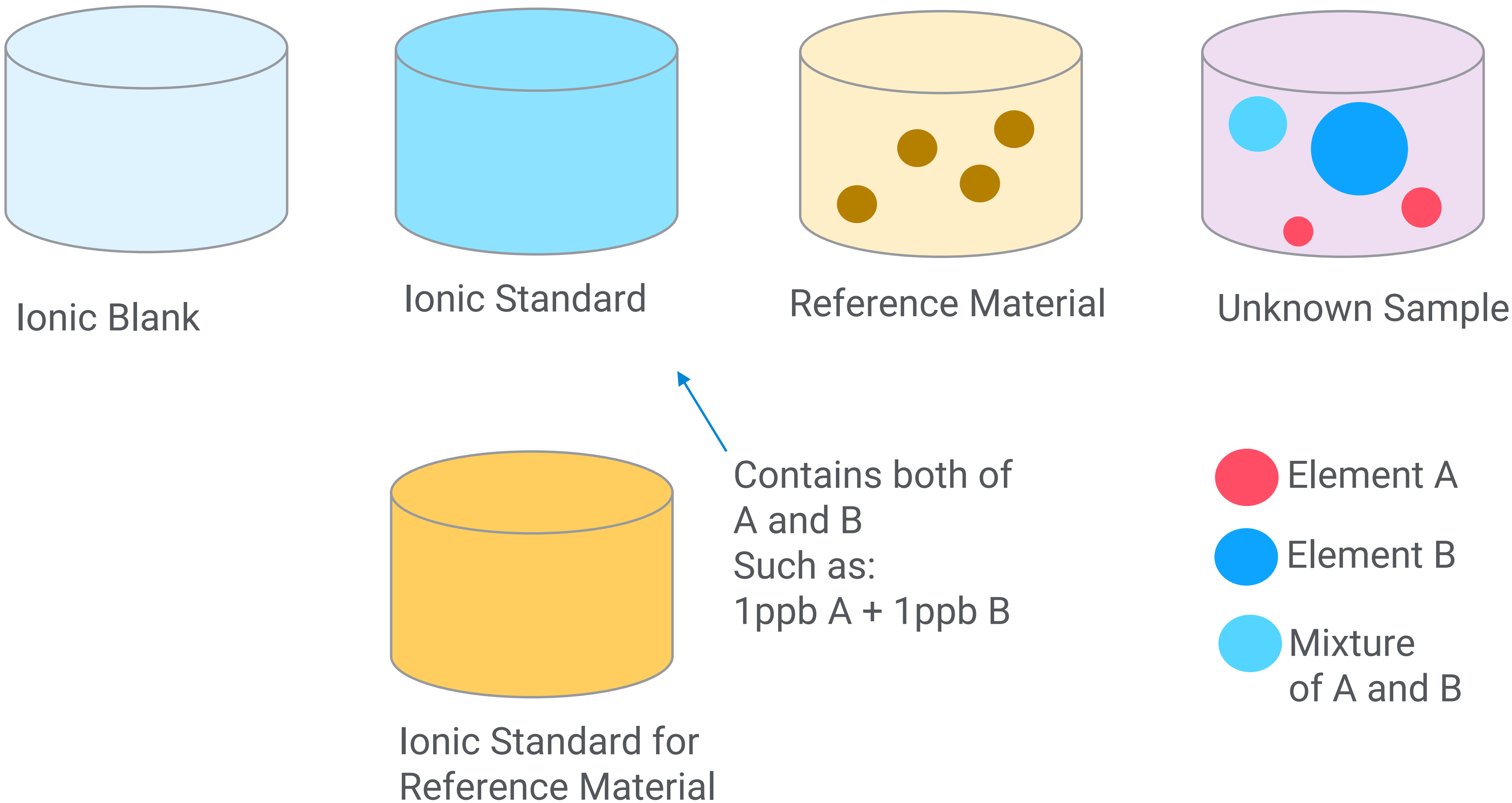
Ag NPs in WWTP process: Conclusions

- Can detect Ag NPs in WWTP process
- Concentrations as Ag NPs in low ng/L
- Around 96% of influent load removed through WWTP (including UF step)
- Most NPs are below 100 nm within the process
- Considerable dissolution of Ag NPs, releasing Ag^+
- sp-ICP-MS is effective for monitoring NP concentrations in WWTP effluent

Cervantes et al., Water Research 2019

Advanced operation – Multi-Element Screening

- Sample prep: In case number of elements is 2+



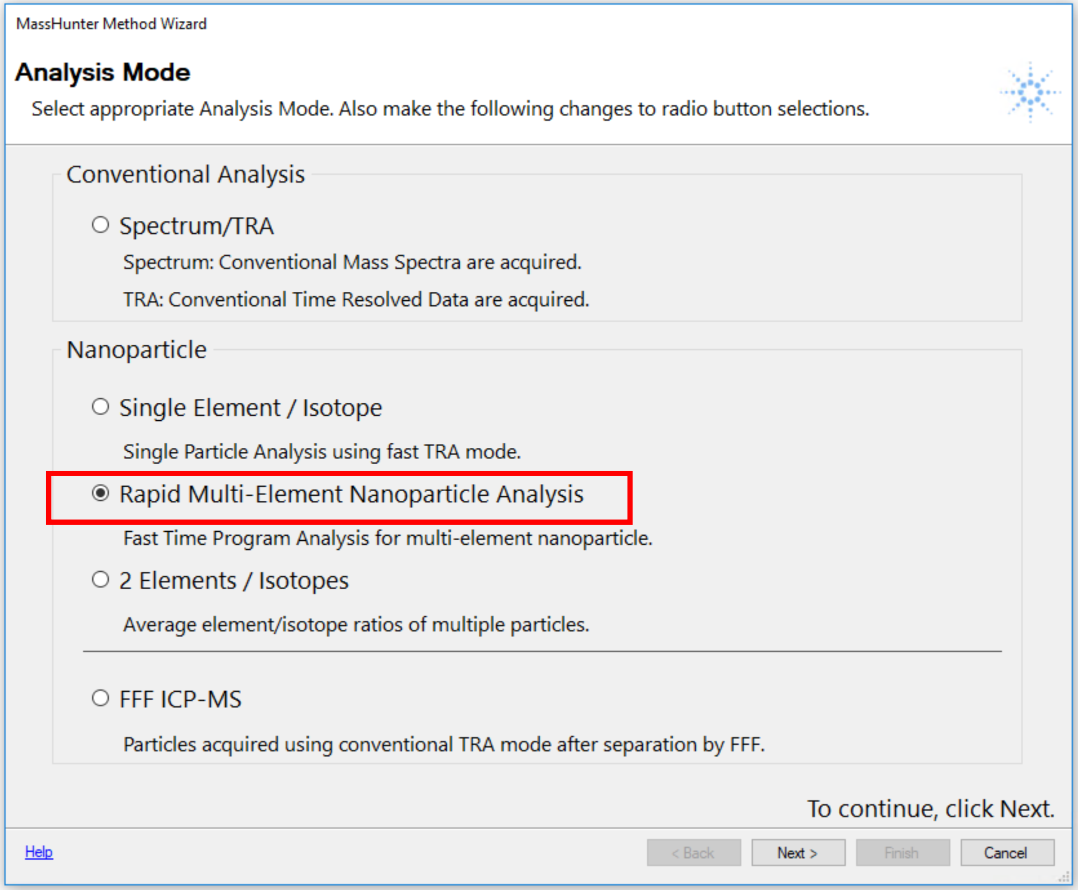
Multi-element sp-ICP-MS analysis

- Very similar operating parameters as single element
- Agilent software able to acquire information for up to 16 elements
- Considered both aqueous phase and sludge
- Sludge was centrifuged at 5,000 RPM for 20 min
- Recovery of spiked Au NPs from sludge was
  - 64% spiked pre-centrifugation
  - 107% spiked post-centrifugation

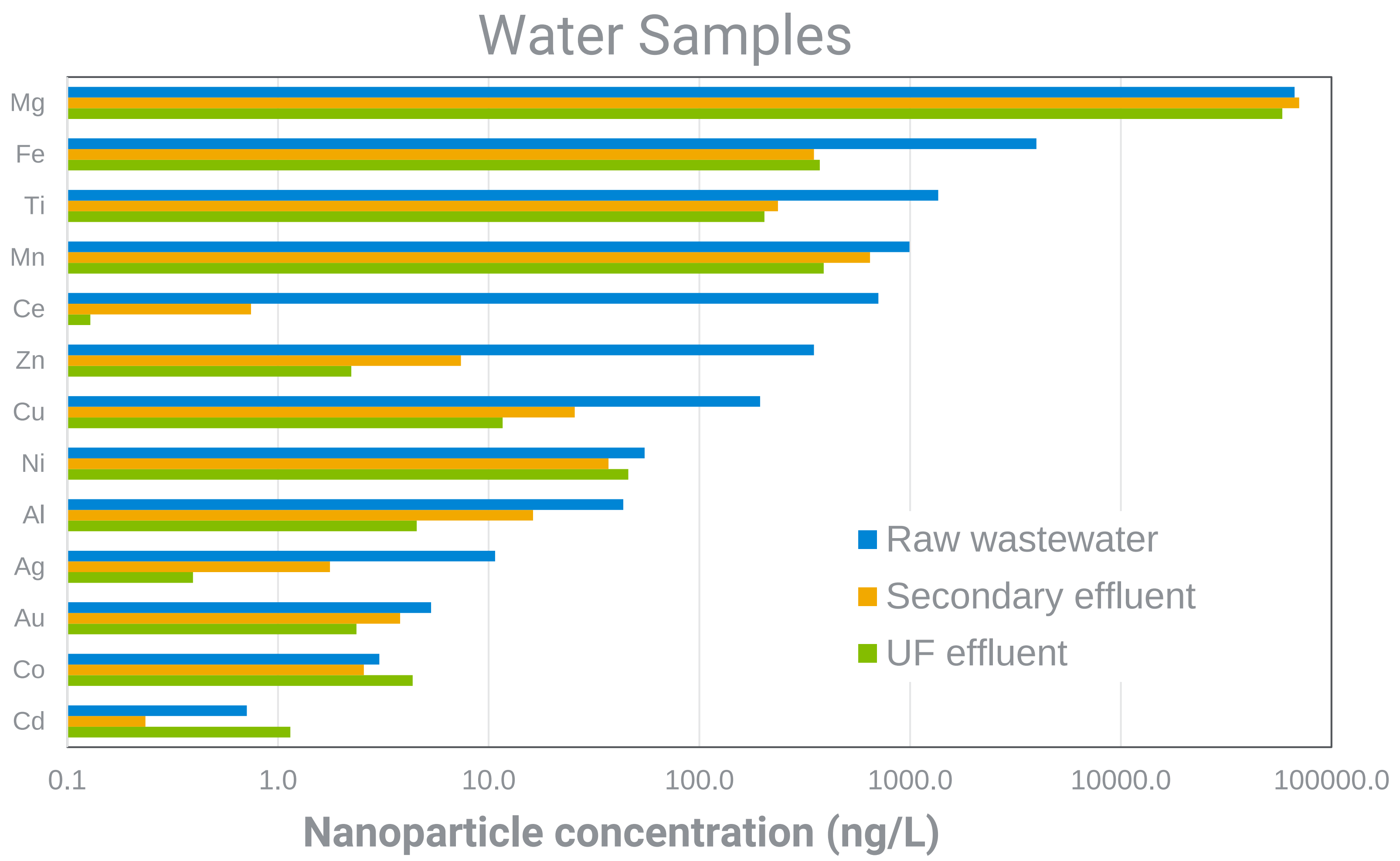
Advanced operation – Multi-Element Screening

➢ Operation

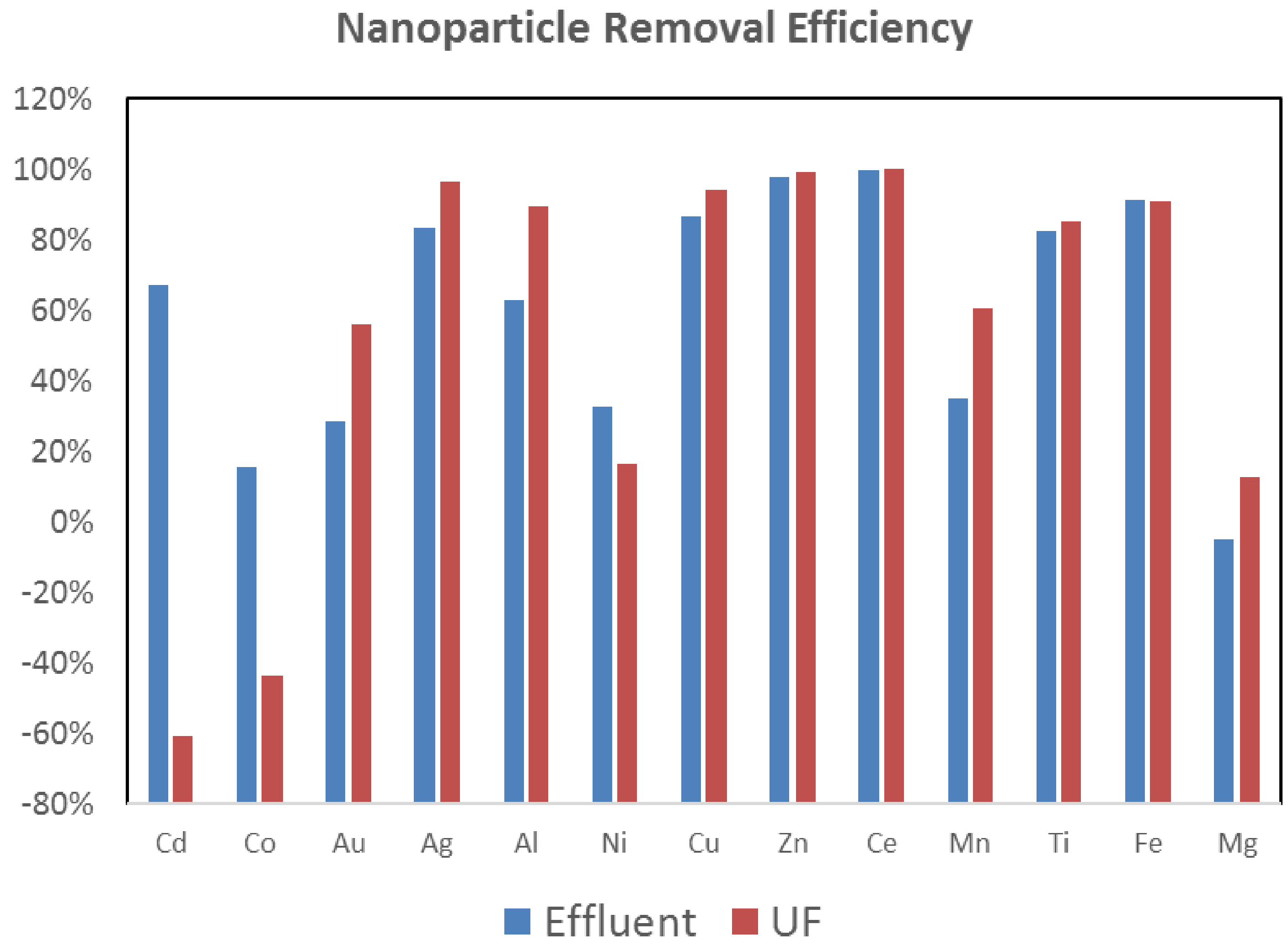
Run Method wizard and Select “Rapid - Multi Element Screening”.



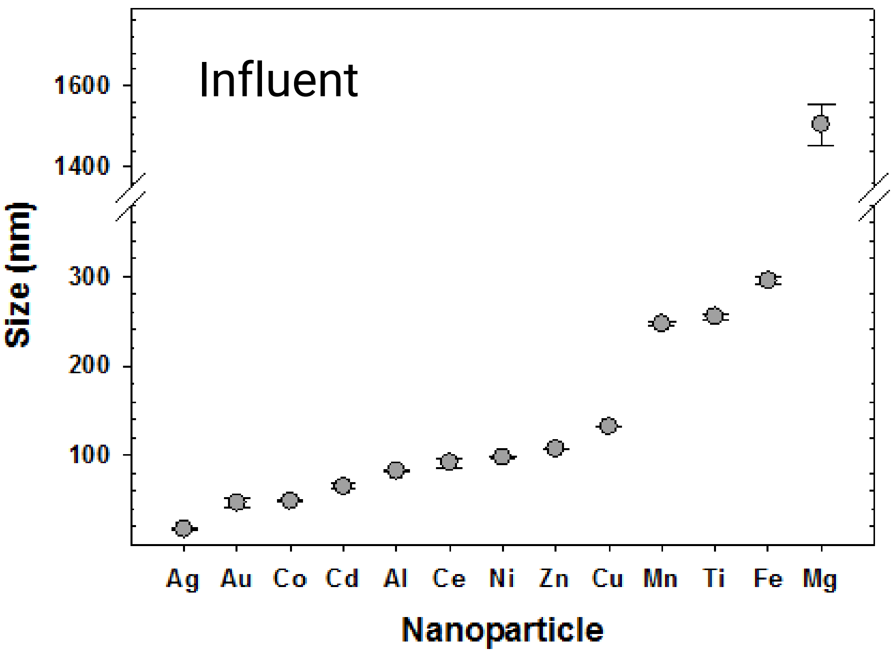
Multi-element sp-ICP-MS analysis

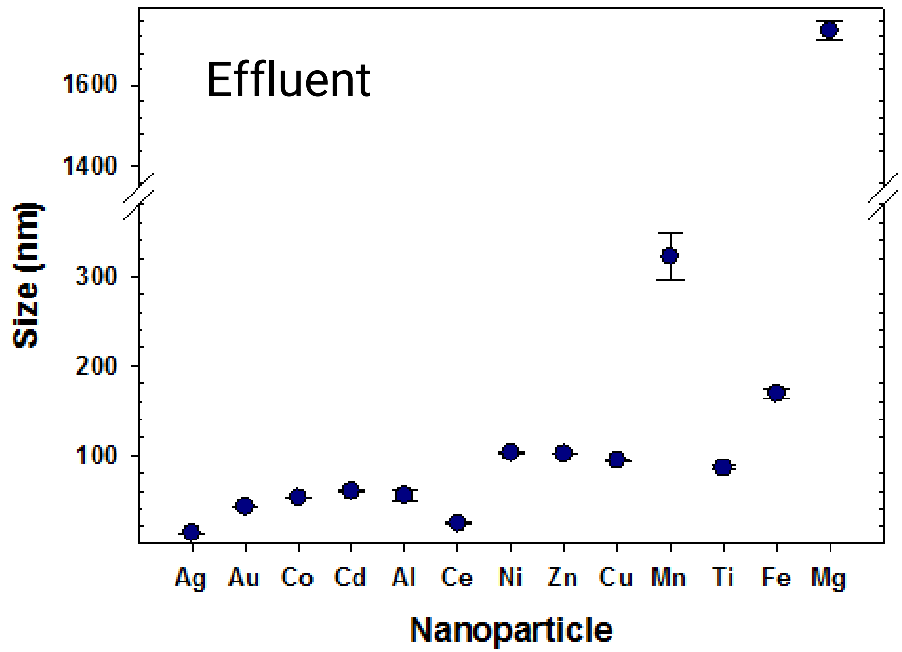


Removal of NPs in WWTP

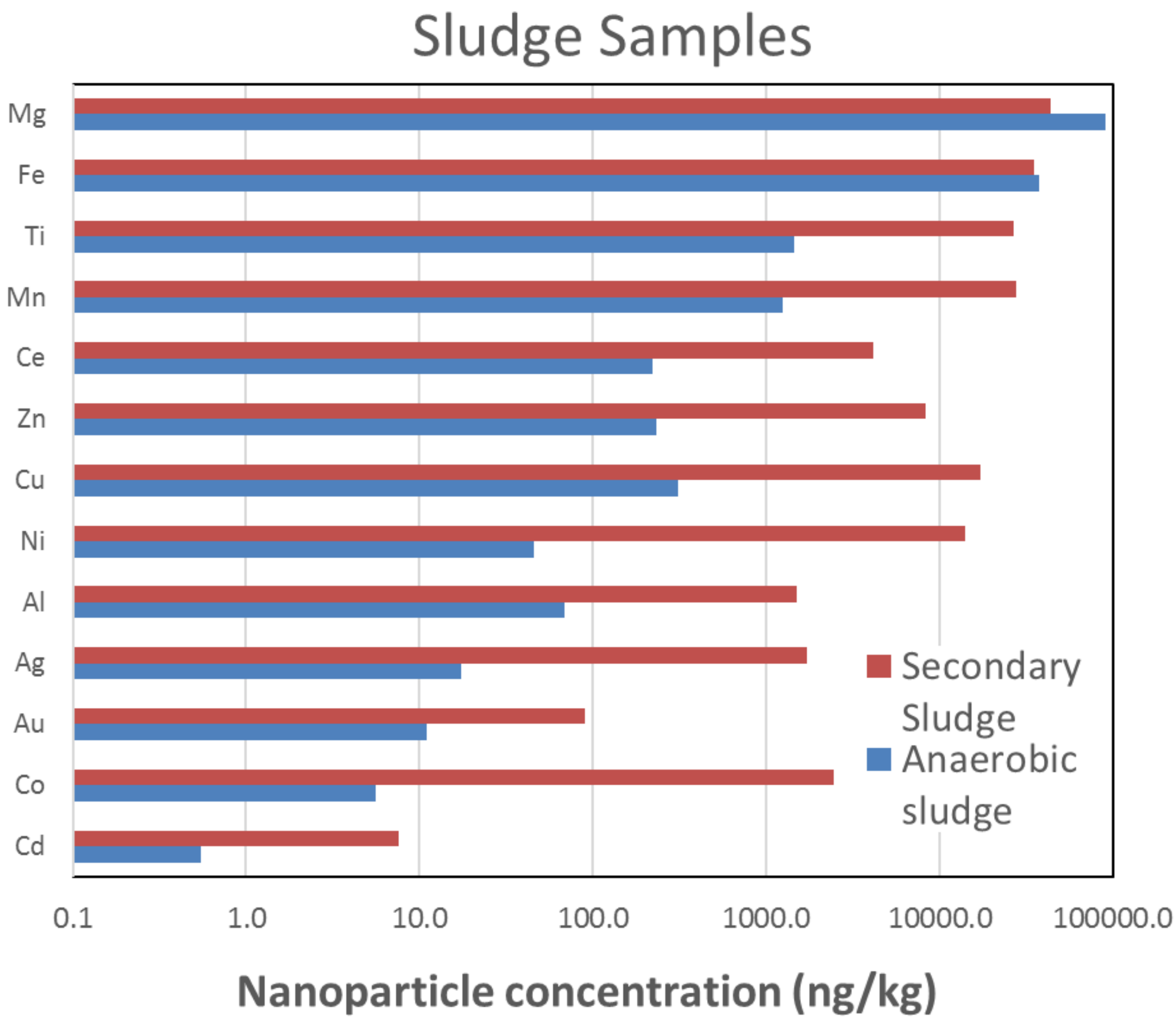


NP size in Water Streams

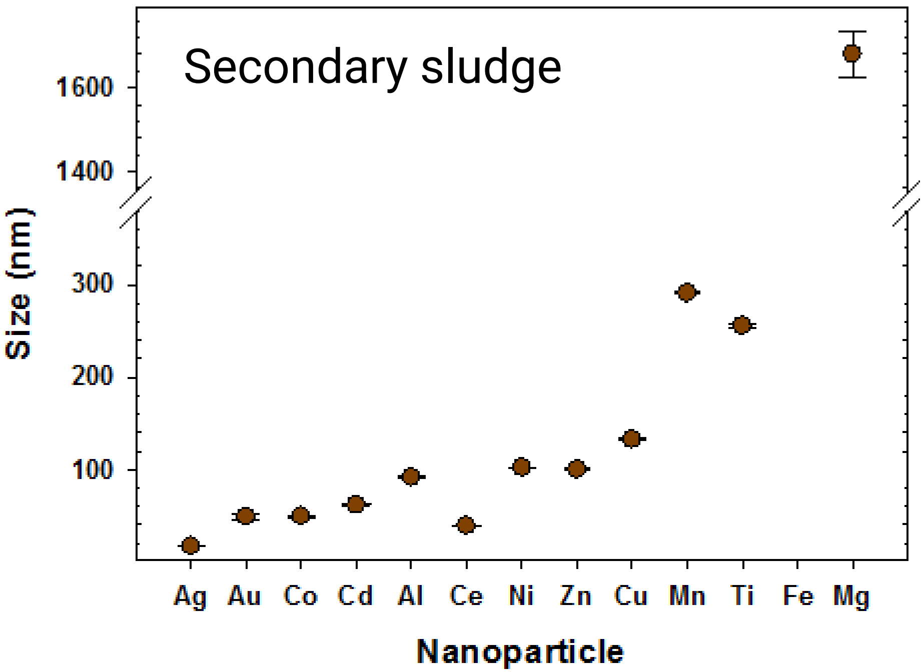


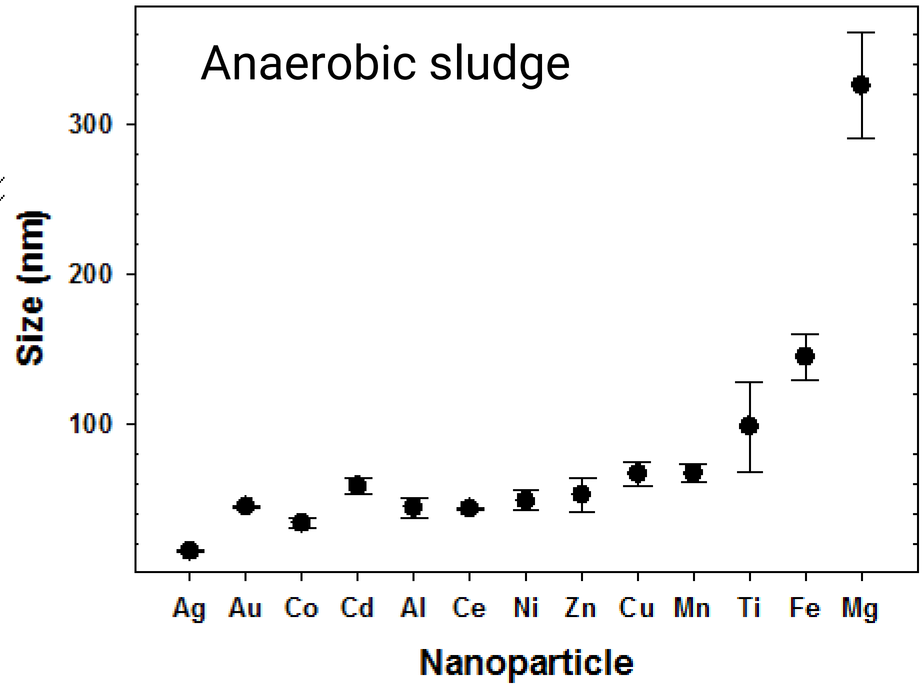


Multi-element sp-ICP-MS analysis

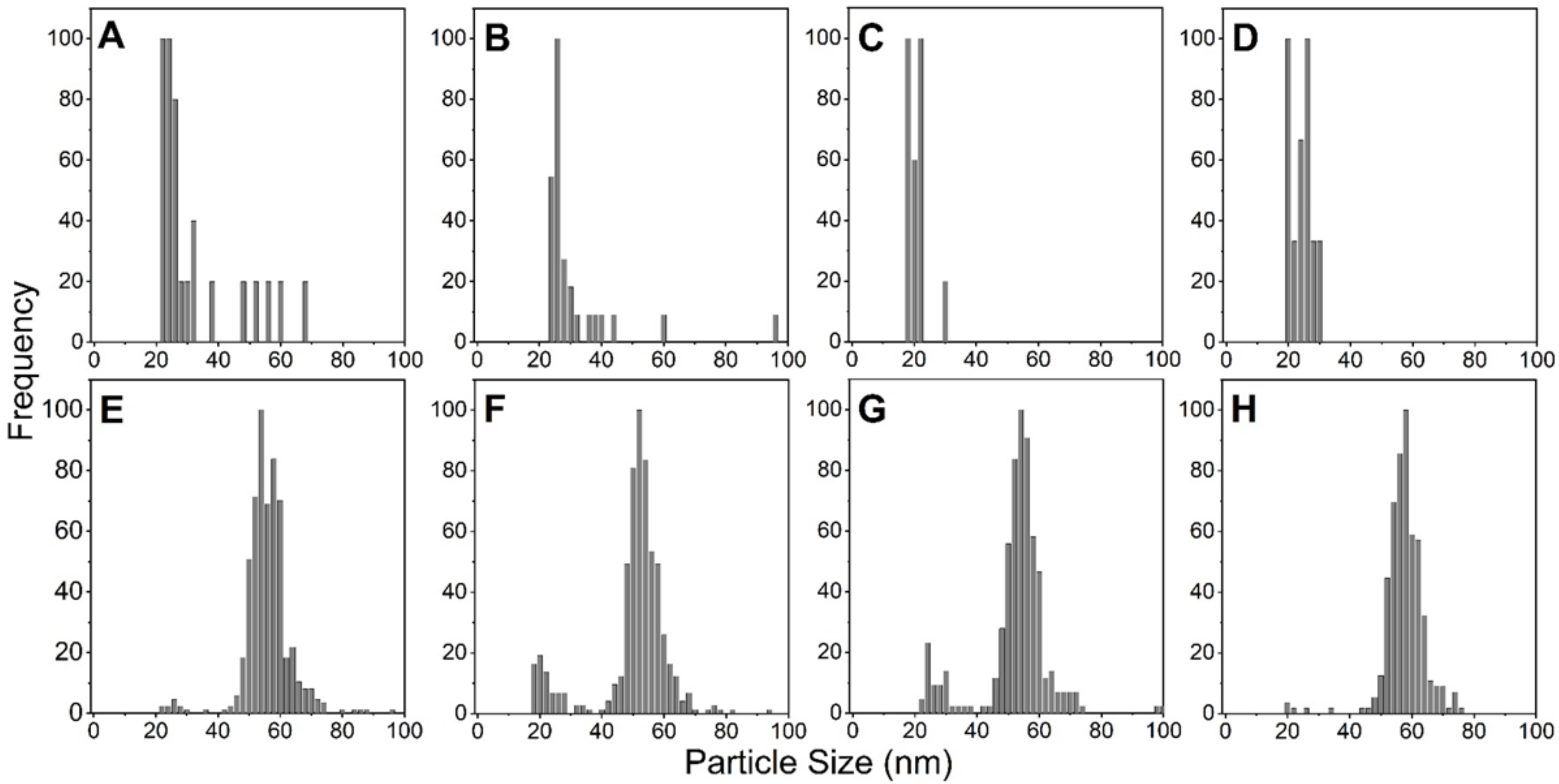


NP size in Sludge





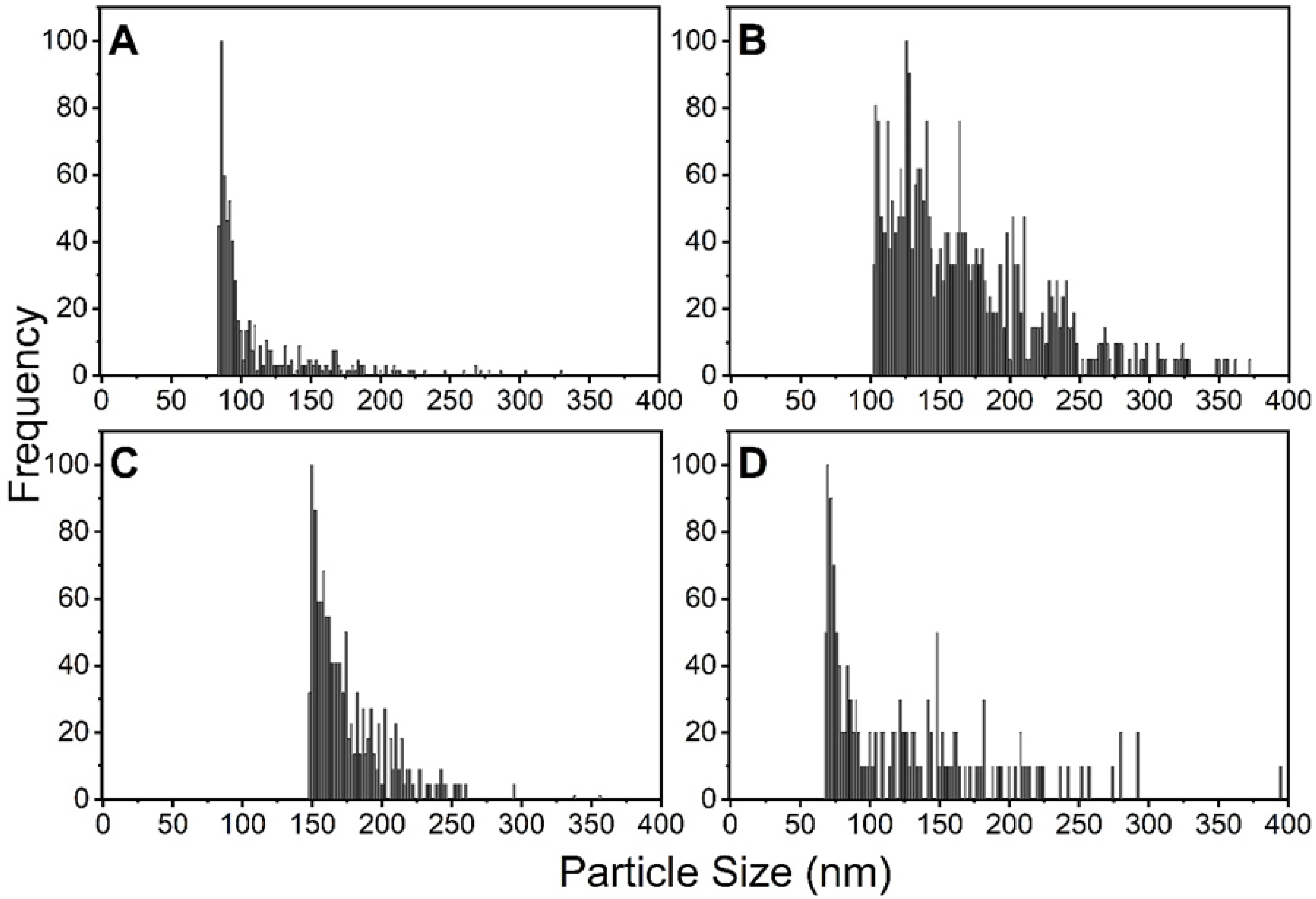
Size Distribution Ag NPs



Size distribution of detected Ag NPs in (A) Raw; (B) Effluent; (C) waste sludge; (D) anaerobic sludge

Pre-centrifugation spiked Ag NPs reference materials (60 nm) in (E) Raw; (F) Effluent; (G) waste sludge; (H) anaerobic sludge.

Size Distribution TiO_2 NPs



TiO_2 NPs in (A) Raw; (B) Effluent; (C) waste sludge and (D) anaerobic sludge samples

Conclusions

- spICP-MS offers the best approach for quantitative analysis of nanoparticles
- Provides concentration, size distribution, composition, dissolved ion concentration
- Can be applied to water and wastewater samples

- Most likely approach for commercial analysis
- Challenges remain with regards to samples that contain high levels of natural NPs

Acknowledgements

Yuxiong Huang, now Prof. at TBSI @ Shenzen

Pabel Cervantes, postdoc at UCSB

Jenny Nelson, Agilent Technologies

Craig Marvin, Agilent Technologies

Tarun Anumol, Agilent Technologies