Detection of Engineered Nanomaterials: Semi-Conductor Facilities and Consumer Devices

(*Task Number: 425.040*)

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Objectives

- **Goal:**
  - **To 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**
- **Objectives:**
  - **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**

ESH Metrics and Impact

1. Provides analytical methods and SOPs using commercially available instruments for EHS monitoring of NMs in air and water

1. Aid in ESH workplace exposure monitoring and assessment of remedial actions to reduce exposures, and in monitoring NMs after they leave fabrication facilities

1. Aids in documenting nanomaterial fate over their life cycle

1. Organized research and industry consortium which procured well-defined CMP solutions for characterization, toxicity and fate testing

Selected Nanomaterials

- As identified in the International Technology Roadmap for Semiconductors (ITRS):
  - CMP: silica, alumina, cerium oxide
  - Carbon nanotubes (MWCNT) in self-assembly or advanced packaging processes (alone and embedded in polymer matrices)
  - Explored detection of nanographene plateletes because of their electronic properties

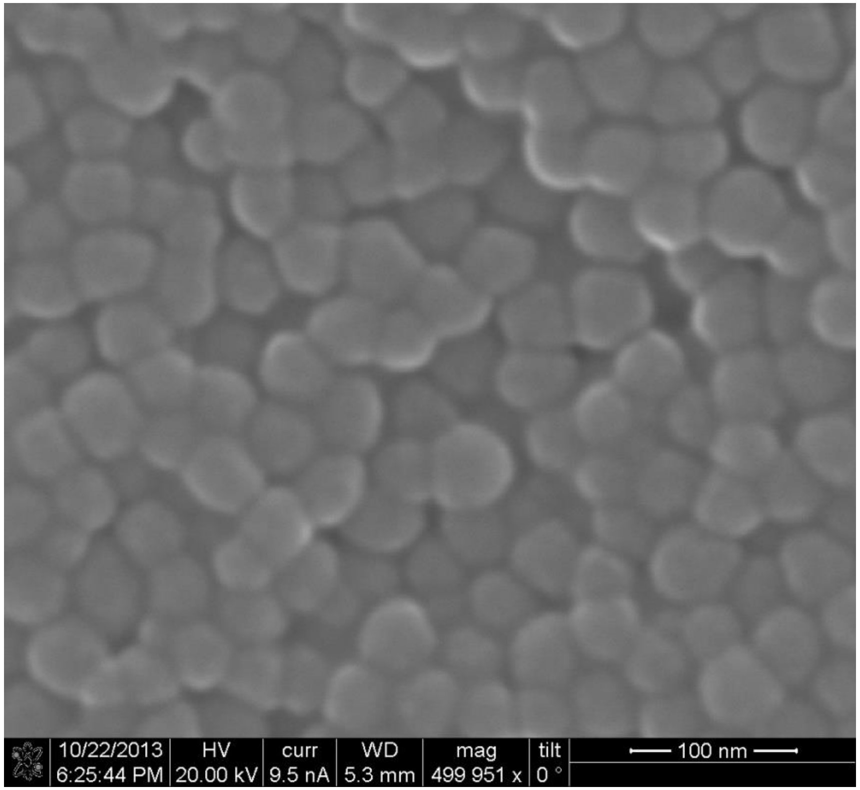
Outline: Detection & Size Characterization of NPs

I. Metallic NPs in consortium CMP slurries
II. Advances on size determination of metallic NPs
III. NP separation from water using cloud point extraction (CPE)
IV. Advances on detection of carbonaceous NPs

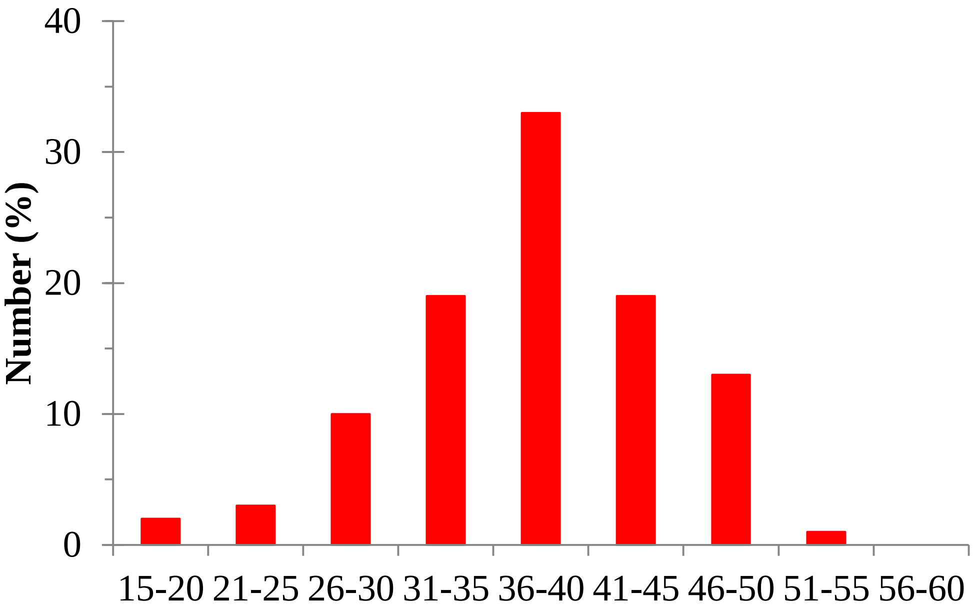
Consortium CMP NPs

Select contributions from our task

#1 Colloidal Silica Nanoparticles



SEM

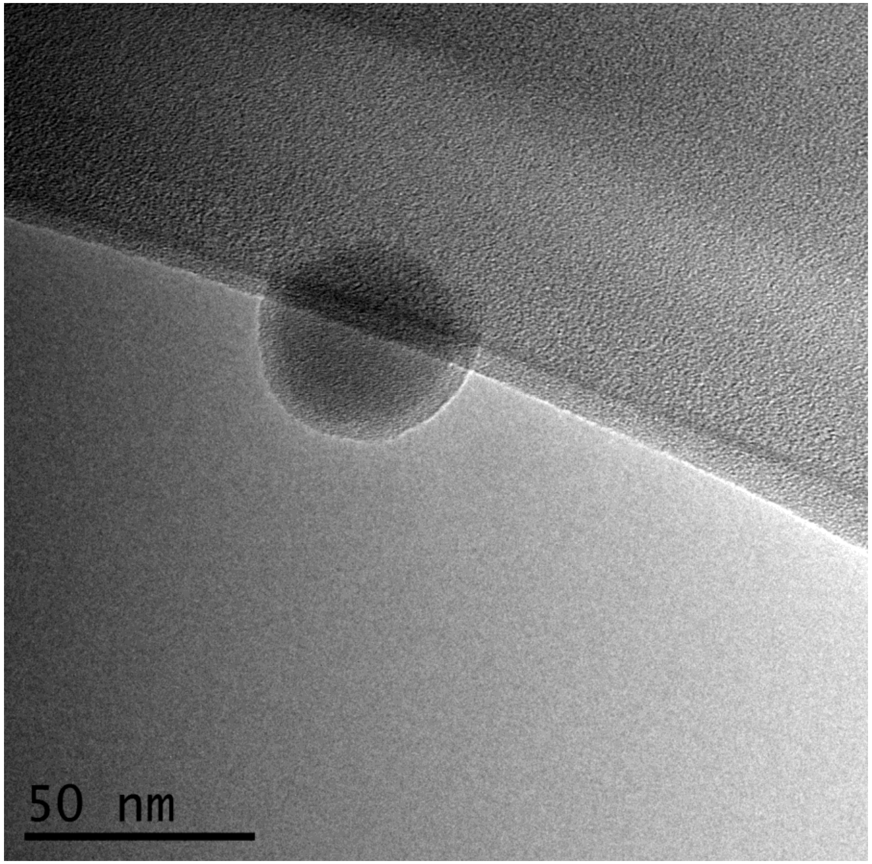


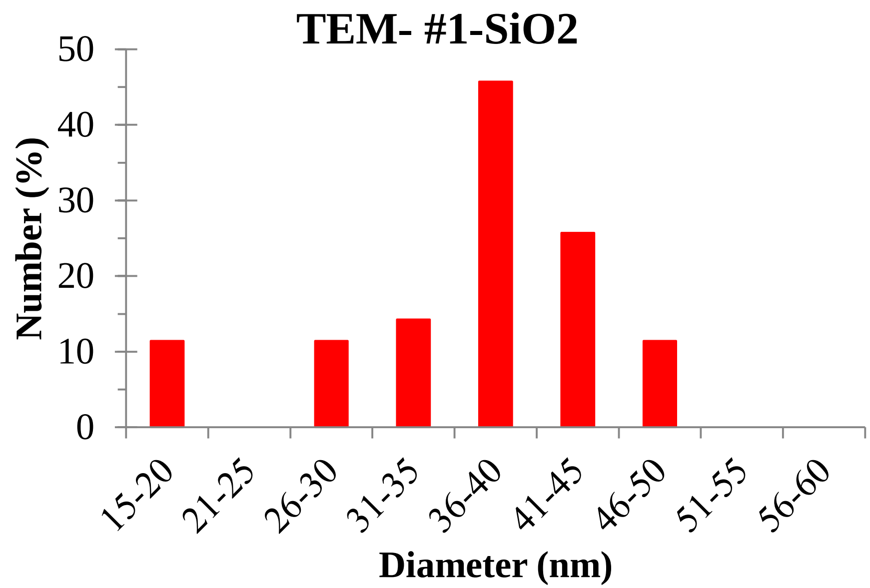
Measuring diameters of 100 particles

Averaged size: 37 ± 7 nm
Min-Max: 15 – 52 nm

	Original Request	Recommended by Cabot Microelectronics
1) Acidic colloidal silica model slurry:		
	3 wt % precipitated silica, ~70 nm particle size	3 wt % precipitated silica, 50 - 60 nm particle size

#1 Colloidal Silica -TEM





Unit (nm)	TEM	SEM
Mean Diameter	36	37
One STD	9	7
Minimum Diameter	13	15
Maximum Diameter	49	52

Original suspension was diluted 500 folds in order to get separated particles .
(TEM analysis: total 42 particle from 13 images).

	Original Request	Recommended by Cabot Microelectronics
1) Acidic colloidal silica model slurry:		
	3 wt % precipitated silica, ~70 nm particle size	3 wt % precipitated silica, 50 - 60 nm particle size

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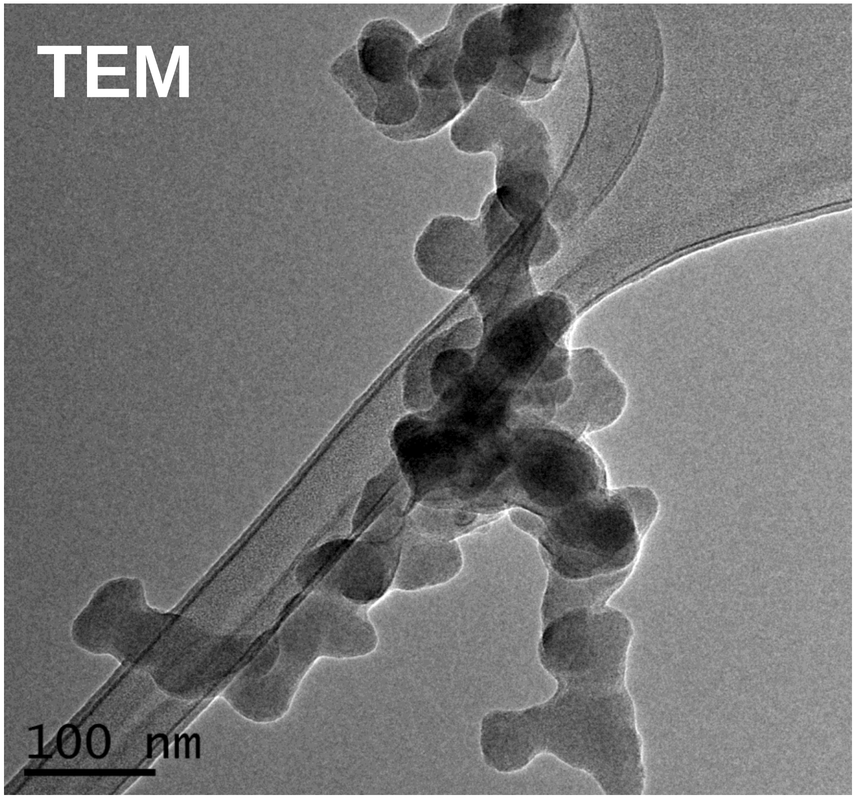
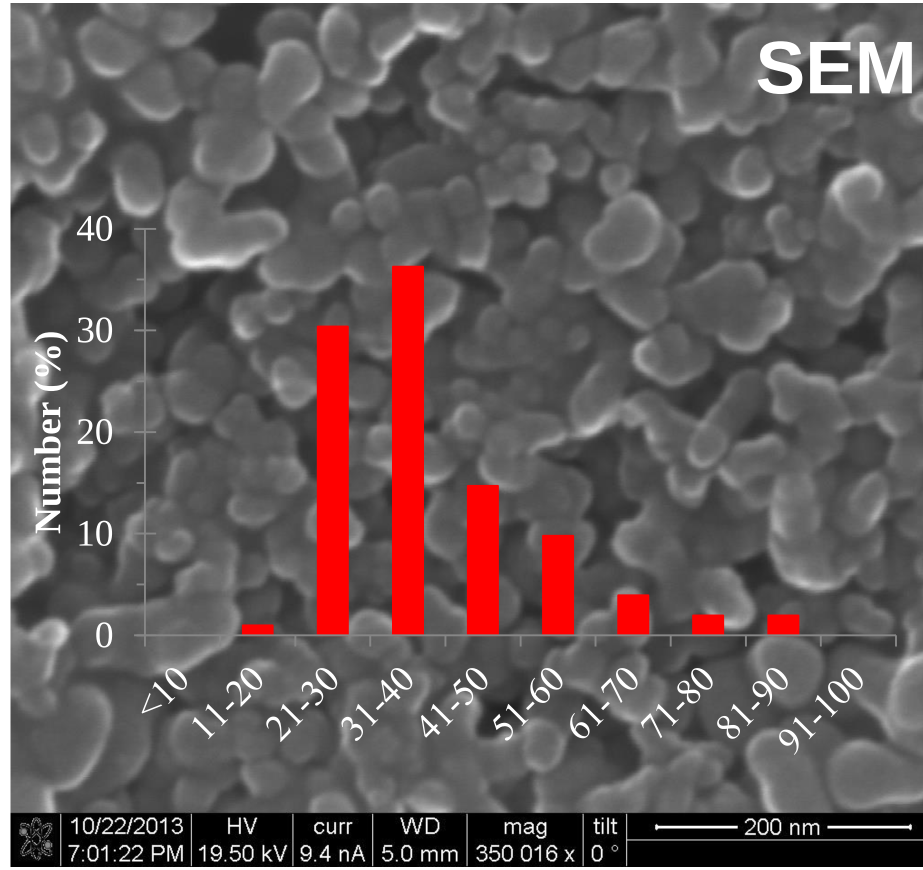
#2 Fumed Silica

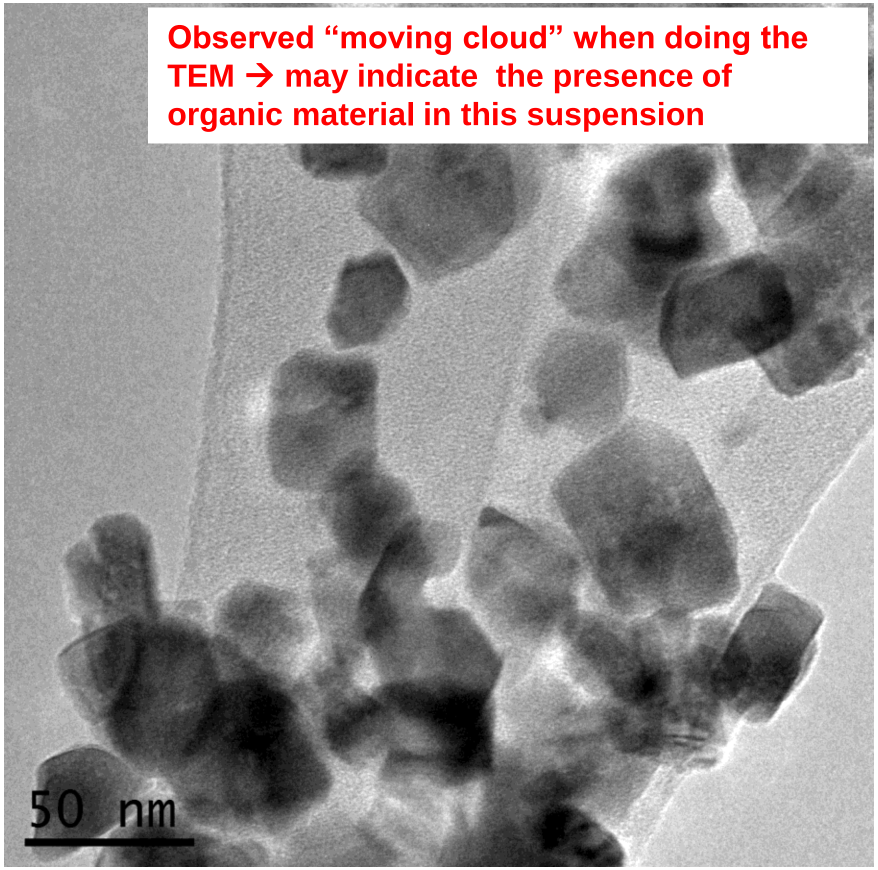


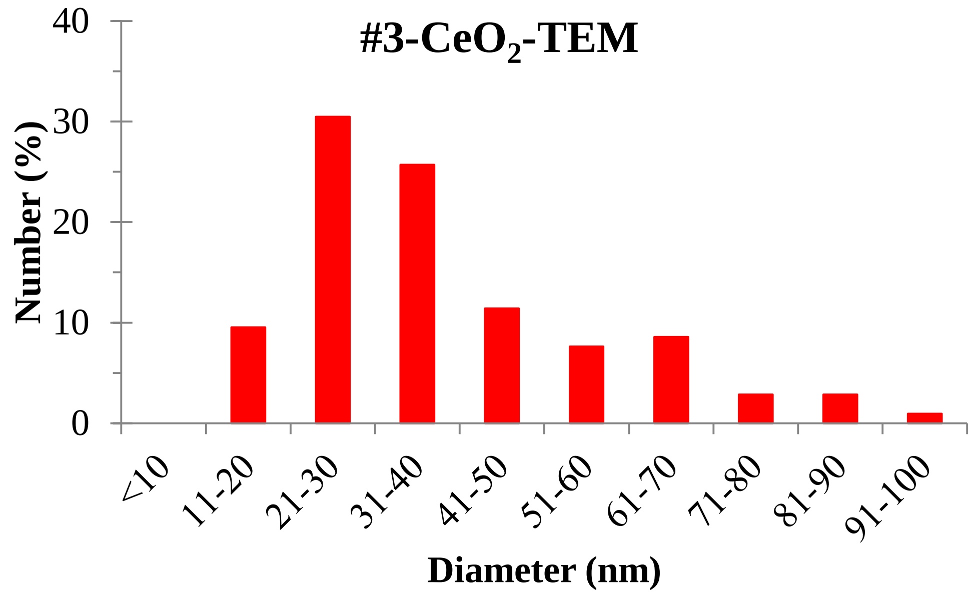


Measuring diameters of 102 particles
Averaged size: 38 ± 14 nm
Min-Max: 20 – 90 nm

2) Basic fumed colloidal silica model slurry:	
5 wt % fumed silica, 100nm stable aggregate	5 wt % fumed silica, , 120-140 nm average

#3 Ceria Nanoparticles





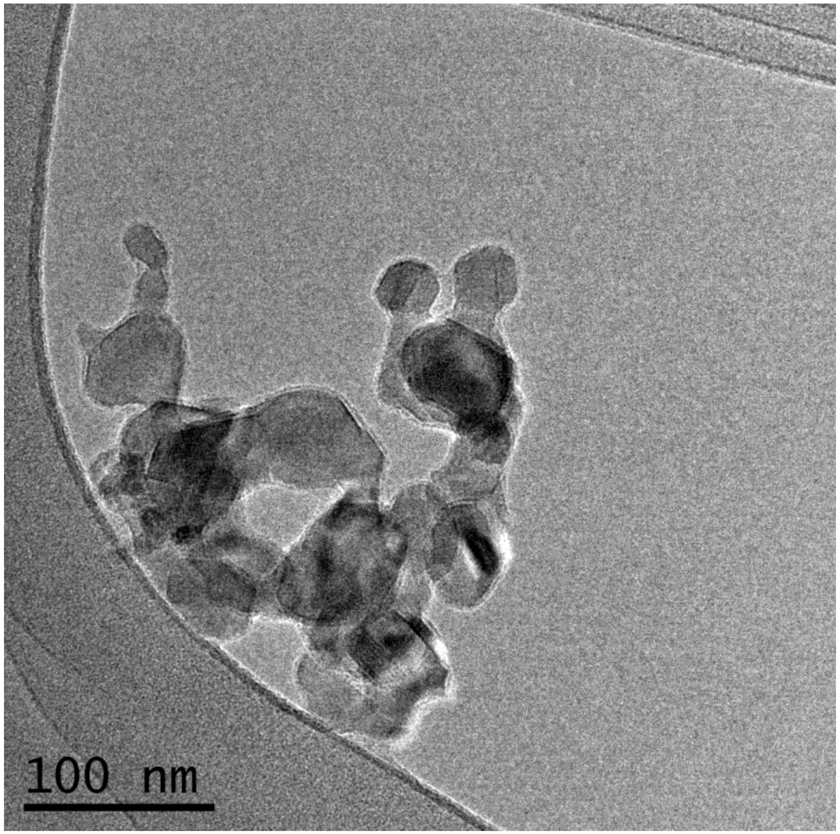
Unit (nm)	TEM	SEM
Mean Diameter	39	43
One STD	19	16
Minimum Diameter	11	15
Maximum Diameter	94	97

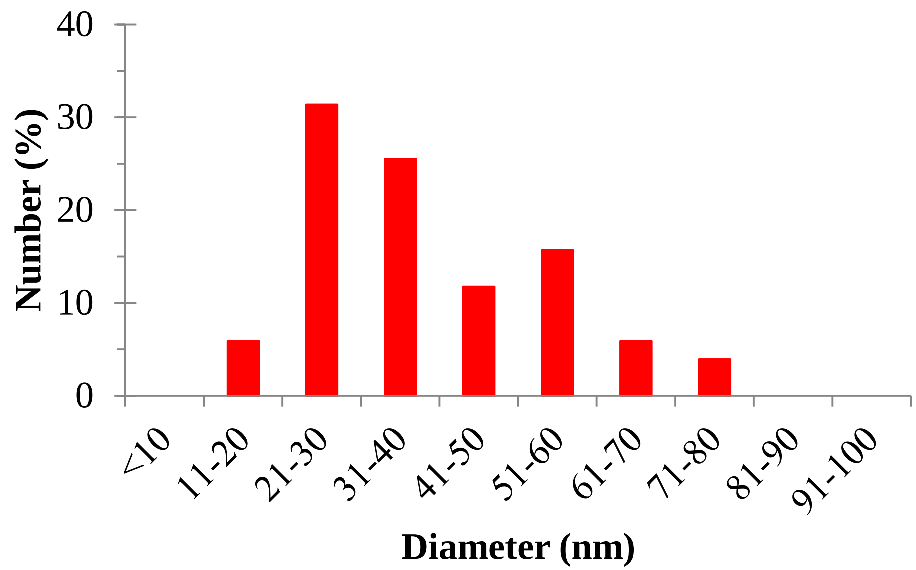
Measuring diameters of 105 particles

One Way ANOVA compare mean diameter → P = 0.10 (no significant difference between SEM and TEM results

3) Ceria model slurry:		
	1 wt % ceria, ~ 100 nm particle size	1 wt % ceria particle, 60 - 100 nm

#4 Aluminum Oxide Nanoparticles

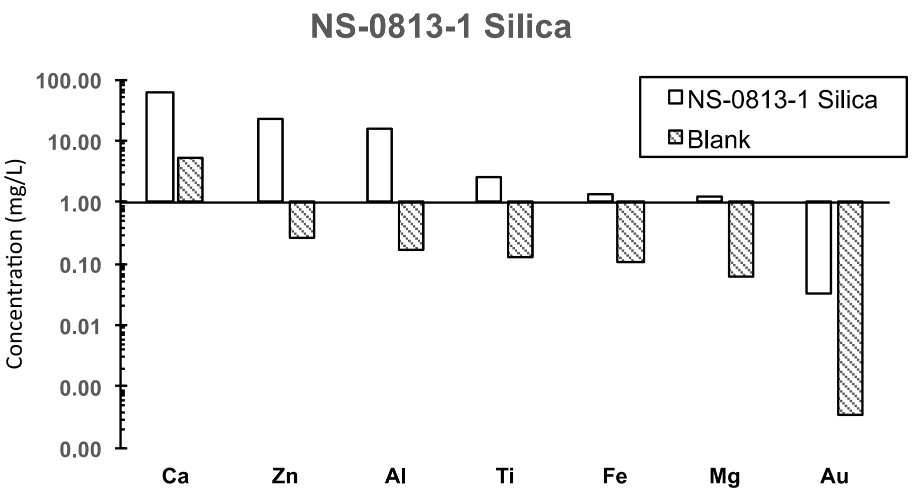


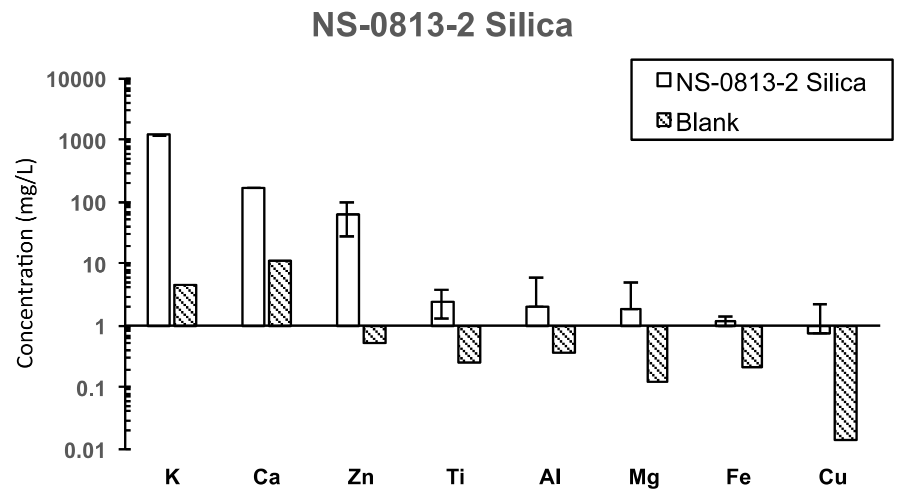


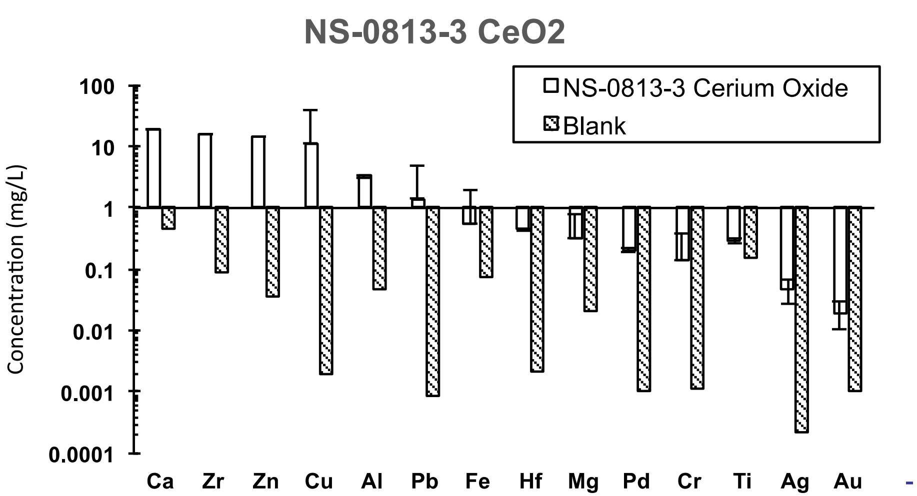
Unit (nm)	TEM	SEM
Mean Diameter	38	85
One STD	16	21
Minimum Diameter	16	36
Maximum Diameter	77	150

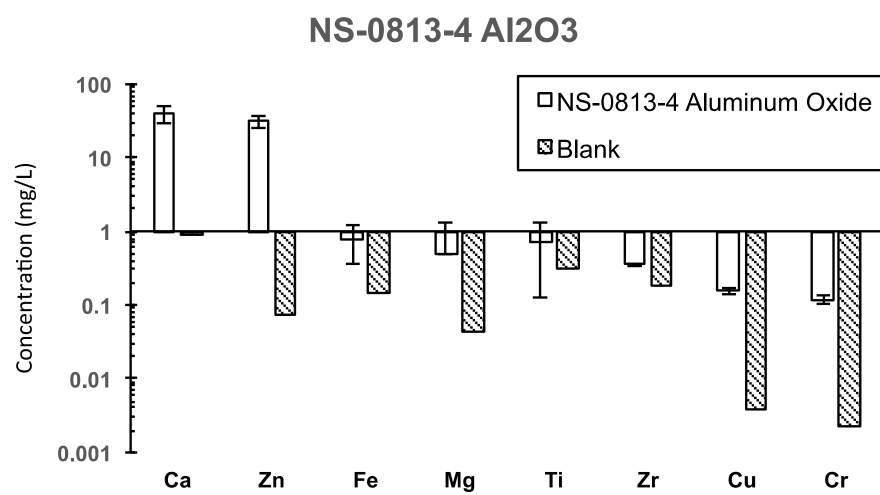
4) Aluminum Oxide Model Slurry (Additional slurry model suggested by CMC.)		
		1 - 5 wt % aluminum oxide, 80-100 nm

Other elements contained in CMP slurry





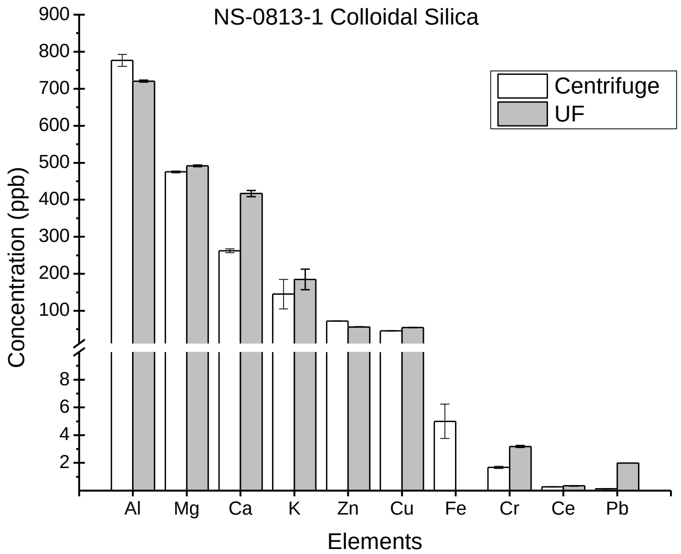


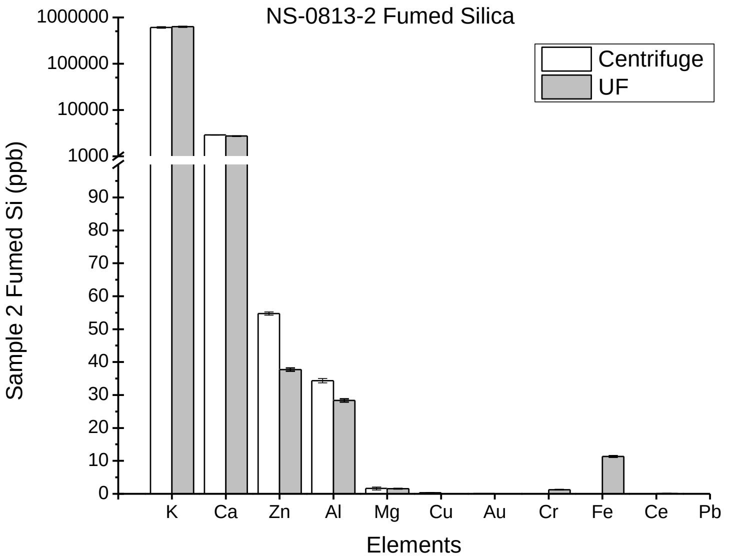


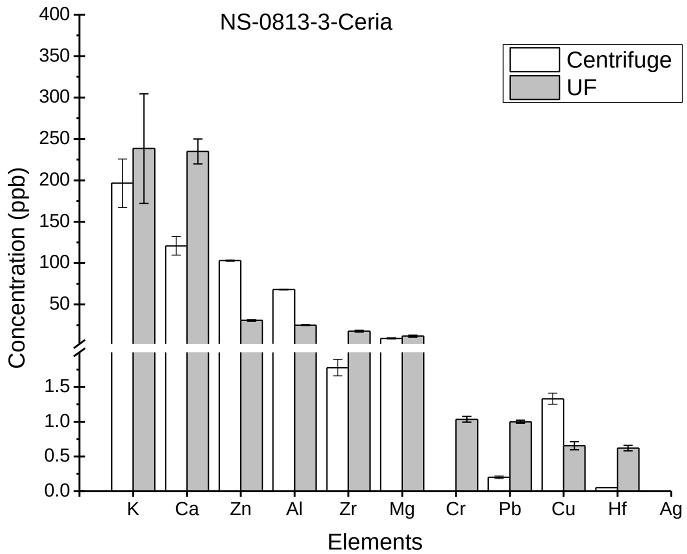
What is in the CMP Slurry other than NPs?

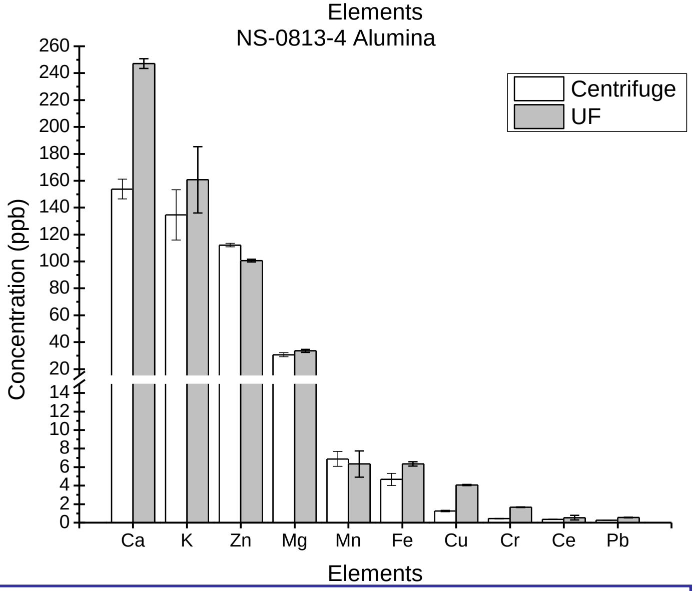
- Removed NPs by:
  - High speed centrifugation (UT-Dallas)
  - Centrifugal Ultrafiltration at lower speed

Concentrations of dissolved elements in CMP slurries. "Centrifuge" corresponds to samples from UTD. "UF" corresponds to samples treated with centrifugal ultrafiltration (30K Da).







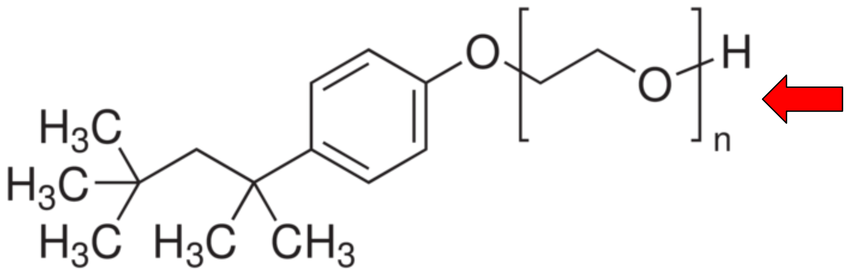


Advances in Size Separation of NPs in water

- Centrifugal ultrafiltration (previous slides)
- Cloud point extraction
- Single particle ICP-MS
  - SOP available on web to SRC members
  - 20+ lab world-wide intra-lab validation study
  - Improvement in signal processing of sp-ICP-MS data (K-means versus 3σ paper submitted for publication)
  - Minimum size detection limit for different elements by sp-ICP-MS
  - Fast-scan sp-ICP-MS
  - User interface development with Perkin-Elmer

Cloud Point Extraction (CPE)

- A surfactant – Trition 114 can be used for CPE *(Liu., et al., Chemical Communication, 2009).*

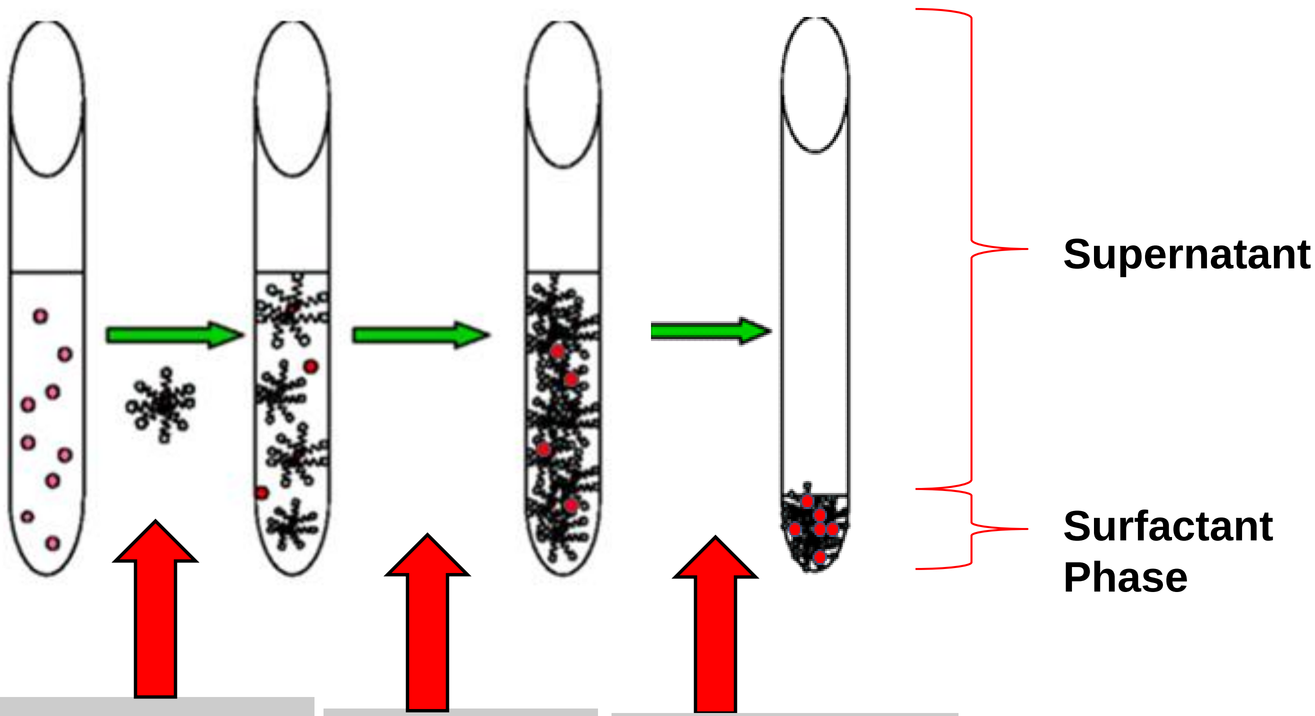


Surfactant : Triton 114

- When the temperature increases above the temperature - cloud point (CPT), the micelles become dehydrated and aggregates, forming cloudy phase.
- Cooling down and centrifuge→ phase separation
- Nanoparticles move from water phase to surfactant phase

Chao et al., Analytical Chemistry, 2011

Cloud-point Extraction Process



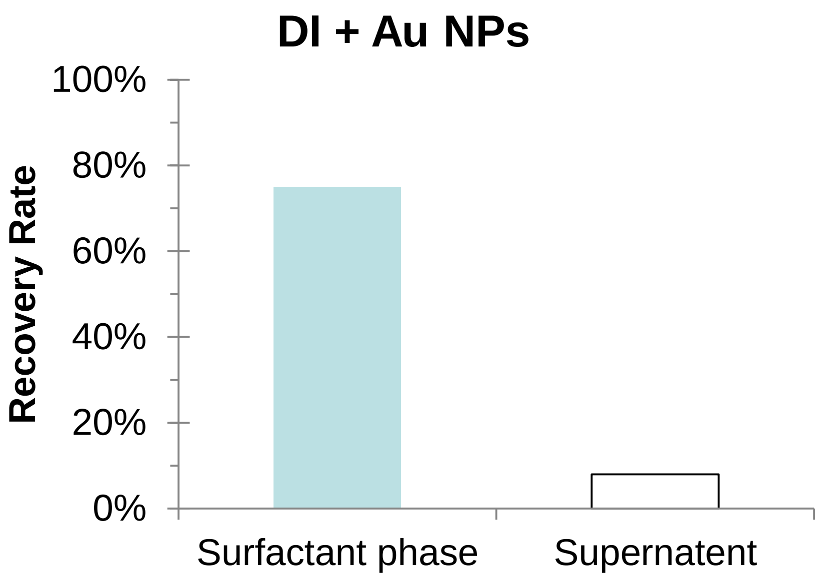
Step 1.
Adding surfactant (Triton 114) to get a final concentration of 5% (W/V)

Step2.
Water bath at 40 °C for 30 minutes

Step 3.
Cooling down, and centrifuge

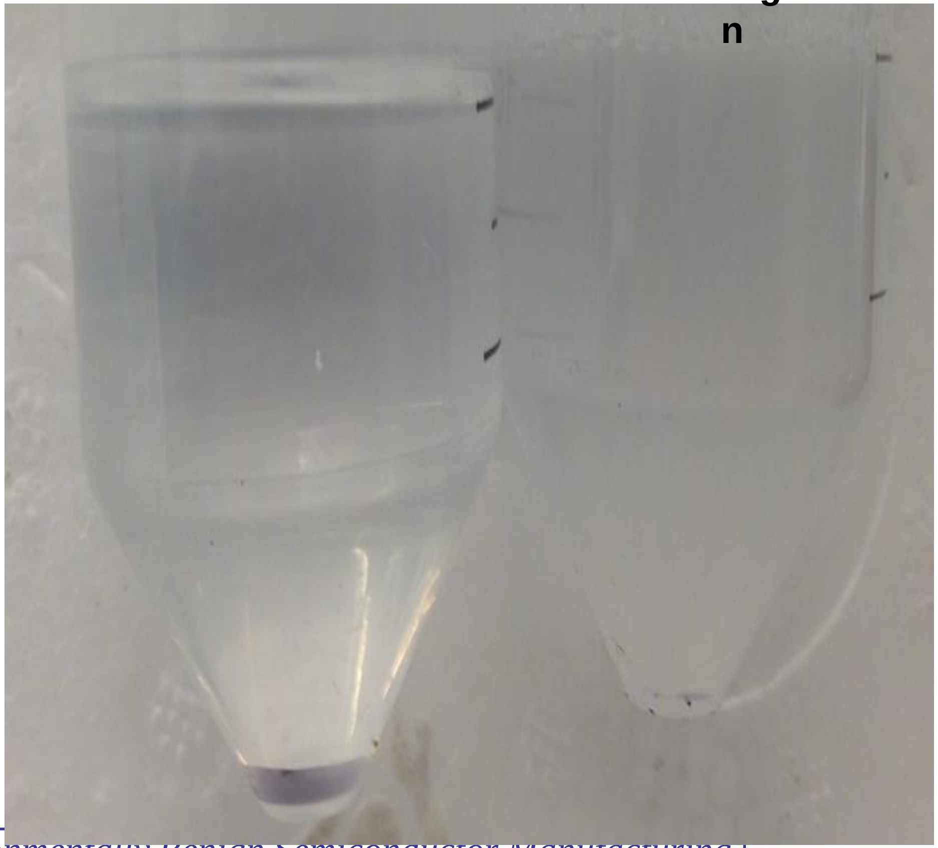
(Ojeda.,et.al., Microchimica Acta, 2012)

Example of CPE: Recovery Rate of Au Nanoparticles from Nanopure water

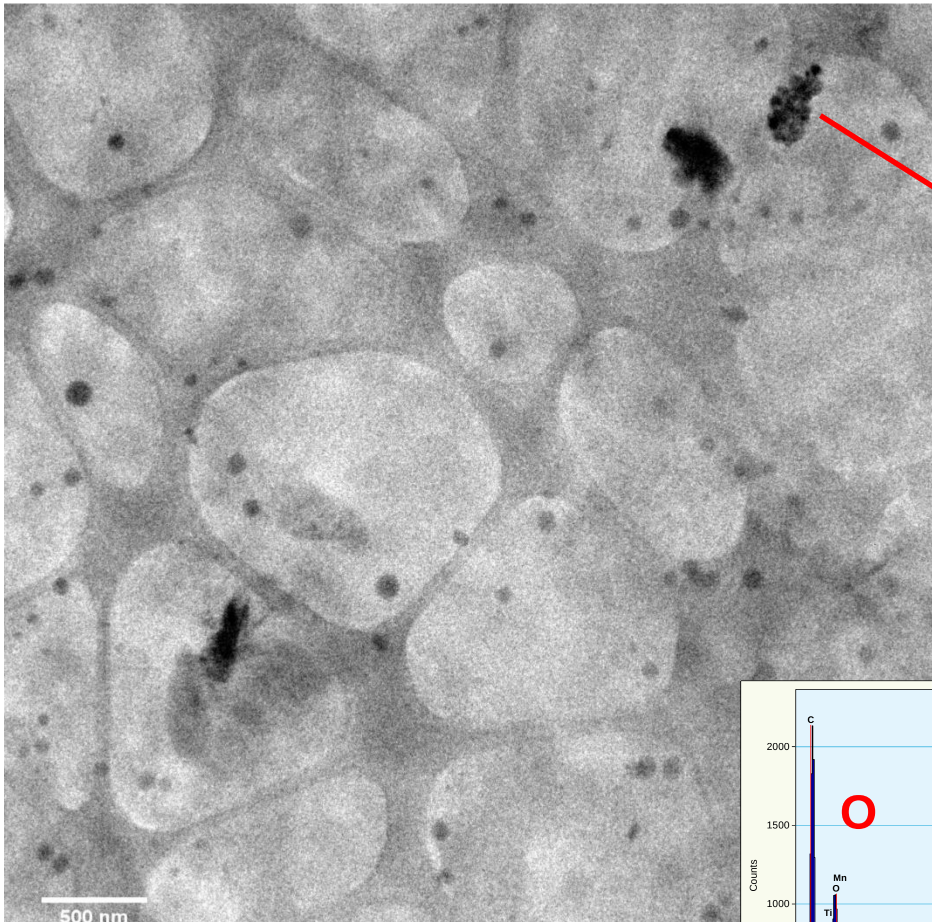


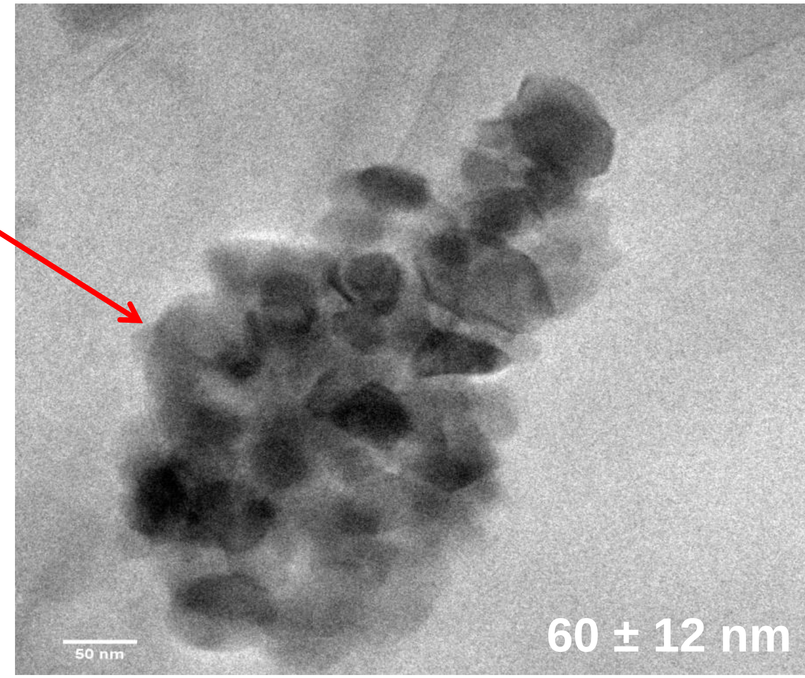
After Centrifugation

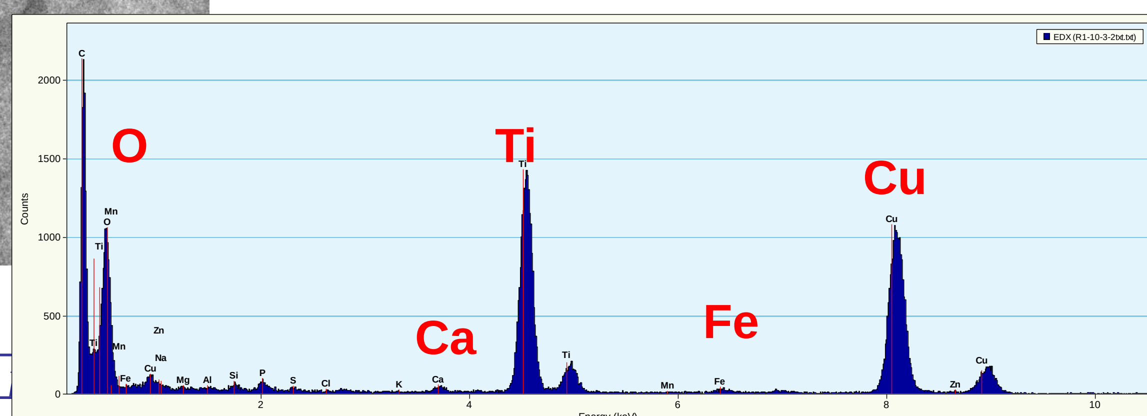
Before Centrifugatio n



Salt River Sample

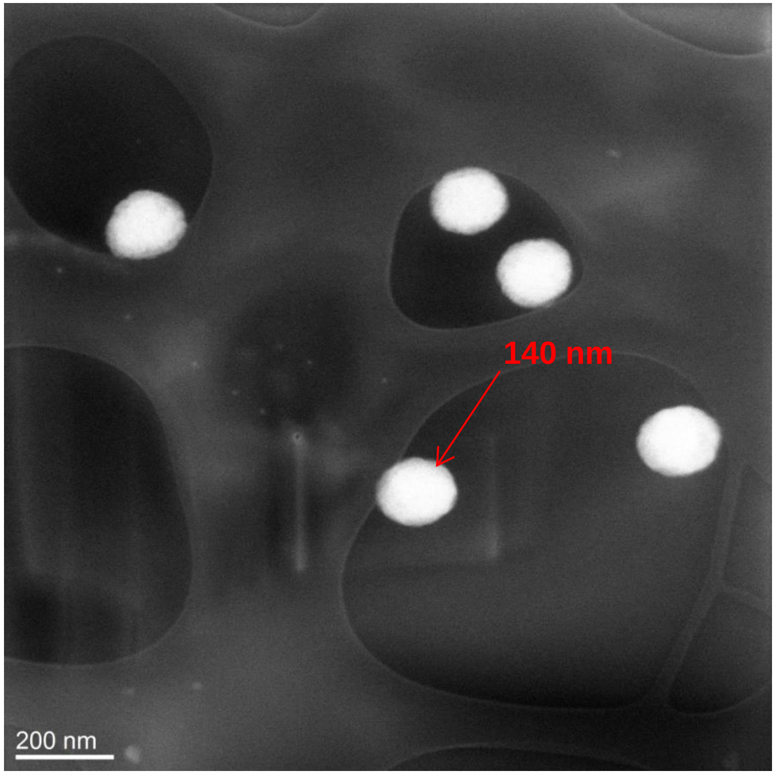


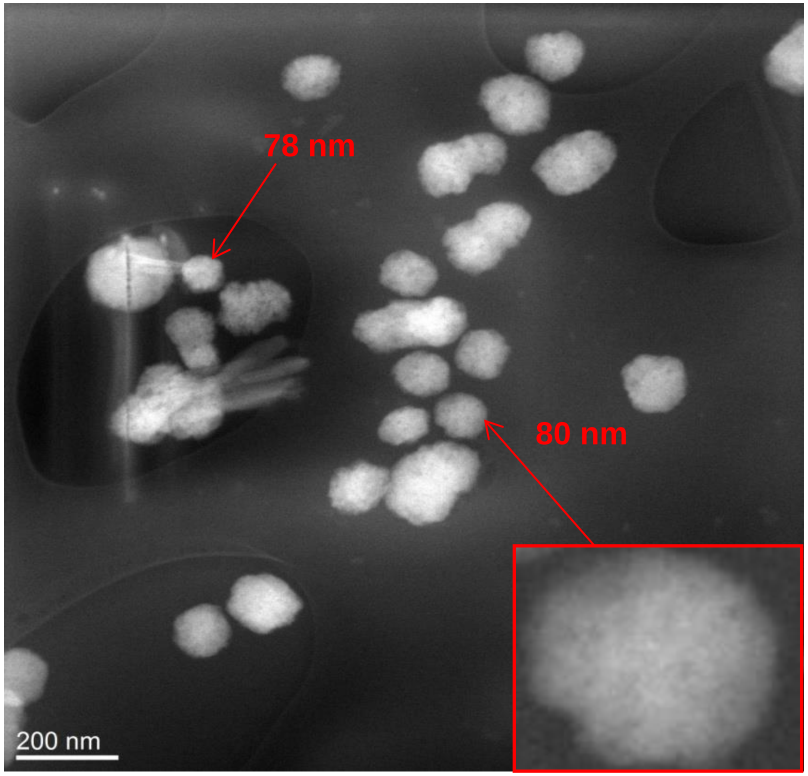




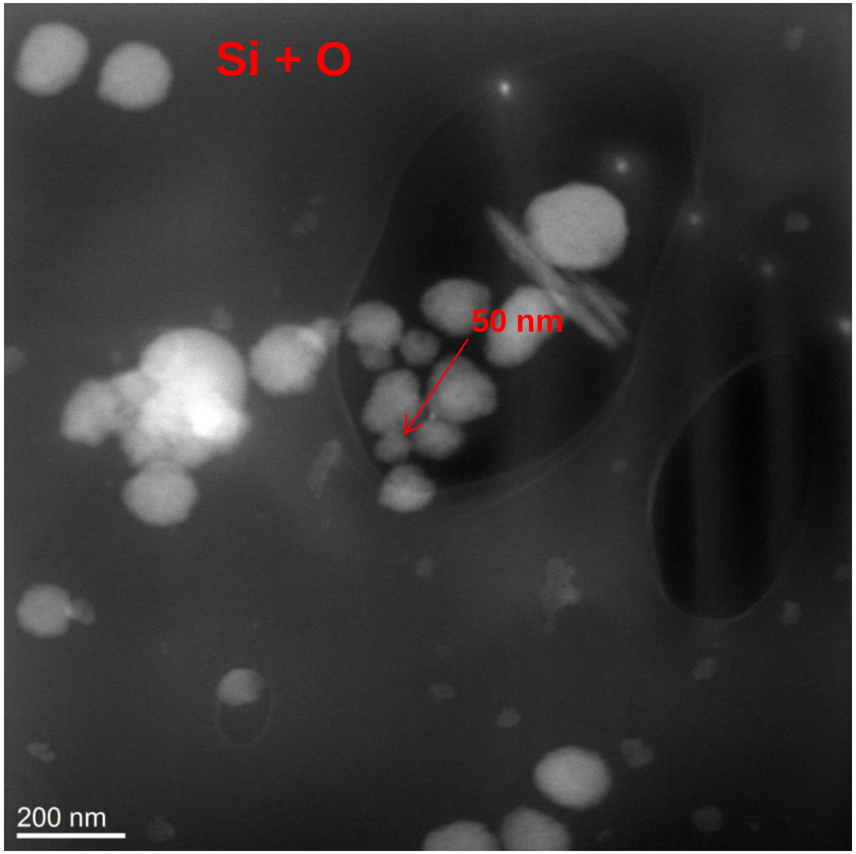
SRC Engineering Research Center

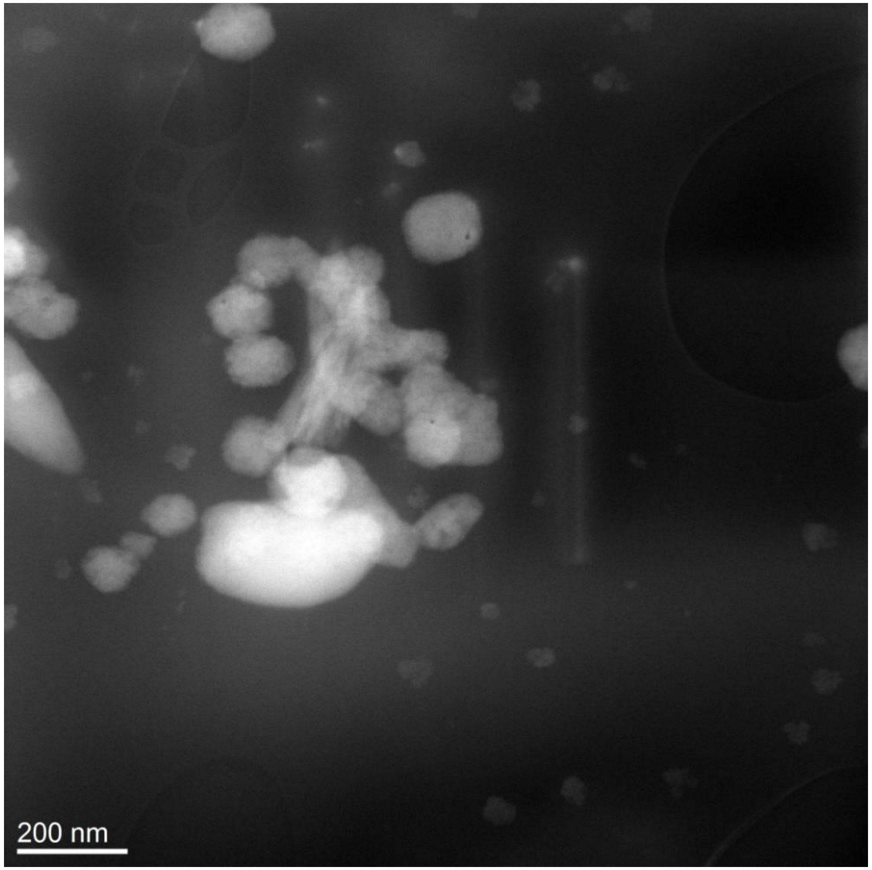
Nanoparticles from Arizona Wastewater Treatment Plants (Spherical SiO_2 NPs – polishing agents?)





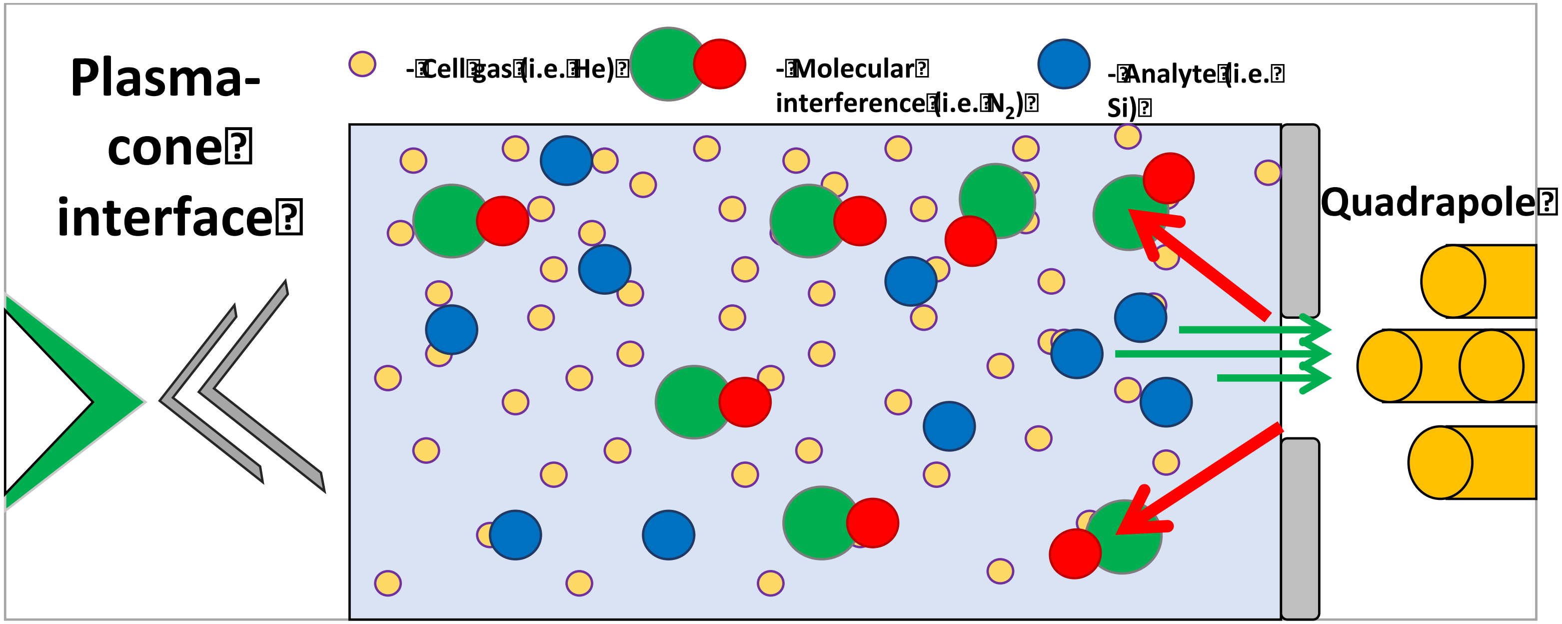
More Nano- and Micron- Silica particles in Wastewater





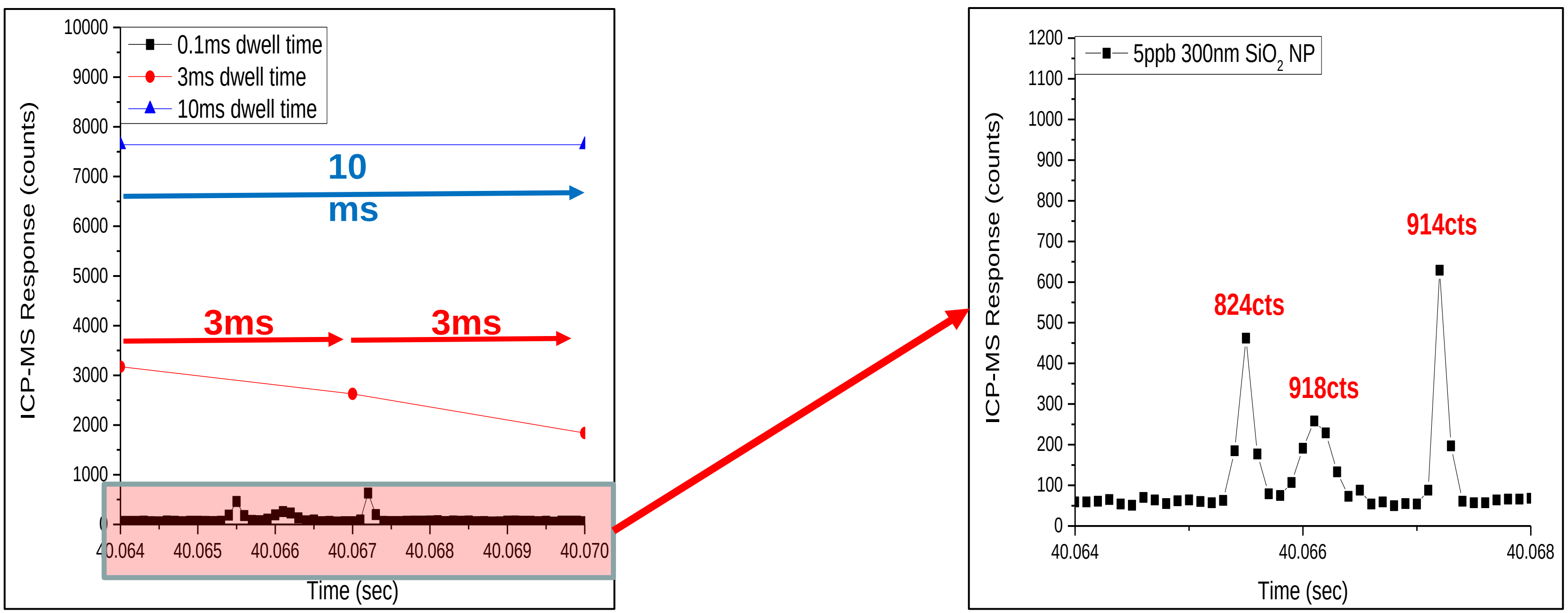
Silica nanoparticle detection

- **Development of microsecond spICP-MS is a new method of eliminating molecular interferences to improve detection limit**
- **Analysis of silica by ICP-MS is impeded by the abundant dinitrogen (N_2) interference (e.g. $^{28}Si = 2 * {}^{14}N$)**
- **Conventional ICP-MS uses a pressurized cell (i.e. helium, ammonia) to reduce or eliminate interference**



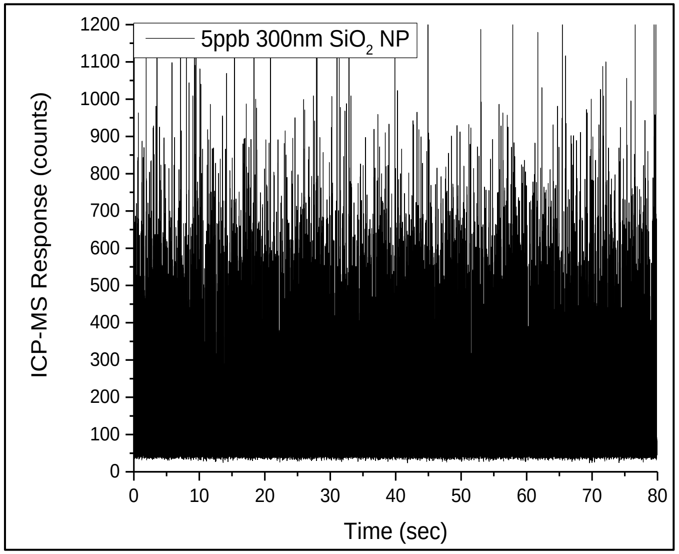
Microsecond spICP-MS (Fast-scan)

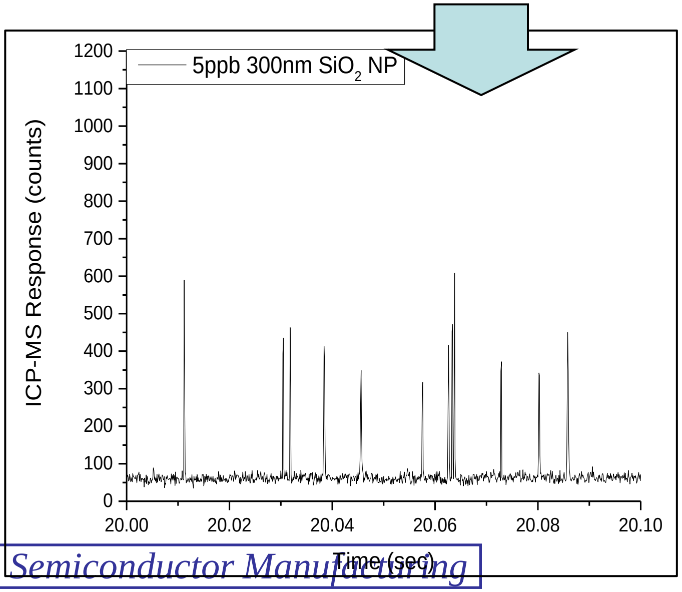
- **By reducing dwell time to microsecond time scales (i.e. 100 µs), greater resolution can be achieved while simultaneously reducing molecular interference**
- **As dwell time is faster than nanoparticle pulse generation, a distribution of pulse intensity is generated, and when summed is equal to the total count intensity of the particle**



Advantages of microsecond spICP-MS

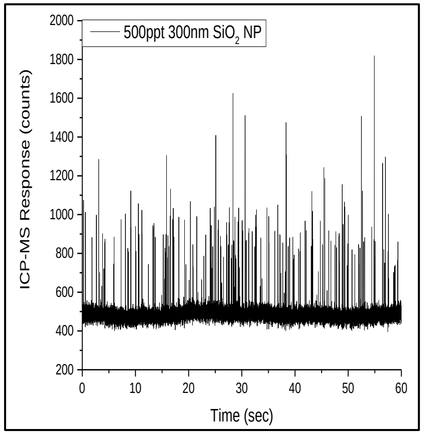
- **Potential interferences (i.e. dissolved background analyte, molecular interferences) are greatly reduced or eliminated**
- **Microsecond dwell times allow for greater resolution between particles and therefore reduce "coincidence"**
- **Higher particle number concentrations can be analyzed increasing working range of spICP-MS (low ng/L – mid µg/L)**

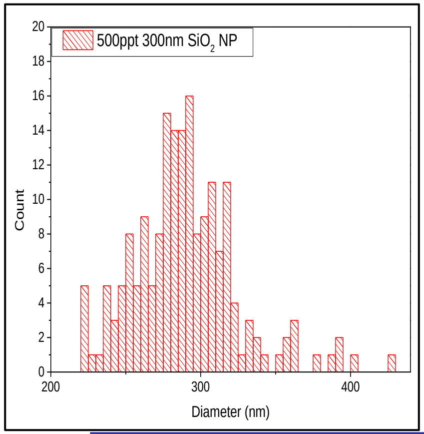




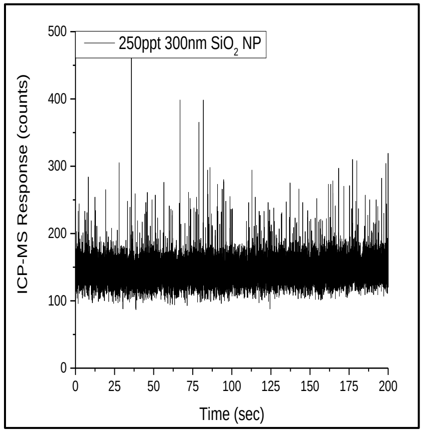
spICP-MS Comparison

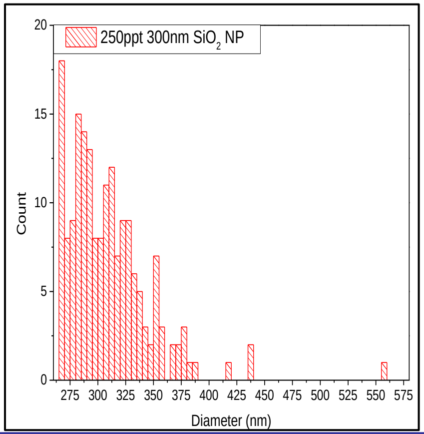
- Nexion 300D (0.15ml/min NH_3)
- 500ppt 300nm SiO_2 NP



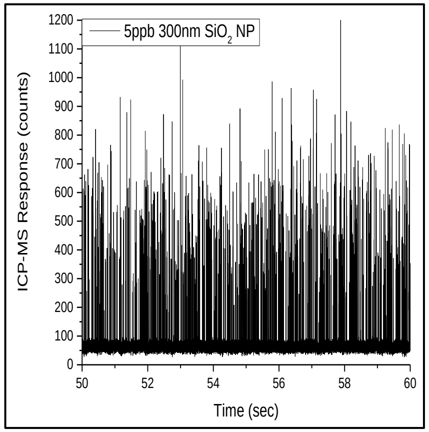


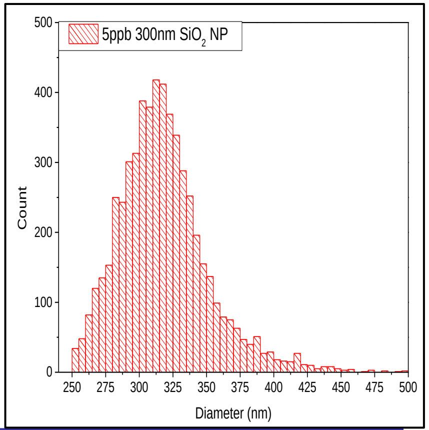
- Agilent 7700x (3.5ml/min He)
- 250ppt 300nm SiO_2 NP





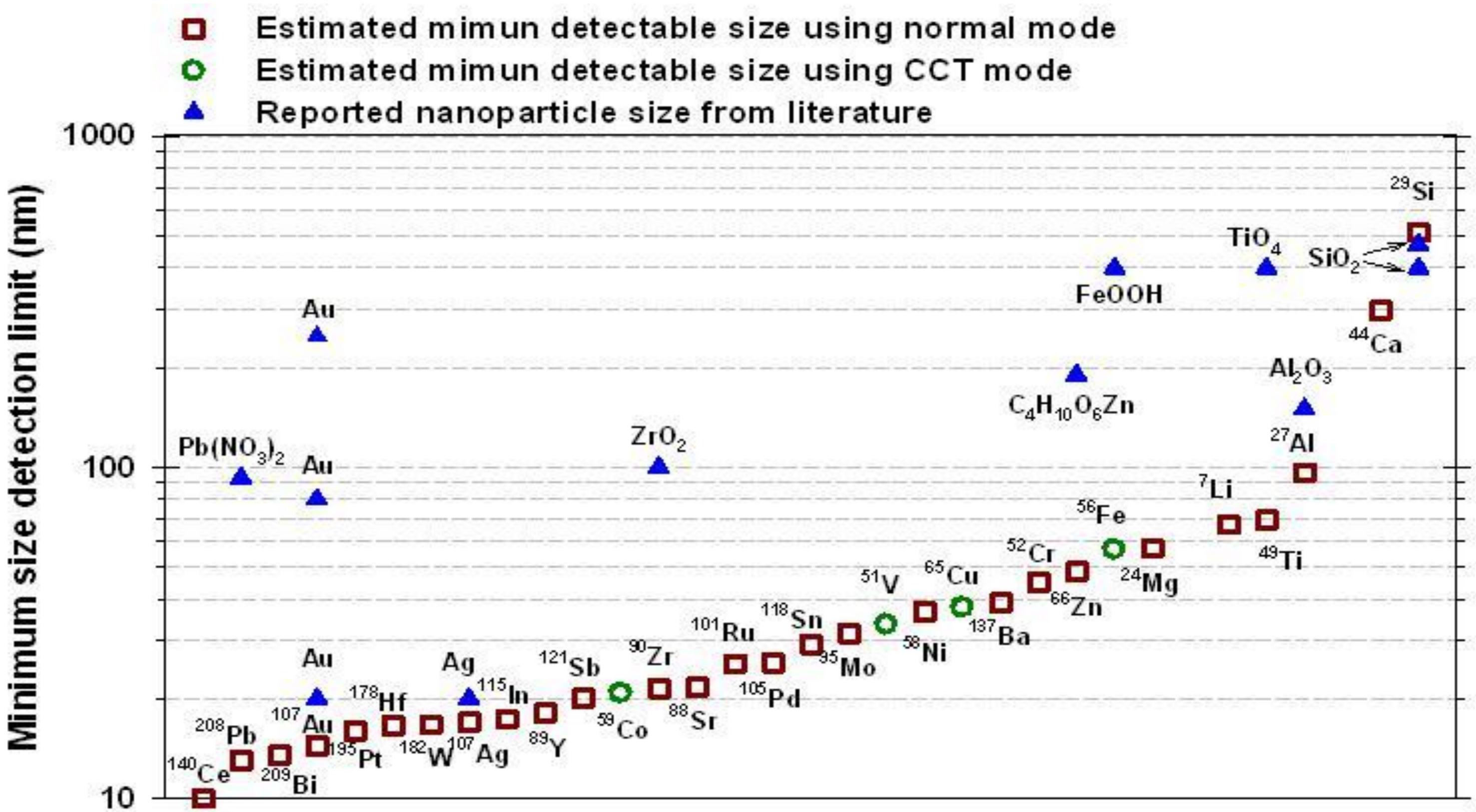
- Nexion 300Q (no cell gas)
- 5ppb 300nm SiO_2 NP





Montaño, M.; Ranville, J.; Majestic, B. *Unpublished Data*, 2013-2014

Calculation of minimum size by sp-ICP-MS for different elements

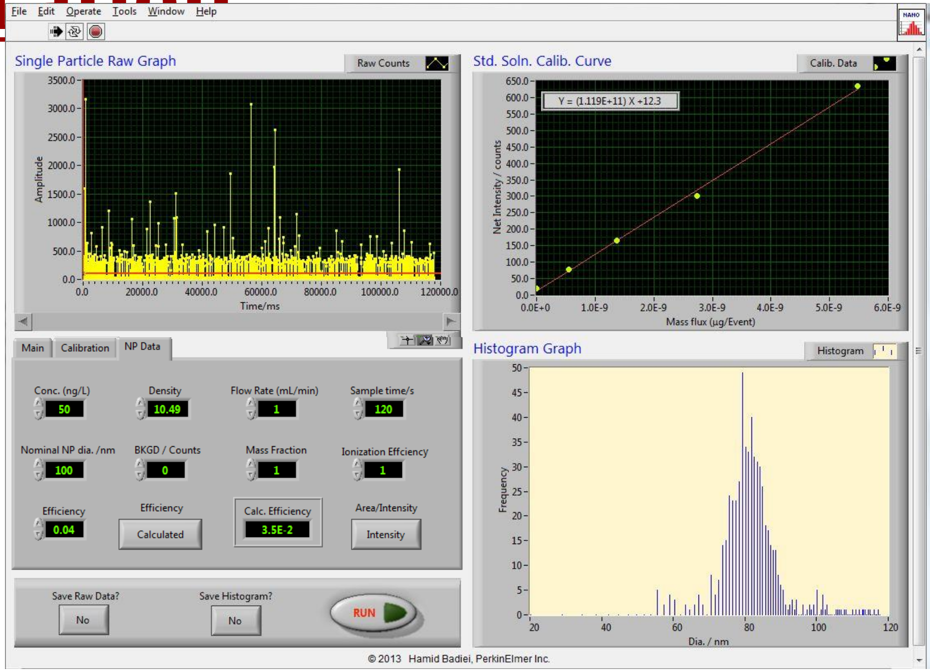


Key factors: background signal at target m/z, isotopic compositions, nebulization efficiency

ICP-MS Industry Collaboration

- Collaborations with University of Denver and Perkin Elmer have allowed ability to use different ICP-MS technologies

- Collaboration with PostNova Analytics is underway to determine potential differences in particle vs. bulk density



Carbonaceous NP Detection

- SWCNT & MWCNT detection
  - PTA method developed & published
  - SOP on-line for SRC members
  - Collaborated with 2 inhalation toxicity groups to study CNT exposures using above methods + new tissue digestion method
  - Embedded MWCNT in thermal-polymers, evaluating release rates (on-going)
  - Evaluated CNT in air using personallized air samplers
- Nano graphene (and GO) platelettes detection
  - Graphene analysis by PTA works
  - Graphene oxide “reduction” + PTW works
  - SOPs & paper being developed

Air Sampling

- Goal: To quantify the presence of CNTs in the presence of background air particulates
- Quartz fiber filters were loading into the personal air exposure monitor (Leland Legacy ® Pump (SKC Inc.)).
- Two air samples were obtained representing
  - an indoor facility (e.g., manufacturing lab)
  - Outdoors in Arizona .
- Air monitor run for 24 hours 10 L/min.
- Each sample location was collected in duplicate.
- Filters then spiked with CNT
- Samples analyzed for organic carbon and CNT by PTA

Recovery of CNTs on air filter samples

(Conclusion: Excellent CNT recoveries indicates viability to monitor CNTs in workplace air)

“Strong” MWCNT

Indoor air

Spiked CNT / ug	TOT data / ug
1	1.00±0.15
5	4.35±0.32
10	9.59±0.58

Outdoor air

Spiked CNT / ug	TOT data / ug
1	0.80±0.17
5	4.48±0.36
10	10.06±0.63

“Weak” MWCNT

Indoor air

Spiked CNT / ug	TOT data / ug
1	0.73±0.14
5	4.82±0.34
10	10.29±0.62

Outdoor air

Spiked CNT / ug	TOT data / ug
1	1.71±0.22
5	4.71±0.37
10	9.70±0.62

Application of Analytical Methods

- Treatability of NPs in CMP fluids

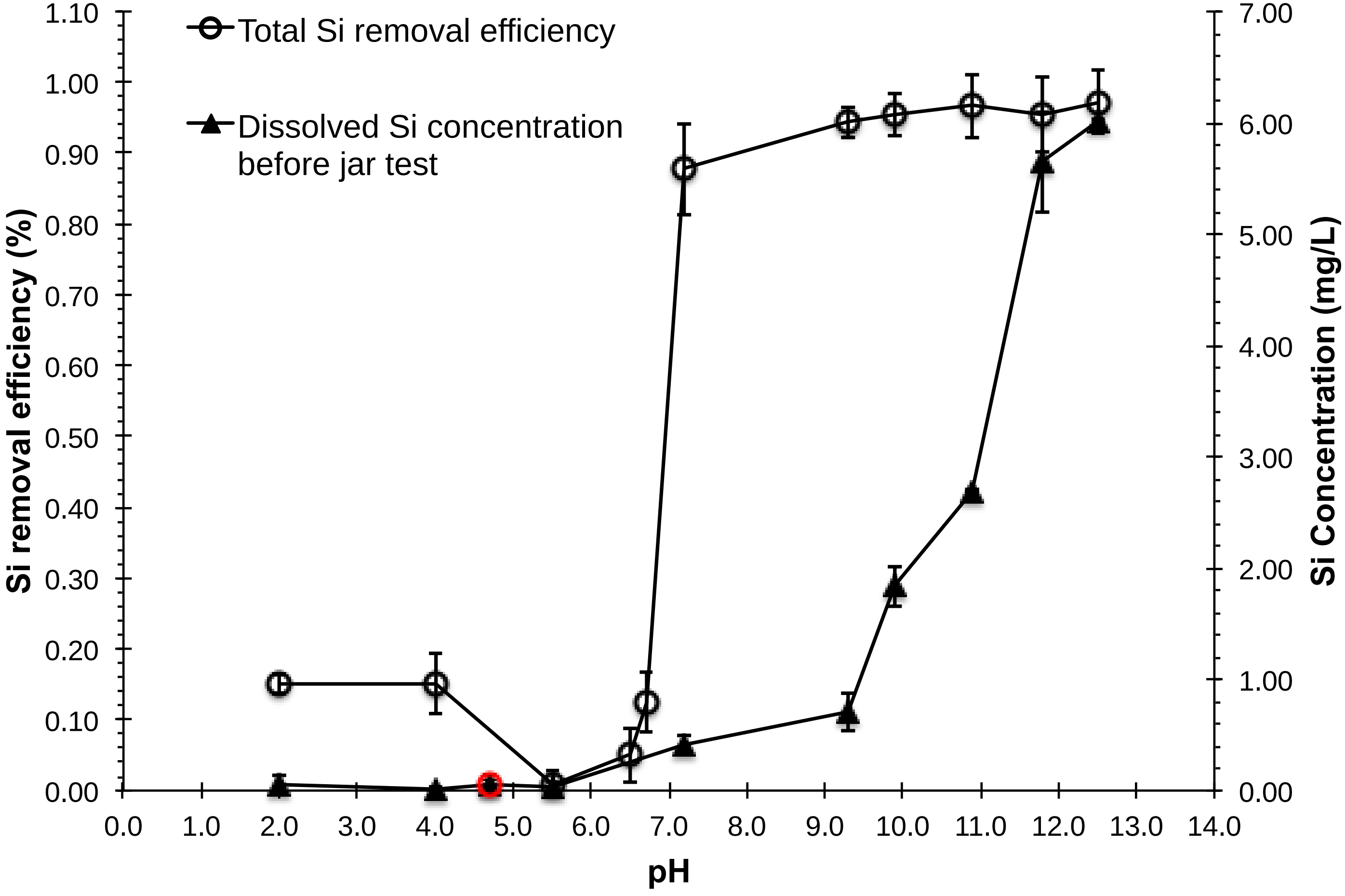
- Sorption of III/V elements on CMP NPs (see slide-deck)

Ga

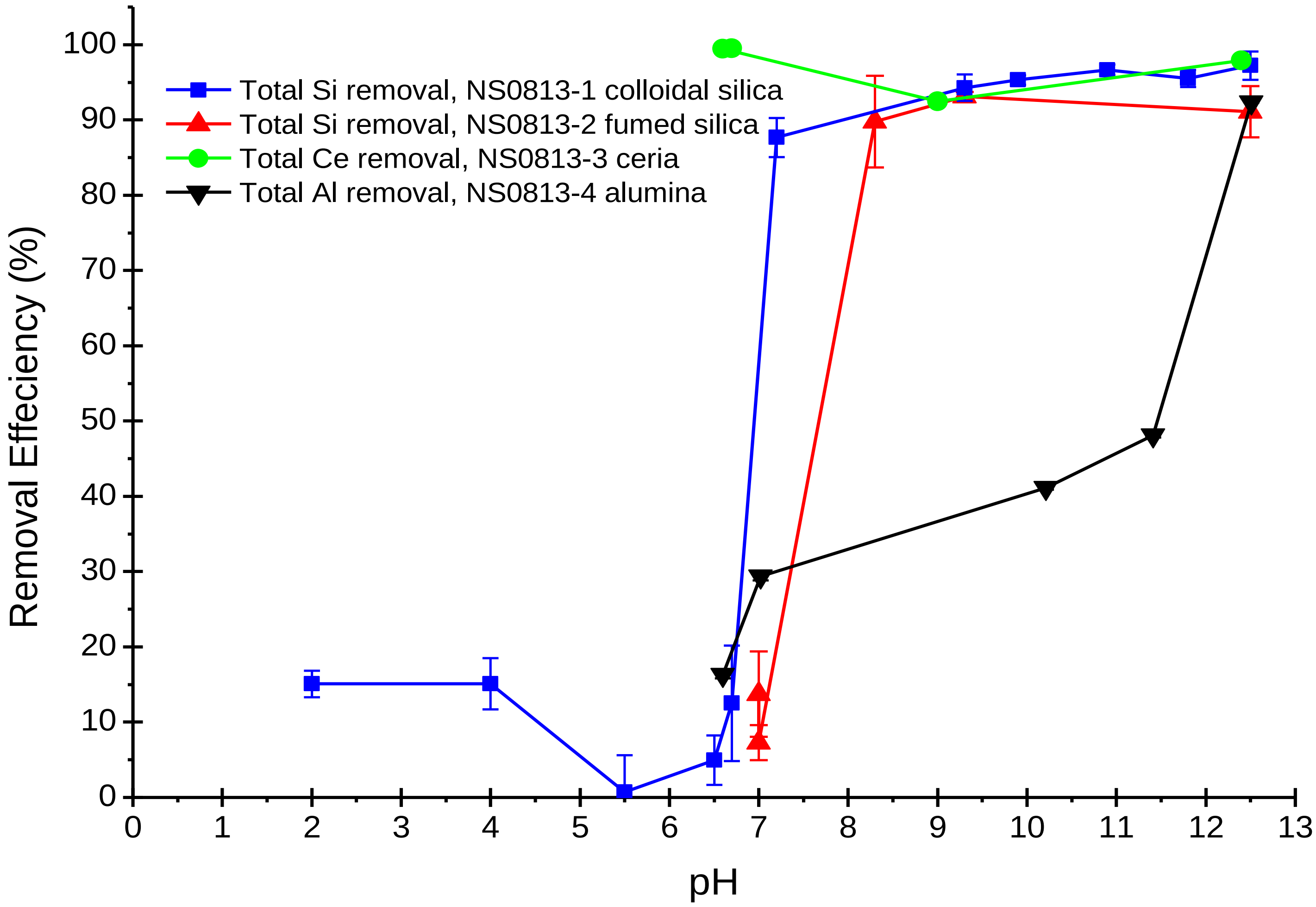
As

In

CMP Slurry – Colloidal Silica



Si removal efficiency and initial dissolved Si at different pH values. Red circle represents the Si removal efficiency of control sample.

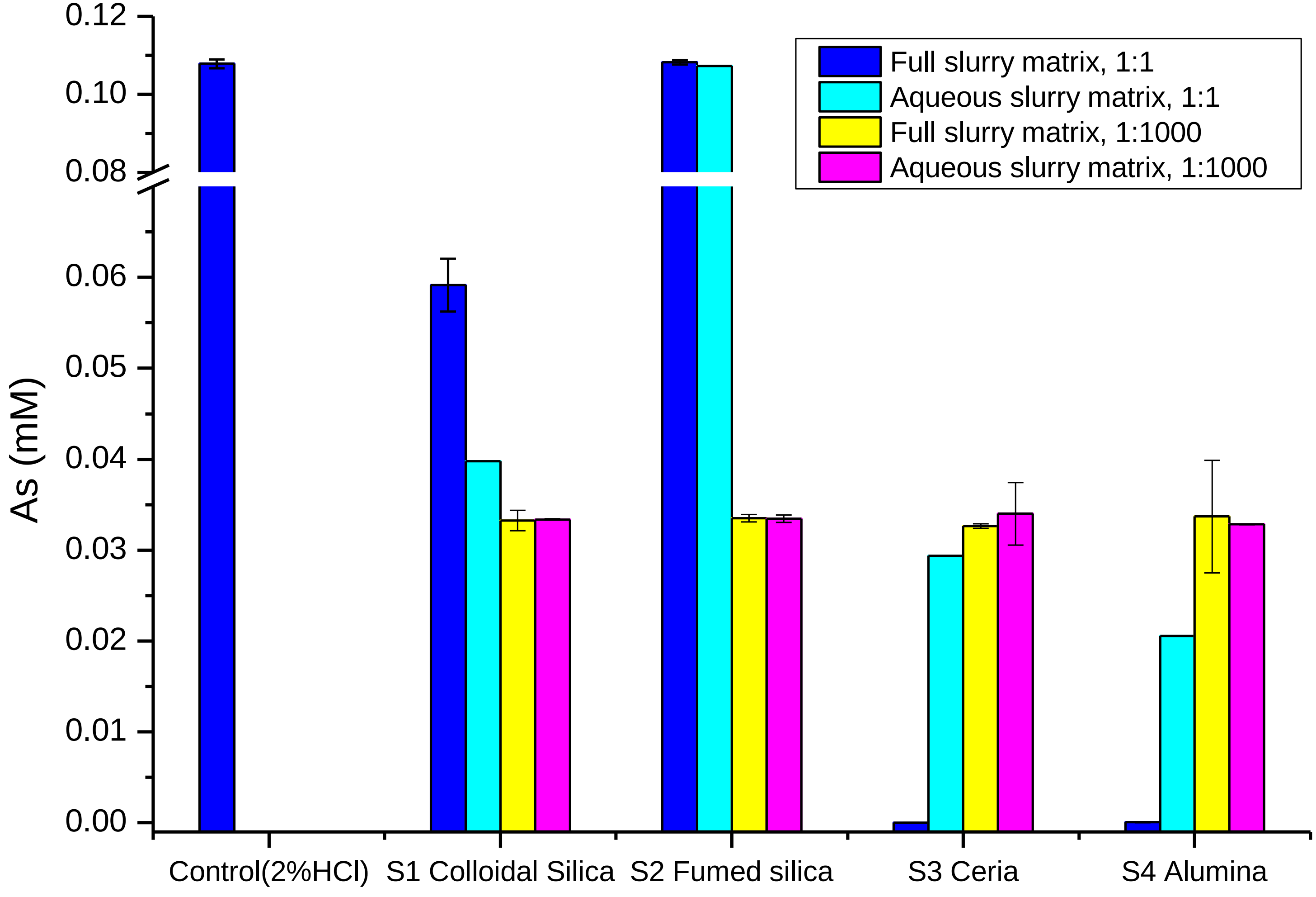


Removal efficiencies of Si, Ce and Al for 4 CMP slurries under different pH conditions. Ca dosage was 2mM in all cases. Started concentrations: $C_{0Si,slurry\ 1}$=24 mg/L, $C_{0Si,slurry\ 2}$=20mg/L, $C_{0Ce,slurry\ 3}$=19.5mg/L, $C_{0Al,slurry\ 4}$=31mg/L. pH values are obtained after jar test when reactions are considered in equilibrium.

Addition of III/V elements to CMP NP slurries

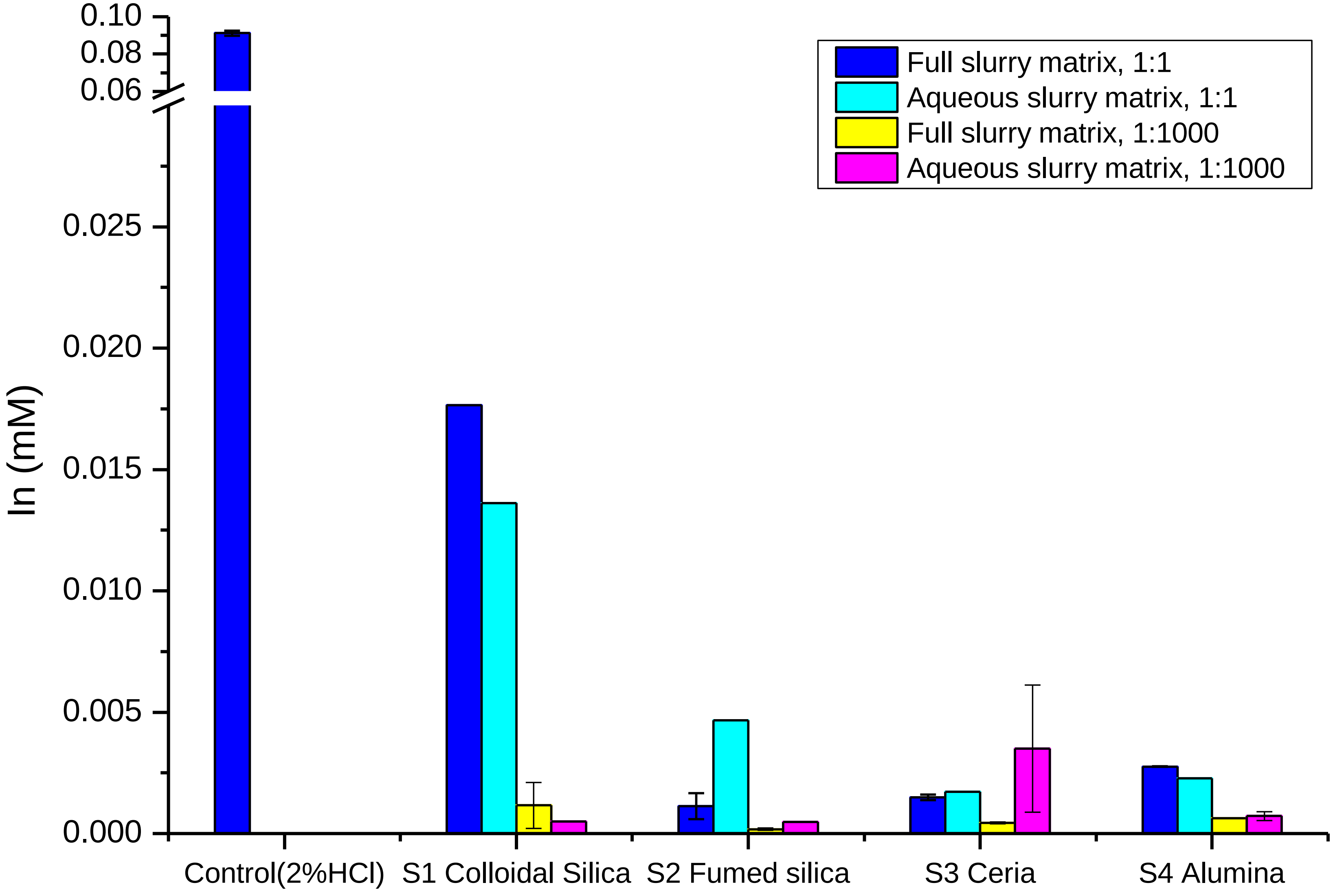
- As(V) or In(III) ions added at 0.1 mM to CMP slurries (no pH adjustment)
- Sorption studied in a screening test
- NPs (with sorbed As/In) separated from slurry using centrifugal ultrafilters

Arsenate



0.12
0.10
0.08
0.06
0.05
0.04
0.03
0.02
0.01
0.00
As (mM)
Full slurry matrix, 1:1
Aqueous slurry matrix, 1:1
Full slurry matrix, 1:1000
Aqueous slurry matrix, 1:1000
Control(2%HCl)
S1 Colloidal Silica
S2 Fumed silica
S3 Ceria
S4 Alumina

Indium



In (mM)
0.10
0.08
0.06
0.025
0.020
0.015
0.010
0.005
0.000
Full slurry matrix, 1:1
Aqueous slurry matrix, 1:1
Full slurry matrix, 1:1000
Aqueous slurry matrix, 1:1000
Control(2%HCl)
S1 Colloidal Silica
S2 Fumed silica
S3 Ceria
S4 Alumina

Industrial Interactions and Technology Transfer

- **Worked closely with IBM on understanding fate of CMP-based nanoparticles in on-site wastewater treatment system**
- **Collaborated in international sp-ICP-MS round robin**
- **Presented for a ERC/SRC monthly webcast**
- **Organized and lead consortium of university researchers**
- **Organized 2013 GRC on Environmental Nanotechnology & invited David Speed as speaker to describe research needs for semi-conductor industry (organizing 2015 GRC)**
- **Working with Perkin-Elmer on sp-ICP-MS data analysis software**

Future Plans

Next Year Plans

- Continue examining removal of CMP NPs by on-site chemical treatment, and removal at municipal biological WWTPs
- Currently examining ROS production by CMP NPs (so far only CeO_2 produces ROS)
- Continue experiments with different III/V elements to assess sorption, removal capability and impacts of NPs to produce ROS
- Evaluate physical abrasion on release of CNTs from thermal packaging
- Optimize sp ICP-MS fast-scan methodology for low level SiO2 analysis
- Compare FFF-ICP/MS to sp-ICP/MS analysis for size determination and aggregation state of CMP NPs

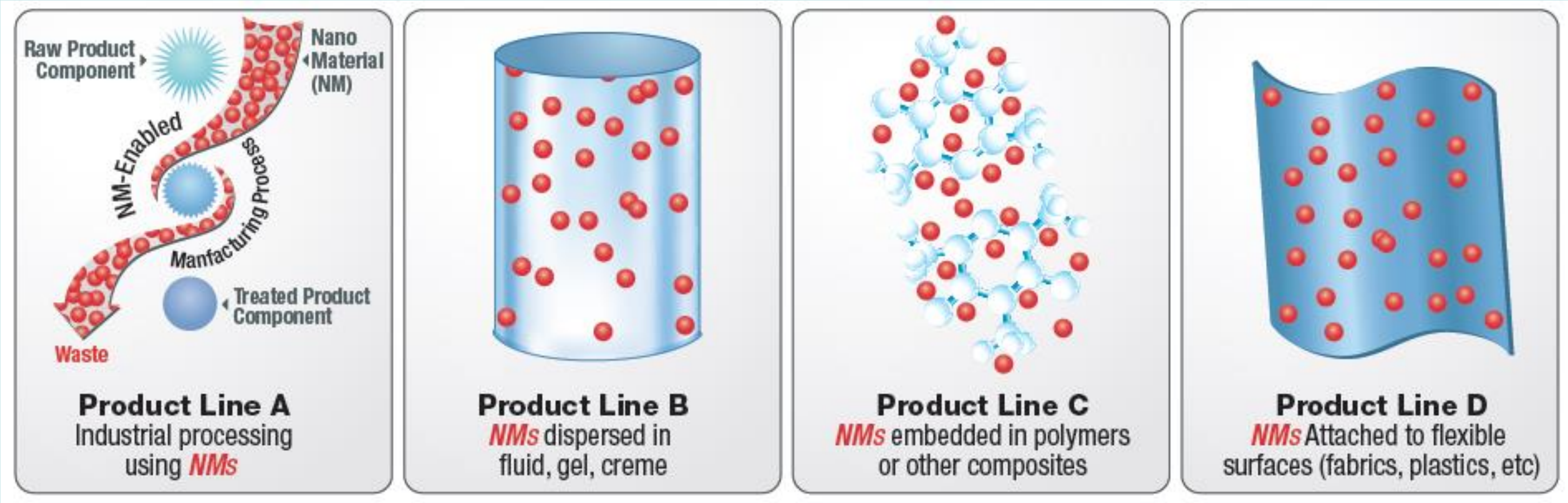
Long-Term Plans

- Attempt to "track" CMP NPs in municipal WWTP biosolids
- Understand NP removal in more complex CMP slurries, with or without III/V elements

Publications, Presentations, and Recognitions/Awards

- **Four publications submitted for review or under preparation**
- **Presentation at TECHCON 2012**
- **Presentation at Rocky Mountain SETAC Meeting 2013 (1st place oral presentation)**
- **Presentation at National SETAC Meeting 2013**
- **Kyle Doudrick – 2013 Simon Karecki awardee**
- **EPA award on Life Cycle of Nanomaterials which incorporates a product line similar to CMP fluids containing NPs**

Life Cycle of Nanomaterials (LCnano)



EPA #RD835580 (Pending final award)

Duke University
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