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

(*Task Number: 425.040)*

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Other Researchers:

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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**
- **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**

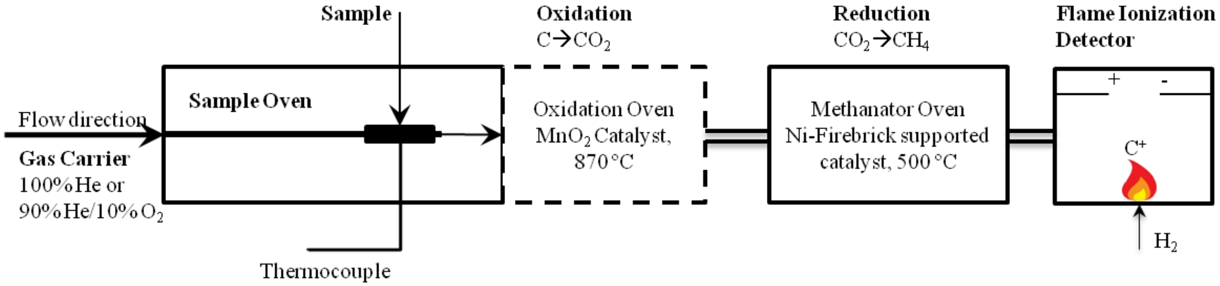
1. **Aid in ESH workplace exposure monitoring and assessment of remedial actions to reduce exposures, and in monitoring NMs after they leave fabrication facilities**

1. **Aids in documenting nanomaterial fate over their life cycle**

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)
  - Exploring detection of nanographene platelettes because of their electronic properties

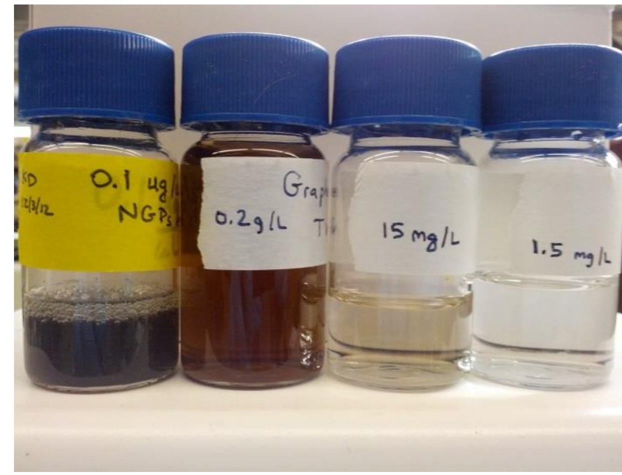
Thermal Optical Transmittance

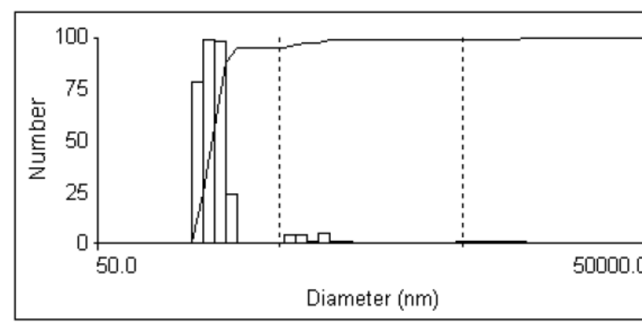


- For MW or SW CNTs
- Uses unique thermal properties of CNTs
- Current detection limit is < 5 ug CNT
- Validated with over 15 different CNTs
- Next step: Use personal air sampler to collect and quantify CNTs (workplace exposure)

Graphene Nanoplateletes

- Highly conductive applications
- Graphene oxides
- 1-15 nm thick
- Analysis strategy:
  - Same as CNTs
  - Also using Raman
  - Preliminary findings indicate TOT analytical method will work for graphene





Multimodal Size Distribution

Metal Oxide Nanoparticle Detection

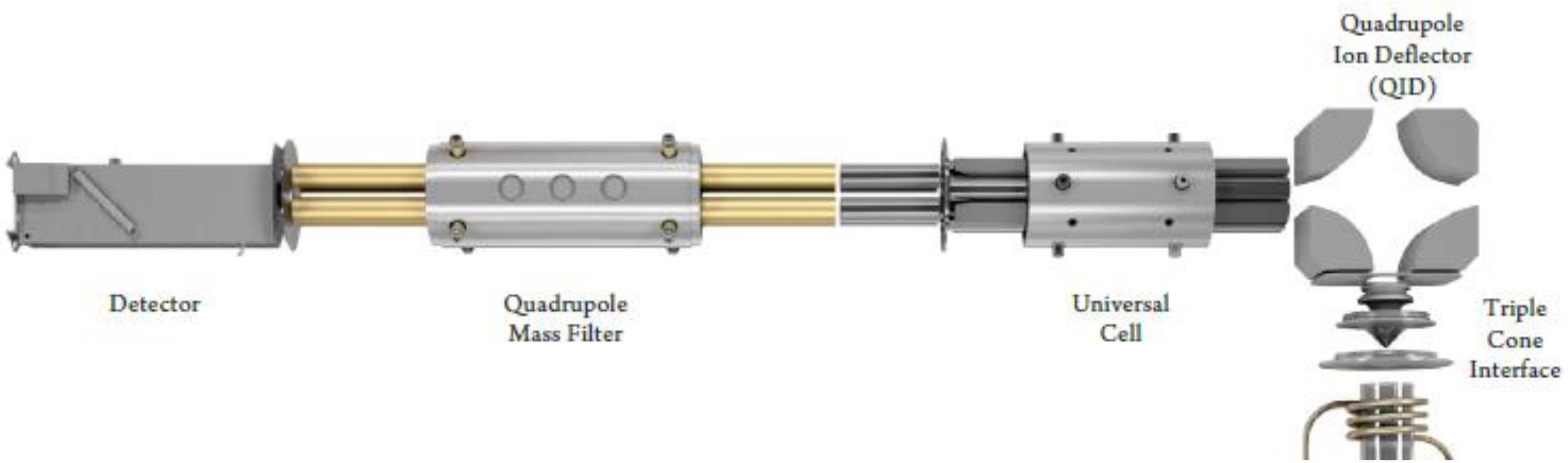
- Single Particle ICP-MS
- Uses instrumentation with modified data collection mode
- Sensitive to ppt levels
- Depending upon element can count NPs down to 5 nm
- Current focus has been spherical NMs, but works for nanowires

World-Wide SP-ICP-MS RoundRobin

- 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

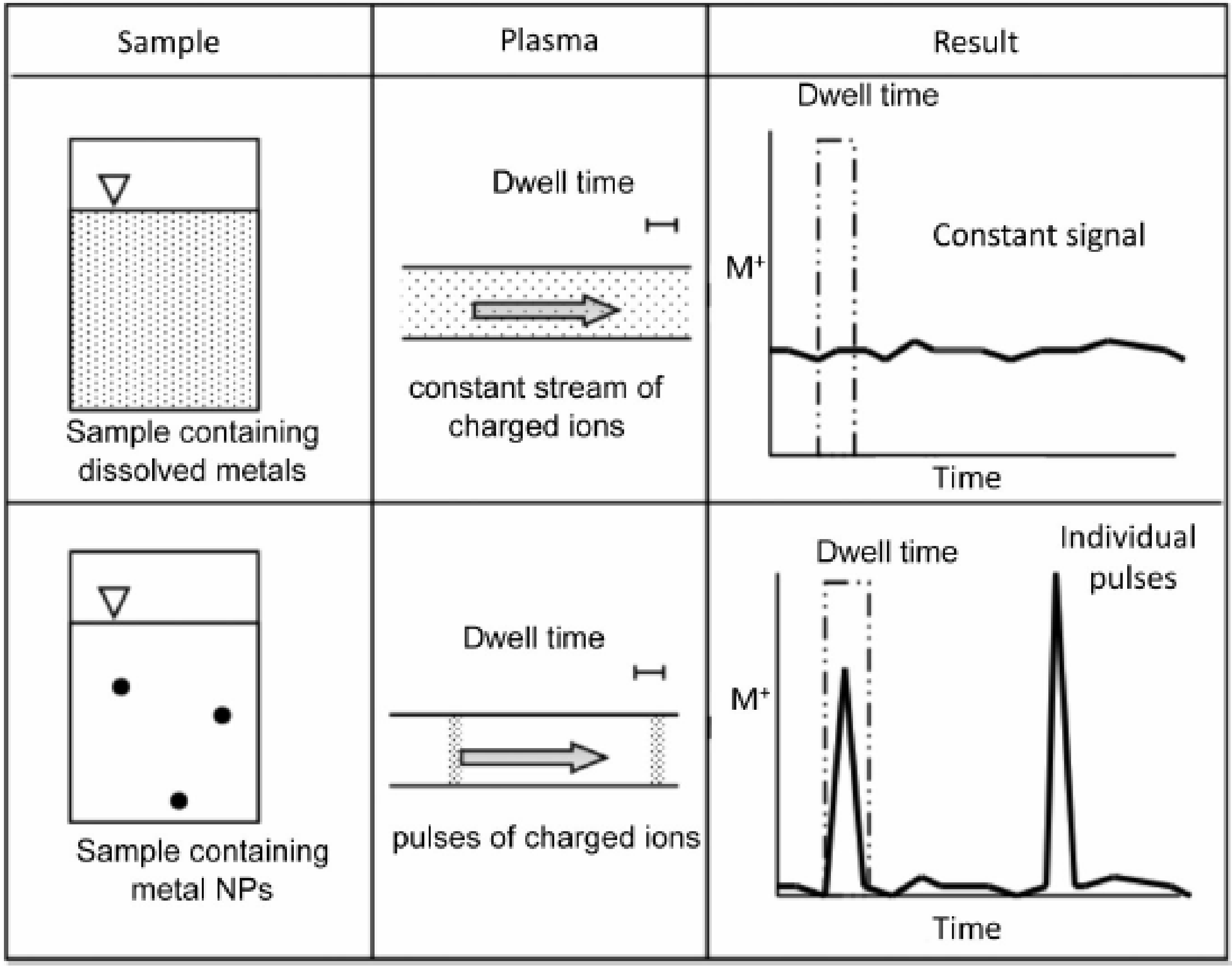
ICP-MS

- Element specific detection
- Detection limits at low part per trillion levels
- Isotopic analysis possible
- Analytical working range over 9 orders of magnitude.



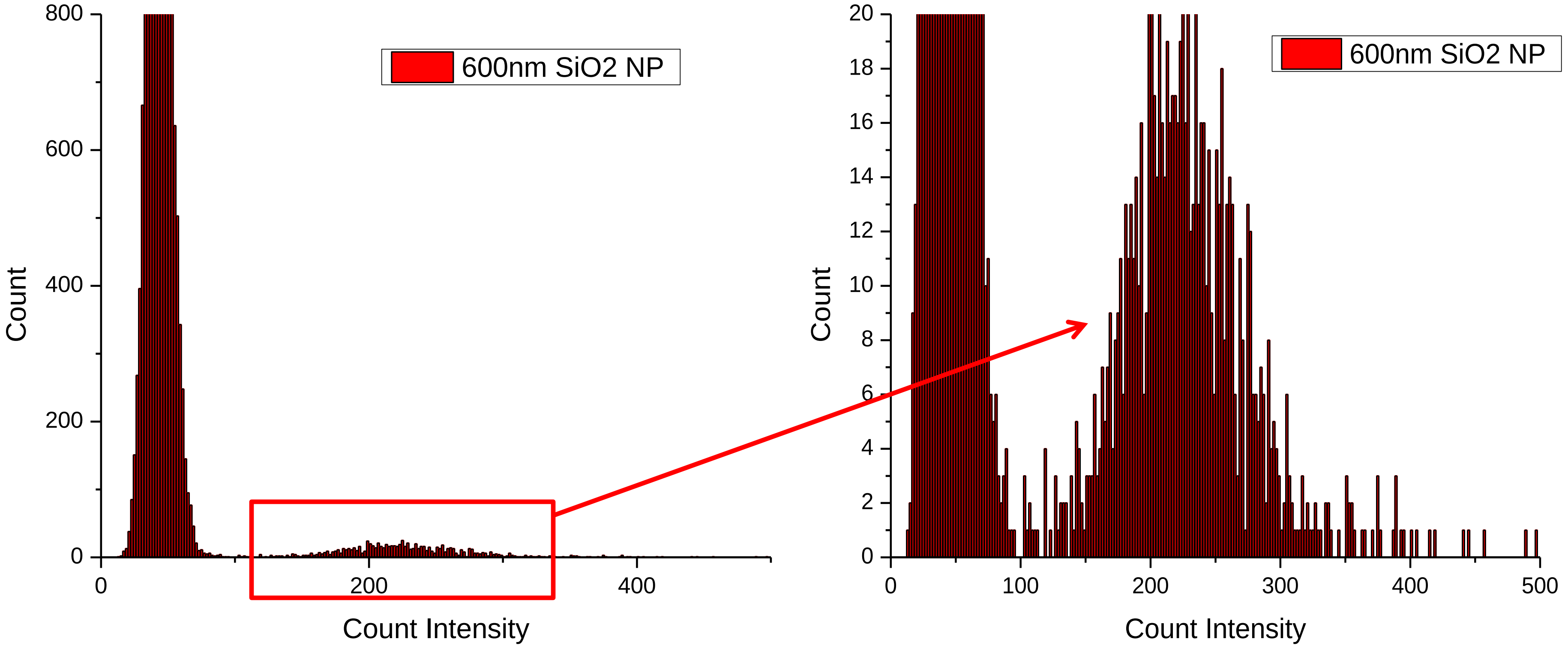
Principles of Single Particle ICP-MS

- **Dissolved analyte gives a constant signal**
- **NP solution dilute: single nanoparticle in a single dwell time**
- **Assumption one pulse = one particle**
- **Number of pulses = number of nanoparticles**



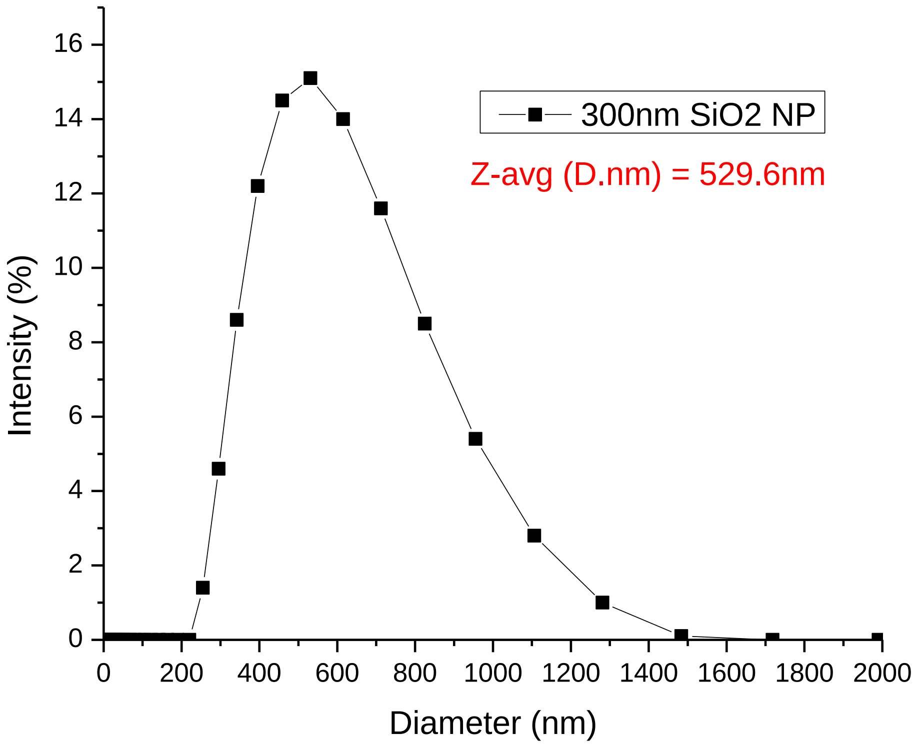
Mitrano, D.; Lesher, E.; Bednar, A. et al. ***Environmental Toxicology and Chemistry*****, 2012**

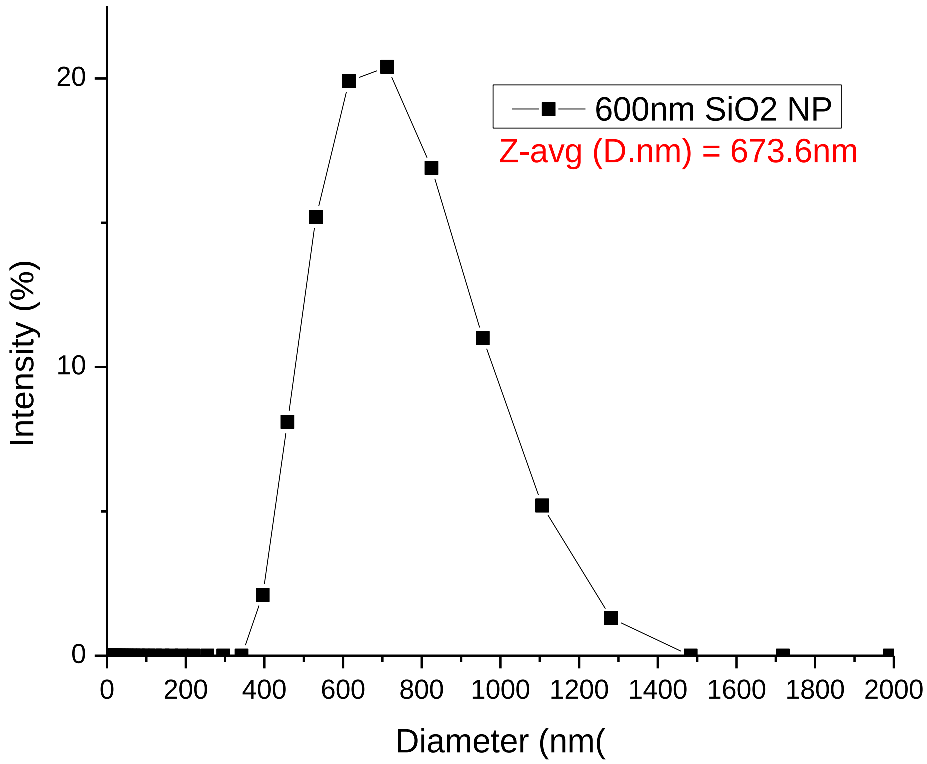
Frequency count of 600nm Data



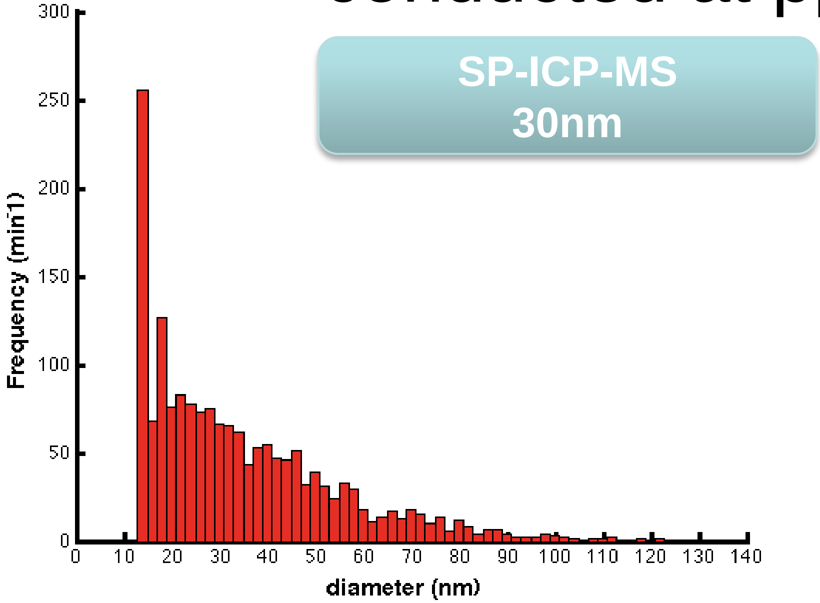
SiO_2 NP DLS

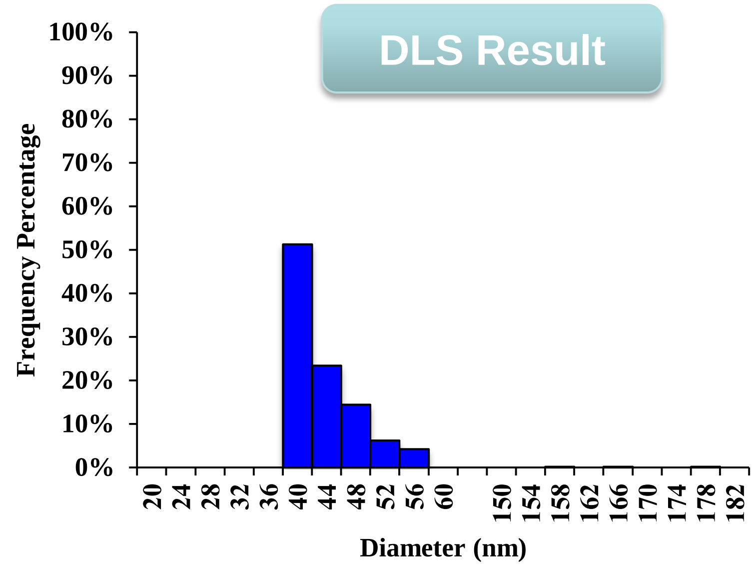
DLS showed particle sizes larger than those reported for 300 and 600 nm SiO_2 nanoparticles

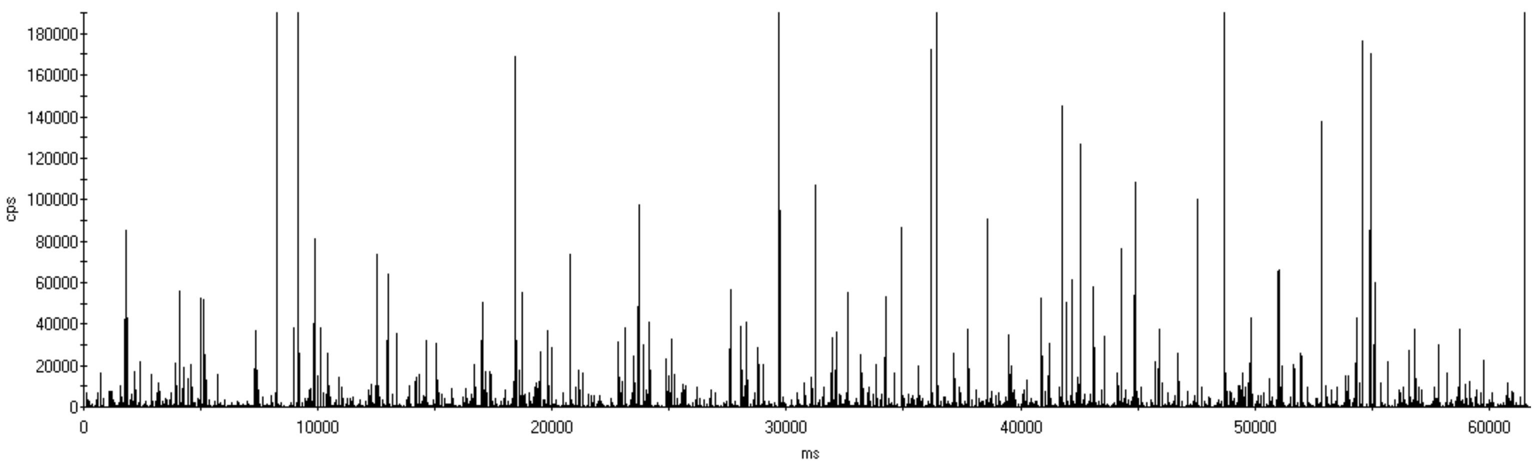




SP-ICP-MS and DLS provide similar size distributions for CeO2, but SP-ICP-MS is conducted at ppt concentrations



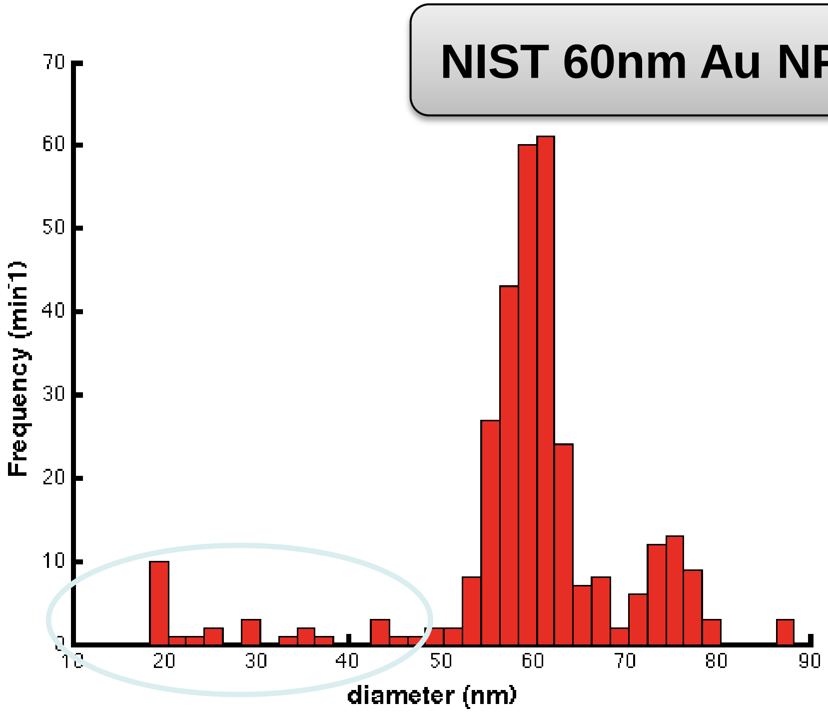


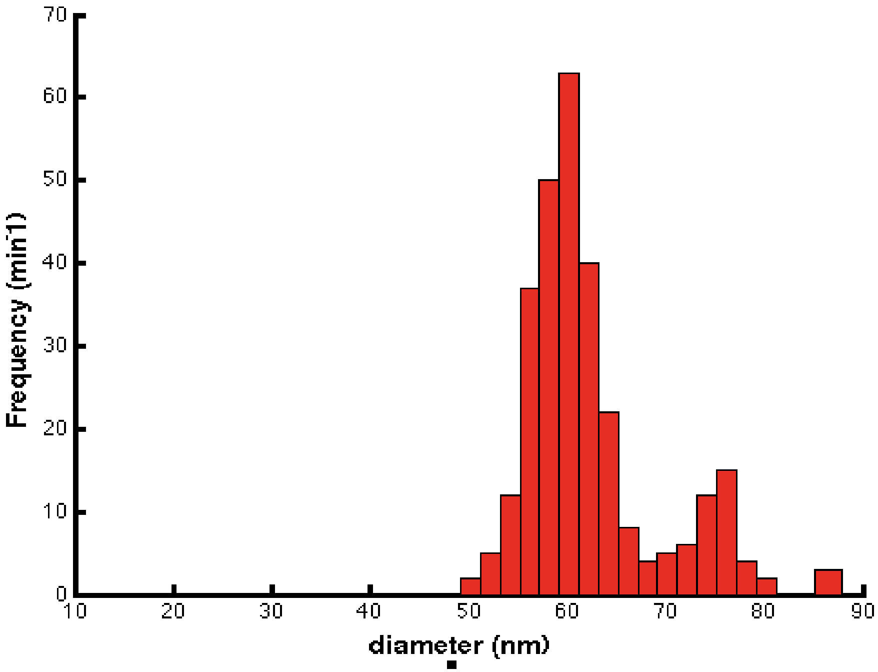


sp-ICP-MS Data Analysis

- Old method: statistical differentiation of signal from background using 4σ
- New method under development: K-Means Algorithm Method Application in particle signal processing in sp-ICP-MS Analysis

An example with Gold Nanoparticles





4 σ --- 316 particles out of 6164 pulses.

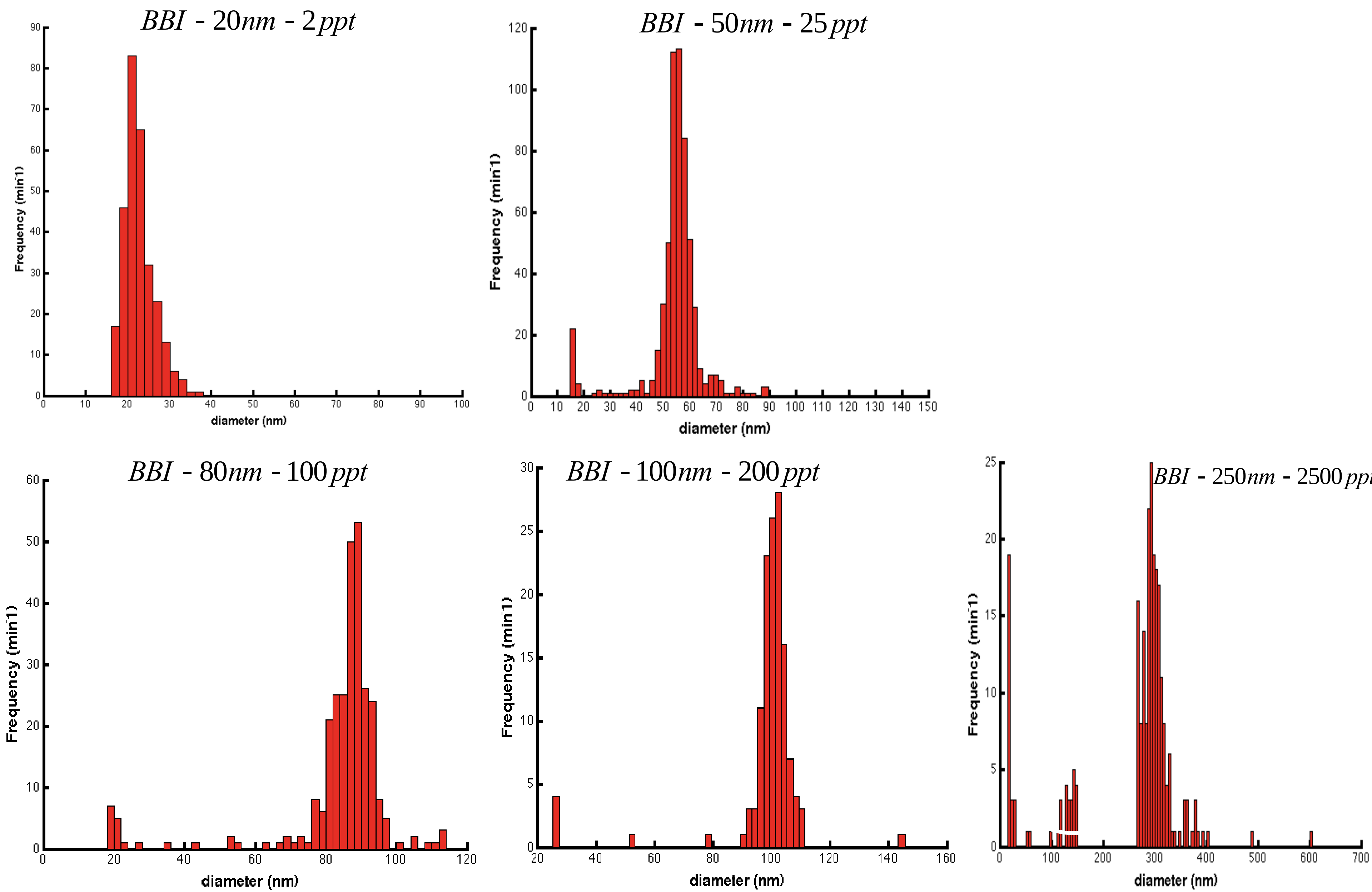
290 particles out of 6164 pulses.

Conclusion: K-means offers a statistically robust data processing strategy for SP-ICP-MS

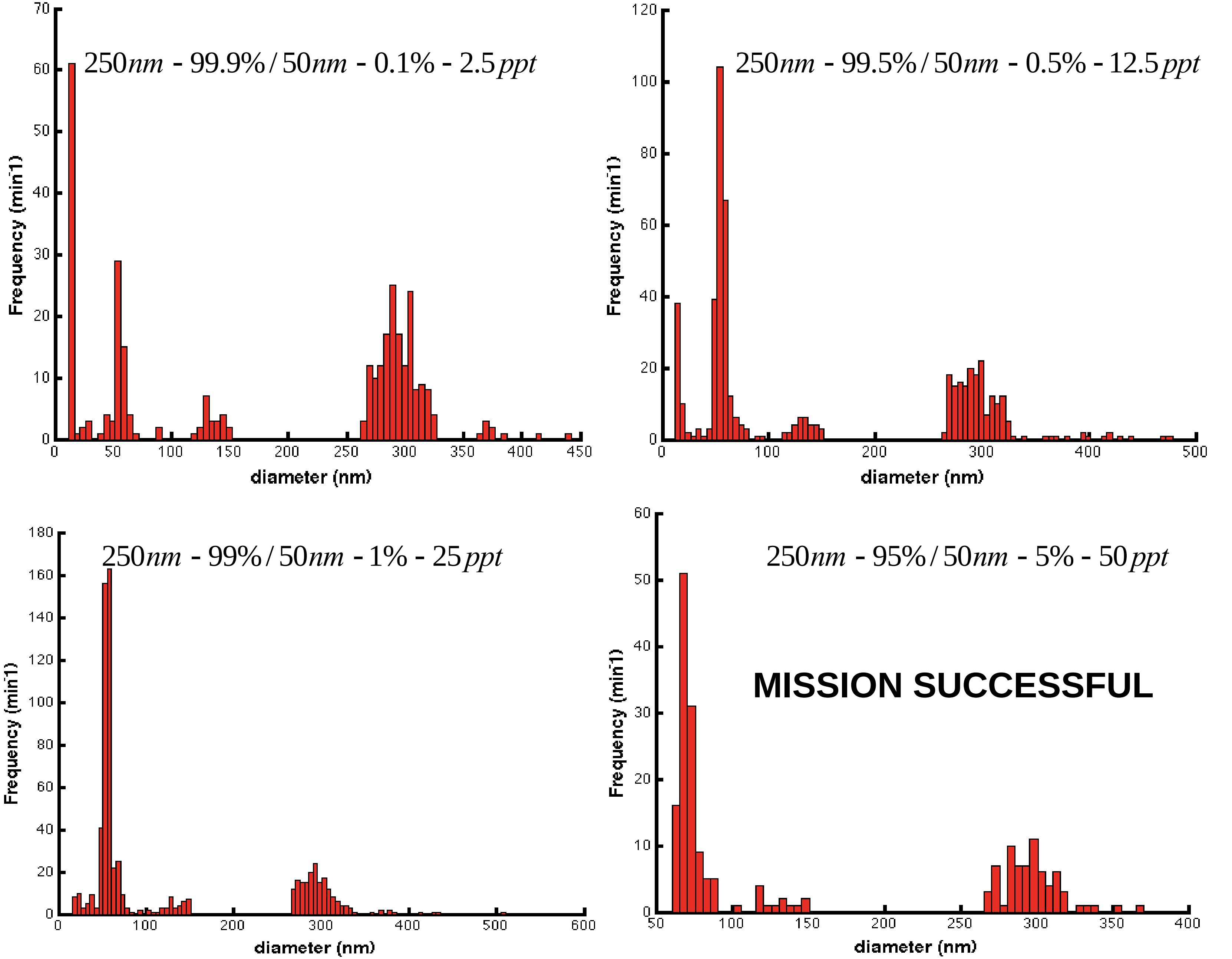
Using SP-ICP-MS to evaluate QA/QC on CMP fluids

- Primary particle size: 250 nm Gold NP
- Impurity sizes: 20nm, 50nm, 70nm, 80nm, 100nm.
- Some parameters:
  - Dwell time: 10ms;
  - 4-sigma-principle differentiation
  - 5-nm bin size;
  - Optimal # concentration.
- Impurity percentage: 0.1%, 0.5%, 1%, 5% (mass-based).

Size distributions of some AuNPs



250nm/50nm mixture



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**
- **Presented in 2012 at SRC annual meeting**
- **Organized and lead consortium of university researchers**

Future Plans

Next Year Plans

- Improve size detection limit for SiO_2 by sp-ICP-MS and/or using ultrafiltration pretreatment
- Finalize CNT analytical SOP
- Demonstrate CNT exposure measurements (from air sampling)
- Finalize development of nanographene analytical technique
- Conduct jar tests to simulate CMP removal during industrial treatment & evaluate improvements to remove SiO_2 nanoparticles

Long-Term Plans

- Conduct on-site training for sp-ICP-MS
- Ability to quantify trace-level CMP-NMs in water leaving fabs and on personal air monitors

Publications, Presentations, and Recognitions/Awards

- **Publications in process**
- **Presentation at TECHCON 2012**
- **Kyle Doudrick – 2013 Simon Karecki awardee**