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Cloud-point Extraction and Characterization of Nanomaterials from Water

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Outline

- Introduction of Cloud-point Extraction (CPE)
- Demonstration of CPE on Extraction of Gold Nanoparticles
- CPE on a Variety of Water and Characterization of Nanoparticles
- Summary
- Future Work & Potential Application

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Potential Release of Nanomaterial from Semiconductor Industry

- The use of chemical-mechanical polishing (CMP) may lead to potential release of nanoparticles to water.

- Some existing methods are capable of detecting nano particles (e.g. single particle ICP-MS), but still needs development to count small nanoparticles (NPs) of Al or Si based CMP.

- To characterize nanomaterials in the water, an enrichment method may be beneficial.

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Benefits of Pretreatment Method for Nanomaterial Characterization

1) Enrichment of nanoparticles into a clean phase to facilitate analysis.

2) Separation of nanoparticle from metallic ions

3) Non invasive method (i.e. does not change size or shape of nanoparticles)

4)Currently such methods are lacking for nanomaterials in aqueous systems or biological fluids, perhaps with exception of ultra-high speed centrifugation.

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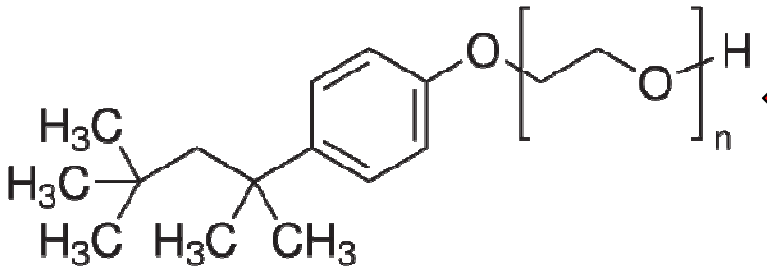
What is Cloud-point Extraction (CPE)?

- 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

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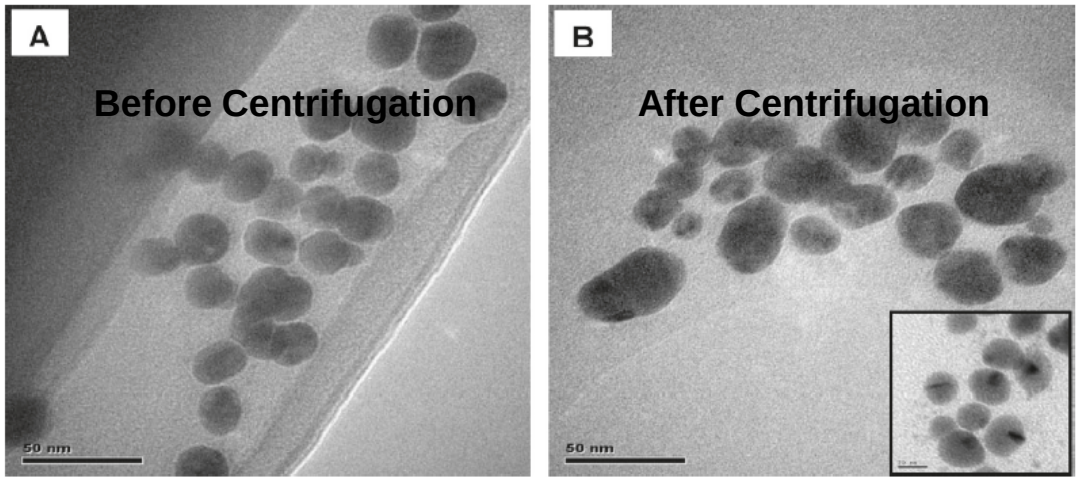
Demonstration of CPE on Nanomaterial Extraction

- Effectively used in a variety of nanoparticles suspended in deionized water, including CdSe/ZnS, Fe_3O_4, (c) TiO_2, Ag, Au, C60,SWCNT.
- No size change of nanoparticles (e.g. silver nanoparticles)

TEM Images



Chao et al., Analytical Chemistry, 2011

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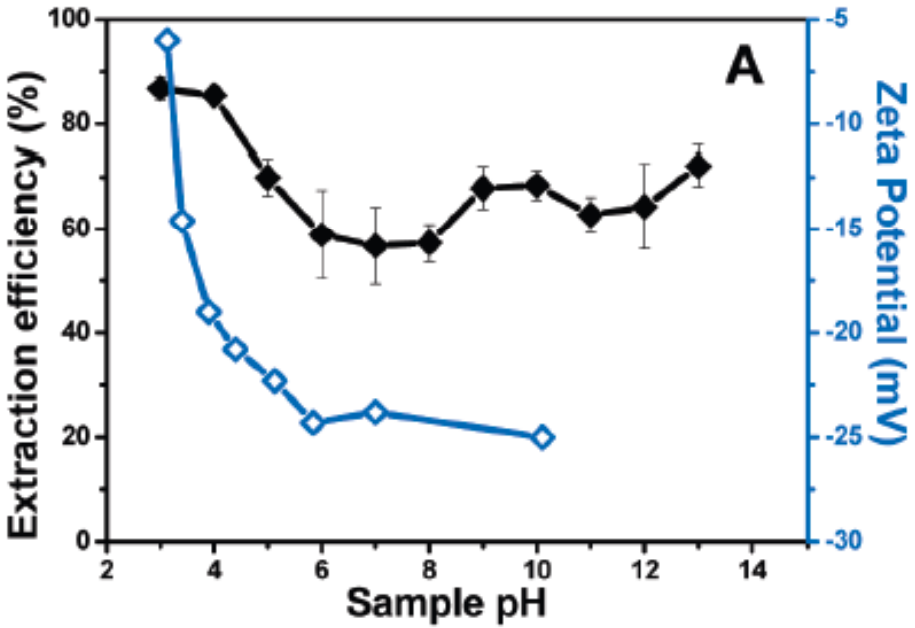
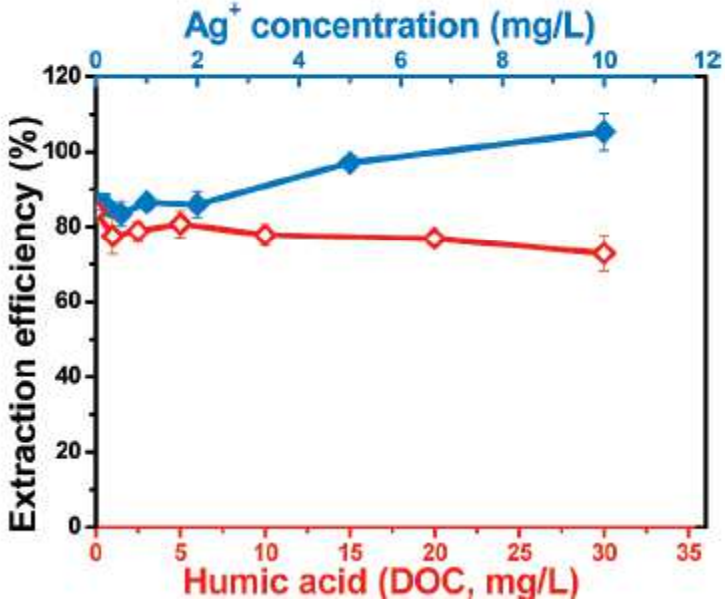
Literature Reports of Factors Affecting Recovery Rate

Effect of pH



Effects of humic acid and initial silver concentration



The importance of recovery rates may vary based upon applications. Low recovery rates may be acceptable in some cases (e.g. characterization of nanoparticles).

Chao et al., Analytical Chemistry, 2011

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Objectives and Approach

1. Objective: To extract nanoparticles existing in rivers, tap, and waste waters (i.e., prospecting for nanoparticles in water)

2. Approach: Apply CPE to lab wasters with known nanoparticles and then to characterize NPs by electron microscopes in more complex “real” matrices after CPE.

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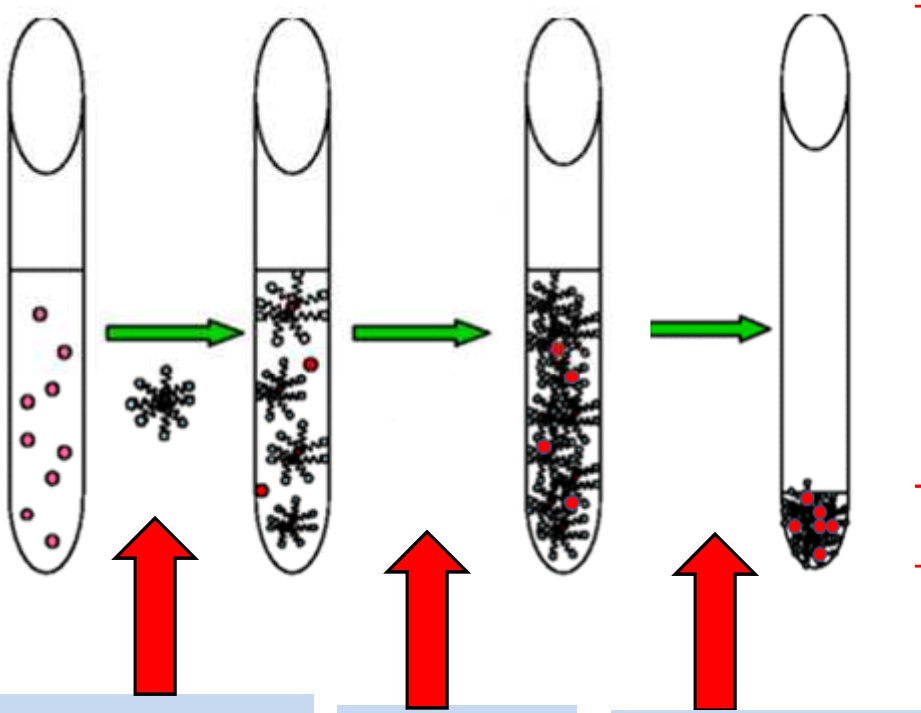
Cloud-point Extraction Process



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

Step2. Water bath at 40 ℃ for 30 minutes

Step 3. Cooling down, and centrifuge

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

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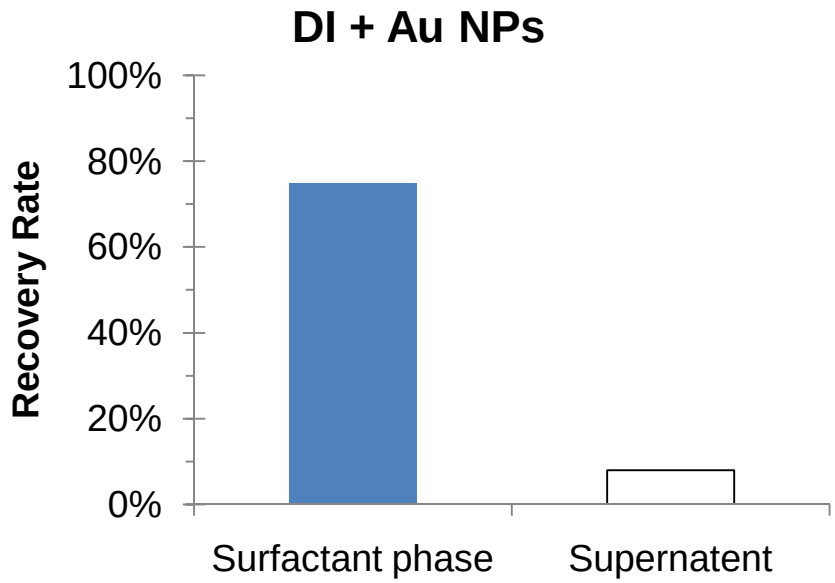
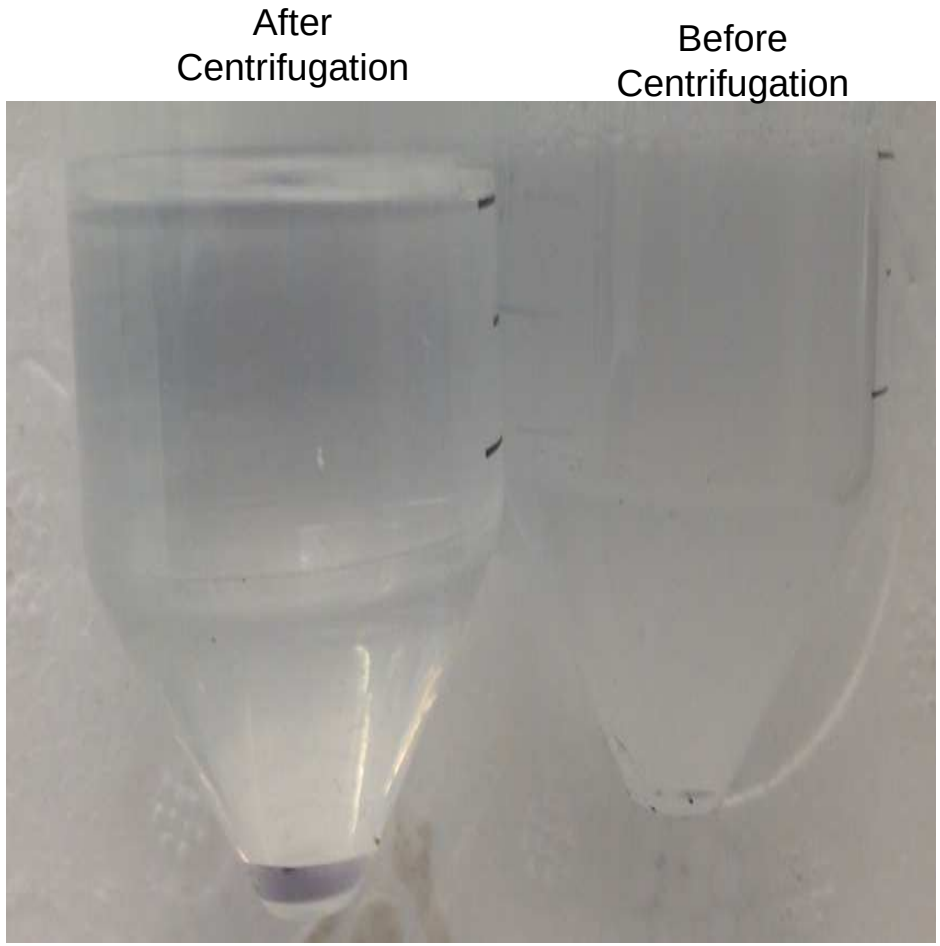
Example of CPE: Recovery Rate of Au Nanoparticles from Nanopure water





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Results

- Nanoparticles in river water
- Nanoparticles in drinking tap water
- Nanoparticles in treated wastewater

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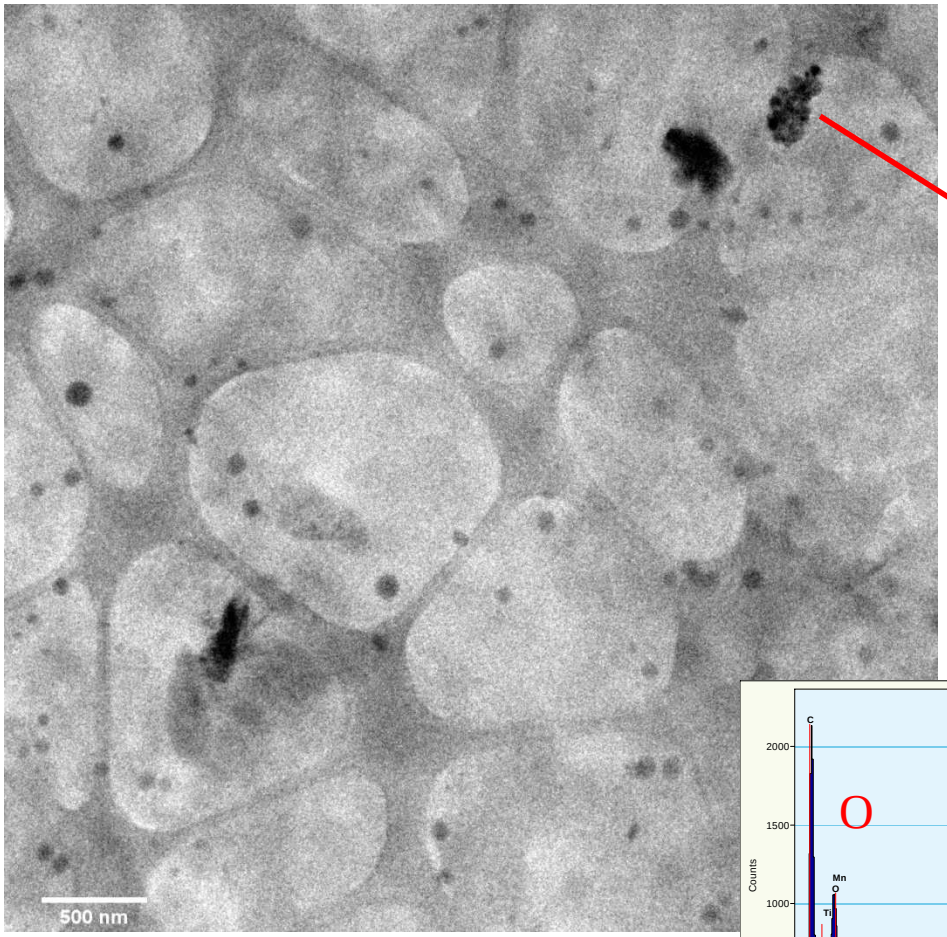
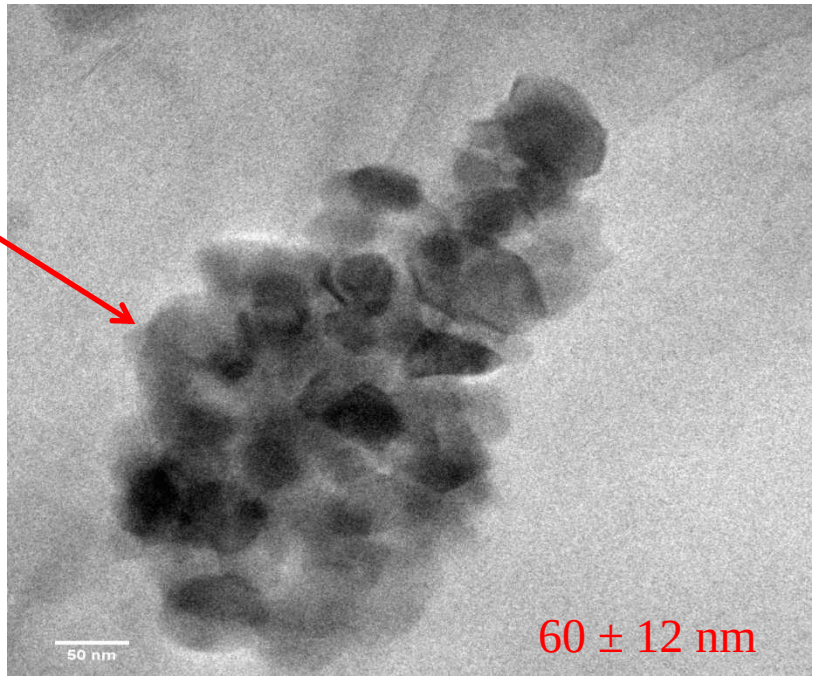
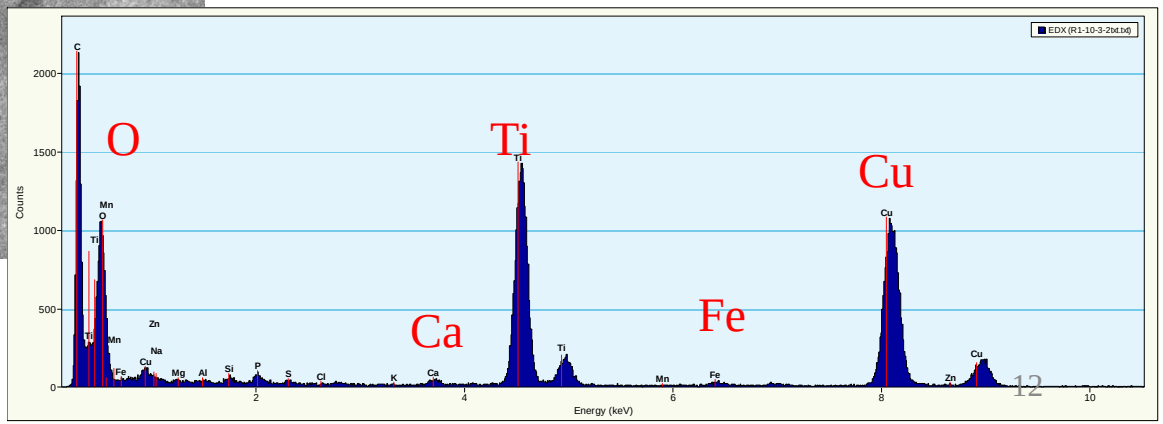
Salt River Sample







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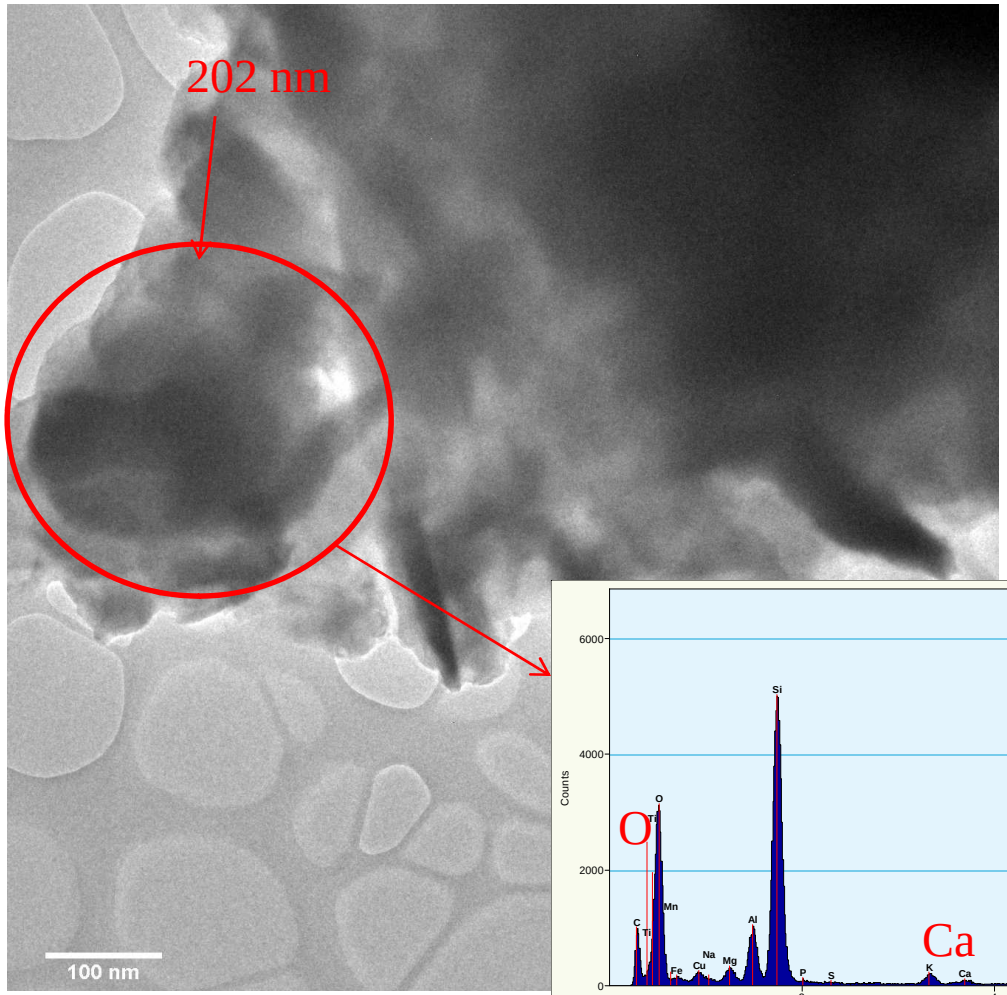
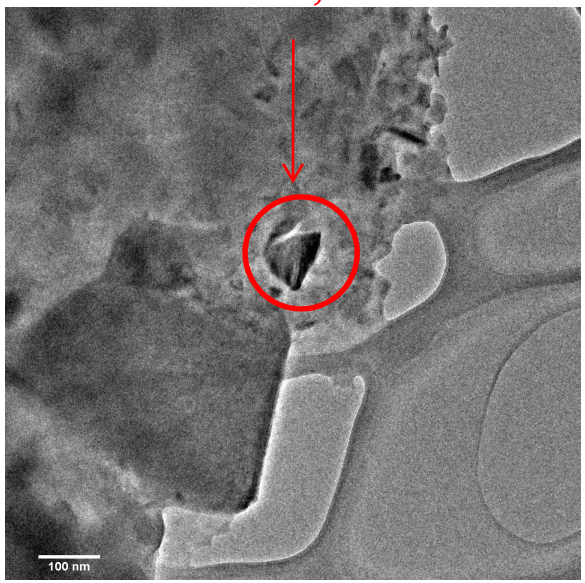
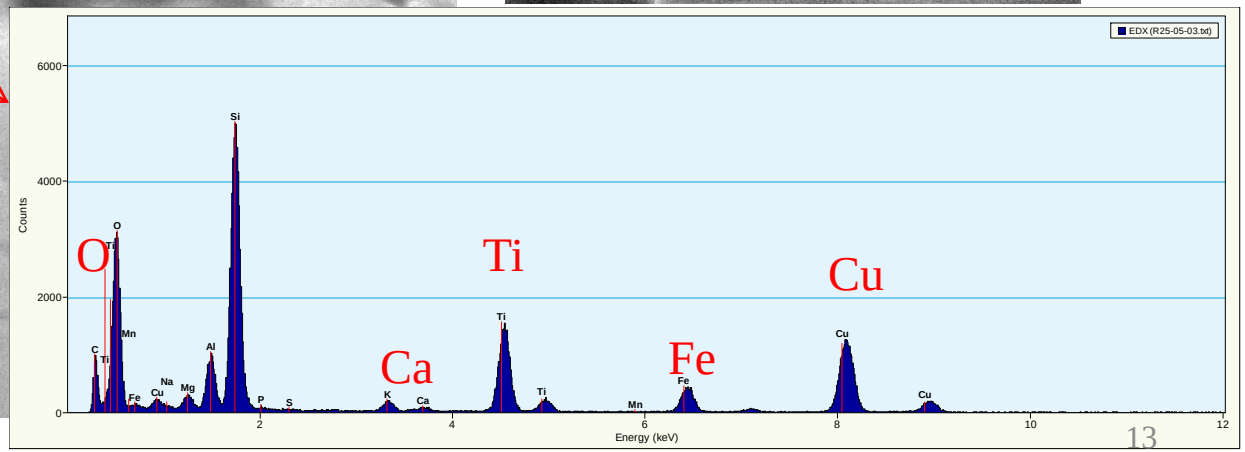
Verde River Sample



Fe +C +O, 93 nm





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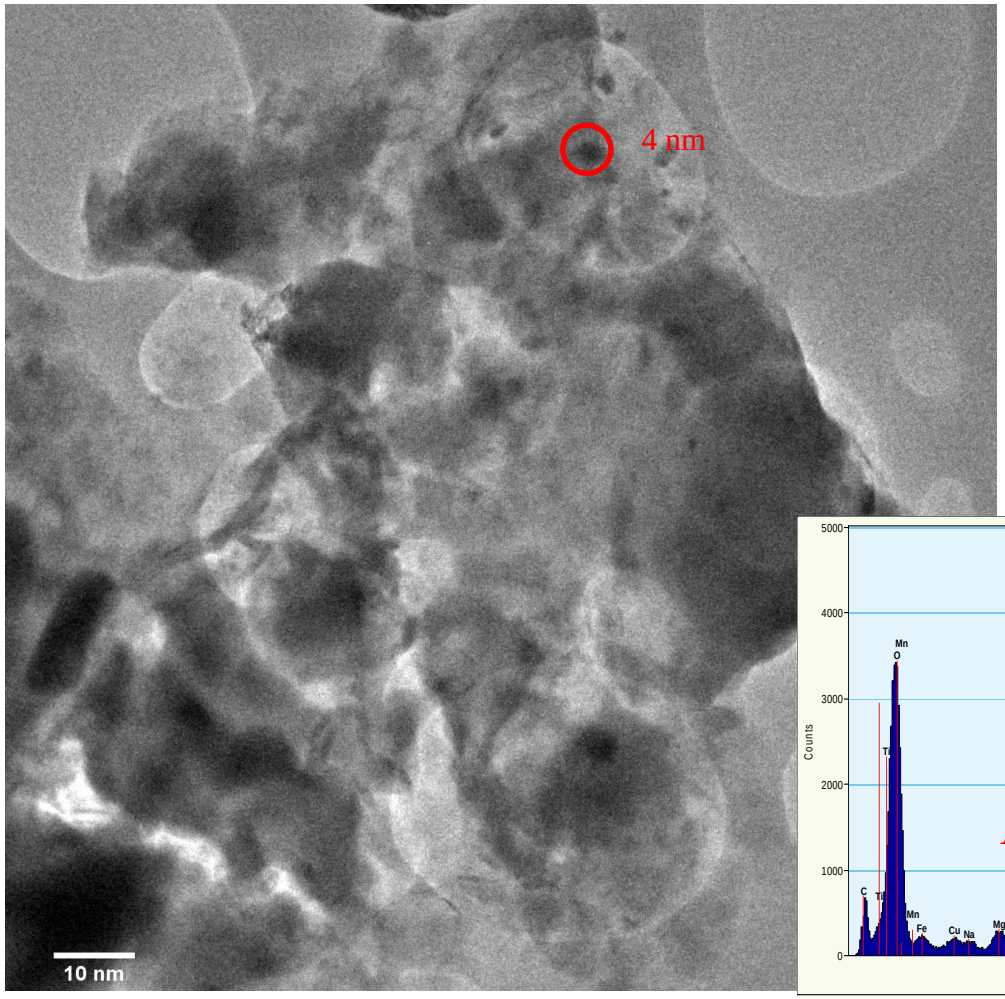
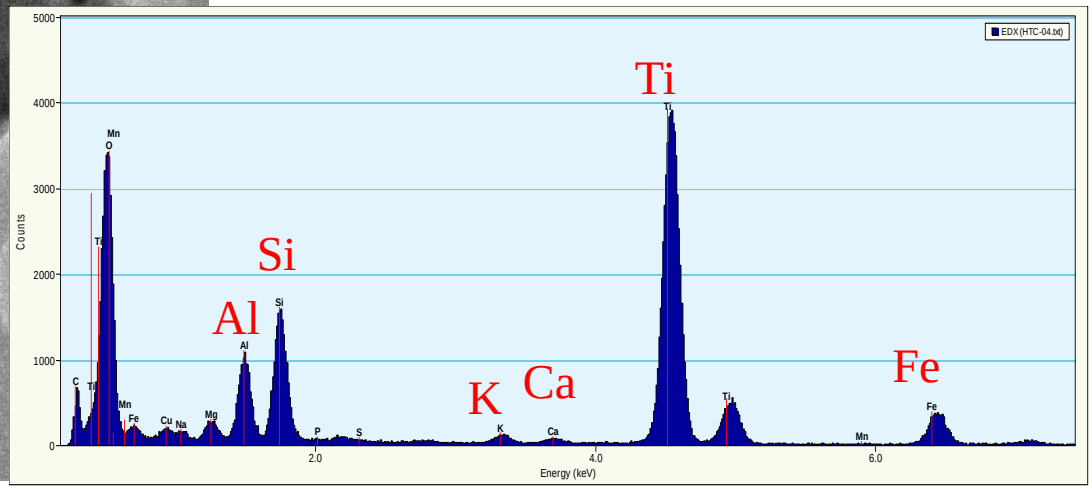
Water Sample from Tempe Canal



The smallest particle containing high concentration of Ti



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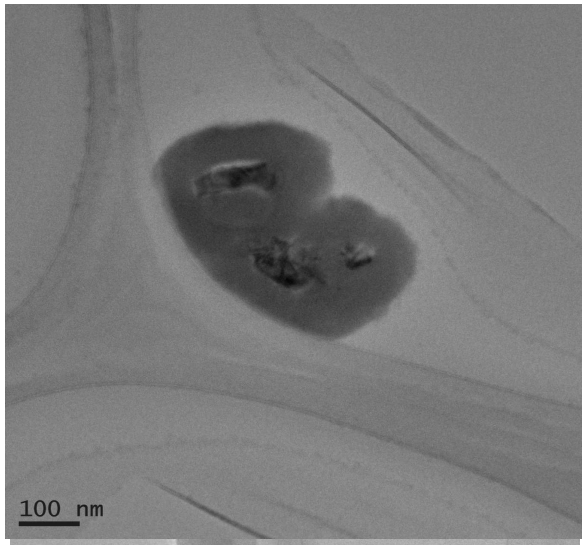
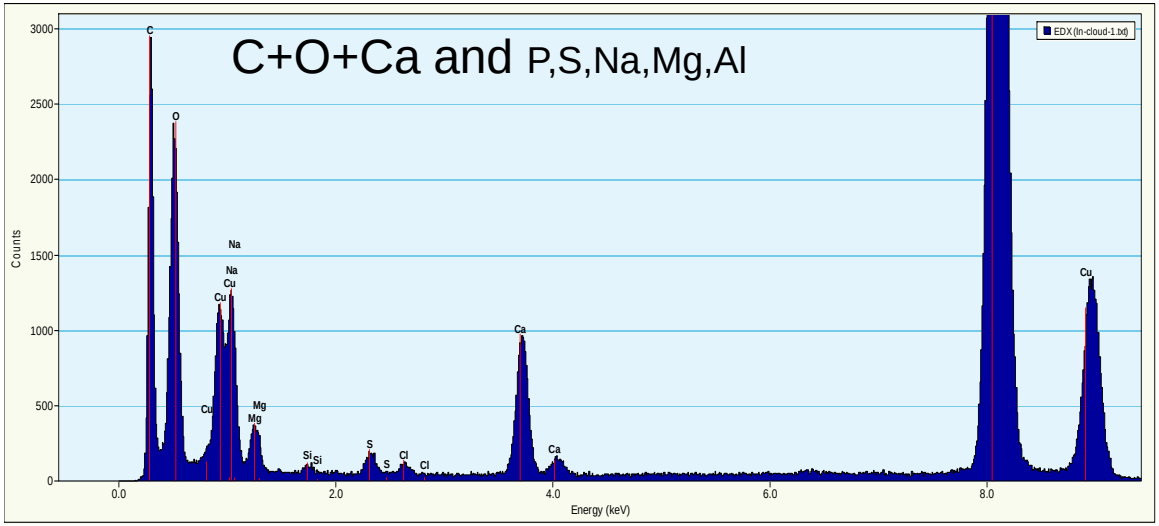
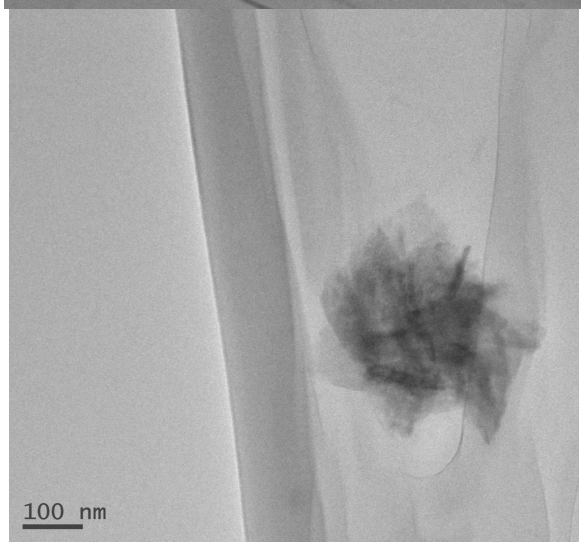
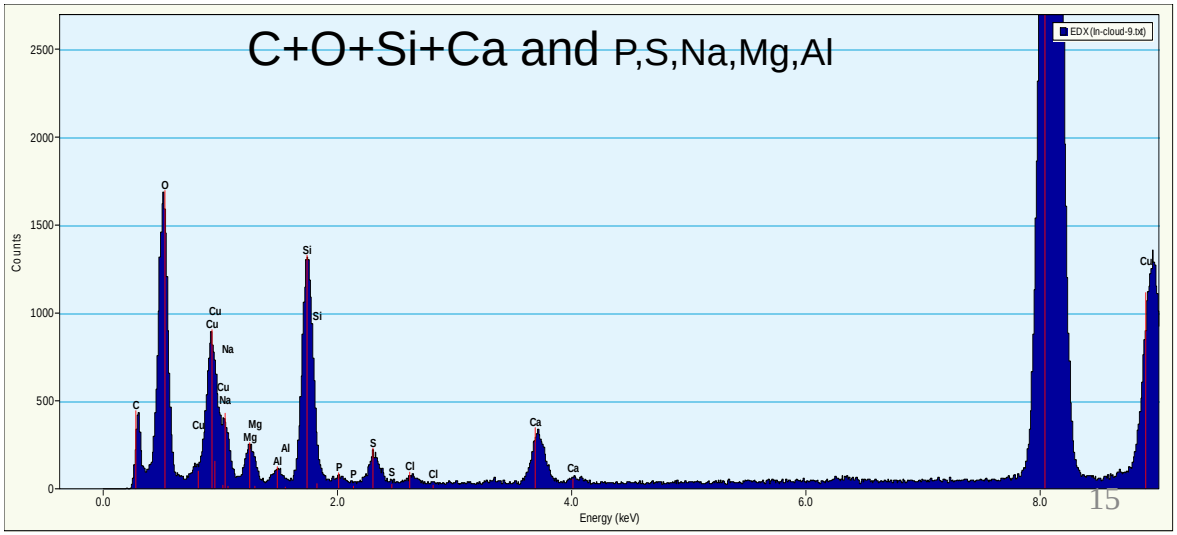
Influent to Potable Water Treatment Plant (WTP) - “between River and Tap Water”









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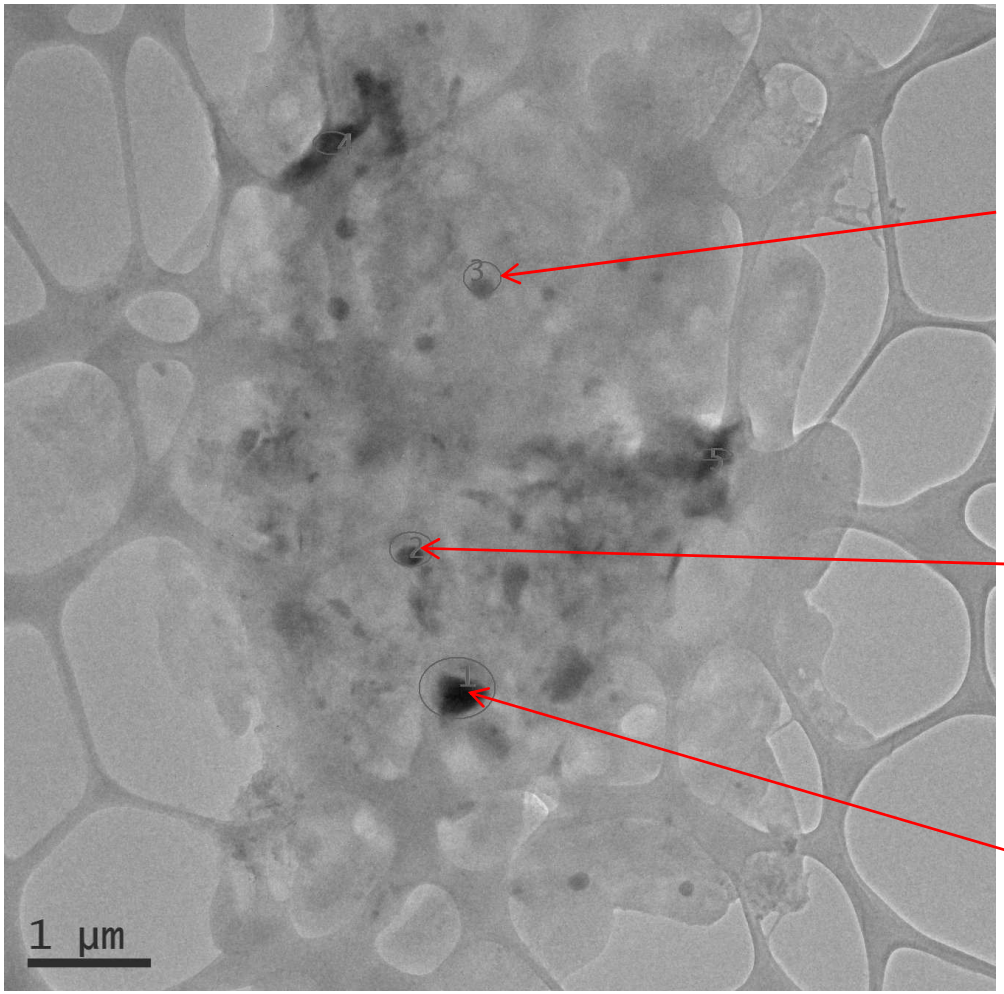
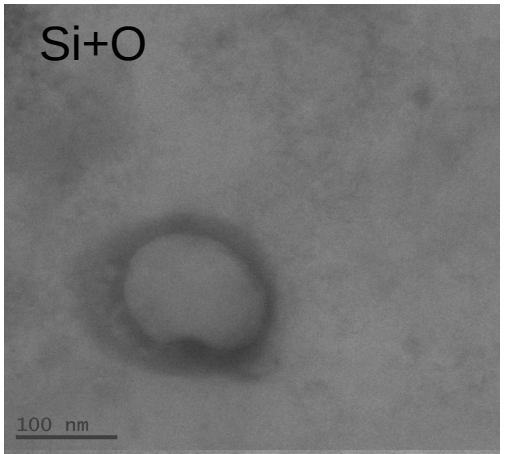
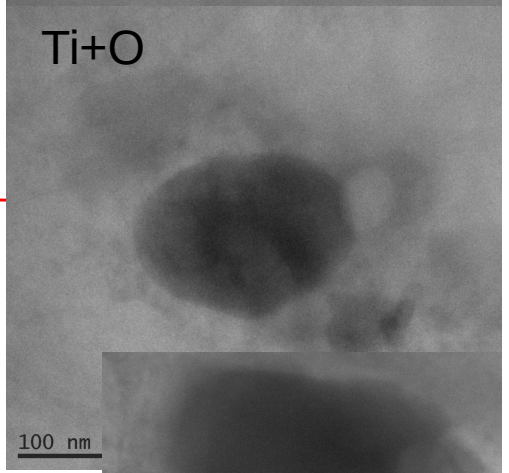
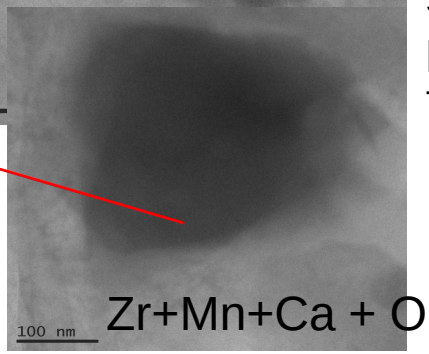
Particles in Tap Water









- One major advantages of CPE in characterization: particle enrichment

- Titanium and silicon containing particles were frequently found.

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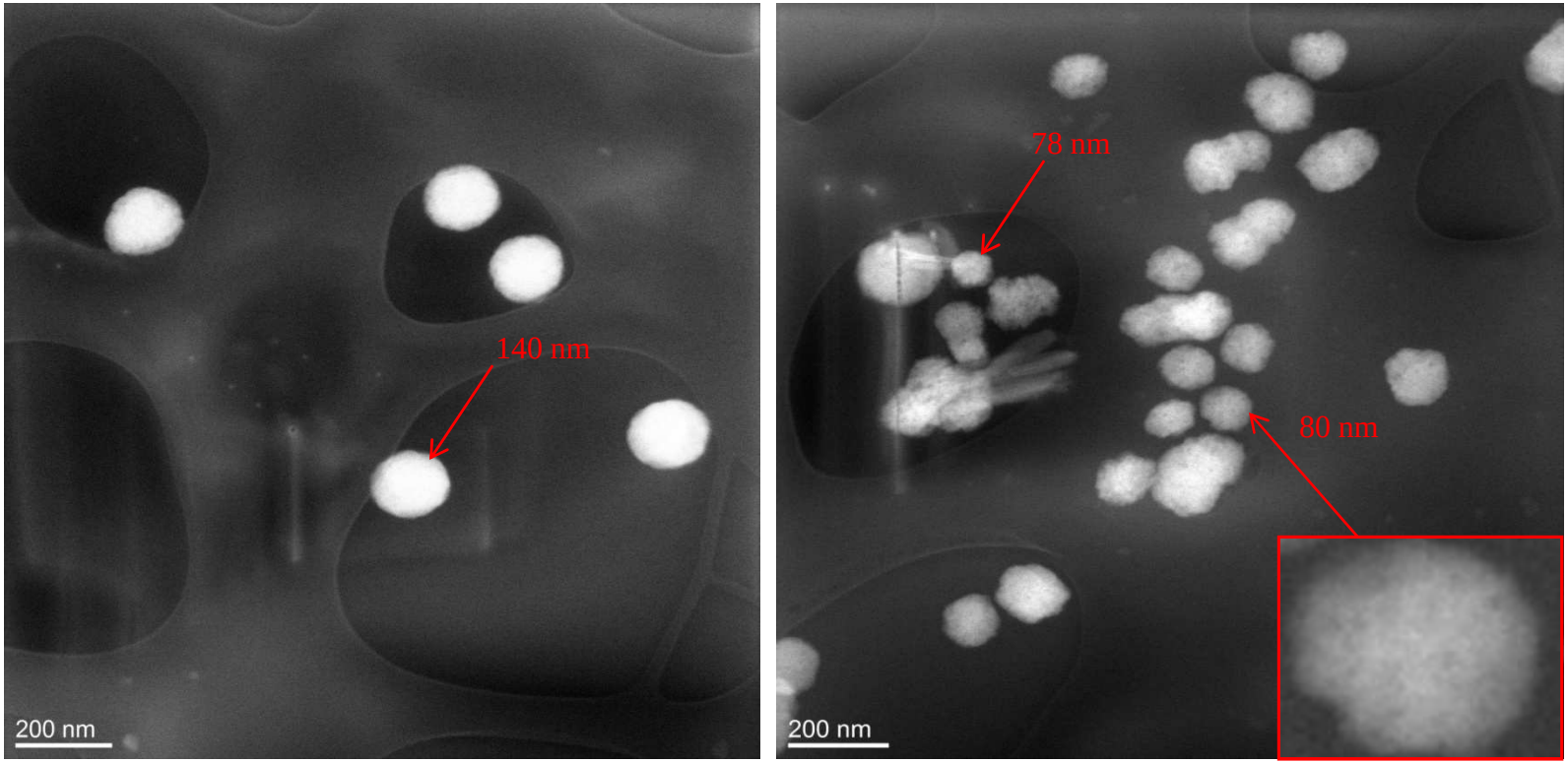
Nanoparticles from Arizona Wastewater Treatment Plants



Silica containing particles. The atomic ratios of elements →

C	O	Si	S	Ca
29	16	4	2	1

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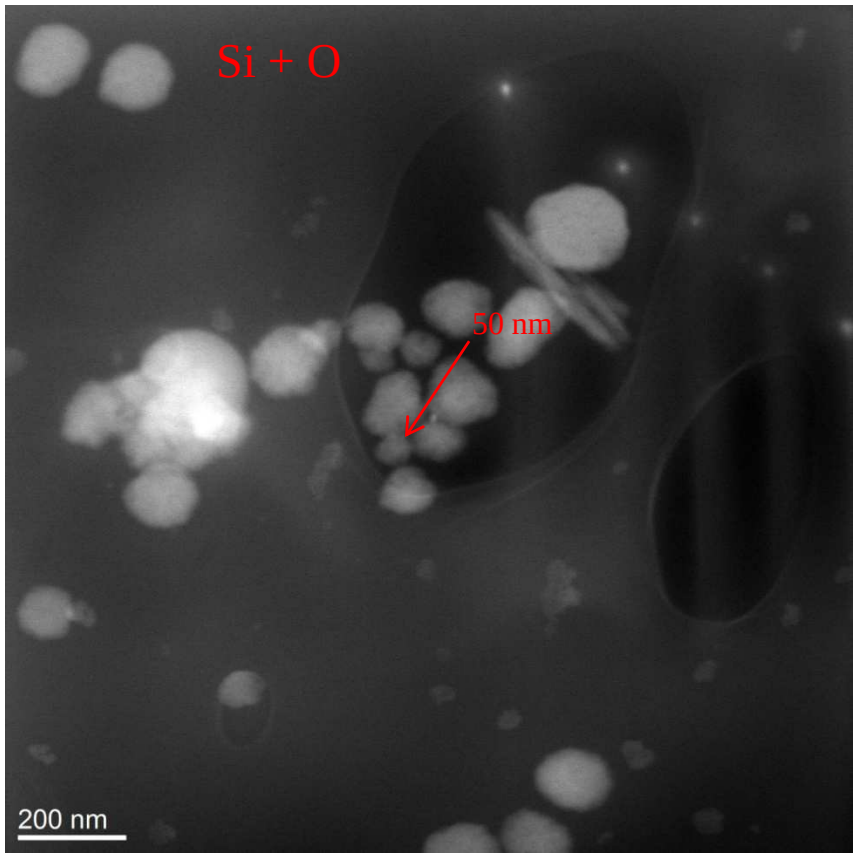
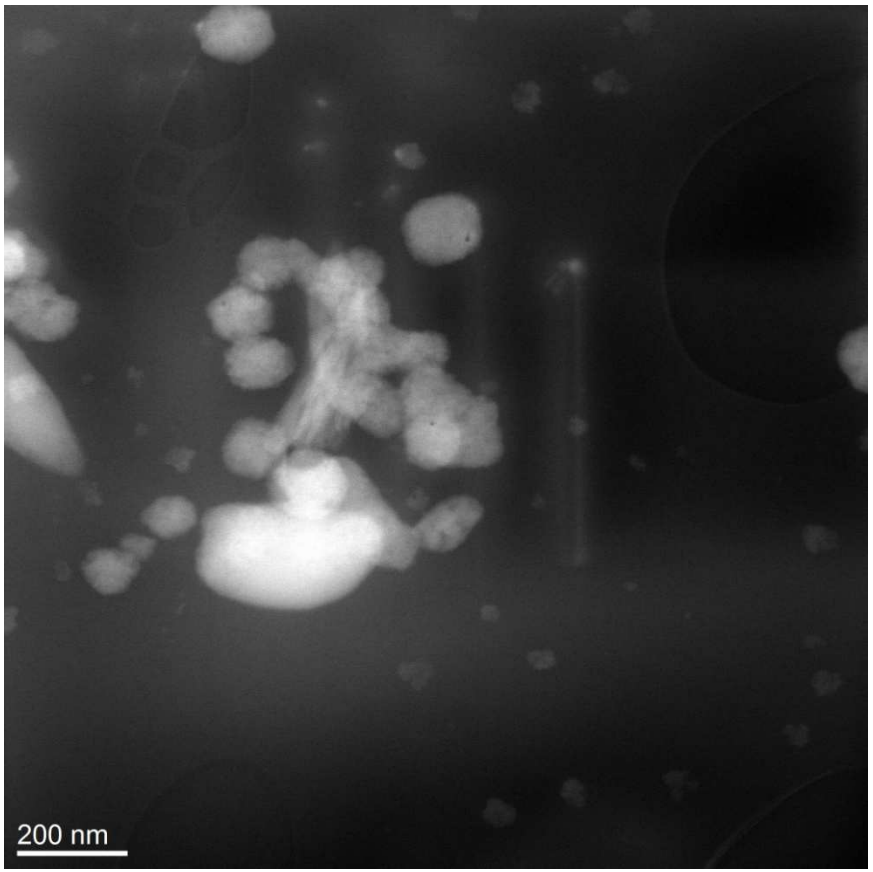
More Nano- and Micron- Silica particles in Wastewater





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Summary of all the Particles Found

Major elements detected by EDX of particulates(likely material)	Approximate Particulate Diameter (nm)	Location
Ti + O (Titanium dioxide)	4, 60 ± 12, 108	Salt, Verde River, Canal, and tap water
Si + O (Silica)	50 - 220	wastewater
C + Ca + O (Calcium carbonate)	61 - 109	River and tap water
Fe + C + O	93	River water
C+O+Si+Ca (Amorphous)	200 - 377	River, tape water, and wastewater
* No silver/gold particles were identified.		

Benefits over sp-ICP-MS : entire composition, shape, morphology of particles.

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Conclusions

- Cloud-point extraction (CPE) by Triton 114 demonstrated the ability to enrich gold nanoparticle from nanopure water about 18 times while preserving the size and shape.

- The most abundant nanoparticles identified so far were silica and titanium containing particles with diameter in the range 4-99 nm.

- Other nanoparticles ranged from 30-65 nm contained a list of major elements, including calcium, magnesium, aluminum, iron, oxygen, sulfur, carbon, and chloride.

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Future Work

- To determine the total metal concentration in cloud phase by ICP-OES, prospecting nanomaterial concentration in water.

  (e.g. concentration of silica NPs = Total concentration of silica × number of nano silica/ total number of silica particles).

- Apply CPE to semi-conductor waste streams, using simulated CMP wasted fluids after laboratory jar tests.

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