# Analysis of Particulate and Nanoparticles In Drinking Waters: Analytical Techniques, Interpretations and Considerations

December 8–10, 2020

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USEPA ORD CESER WID DWMB

virtual summit

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WATER QUALITY & INFRASTRUCTURE

# Objectives

- Why particle analysis is important
- Analytical methods
- Sample preparation techniques
- Strengths and weaknesses of analytical techniques

# Importance of Particle Analysis

- There is recognition that particulate material (chemical and biological) can be an important source of drinking water contamination.
- Particle analyses inform on source water issues, treatment effectiveness and distribution system issues.
- In the distribution systems (post precipitation- $CaCO_3$, corrosion - red water or lead)
- Particle properties can be important to the understanding how chemical treatment (e.g. orthophosphate) affects the system (predicting layers but forming particles)
- Particle analysis may indicate the source: e.g. lead particles associated with tin may point to the origin being solder joints not service lines

# Information Needed from Particle Analysis

- Morphology
- Size
- Elemental composition
- Mineralogy
- Charge
- Dispersion

# USEPA Advanced Materials and Solids Analysis Research Core (AMSARC)


## Electron Microscopes

- JEOL 6490 LV SEM Oxford Aztec EDS
- JEOL JEM7600 FESEM Oxford Aztec EDS
- JEOL 2100 TEM Oxford Aztec EDS Electron Diffraction

## Powdered X-ray Diffraction

- PANalytical X'pert Pro theta/theta X'celerator RTMS Detector

## Zeta Sizer

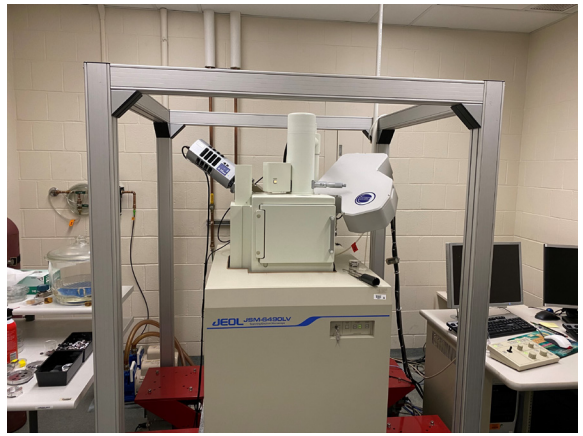
- Malvern PANalytical Zetasizer Nano-ZS90

# SEM Analysis

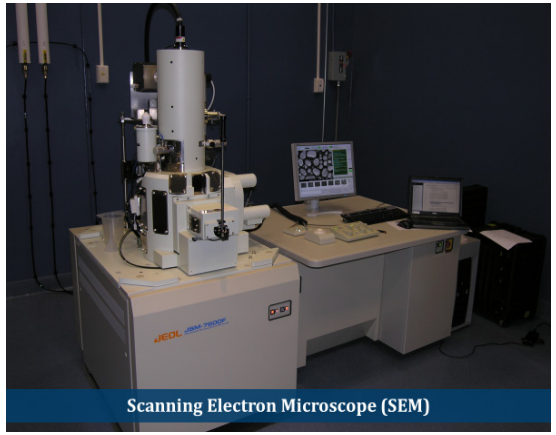
# What Data can SEM Provide?

- Morphology
- Size
- Elemental composition
- Mineralogy
- Charge
- Dispersion

# Scanning Electron Microscopy



**JEOL 6490 LV**

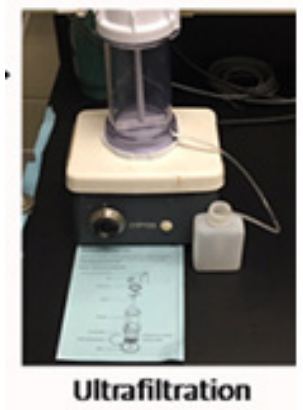



**JEOL JEM7600FE**

- Standard SEM. Magnification 10-300,000x. **Samples must be conductive to prevent charging**. Non-conductive samples are coated with metal (gold, palladium, chromium, carbon e.g.) Operated at high vacuum 1 Pa (10-3 Torr)
- Variable pressure SEM. Magnification ~10-150,000x. The beam becomes 'skirted' reducing resolution. Air or an inert gas is bled into the sample chamber to help reduce charging. **(No coating needed)** Operating pressures can approach 270 Pa (~2.03 Torr)
- Field Emission SEM. Very small probe size and high vacuum allow magnifications 50-1,000,000x. **Can analyze nanoparticles**. Some non-conductive samples can be examined with the use of gentle beam or backscatter electron detection

# Filtering for Particulate

0.2 µm syringe filter

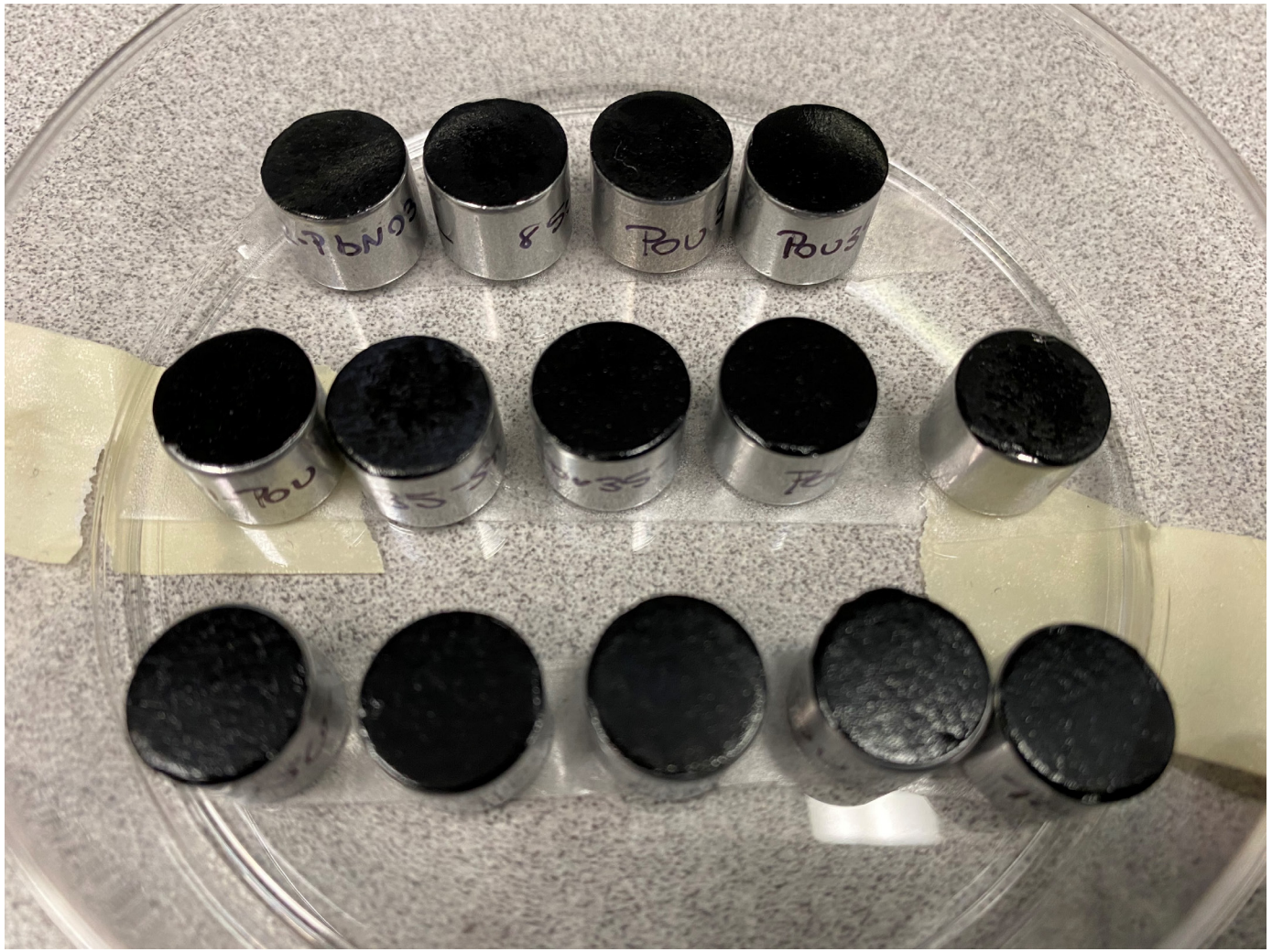


Ultrafiltration

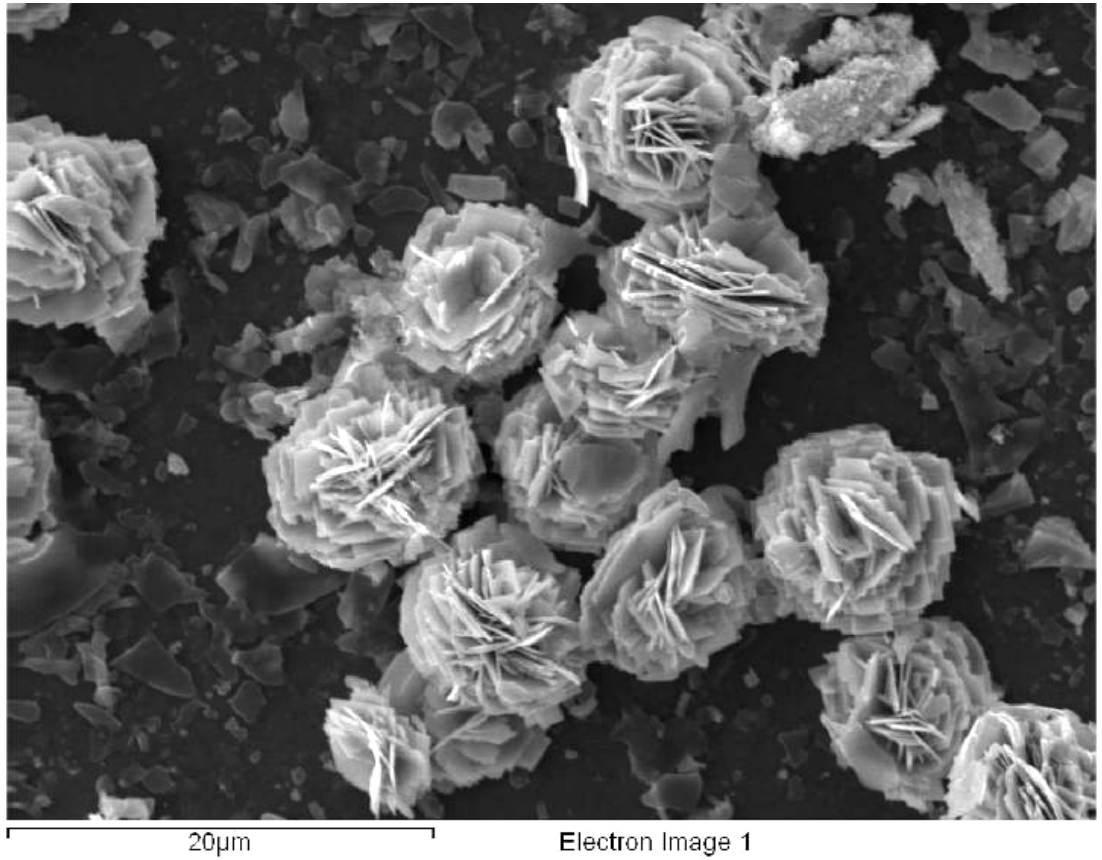
- Should be done in the field ASAP if possible
- Syringe Filter Filtration – 60 ml through 0.2 µm pore size
- Ultra-Filtration - ~100 ml through 30 kDa ultrafilter – est. pore size 0.01 µm
- retained particulate may be smaller than pore size due to clumping

# Sample Preparation

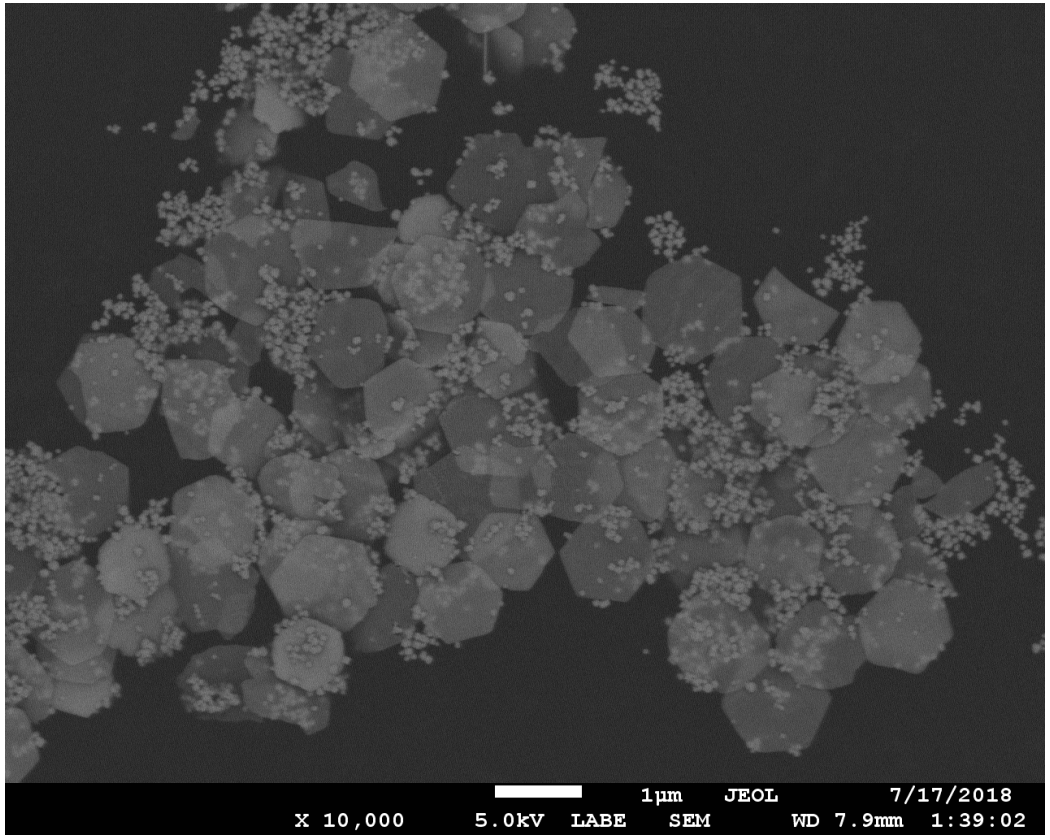
- SEM
  - Water filtered through preselected filter; particles may clump together resulting in retention
  - Filters harvested
  - Can analyze filter directly (limitations)
  - 12mm SEM stubs with adhesive carbon tabs dabbed on the filters to transfer particulate
  - (coated or uncoated)  issues with nanoparticles



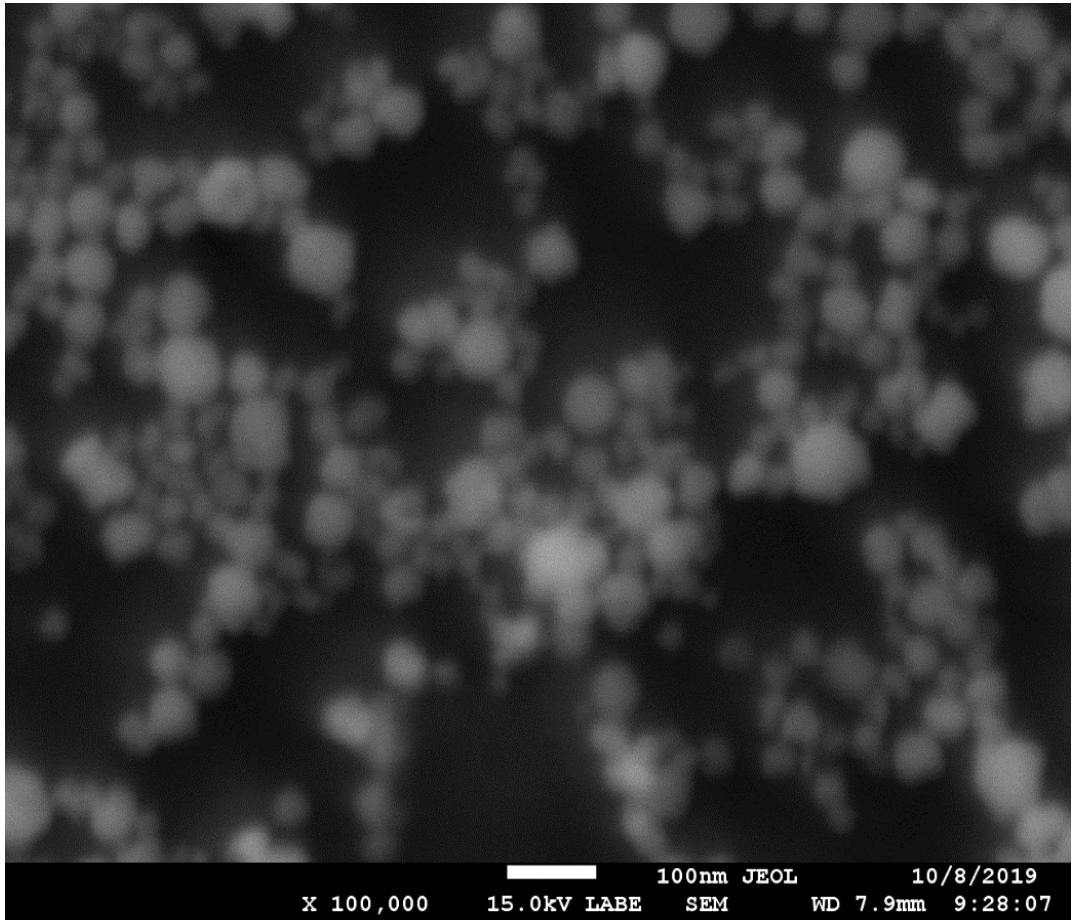
- 12mm SEM stubs with carbon tabs
- Particles transferred by touching carbon tab to filter

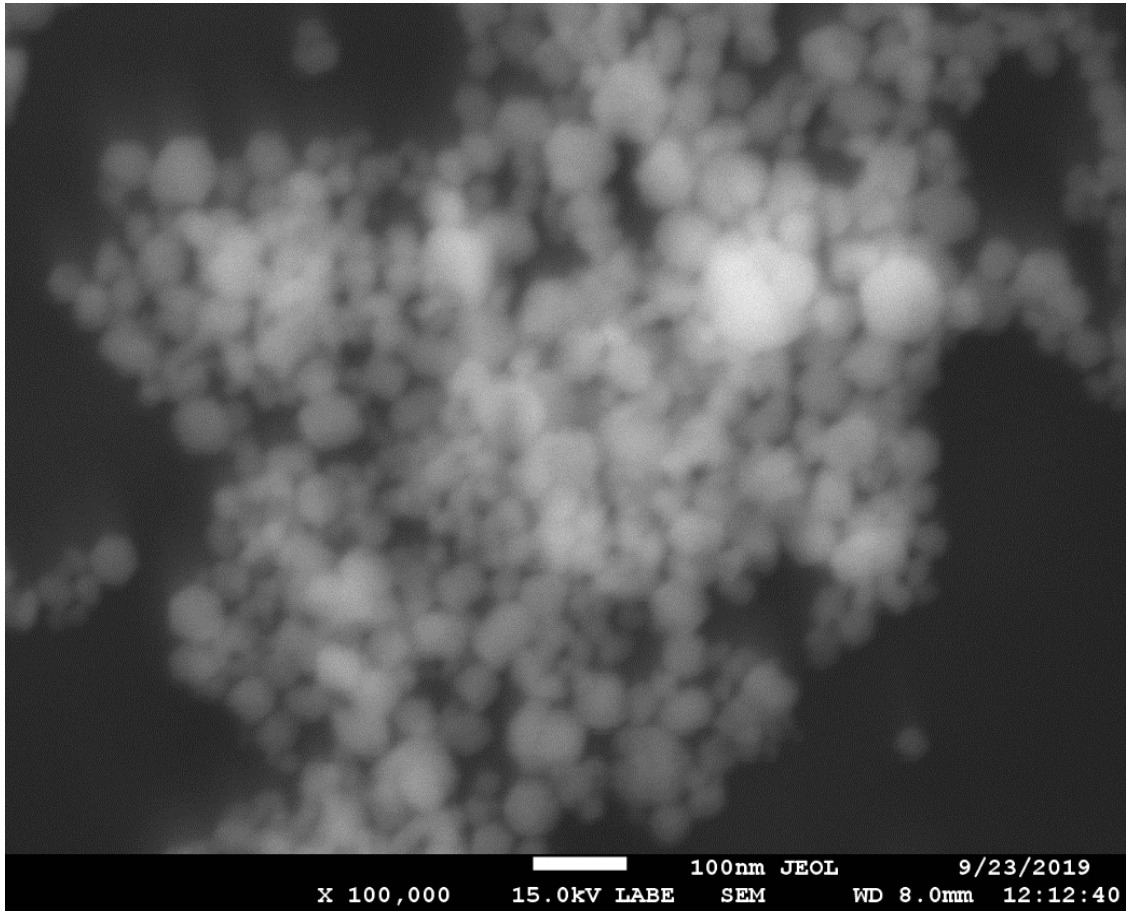



SEM micrograph of lead particles in the presence of pyrophosphate




FESEM LABE Micrograph of laboratory generated hydrocerussite (large particles) and pyromorphite (Small Particles)

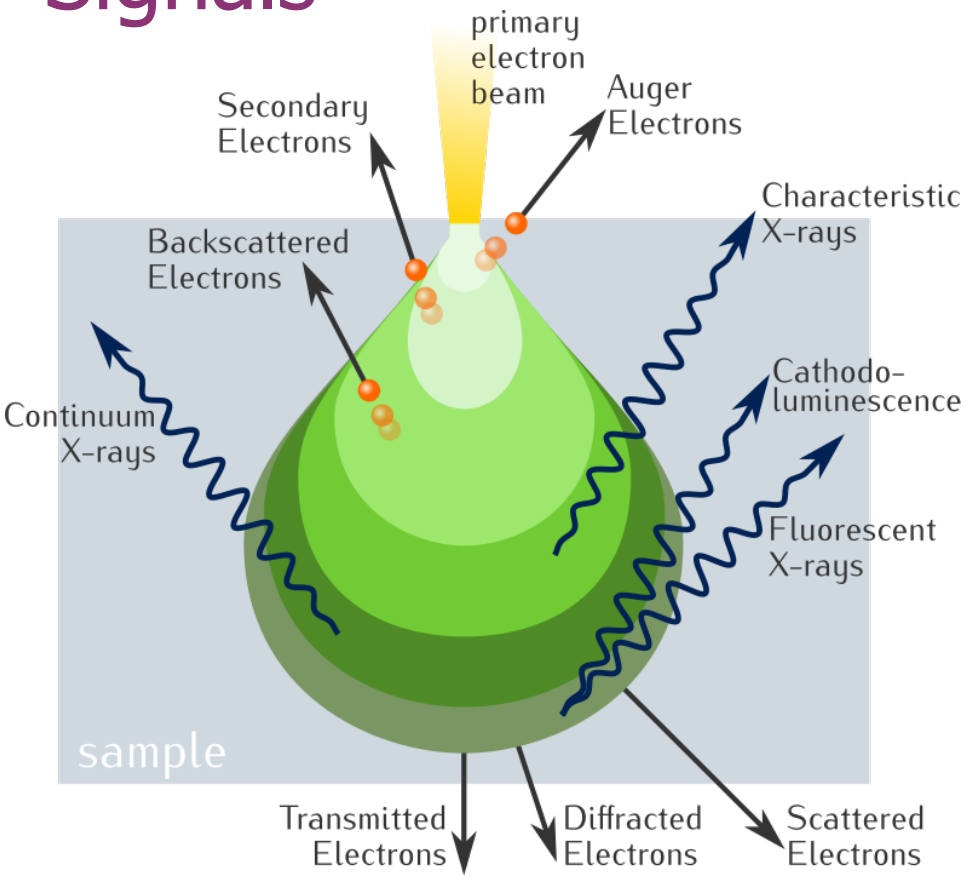


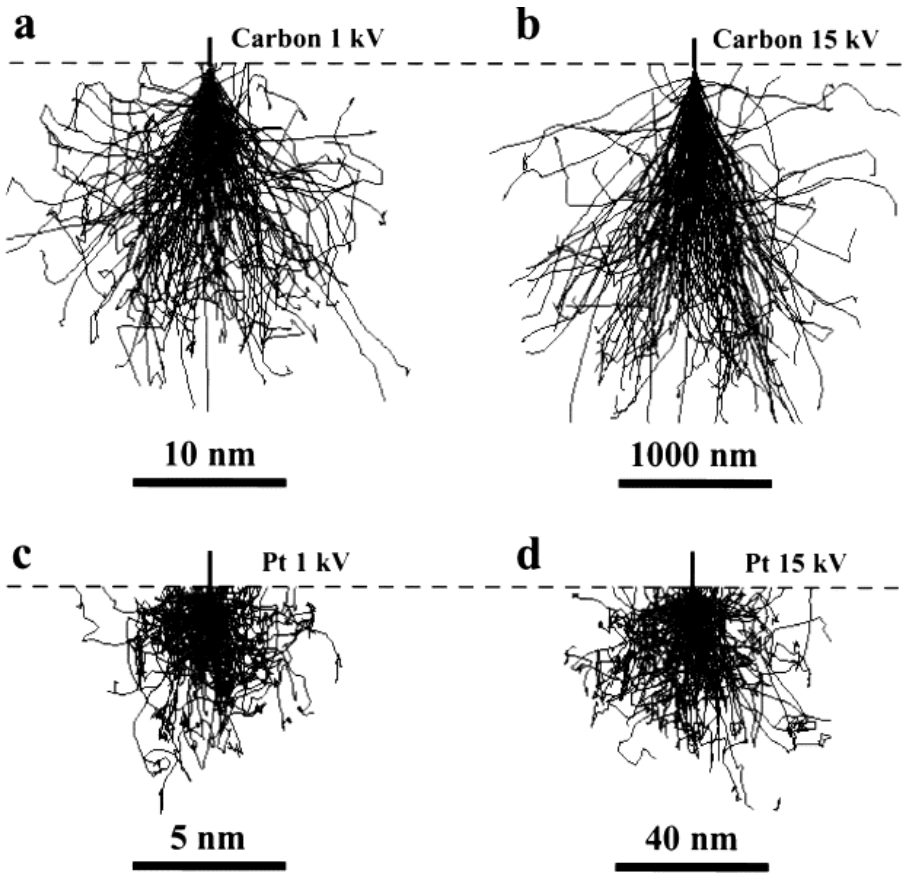




FESEM Backscatter micrographs from inhouse studies showing particle size and morphology

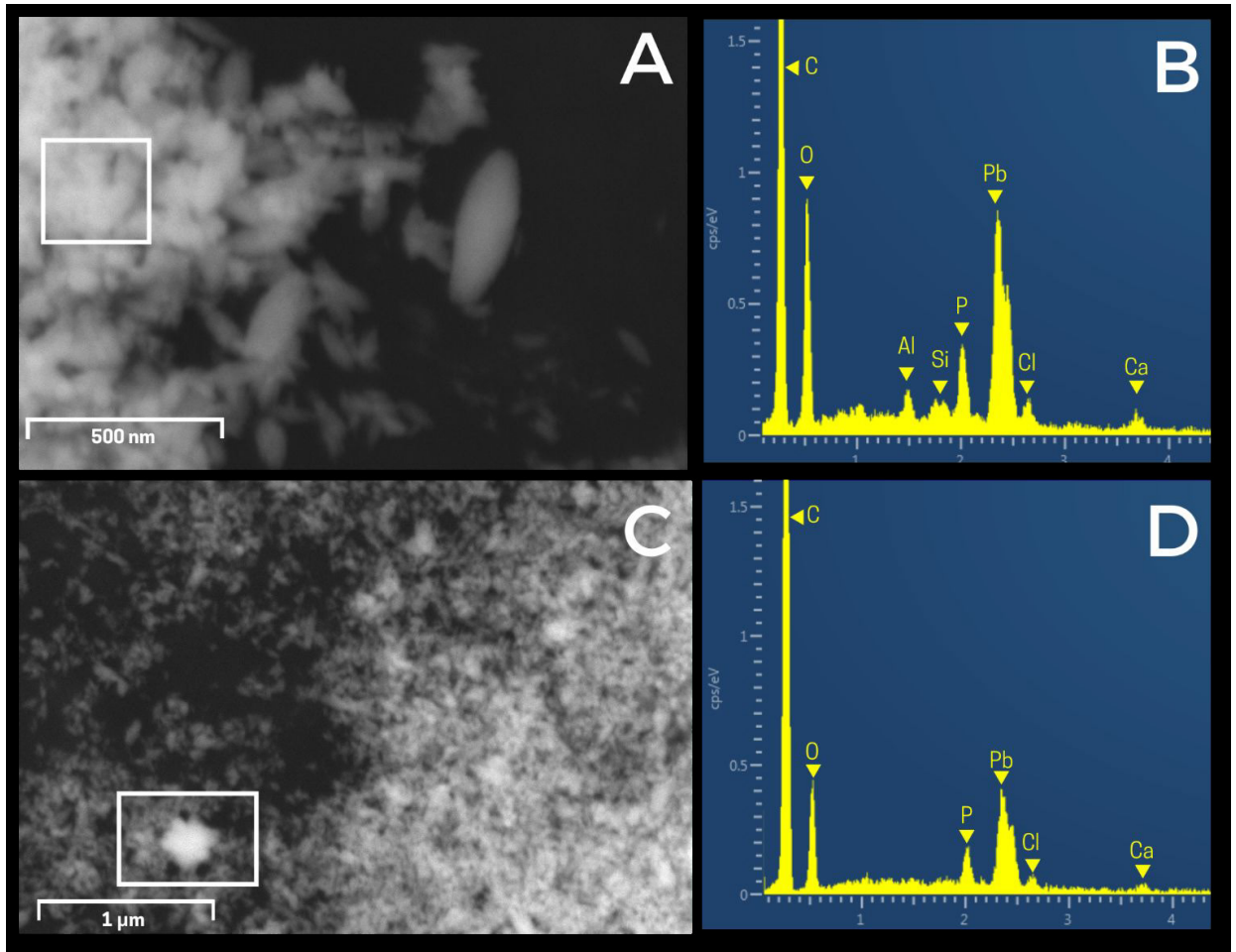
# SEM Qualitative EDS Analysis

# Electron Beam Interaction Volume and Characteristic Signals



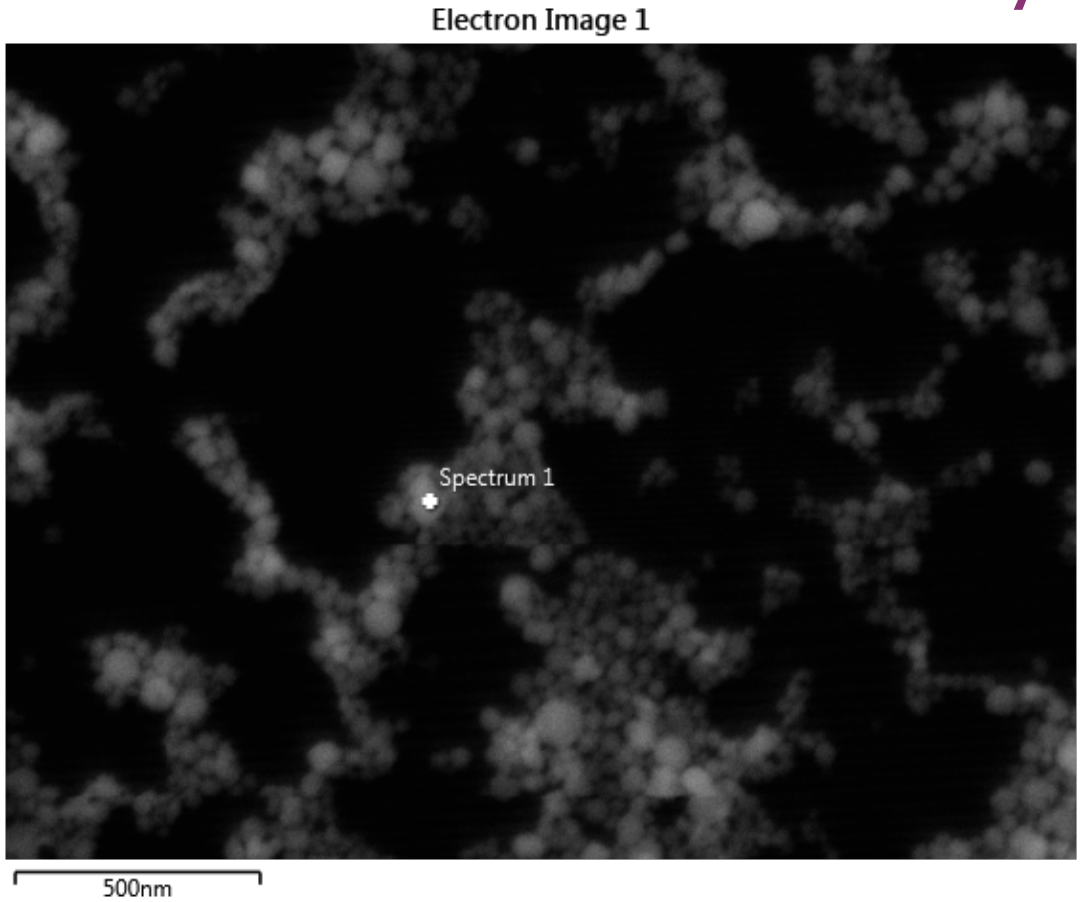



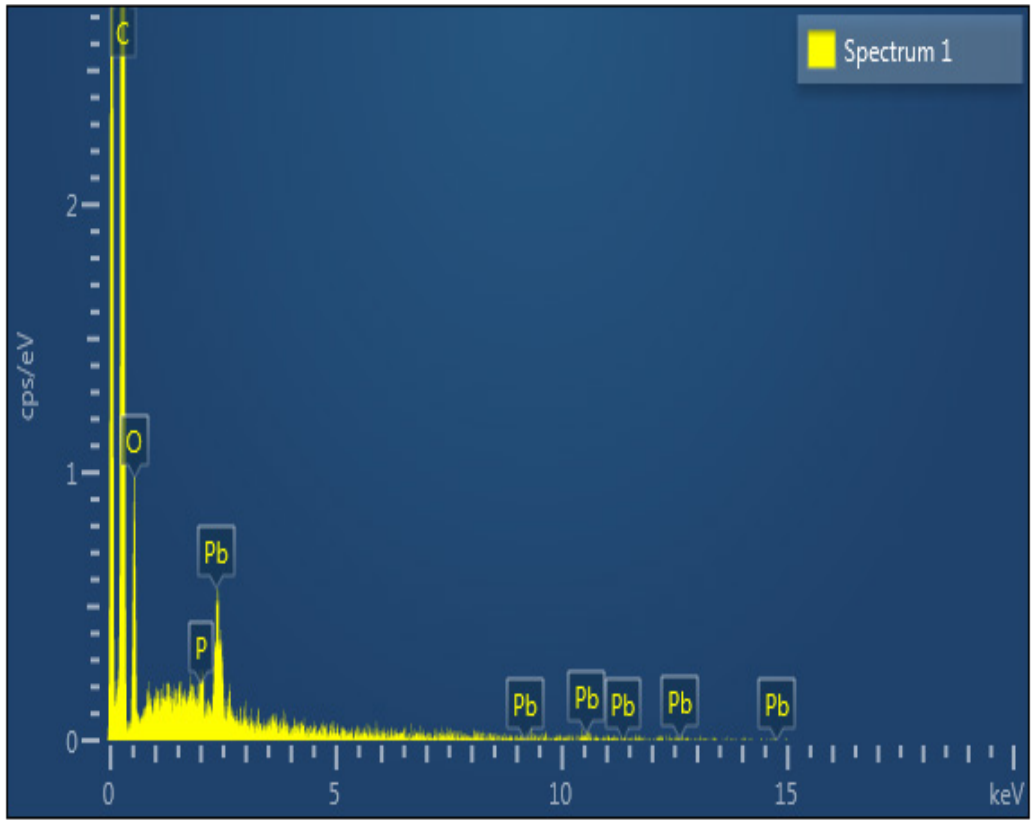
# FESEM EDS Particle Analysis from Field Experiment




- Field Emission Scanning Electron Micrographs with Energy Dispersive Spectroscopy Spectra
- Morphology
- Size
- Elemental composition

# FESEM EDS Particle Analysis from Lab Experiment



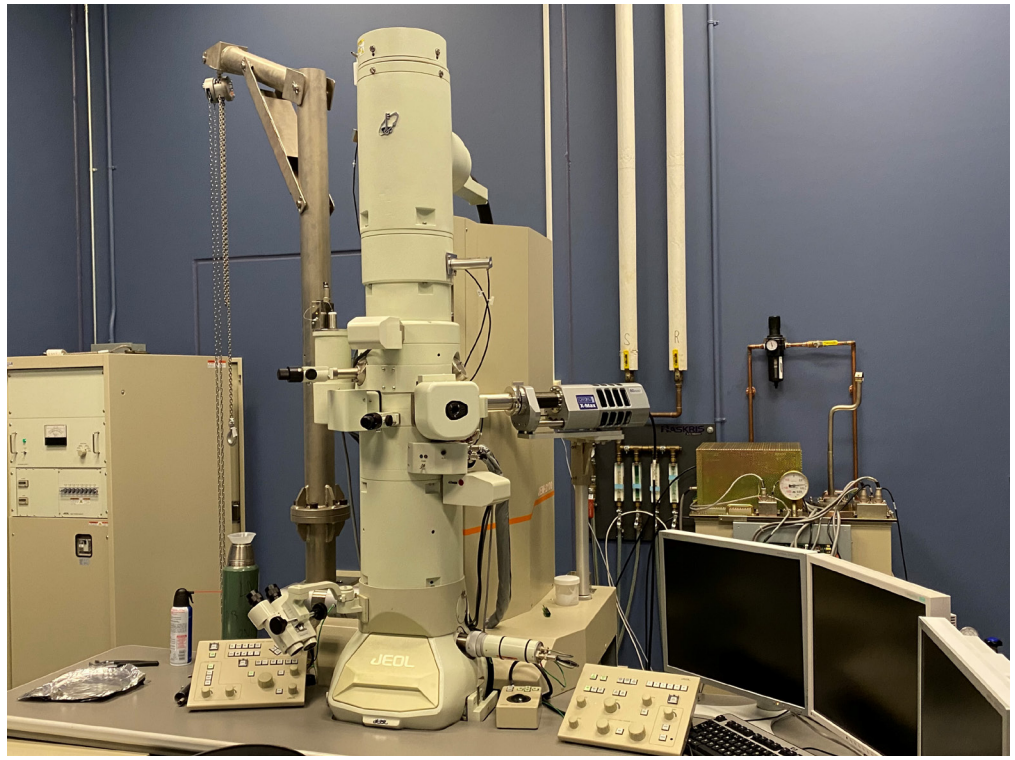

- Morphology
- Size
- Elemental composition

# TEM Analysis

# What Data can TEM Provide?

- Morphology
- Size
- Elemental composition
- Mineralogy
- Charge
- Dispersion

# Electron Microscopy

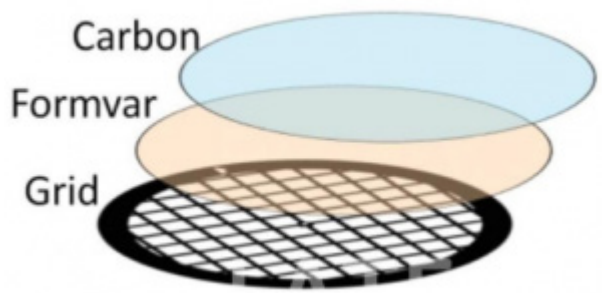



**JEOL JEM-2100 TEM**

- Transmission Electron Microscopy. Magnification 100-1,000,000x  Samples must be electron transparent to view internal structure.  Operated at high vacuum and 200kV.

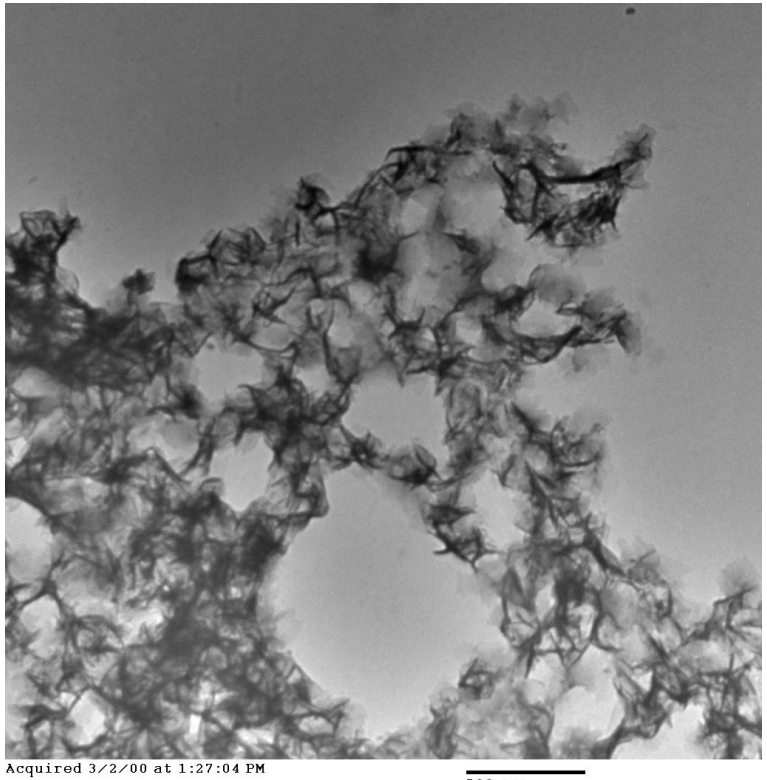
# Sample Preparation

**TEM**



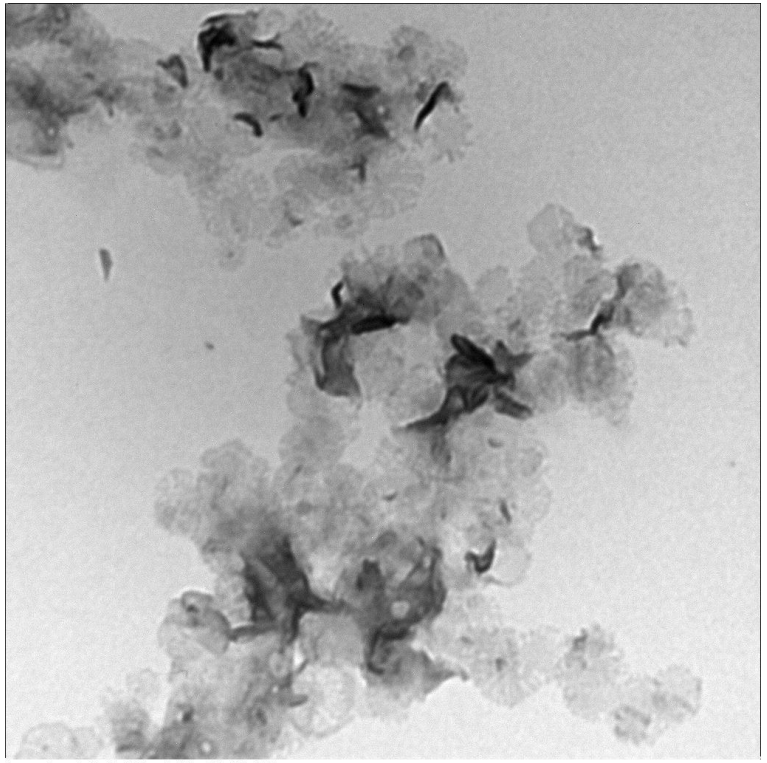

- 3 mm diameter copper grids with formvar and carbon coatings
- Grid held in place with self-closing forceps
- 1 mL polypropylene disposable pipette used to transfer 1 drop to grid.
- Incubated until water evaporated and particles left on grid

# TEM Micrographs of Iron Colloid Particles



Acquired 3/2/00 at 1:27:04 PM
0210000103

500 nm
TEM Mag = 25000 x
Print = 53997x @ 6.75 in
Instrument jeol 1200ex



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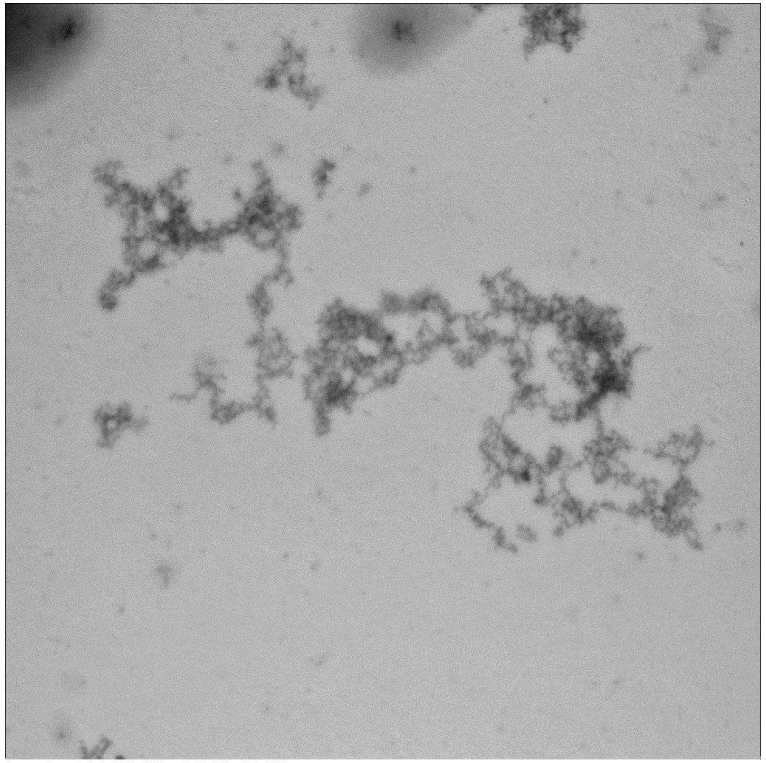
02240004

100 nm
TEM Mag = 50000 x
Print = 107993x @ 6.75 in
Instrument jeol 1200ex



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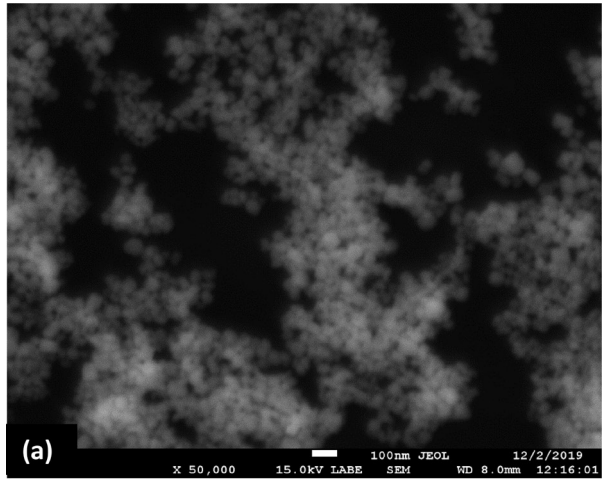
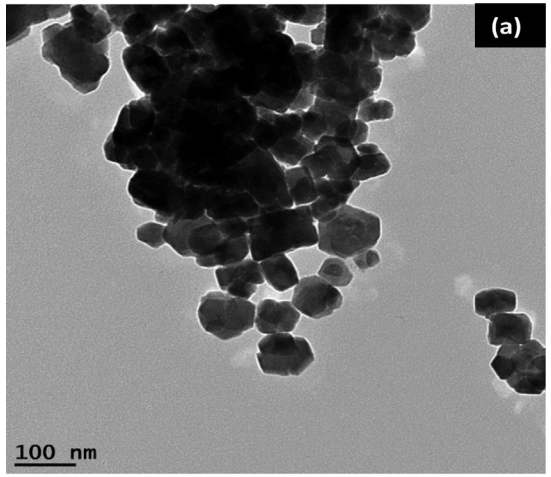
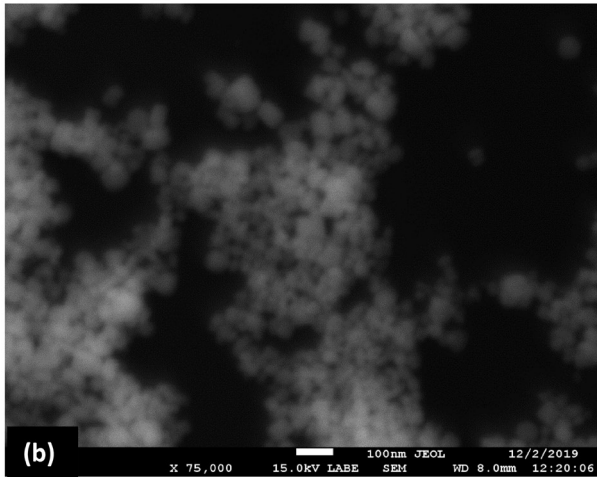
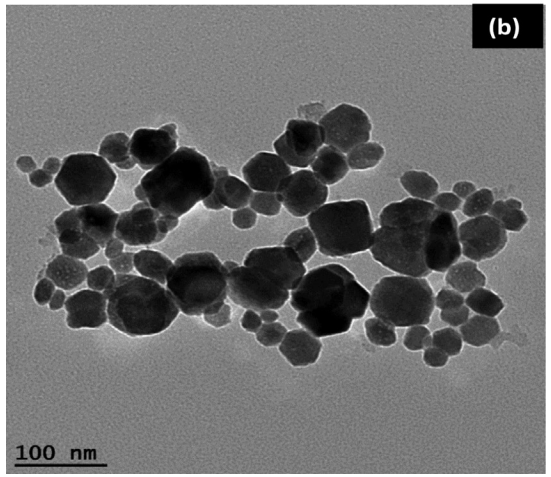
500 nm
TEM Mag = 12000 x
Print = 26878x @ 7 in
Instrument jeol 1200ex

# Comparison FESEM and TEM



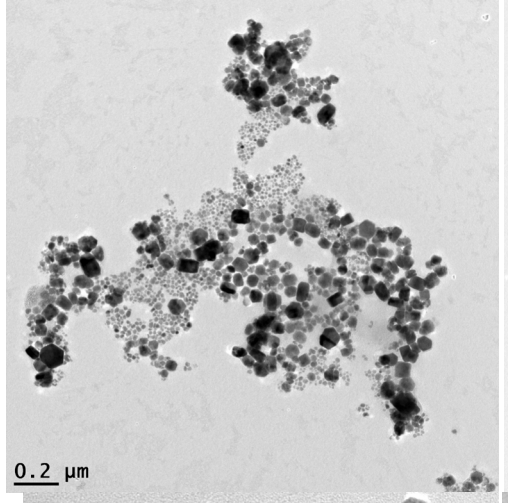



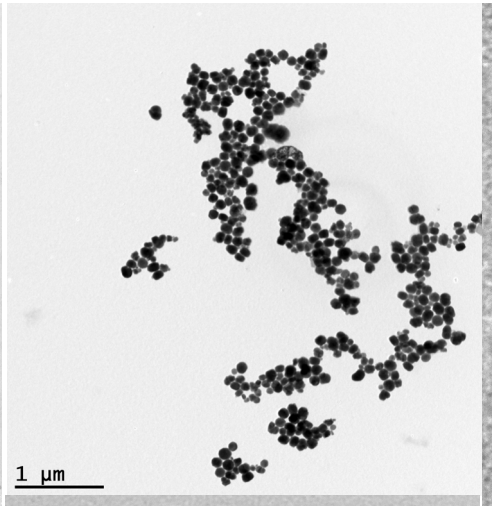



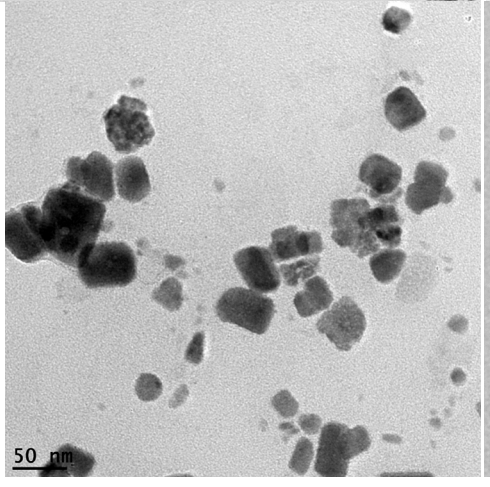



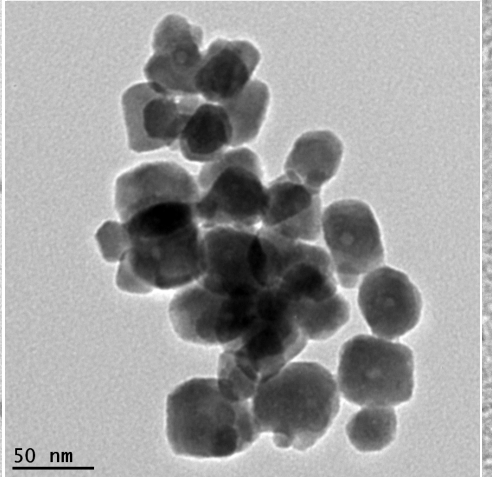

- Laboratory generated lead nanoparticles
- Morphology of individual nanoparticles clearly visible by TEM

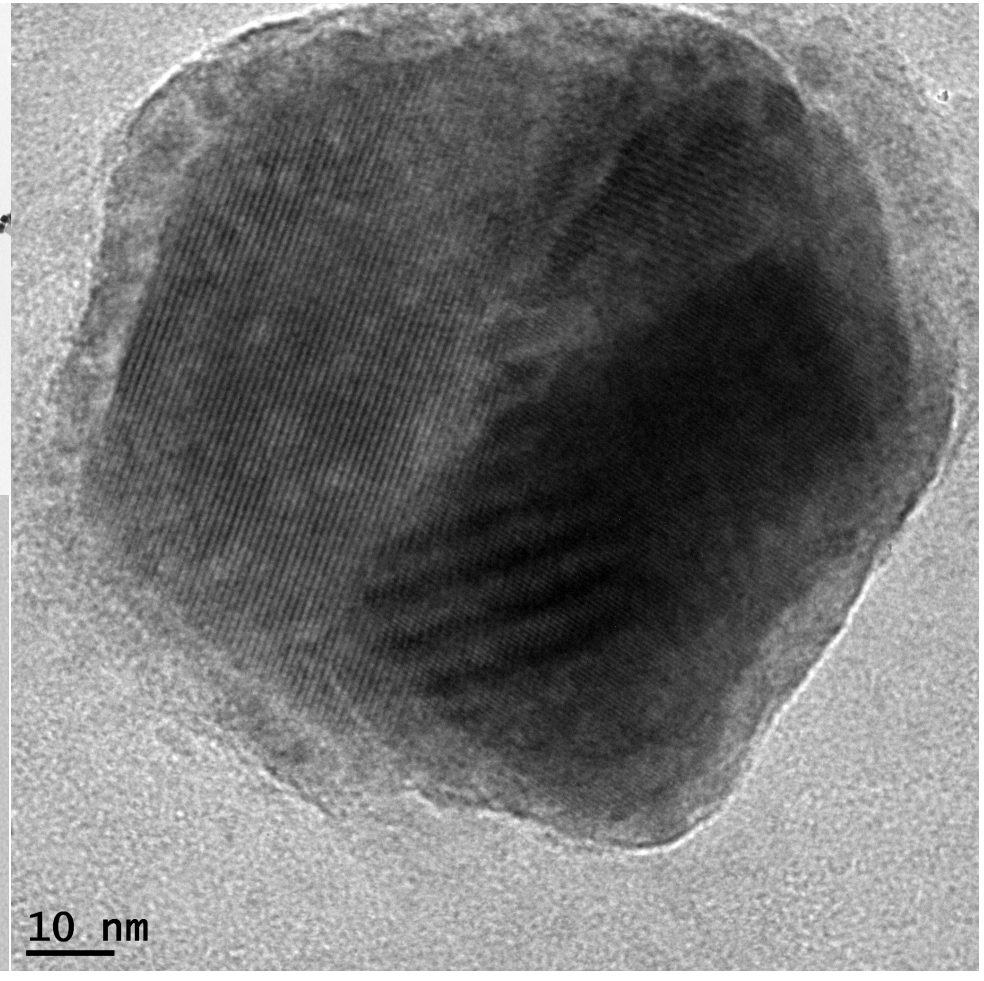
# TEM Micrographs of Particles



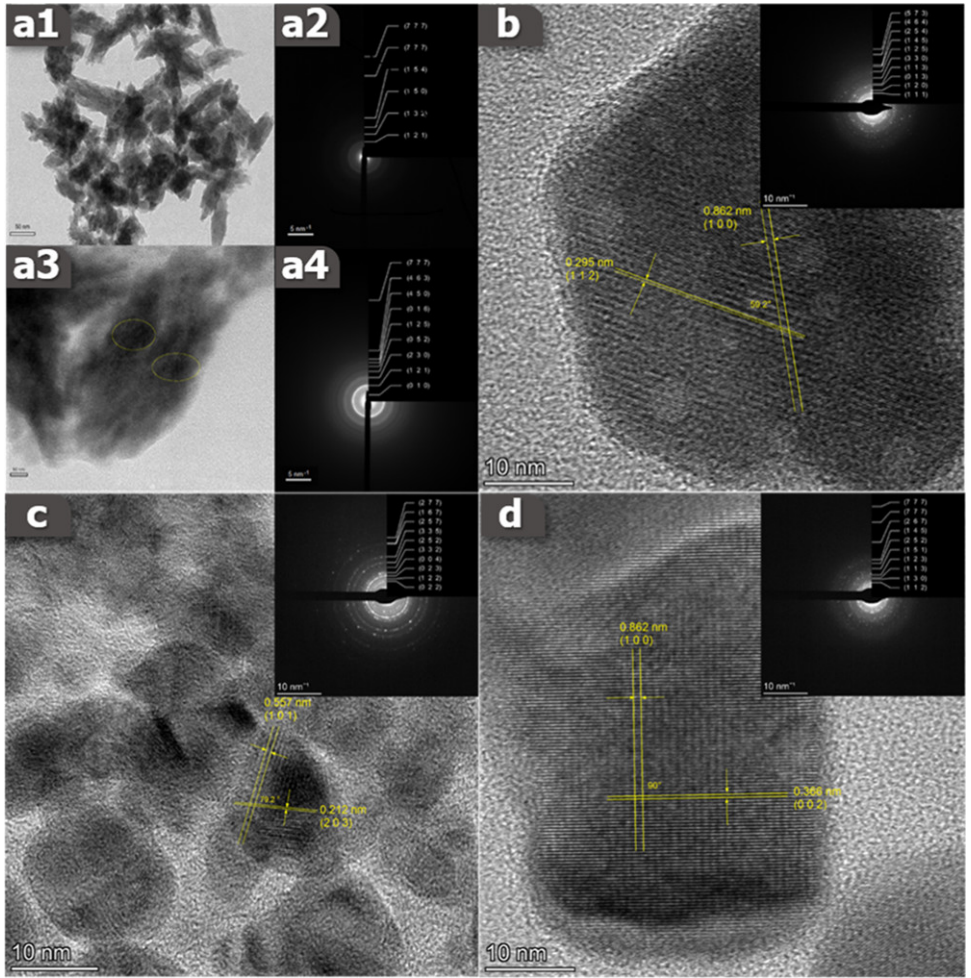




- Lead Particles
- Higher resolution than FESEM
- Crystal lattice visible

# TEM Micrographs with Electron Diffraction



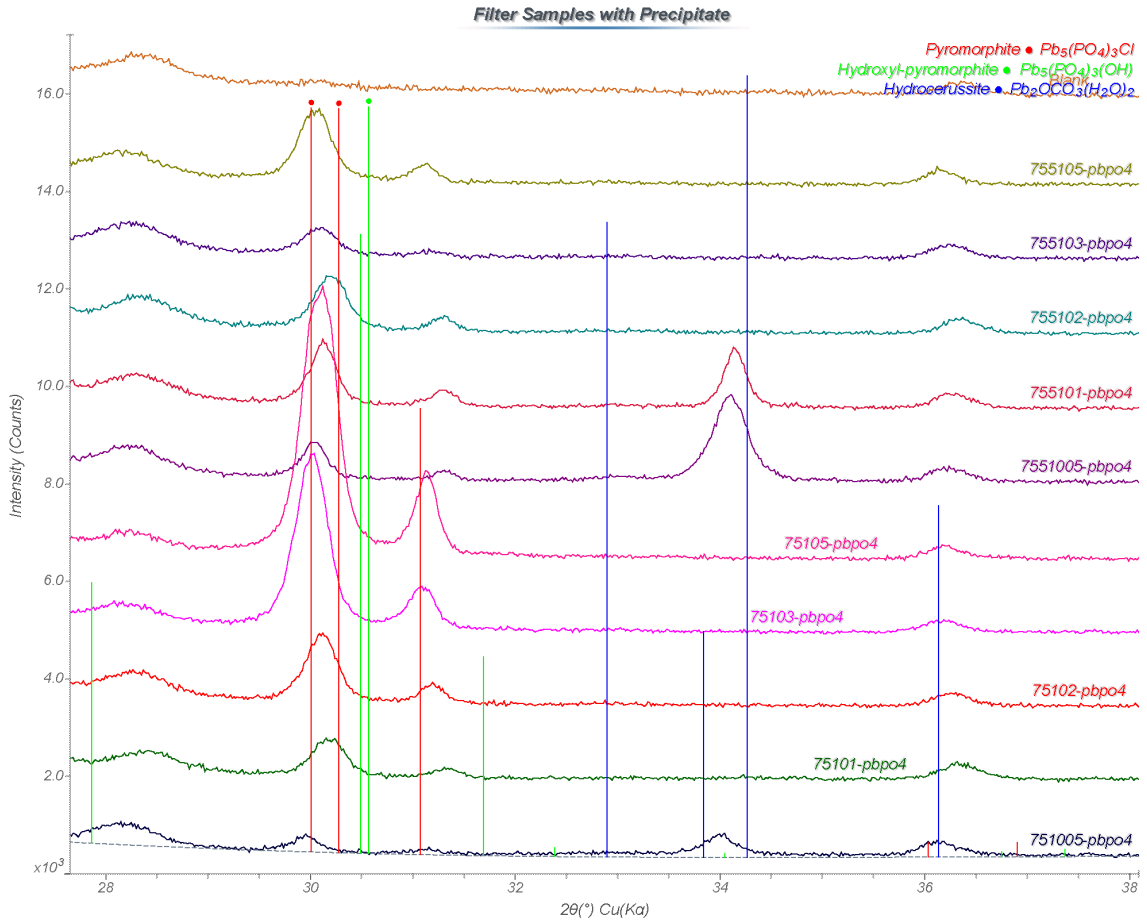

- Lead Nanoparticles
- ImageJ was used to process images
- CrysTBox subprogram of MATLAB used for electron diffraction analysis
- All four samples here indexed to pyromorphite

# Powder X-ray Diffraction

# What Data can Powdered XRD Provide?

- Morphology
- Size
- Elemental composition
- Mineralogy
- Charge
- Dispersion

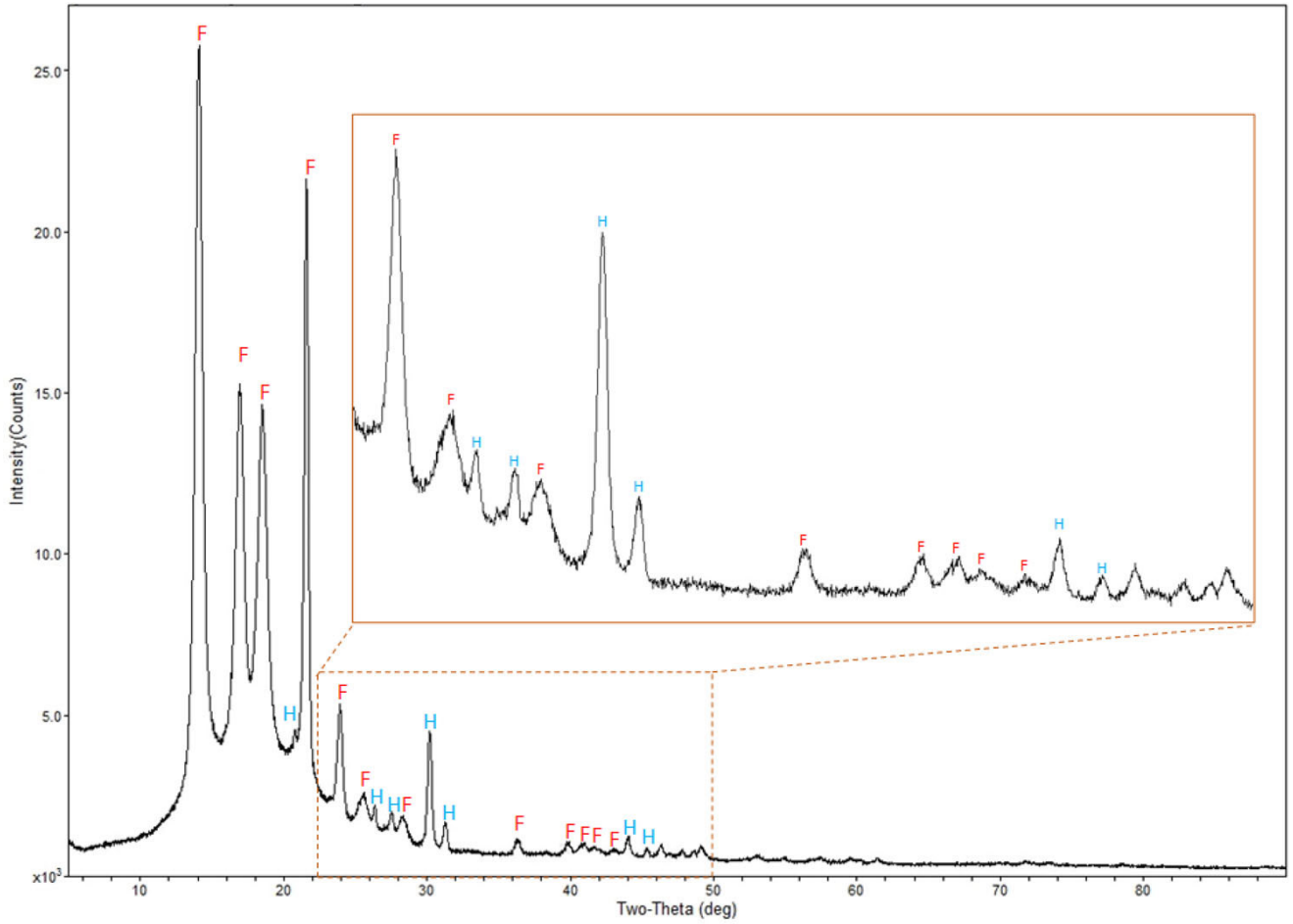
# Powdered X-ray Diffraction




751005-pbpo4

- Series of XRD tracings of lead particles on filters
  - Filters cut and directly mounted to XRD sample holders
  - The small size of the particles cause line broadening which make identification difficult
  - Filter itself has identifiable peaks which complicate material

# Powdered X-ray Diffraction




- Filters removed and directly analyzed
  - Software can give particle size estimations
  - The small size of the particles cause line broadening which make identification difficult
  - Filter itself has many identifiable peaks which complicate analysis.
  - Filtration can cause preferred orientation issues (analysis assumes random orientation)

# Zeta Sizer

# What data can Zetasizer Provide?

- Morphology
- Size
- Elemental composition
- Mineralogy
- Charge
- Dispersion

# Malvern PANalytical Zetasizer Nano-ZS90

- Measure the **particle size** of dispersed systems from sub-nanometer to several micrometers in diameter, using the technique of Dynamic Light Scattering (DLS).

- Dynamic Light Scattering (also known as PCS - Photon Correlation Spectroscopy) measures Brownian motion and relates this to the size of the particles. It does this by illuminating the particles with a laser and analysing the intensity fluctuations in the scattered light.
- Need high concentration of particles of the same composition.  Limited use outside lab studies

# Analytical Comparisons

# Particle Size Analytical Method Comparison

| | Zetasizer | SEM | TEM | XRD |
|---|---|---|---|---|
| | Average (nm) | Average (nm) | Average (nm) | Average (nm) |
| **Pyromorphite** | 82±47 | 68±6 | 63±21 | 28±5 |

# Conventional SEM

- Strength
  - Ease of sample preparation
  - Very little sample required
  - Secondary and backscatter emission imaging
  - Moderate skill needed to prep. and run samples.  Considerably more experience necessary for complicated matrixes
  - Semi-quantitation standardless EDS analyses
  - X-ray mapping showing in situ elemental concentrations
- Weakness
  - Samples must be coated (except LV)
  - Sample must be beam stable
  - Resolution not enough for nanoparticle work
  - Skirting of the beam in LV mode makes resolution worse and complicates EDS

# FESEM

- Strength
  - **Can resolve and analyze nanoparticles**
  - Relative ease of sample preparation
  - Very little sample required
  - Secondary and backscatter emission imaging
  - Semi-quantitation standardless analyses for many materials
  - X-ray mapping showing in situ elemental concentrations
- Weakness
  - Sample must be non-magnetic and firmly attached to stubs (high vacuum)
  - Sample must be beam stable
  - Non-coated samples can be run in backscatter mode, but the scanning speed is very slow and makes the analysis **TEDIOUS!**
  - Experienced analyst

# TEM

- Strength
  - Can easily resolve and analyze nanoparticles
  - Very little sample required
  - Semi-quantitation standardless EDS for many materials
  - **Can resolve crystal lattice and use electron diffraction for identification**
- Weakness
  - Sample must be electron transparent
  - 3mm grids can be difficult to handle
  - Sample must be beam stable
  - Analysis is time consuming
  - Experienced analyst
  - Elemental data is qualitative on nanoparticles (beam volume)

# Powdered X-Ray Diffraction

- Strength
  - Ease of sample preparation
  - Well established automated searchable database for automated peak matching
  - Moderate skill needed to prep. and run samples. Considerably more experience necessary for complicated mixtures, substituted metastable compounds
  - Particle size estimates
- Weakness
  - Samples must be crystalline
  - Requires a fair amount of sample. Assumes infinite thickness
  - Filter material can cause spurious peaks
  - Nanoparticles cause line-broadening
  - Preferred orientation can cause departures from reference patterns

# Zetasizer

- Strength
  - Ease of sample preparation
  - Estimate of particle size
  - Estimate of particle shape
- Weakness
  - Needs larger abundance of particles than are usually present in distribution system
  - Will average the size of all particles . . . Works best with one general particle size
  - Generally limited to laboratory studies

# Summary

- Why particle analysis is important
- Analytical methods
- Sample preparation techniques
- Strengths and weaknesses of analytical techniques

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# Stephen M. Harmon
## Physical Scientist

**Physical Scientist at the United States Environmental Protection Agency, Office of Research and Development, Center for Emergency Solutions and Emergency Response, Water Infrastructure Division, Drinking Water Management Branch**

**29 years of experience doing analytical chemistry and materials analysis concentrating on drinking water distribution system materials, corrosion, deposits and particle analysis. Areas of specialization include: powdered X-ray diffraction, X-ray fluorescence spectroscopy, scanning electron microscopy with energy dispersive spectroscopy, and transmission electron microscopy with energy dispersive spectroscopy. Currently a primary investigator and USEPA's AMSARC facility in Cincinnati, OH.**

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