

## Background and Opportunity

- Pesticides containing nanoparticles are becoming increasingly common, but their behavior in the environment and their toxicological effects on aquatic organisms are largely unknown
- Current methods for pesticide characterization may not be applicable to those that contain nanoparticles
- Nanopesticide formulations contain both nano and micro fractions such as those seen in Figure 1. These need to be separated to determine their contribution to the fate, transport, and toxicity of the pesticide

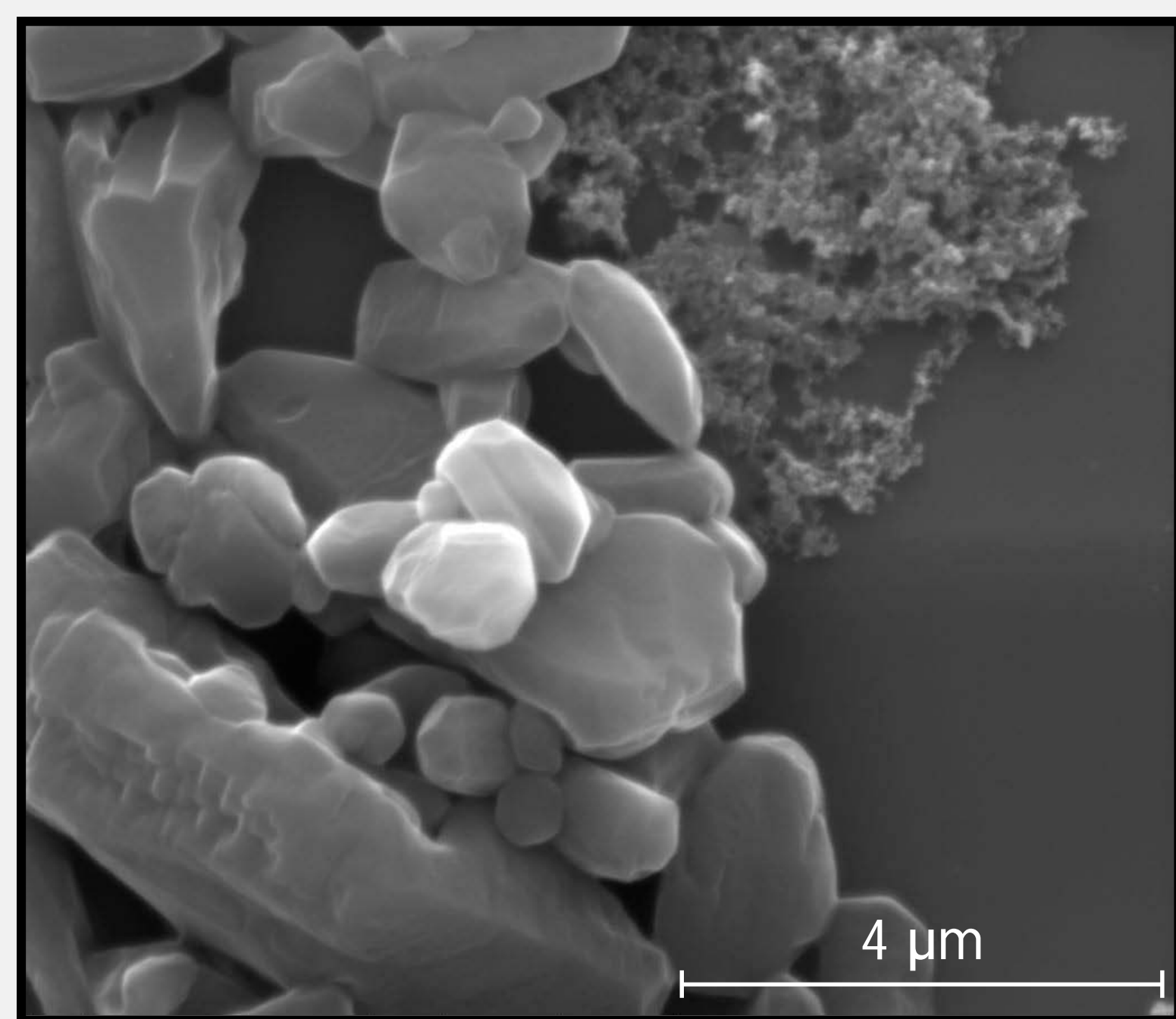


Figure 1: Tempo SC pesticide scanning electron microscope image at 4 μm scale. Note the presence of large particles in the foreground and smaller agglomerated particles in the back.

## Objectives

- Develop fractionation methods for several pesticides
- Characterize micro and nano fractions based on concentration of active ingredient (AI)
  - Nano less than 1 micron
  - Micro greater than 1 micron
- Investigate fate and transport of fractions in water column

# Fractionation of Nanopesticides and their Stability in Environmental Matrices

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## Materials and Methods

### Pesticides

- Optimate CS
- Cyonara 9.7
- Tempo SC
- Safari
- Bravo Weatherstik

### Fractionation

- Centrifugation
- Filtration

Centrifuge speed and time determined using Stoke's Law for particle settling to estimate centrifuge time.

$$v_p = \frac{g d_p^2 (\rho_p - \rho_f)}{18 \mu}$$

- $d_p$  - particle diameter
- $\rho$  - density
- $\mu$  - viscosity

### Characterization

- Dynamic Light Scattering (DLS)
- Spectrophotometry
- Scanning Electron Microscopy (SEM)

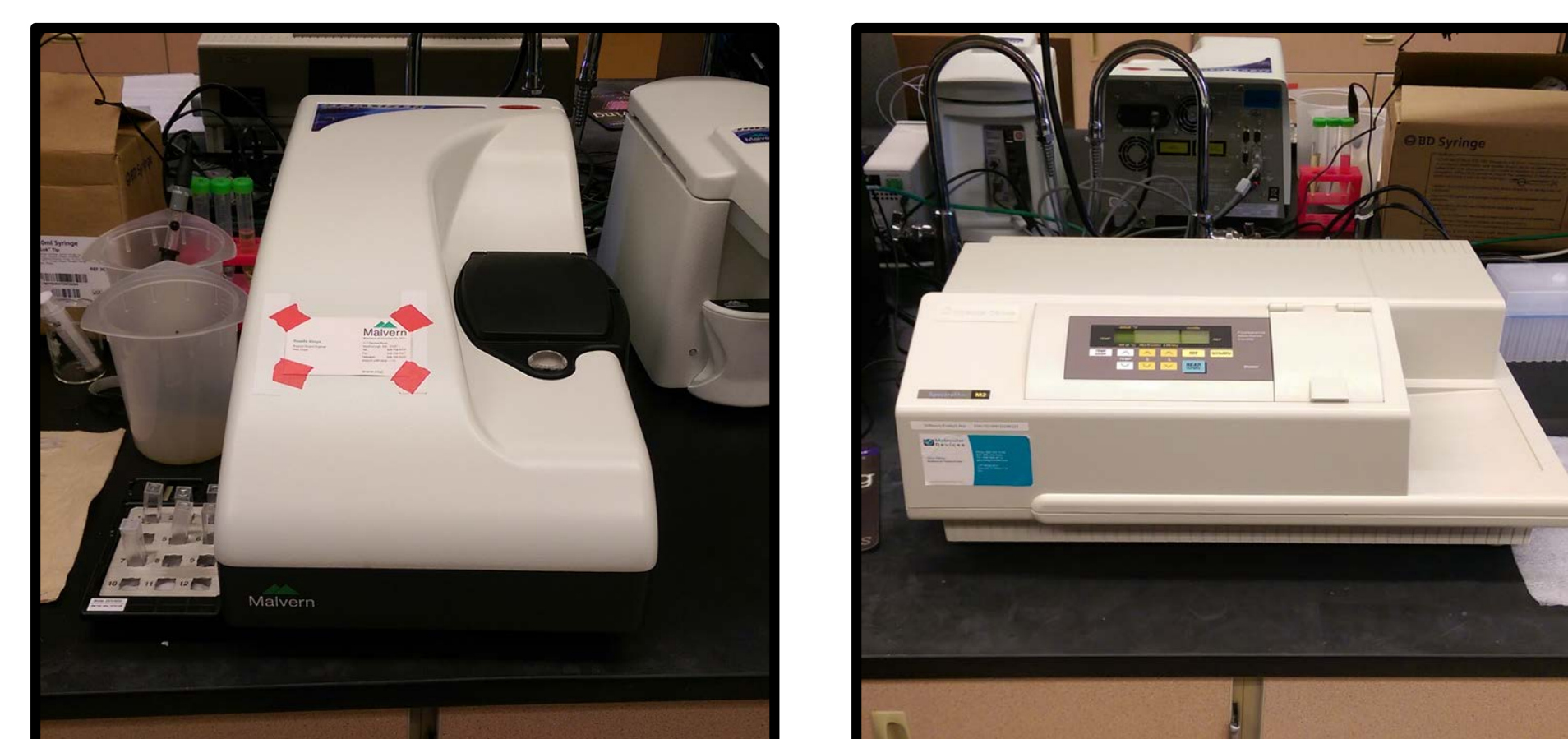


Figure 2: Malvern DLS (left) and spectrophotometer (right) used to determine particle size and concentration of AI respectively.

Concentration of AI determined using spectrophotometer. Beer's Law relates concentration to absorbance, the molar extinction coefficient, and path length.

$$A = \epsilon b c$$

- A - Absorbance
- $\epsilon$  - Molar Extinction Coefficient [ $L \text{ mol}^{-1} \text{ cm}^{-1}$ ]
- c - concentration

## Stability Testing

- Make the concentration of AI equal in fractions to test in separate matrices
- Water
- Water with salt
- Water with salt and humic acid
- Measure size, zeta potential, pH, and turbidity over five days

## Results

The size of each fraction decreased with centrifugation and filtration as shown in Figures 3 and 4.

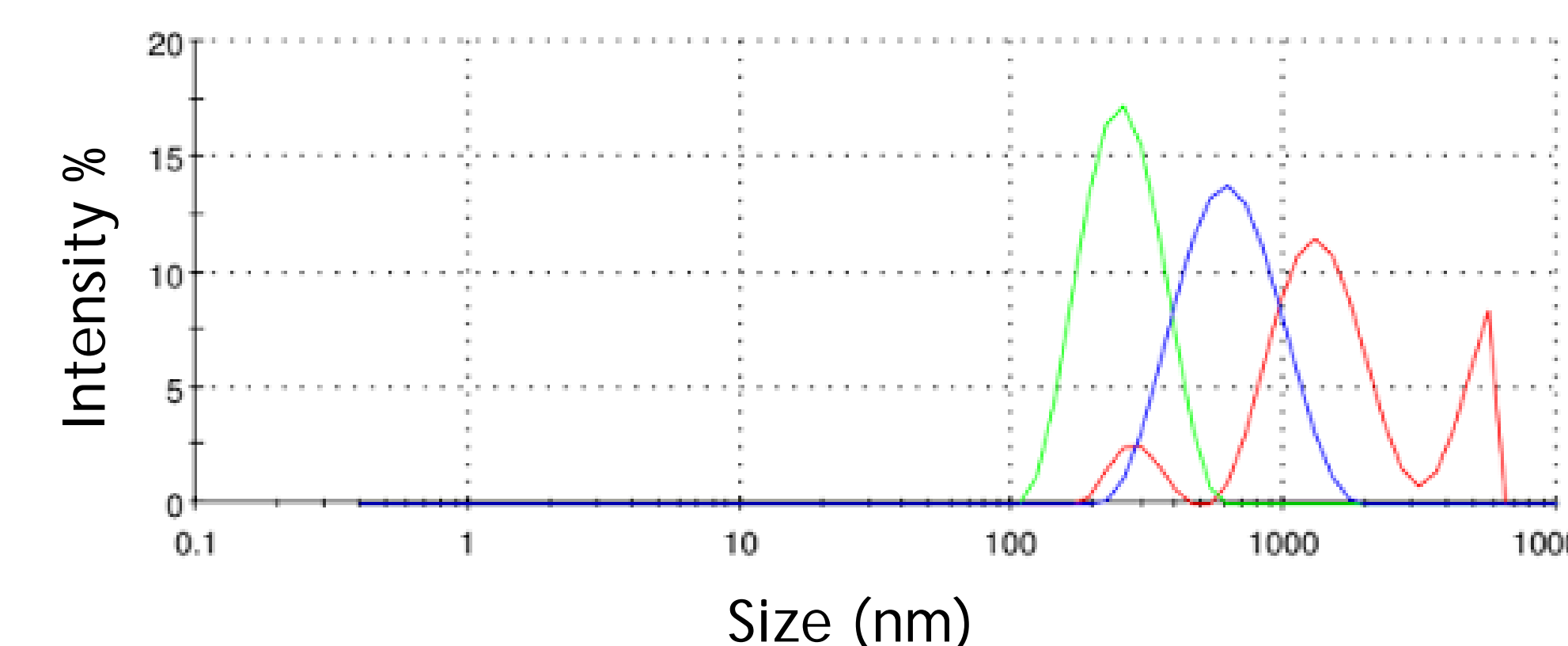


Figure 3: Size distribution of complete (red), centrifuged (blue), and filtered (green) fractions of Optimate CS.

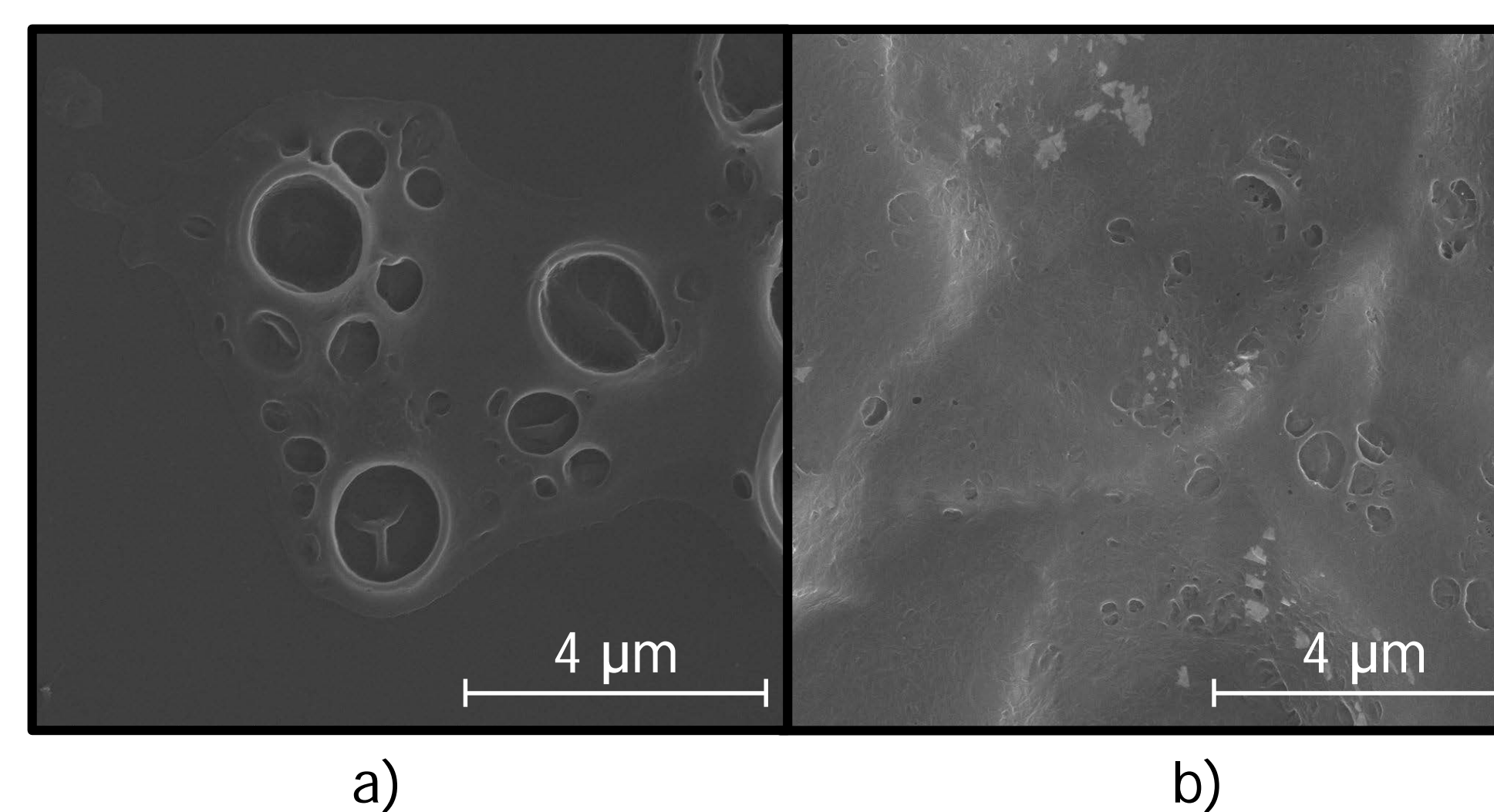


Figure 4: SEM images of a) complete formulation and b) micro fraction of Optimate CS at 4 μm scale. The lack of larger encapsulations in the micro fraction indicates they were removed during centrifugation.

- Calibration curves created in spectrophotometer for each pesticide
- Optimate and Bravo pesticides presented non-linear curves and cannot be characterized by spectrophotometer

## Results Continued

AI in Cyonara micro and nano fractions determined to be approximately 14% and 86% of complete based on results from standard curve.

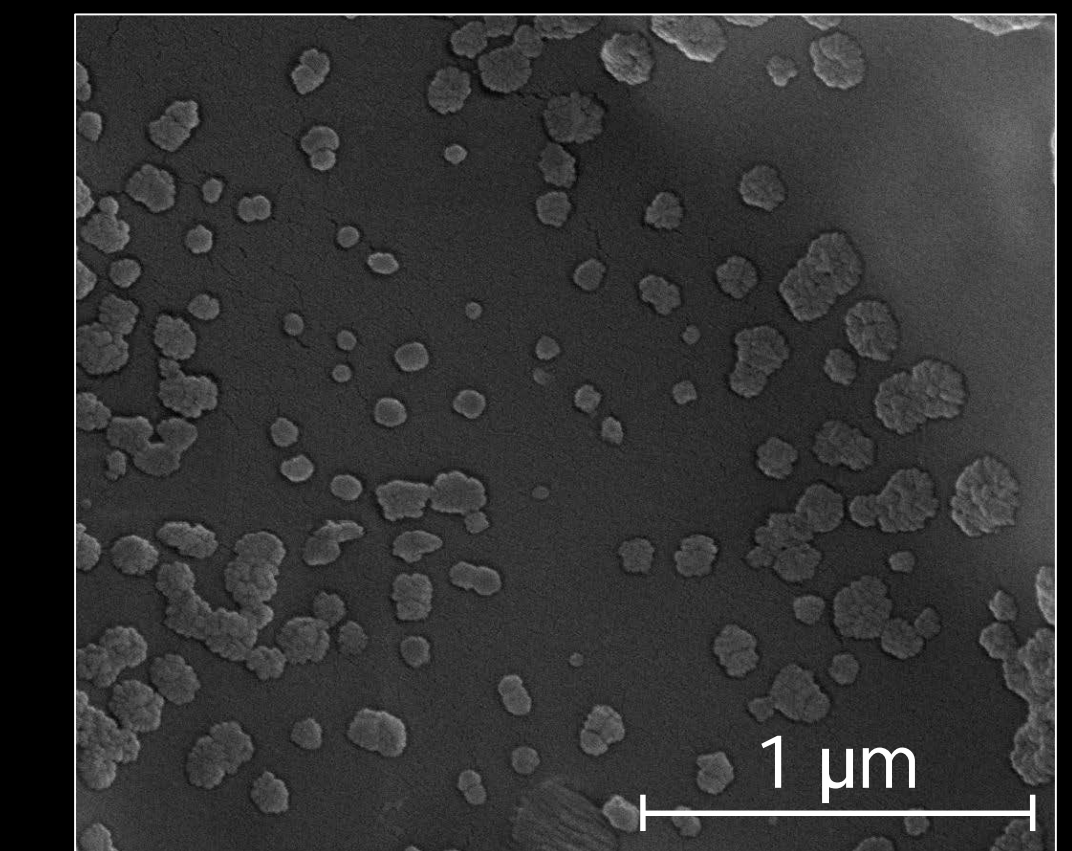


Figure 5: SEM image of Cyonara at 1 μm scale. The high number of particles may confirm the spectrophotometer results that indicate high concentration of AI in the nano fraction.

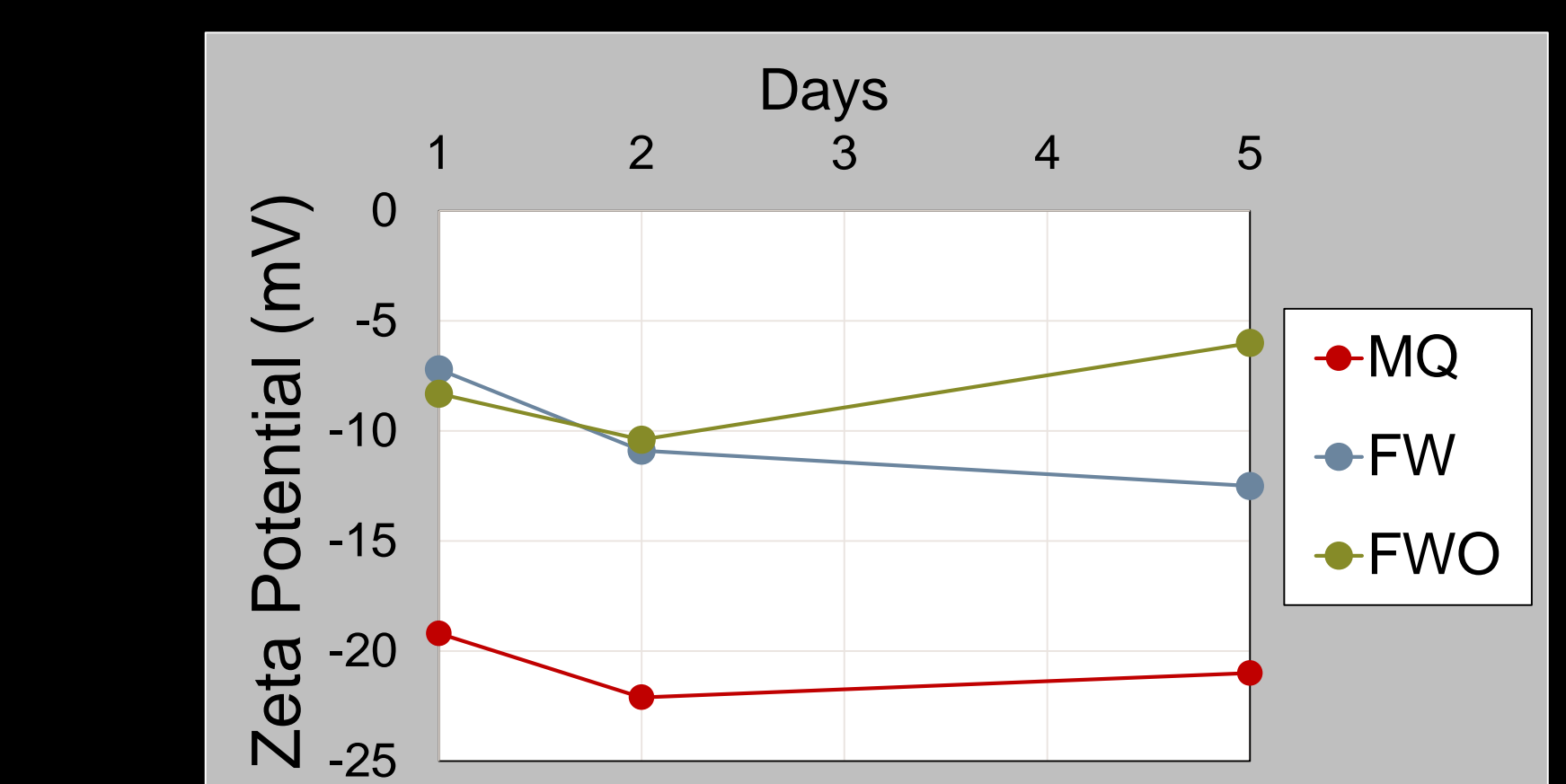


Figure 6: Stability results for Cyonara micro fraction in water (MQ), water with salt (FW), and water with salt and humic acid (FWO). Results may indicate lower stability in FW and FWO compared to MQ.

## Future Work

- Investigate the toxicity of nanopesticides using an embryonic zebra fish assay
- Stability testing with additional pesticides
- Investigate absorbance interference from other ingredients

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