

Introduction

Nanoparticles and their applications have been the focus of scientific investigation from multiple approaches. However, manufactured nanoparticles released to the environment may pose a critical threat to the environment and living organisms.^[1,2]

In-depth investigation of how nanoparticles interact with the environment is currently difficult because traditional methods for detecting and quantifying them are limited.

The concentration of nanoparticles in natural water samples is too low to be detected easily; highly sensitive instrument such as ICPMS is very costly and requires high maintenance.^[3]

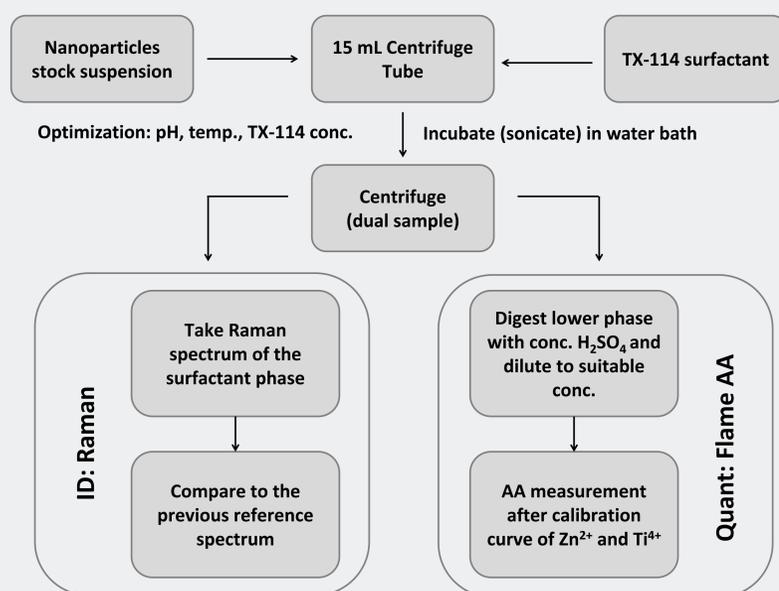
Developing easier methods to detect, identify and quantify metal oxide nanomaterials may lead to more rapid assessment of nanoparticle levels in the environment and better understanding of their fate and transport.

Preconcentration of the samples through cloud point extraction followed by Raman scattering and flame atomic absorption spectroscopy offers the advantage of identifying and quantifying nanoparticle species in aquatic environment.^[4-6]

Objective

The goal of this project is to achieve maximum cloud point extraction efficiency of zinc oxide and titanium dioxide (rutile and anatase) nanoparticles in water samples into the non-ionic surfactant-rich phase through optimization of CPE factors.

Methodology



Results

Pure anatase nanoparticles and TX-114 surfactant were mixed to simulate the surfactant phase after cloud point extraction. Four samples were prepared with different anatase concentrations of 500, 1000, 2000, and 4000 ppm as shown in figure 1. These samples gave the Raman spectra shown below. (B&W Tek i-Raman, 785 nm laser, ~150 mW at sample, 3 second integration times)



Figure 1. Anatase TX - 114 mixture



Figure 2. Anatase sample after CPE

Cloud point extraction of anatase nanoparticles suspended in water (1.0 mg/L) was carried out, giving two distinct layers with the surfactant-rich phase at the lower layer as shown in figure 2. The surfactant phase volume was measured to be less than 0.2 mL, which allows 50x greater concentration.

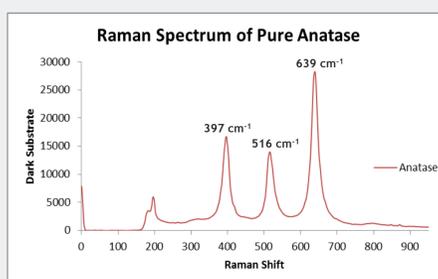


Figure 3. Raman spectrum of pure anatase

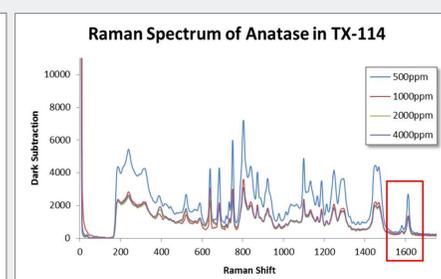


Figure 4. Raman spectrum of anatase TX - 114 mixture

The absolute intensity of the Raman signal depends on the film thickness and focusing. The concentration of TX-114 in the surfactant layer is relatively constant, and therefore we use the band at 1612 cm⁻¹ as an internal standard (figure 4). This sharp isolated band from TX-114 is thought to come from the helical structure of the ethylene oxide units saturated with water.^[7]

After normalizing the Raman spectrum of anatase and TX-114 mixture, the three characteristic peaks of anatase (397cm⁻¹, 516cm⁻¹, 639cm⁻¹) could be easily identified on the graph as the interference peak became overlap (figure 5). The graph of normalized data at 639cm⁻¹ versus concentration of anatase in TX-114 was plotted (figure 6). A good linear response was obtained from the plot.

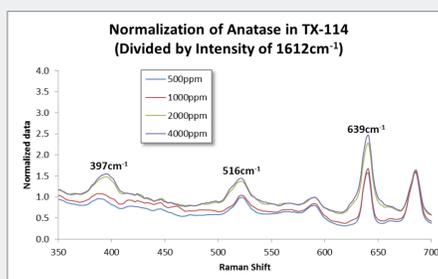


Figure 5. Normalized spectrum

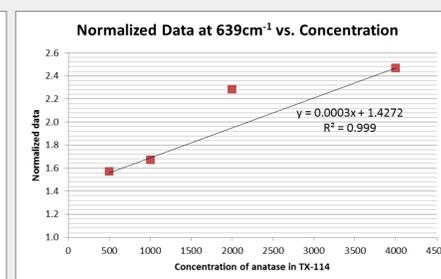


Figure 6. Graph of normalized data vs. concentration

Results

10 ppm of anatase in water sample was subjected to cloud point extraction and the Raman spectrum of the surfactant phase was obtained as shown in figure 7. The characteristic peaks of anatase are easily seen.

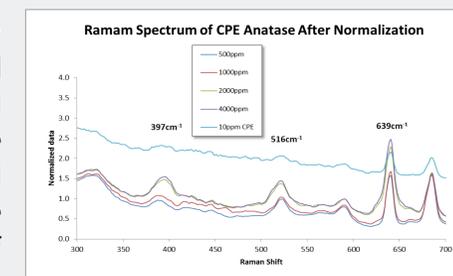


Figure 7. Raman spectrum of 10 ppm anatase

The Flame AA calibration curve for Zn²⁺ and Ti⁴⁺ (figure 8) shows non-linear response at higher concentration. This is easily explained by self-absorption. Application of flame AA to the detection of Ti and Zn from nanoparticle samples after cloud-point extraction is currently in progress.

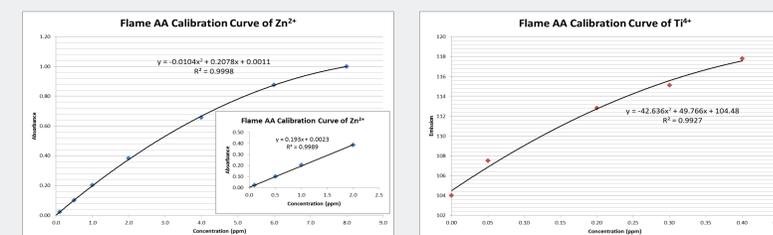


Figure 8. Flame AA Calibration curve of Zn²⁺ (left) and Ti⁴⁺ (right)

Conclusions

- Raman spectroscopy combined with cloud point extraction can detect anatase in water at concentrations as low as 10 mg/L.
- Flame AA spectroscopy combined with cloud point extraction is expected to easily quantify Ti and Zn from NPs at very low levels.

References

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