APPLICATION NOTE

ICP - Mass Spectrometry

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Quantitative Evaluation of Nanoparticle Dissolution Kinetics using Single Particle ICP-MS: A Case Study with Silver Nanoparticles

Introduction

Accurate data on engineered nanoparticle (ENP) environmental behavior and the interplay between ENP size, dissolution rate, agglomeration, and interaction with the sample matrix is critical to appropriately characterize the risks these novel materials may pose to environmental health. The advancement of the single particle ICP-MS (SP-ICP-MS) technique is a great benefit for the study of ENPs in natural systems at environmentally relevant (ng/L) concentrations. Previous studies may have obscured environmentally-relevant transformations because of artificially high ENP concentrations used in the experiments[1]. Therefore, the SP-ICP-MS method is at the forefront to garner the type of information most relevant for environmental risk assessments, namely the precise tracking of changes in ENP size, associated dissolved metal concentration, and determining polydispersity of an ENP sample, all at dilute concentrations in complex solutions. Because dissolution rate is surface-area controlled, the time to complete dissolution is highly dependent on the initial and (potentially stable) intermediate particle sizes. By measuring the change in particle size, as well as the evolution of $Ag^+(aq)$ in solution, using SP-ICP-MS, potential pitfalls related to loss of Ag^+ to experimental materials and to other environmental surfaces, such as suspended sediments or biota in the case of complex matrices, may be avoided.

SP-ICP-MS Technique

The theoretical basis of detecting and measuring single particles by SP-ICP-MS has been well-studied in recent years[1-8]. This basis relies on the assumption that at sufficiently short dwell times and low particle number concentrations, detected pulses represent individual particle events. As a result, analysis in single particle mode uses thousands of fast, individual readings with the goal of capturing one (or a slice of one) ENP event. The particle mass can then be determined by the intensity of the ICP-MS response. If the ENP's element is also present as a dissolved species (i.e. dissolved silver vs. a silver nanoparticle), an increase of the baseline is observed in single particle mode. This increase is directly proportional to the instrument's calibration curve of the dissolved species.

In this study, we used the Syngistix™ Nano Application Module for particle measurement/detection and automated data treatment. Determination of the transport efficiency (i.e. the percentage of particles in solution that are detected) is critical to determining the ENP size when using calibrations based on dissolved standards. To avoid coincidence (i.e. two particles being detected in the same pulse), particle concentrations were adjusted so that no more than 1500 particles were detected in 60 s acquisition time[2,6].

Experimental

Materials

Ag ENPs (100 nm diameter, NanoXact, NanoComposix, USA) with polyvinylpyrrolidone (PVP) as a capping agent were examined. ENP suspensions were made by diluting stock solutions (20 mg/L Ag ENPs) with water to yield a final concentration of 50 ng/L Ag ENPs. To match the peak intensities observed by SP-ICP-MS, dissolved Ag standards (High-Purity Standards; QC-7-M) were used for calibration and diluted in 2% HNO_3 (Optima grade) for final concentrations ranging from 0.1-1 µg/L. For determination of nebulization efficiency, 100 nm Au NPs were obtained from BBI™ Solutions (Cardiff, UK) and prepared daily as a 100 ng/L ENP solution in distilled (DI) water.

Water samples analyzed included deionized water (DI, 18.3 M-ohm cm Nanopure), tap water (Colorado School of Mines campus, Golden CO) and surface water. The surface water sample, collected in June 2012 from Clear Creek in Golden, CO, was taken just beneath the water surface, approximately 1 m from the creek bank, and passed through a 0.45-micron filter. The sample was stored in a polyethylene bottle at 20 °C prior to use. The tap water contained approximately 1 mg/L free chlorine, as tested by the Golden, Colorado water treatment facility.

Instrumentation

A PerkinElmer NexION® 350Q ICP-MS was used for analysis. Operating conditions were optimized to produce maximum $^{107}Ag^+$ intensity. Data was collected for 120 seconds, using a dwell time of 100 µs. Aqueous calibration standards included a blank and four dissolved Ag solutions (0-1 µg/L). SP-ICP-MS dissolved standards were made both in 2% HNO_3 and matrix matched to the water chemistry. Acidified samples served as a check standard and a measure of instrument sensitivity, where the latter calibration curve was used for particle sizing. To monitor instrumental drift over time, a single 100 ng/L Ag dissolved calibration check standard was analyzed in SP-ICP-MS mode after every ten ENP samples. All data collection and analysis was done in SP-ICP-MS mode using the Syngistix Nano Application Module.

Analytical Results

Data Collection and Interpretation

Data demonstrating the dissolution of 100 nm PVP Ag ENPs (50 ng/L) in DI are provided in Figure 1, with the decrease in raw pulse intensities being direct evidence of size reduction over time. The corresponding dissolved Ag^+ increase over time was also observed by the elevated background counts (i.e. in the region below 50 counts, in this analysis).

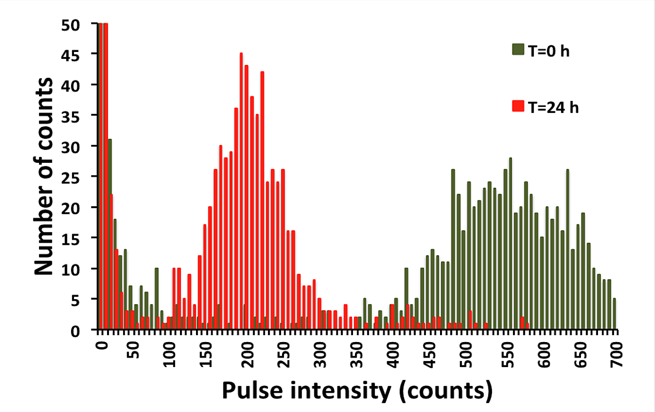

Figure 1. Raw data of 100 nm PVP capped Ag ENPs suspended in DI water, analyzed at 0 h (start of experiment) and after 24 h. Note decreased pulse intensity of main particle distribution histogram and increased background counts in the 24 h sample, indicating increased Ag^+ in solution.

Comparison of Dissolution in Various Water Chemistries

The dissolution of Ag particles was studied over 24 h in deionized (DI) water, tap water, and creek water. Particle distribution histograms were generated for each of the waters (Figure 2). The evolution of particle size and relative distribution can be noted both 1) within a given dissolution set and 2) across water chemistries by comparing diagrams. The average size was computed so the speed of dissolution could be more easily visualized (Figure 3). Dissolution in chlorine-containing tap water was faster than all other solutions examined. This result is expected since chlorine can act as an oxidizing agent, expediting dissolution in this system. Very little change in particle size was observed in the creek water. Natural systems are inherently complex, and thus difficulties arise in pointing to the factors which contribute to particle stability. However, the results from this study suggest dissolved organic carbon in the creek water may be one of the most relevant predictors of dissolution in natural waters, either by acting as a sink for oxidants in the system or physically protecting particle surface from oxidation/dissolution.

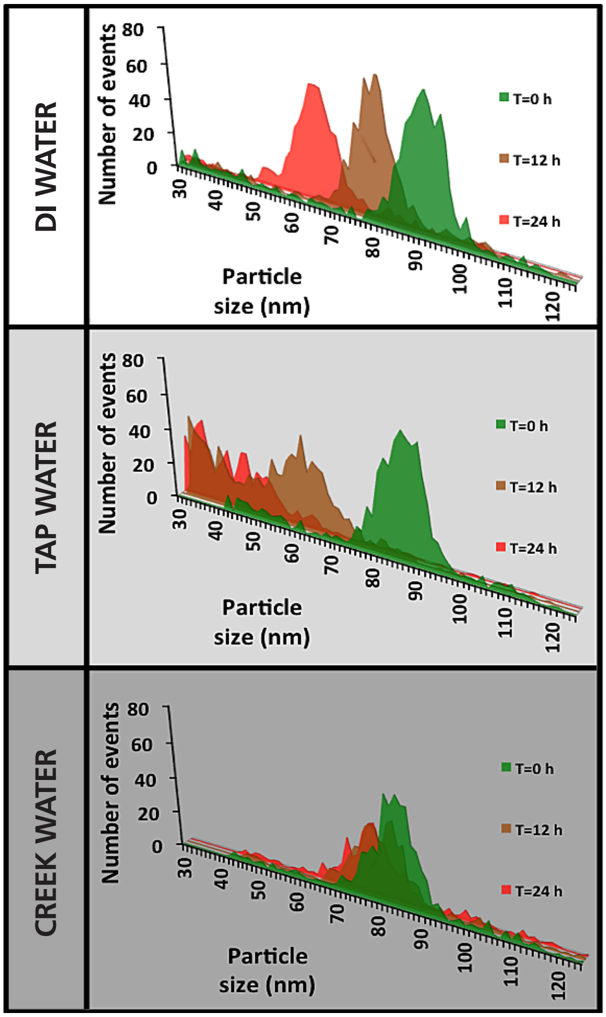

Figure 2. Particle size distribution of Ag ENP suspended in various water chemistries (DI, tap, and creek waters) over 24 h. Evidence of decreasing particle diameter with time through particle oxidation and dissolution in some samples (e.g. DI and tap waters) with less change in particle size observed in other samples, (e.g. creek water).

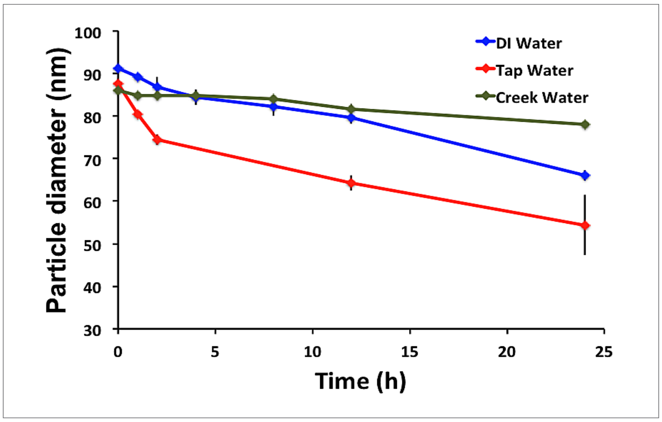

Figure 3. Comparison of Ag ENP dissolution in various waters over 24 hours. Error bars represent standard deviation from triplicate experiments.

Calculating Dissolution Rate Kinetics

Computation of dissolution rates is possible with the information that was collected using SP-ICP-MS. Using the instantaneous average particle diameter, the mass of Ag lost from the original particle can be calculated. After normalizing by calculated geometric surface area for that size particle (assuming spherical particles), the mass of Ag lost per surface area (mol/cm^2) versus time can be examined to obtain the dissolution rate constant. As shown in Figure 3, Ag ENP dissolution follows the first-order kinetics under the studied conditions. However, an inspection of the resultant data indicated that the dissolution rate was not necessarily constant for all time points – two rates were calculated for longer (up to 168 h) experiments: one rate for the < 24 h and one for time points > 24 h. For a more detailed description, see Mitrano et. al[1].

Conclusions

Dissolution potential could be a key component of the screening process for categorizing ENPs with common hazard potential based on their release of ionic species. This study demonstrates the utility of SP-ICP-MS to quantitatively evaluate dissolution kinetics for Ag ENPs under a wide range of conditions. This is particularly important in that only a limited number of methods can be directly applied to aqueous samples, especially considering expected ENP concentrations. Two specific highlights of the benefits of using the SP-ICP-MS technique to measure dissolution in complex samples include:

1) The measurement of primary particle size as the metric of dissolution is more direct than attempting to measure the increase of Ag$^+$ in solution and

2) This is possible even when known sinks in the system for Ag$^+$ exist (e.g. sediments, biota, sampling container).

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