APPLICATION NOTE

ICP – Mass Spectrometry

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Measurement and Analysis of Silver Nanoparticles in Wastewaters with Single Particle ICP-MS

Introduction

The drastic increase in production and consumption of engineered nanoparticles (ENPs) has raised the concern and questions about their release into the environment and potential harm to aquatic and terrestrial species. The characteristic properties of nanoparticles, such as small size and high specific surface area and reactivity, make them desirable for their use in various products.

Silver (Ag) nanoparticles are among the most commonly used nanoparticles in consumer products due to their antimicrobial properties. Therefore, it is expected that Ag ENPs will find their way into the environment, necessitating a way to accurately and rapidly detect and characterize them in a variety of environmental matrices. Work has already been performed demonstrating the ability to successfully characterize Ag ENPs in a variety of water samples[1-3] and biological media which may be exposed to Ag ENPs in the environment[4].

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A major source of environmental release is wastewaters, a complex matrix which must be evaluated for the fate of Ag ENPs. The complexity and variety of the wastewater matrices can make the analysis of ENPs challenging.

This work evaluates the ability of SP-ICP-MS to characterize Ag NPs in a dissolved organic solution containing alginate (a common wastewater component) and two wastewater matrices: mixed liquor and effluent.

Experimental

Samples and Sample Preparation

The water samples were collected from a wastewater treatment plant near Montreal, Quebec, Canada. The effluent wastewater was collected after the secondary settling tank, while the mixed liquor was collected from the secondary aeration tank. Both water types were collected in acid-washed, dark glass bottles and sealed. Effluent wastewater is the ultimate treated wastewater which is discharged to the river from this treatment plant, while the mixed liquor is the wastewater which leaves the aeration tank after biological treatment to the secondary settling tank for the suspended solids to sediment. As a result, the mixed liquor has much higher levels of suspended solids and relatively higher dissolved carbon content compared to the effluent wastewater.

Alginate is a polysaccharide which is detected in wastewaters at ppm levels and comprises the dissolved organic carbon fraction of wastewaters. The alginate solution was used as a known control/surrogate for comparison with the wastewater samples. The alginate solutions were prepared from alginic acid sodium salt from brown algae (Sigma-Aldrich, St. Louis, Missouri, USA) at 6 ppm in deionized water by shaking end-over-end for an hour.

Ag ENPs capped with polyvinylpyrrolidone (PVP) with a mean diameter of 67.8±7.6 nm (as determined with transmission electron microscopy [TEM], nanoComposix™ Inc., San Diego, California, USA) were spiked into 10 mL of all samples at a concentration of 10 ppb (5 million particles/mL). The samples were then diluted 10-1000x with deionized water and sonicated for five minutes prior to analysis. All samples were prepared in triplicate.

Instrumental Conditions

All analyses were carried out on a PerkinElmer NexION® 300D/350D ICP-MS operating in SP-ICP-MS mode using the Syngistix™ Nano Application Software Module. Instrumental parameters are shown in Table 1. With these parameters, a transport efficiency of 8.3% was determined.

Table 1. NexION 300D/350D ICP-MS Instrumental Parameters

Parameter	Value
Sample Uptake Rate	0.3 mL/min
Nebulizer	Glass Concentric
Spray Chamber	Glass Cyclonic
RF Power	1600 W
Analyte	Ag107
Analysis Time	100 sec
Dwell Time	100 µsec

Results and Discussion

To determine the accuracy of SP-ICP-MS, the Ag ENPs were added to deionized (DI) water at a concentration of 0.1 ppb (50,000 particles/mL). SP-ICP-MS measurement determined the mean size of the Ag ENPs to be 63.2±0.2 nm (which agrees with the TEM measurements), and the concentration to be 53,758±1363 particles/mL, thus validating the accuracy of the measurements. The values and standard deviations are from the mean of three replicate analyses.

Next, the Ag ENPs were measured in a 6 ppm alginate solution. Figure 1 shows the Ag particle size distribution for 0.1 ppb (50,000 particles/mL), which corresponds to a mean particle size of 66.1±0.1 nm, with a concentration of 52,302±2102 particles/mL. The agreement between the measured and TEM-determined particle sizes indicates that the alginate matrix does not affect the measurement accuracy.

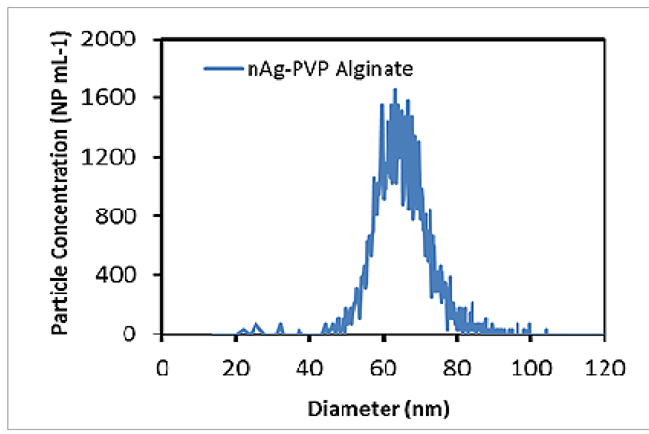

Figure 1. Measured Ag particle size distribution in 6 ppm alginate solution.

With the accuracy of the technique established in the alginate solution, the effluent wastewater and mixed liquor samples were measured next. First, the total Ag concentration was measured in both wastewater samples and was found to range from 25-40 ppt, a level which should not inhibit the determination of Ag ENPs. Figures 2 and 3 show the measured particle size distributions for the effluent and mixed liquor, respectively. The samples were diluted 100x prior to analysis, with Table 2 showing both the measured particle sizes and particle concentrations. Again, the mean particle size agrees with the certificate value, and the particle concentration is close to the calculated value, indicating that neither of the wastewater matrices affects the measurement. These results indicate that Ag ENPs can be successfully measured in wastewater samples.

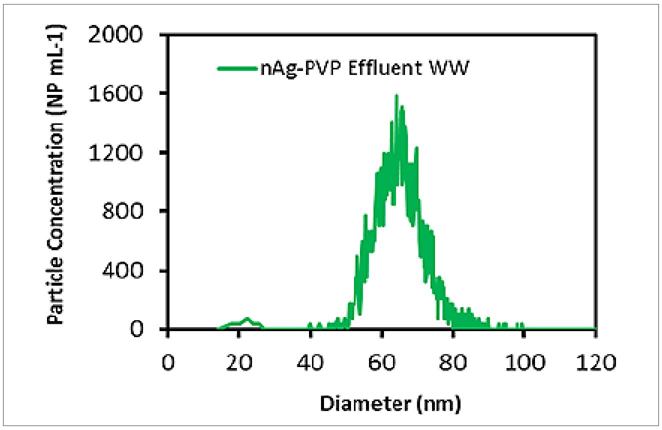

Figure 2. Measured Ag particle size distribution in effluent wastewater diluted 1000 times.

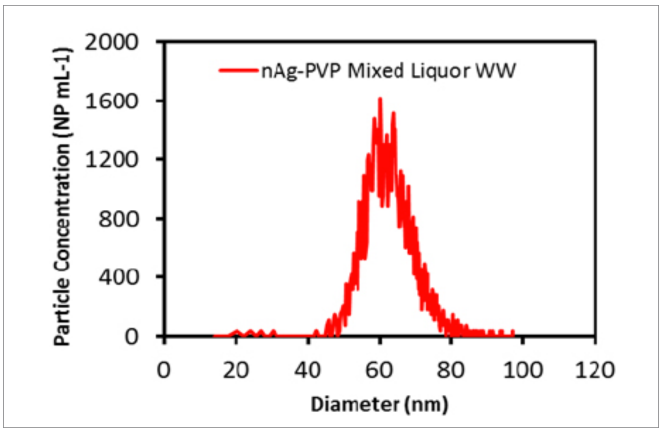

Figure 3. Measured Ag particle size distribution in mixed liquor wastewater diluted 1000 times.

Table 2. Results from Analysis of Wastewater Samples Spiked with Ag NPs.

Sample	Mean Particle Size (nm)	Spiked Particle Conc. (particles/mL)	Measured Particle Conc. (particles/mL)
Effluent Wastewater	66.3±0.2	50,000	54,691±1185
Mixed Liquor Wastewater	63.7±0.4	50,000	53,123±1216

The detection limits for both the Ag particle size and concentrations in the wastewaters were determined. For the determination of particle size detection limits, the diluted samples were analyzed without any Ag ENPs being added. The detection limit was determined by running the unspiked wastewater matrices and observing the particle size which corresponded to the smallest peak recorded in the Syngistix Nano Application Module. For the effluent, the detection limit is about 18 nm, while for the mixed liquor, it is about 12 nm.

To determine the lowest concentration of Ag ENPs which could be detected, Ag ENPs were spiked into DI water and diluted multiple times. The measured particle concentration was then recorded for each concentration. The particle concentration detection limit was determined to be the spiked particle concentration where the measured concentration did not change when the sample was diluted. In this work, the Ag ENP particle concentration detection limit was determined to be 25 ppt (12,500 particles/mL). Since the wastewater matrices did not affect the results, the detection limit was only measured in DI water.

Conclusion

This work has demonstrated the ability of SP-ICP-MS to accurately detect and measure silver nanoparticles in three different types of wastewater samples. Although wastewater matrices are complex, they do not inhibit the ability of SP-ICP-MS to accurately measure the size and nanoparticle concentration.

References

1. Mitrano, D., Ranville, J.F., Stephan, C., "Quantitative Evaluation of Nanoparticle Dissolution Kinetics using Single Particle ICP-MS: A Case Study with Silver Nanoparticle", PerkinElmer Application Note, 2014.
2. Hadioui, M., Wilkinson, K. "Assessing the Fate of Silver Nanoparticles in Surface Waters using Single Particle ICP-MS", PerkinElmer Application Note, 2014.
3. Dan, Y., Zhang, W., Xingmao, M., Shi, H., Stephan, C. "Gold Nanoparticle Uptake by Tomato Plants Characterized by Single Particle ICP-MS", PerkinElmer Application Note, 2015.
4. Gray, E., Higgins, C. P., Ranville, J.F. "Analysis of Nanoparticles in Biological Tissues using SP-ICP-MS", PerkinElmer Application Note, 2014.

Consumables Used

Component	Part Number
Green/Orange (0.38 mm id) PVC Sample Uptake Tubing	N0777110
Gray/Gray (1.30 mm id) Santoprene Drain Tubing	N0777444
Sample Tubes	B0193233 (15 mL) B0193234 (50 mL)

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