

ICP - Mass Spectrometry

Authors:

Michail-Ioannis Chronakis

Emmanuel Mavrakis

Spiros A. Pergantis

University of Crete
Greece

Roberto R. Álvarez-Fernández García

University of Oviedo
Spain

Chady Stephan

PerkinElmer Inc.
Woodbridge, ON, Canada

Monitoring the Fate of Silver Nanoparticles in Seawater Using Single Particle ICP-MS

demonstrated tremendous potential for the measurement and characterization of metal-containing nanoparticles (NPs) in a wide range of sample types, including biological, environmental and food samples. One of the most challenging matrices is seawater due to its high salt content, which causes severe difficulties when analyzed for NPs due to matrix suppression and cone clogging. However, even though sample dilution prior to analysis would be a straightforward way to overcome these difficulties, we have decided to avoid it because it may cause NP transformation due to changes in the ionic strength and/or the organic content of the seawater matrix. Instead, we are using a sample introduction system that can perform such a dilution only milliseconds before the sample is nebulized into the ICP-MS. In addition, it is imperative that the SP-ICP-MS system used for monitoring NPs in seawater has appropriate characteristics that provide the required analytical performance, including:

- A sample introduction system that allows for the continuous and high-throughput introduction of undiluted seawater into the ICP-MS;
- An ICP-MS quadrupole mass analyzer and detector system that can operate under extremely short dwell times (μs) with zero settling time;
- Data processing software that can automatically process single particle data in near real time.

Introduction

Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) is an analytical technique that has

The work presented here demonstrates the ability to measure and characterize silver (Ag) nanoparticles in seawater samples taken from tanks that are part of a large-scale seawater mesocosm experiment. The main challenge, apart from the seawater matrix, was the time-sensitive nature of the sample analysis. Ag nanoparticles will transform quickly in seawater, so samples must be analyzed immediately upon arrival in the laboratory, without prior dilution. Being able to process the acquired SP data in almost real time was vital for monitoring the progress of the overall seawater mesocosm experiment and for taking corrective action rapidly when required.

Experimental

Mesocosm Experiment

Samples were collected from a mesocosm experiment similar to one previously described.¹ In brief, six mesocosm tanks were each filled with 3000 L of seawater. Three tanks served as controls, whereas the other three tanks were each spiked daily with Ag NPs at 50 ng/L Ag. The 60 nm Ag NP material used here was coated with branched polyethylenimine (BPEI). Seawater samples were taken in the morning from each tank, just before the daily addition of “fresh” Ag NP suspensions, for ten consecutive days. Samples were then transferred to the laboratory for immediate SP-ICP-MS analysis.

More specifically, every morning 50 mL of seawater was collected from each mesocosm tank using silicone tubing, permanently placed in the center of each tank 1 to 1.5 m beneath the water surface. A large-volume syringe was used to create light suction and thus transfer seawater via this tubing into sampling tubes. The samples were transferred to the laboratory for immediate analyses. Subsequently to the sampling, a Ag NP suspension (1 L of approximately 150 µg/L Ag, depending on the daily volume of each mesocosm tank) was added daily to each of the three tanks by releasing it onto the seawater surface of the mesocosm tank. Finally, the seawater content of each tank was gently mixed using a dedicated paddle for each tank.

Instrumental Conditions

A modified version of the sample introduction system already described was used in this study (Figure 1).² The modification involved using a syringe pump with a 500 µL glass syringe, thus avoiding the need to use a sample injection loop, which in some cases could cause NP contamination. The modified sample introduction system proved to be extremely efficient, stable, versatile and easy to clean, showing both its improved robustness and viability for continuous use for high throughput NP determination in seawater samples. Approximately 200 µL of each seawater sample were taken up in a glass syringe and analyzed. The syringe pump delivered the sample at a flow rate of 20 µL/min. Samples were diluted 40x online using a T-piece at the tip of the pneumatic nebulizer, so essentially the sample is analyzed immediately giving no time for Ag NP transformation to occur, as the mixing due to dilution lasts for approximately 200 ms prior to nebulization.

All analyses were executed on a NexION® ICP-MS, using the conditions given in Table 1. A dwell time of 75 µs was used. Data acquisition and analysis were performed using the Syngistix™ Nano Application software module.

Table 1. NexION ICP-MS Instrumental Parameters for the Determination of Ag NPs in Seawater.

Parameter	Value
Sample delivery rate via syringe pump	20 µL/min
Deionized water makeup rate via peristaltic pump	800 µL/min
Nebulizer	Glass Concentric MEINHARD® Type C modified with the insertion of a fused silica capillary (100 µm id, 200 µm od) via the central nebulizer channel (for details, see Figure 1)
Spray chamber	Glass Cyclonic
RF power	1600 W
Analyte	¹⁰⁷ Ag
Analysis time	2 x 3 min
Dwell time	75 µsec

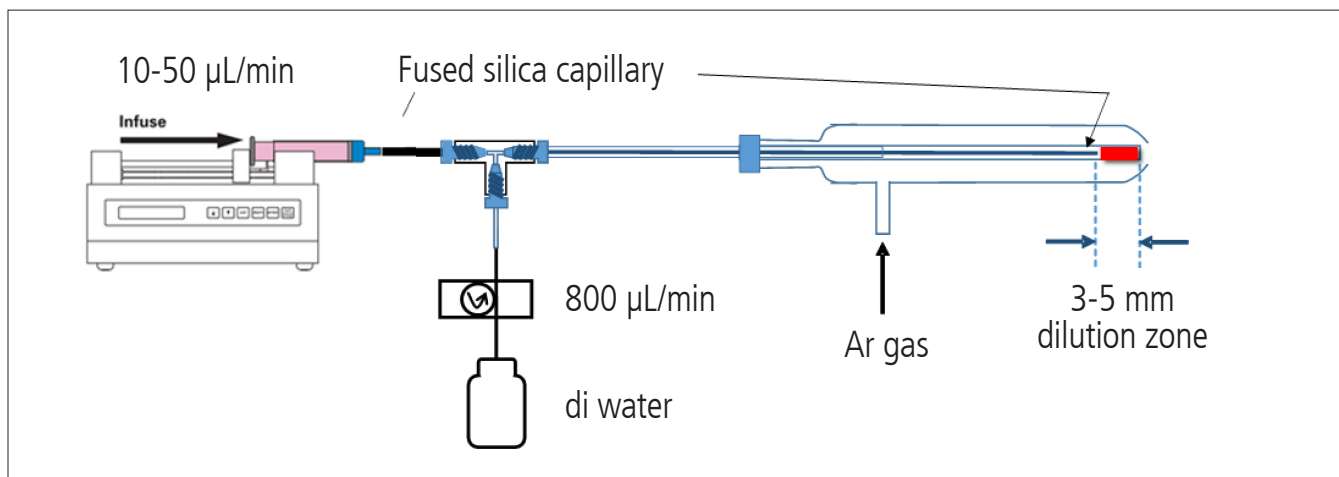


Figure 1. Sample introduction system used for the analysis of Ag NPs in seawater.

Samples and Standards

Seawater samples were taken daily from the mesocosm tanks and immediately transferred to the laboratory for analysis (20-30 min travel time). Samples were not filtered or diluted prior to analysis using SP-ICP-MS.

Ag NPs coated with branched polyethylenimine (BPEI) were used throughout this study, both for spiking the mesocosm seawater and for preparing NP standards. Ag BPEI NP standards were made from a control seawater solution into which 100 ng of 60 nm Ag (Ag BPEI) NPs per L were added (this corresponds to approximately 42000 Ag BPEI NPs per mL). This standard was analyzed immediately in order to avoid the occurrence of NP dissolution (Figure 2) and was used both to calibrate for Ag NP size and to determine the transport efficiency (TE) in combination with the counting approach.

Results and Discussion

The results presented in this application note correspond to the analysis of samples taken from a seawater mesocosm tank in which Ag BPEI NPs were introduced in the morning on a daily basis for a total of 10 days. More specifically, samples were taken daily just prior to the spiking of "fresh" Ag NP suspensions. The amount of Ag added as Ag NPs in each spiking session gave the tank an additional 50 ng/L Ag each day for a total of 10 days, thus a total Ag concentration of 500 ng/L throughout the experiment.

Figures 3 A-C show the size (diameter) distributions for the Ag NPs determined in the tank on day 0 + 2 hours, on day 5 and on day 10, as determined using the SP-ICP-MS setup shown in Figure 1. It is proposed that the Ag NPs gradually dissolve, as shown by the appearance of smaller-sized Ag NPs over time. However, the fact that "fresh" Ag NP suspensions are added daily contributes to the broadening of the NP size distribution towards higher sizes. Thus, much broader size distributions are observed the longer the NPs are present in the seawater and spiking continues.

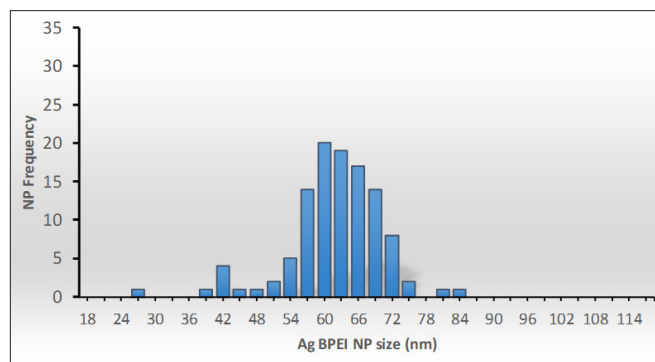


Figure 2. Ag BPEI NPs analyzed immediately after being added to control seawater to make a 100 ng/L Ag containing suspension. This suspension, made daily and immediately prior to sample analysis, was used as a particle calibration standard in the seawater matrix.

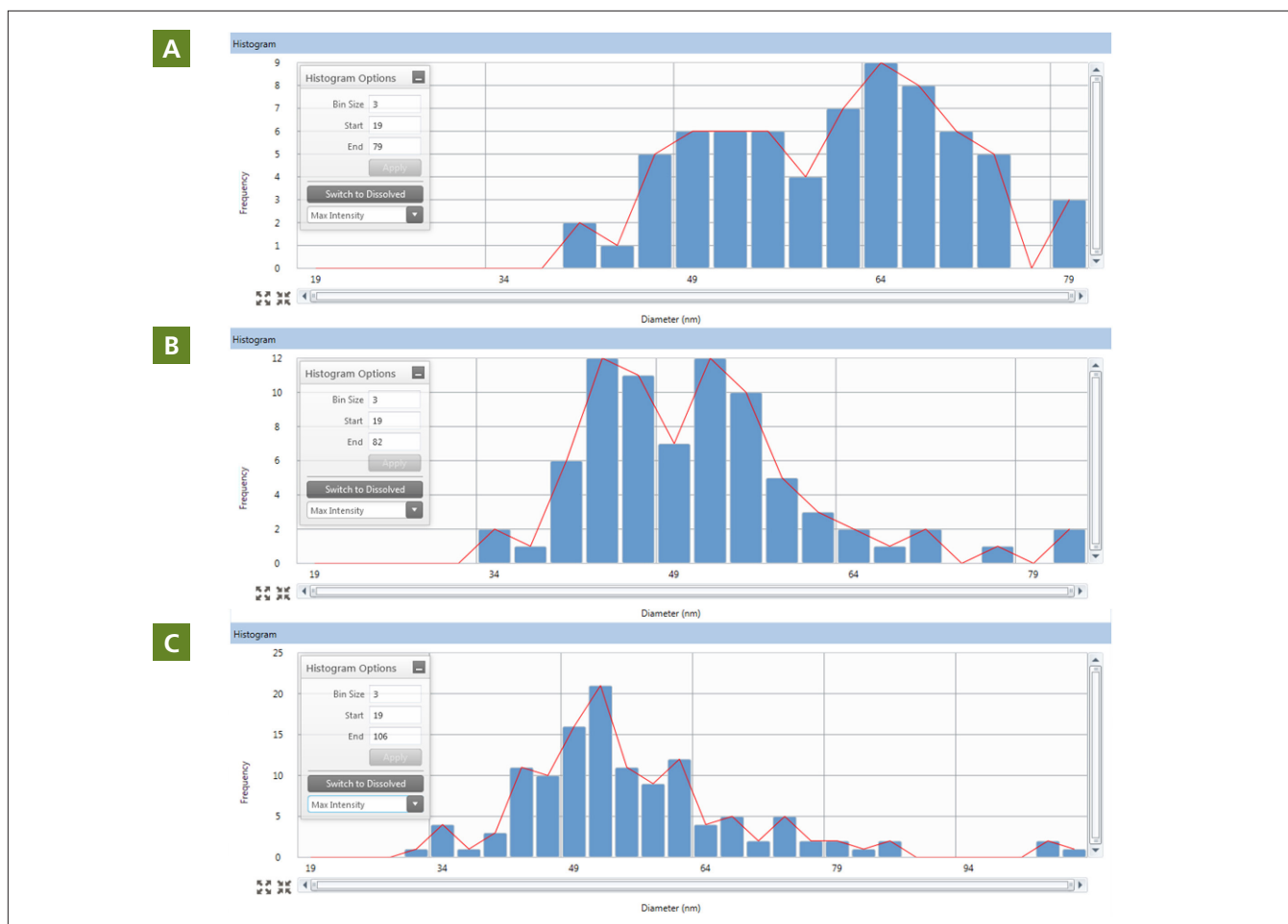


Figure 3. Ag NP size distributions as determined using SP-ICP-MS samples taken on day 0 + 2 hours (top-A), day 5 (center-B) and day 10 (bottom-C).

The dissolved Ag (i.e. Ag⁺) content of the samples was also determined during the SP-ICP-MS analysis. As expected, the dissolved Ag content increases over the mesocosm experiment's duration (Figure 4, dotted grey line). The system's Ag mass balance could be examined using SP-ICP-MS. It was observed that the total Ag mass (blue line) corresponding to the sum of the detected Ag NP (yellow dotted line) and the mass corresponding to the dissolved Ag (grey line) was in good agreement with the total Ag spiked into the mesocosm tank as Ag NPs (orange double line). This shows that the analytical system used was capable of accounting for almost all of the Ag mass added to the seawater mesocosm tanks, even though it had partially transformed into dissolved Ag.

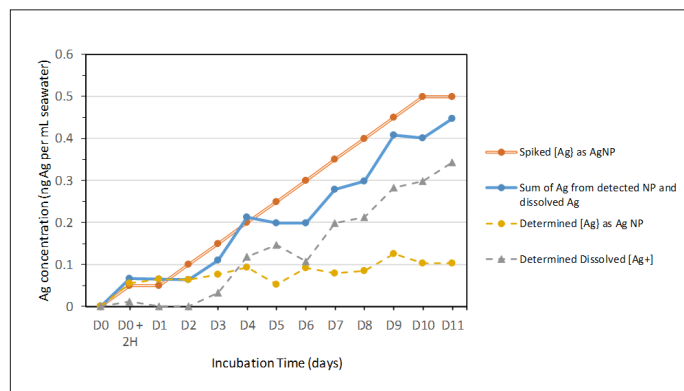


Figure 4. Mass balance diagram showing the levels of Ag spiked daily as Ag NPs, as well as the determined Ag corresponding to Ag NPs (grey dotted line) and to dissolved Ag⁺ (yellow dotted line). Finally, the sum of the latter two (NP Ag plus dissolved Ag - blue line) are compared to the daily Ag spike levels (orange double line).

The unique capabilities of SP-ICP-MS also allowed for the determination of Ag NP number concentrations (Figure 5), which seemed to exhibit a net increase up to day 10. This was the result of daily replenishment as new Ag BPEI NPs were added daily at a rate greater than that of their dissolution.

Finally, it is worth stressing the tremendous stability and rapid computing power of this system. The complete mesocosm experiment, conducted for 11 days (and not explained in full detail in this application note), required the analysis of nine samples per day, analyzed three times each, plus the calibration standards (particle standard in seawater, as well as dissolved Ag standard in seawater). All data processing was provided in almost real time, and seawater samples could be analyzed continuously throughout the day without any signal reduction. Monitoring the results in such an automated fashion was vital for successfully conducting this type of seawater experiment, in collaboration with an interdisciplinary team of marine biologists and chemists.

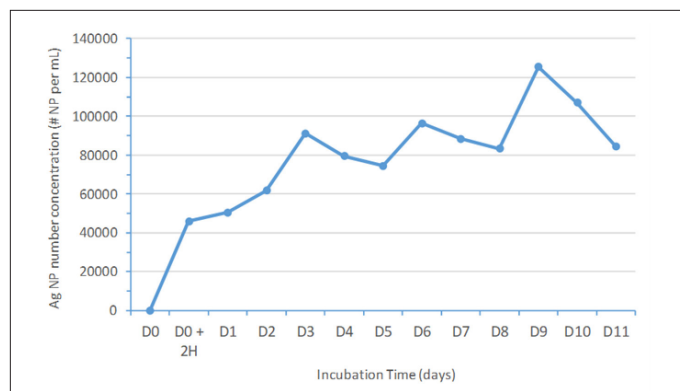


Figure 5. Ag NP number concentration variation with incubation time. On a daily basis, approximately 42000 Ag BPEI NP per mL with a diameter of 60 nm were added from day zero (D0) until day 10 (D10).

Conclusion

Recent advances in ICP-MS instrumentation and software have improved our ability to conduct single particle analysis even in very difficult matrices such as seawater, allowing for such large-scale experiments which would have been extremely difficult using manual data processing. In contrast, present capabilities offered by PerkinElmer in the form of single particle analysis software (Syngistix Nano Application module) allow for almost real-time data analysis, which is vital for conducting such a large-scale incubation experiment in which "fresh" Ag NPs are added daily.

References

1. Tsiola, A.; Toncelli, C.; Fodelianakis, S.; Michoud, G.; Bucheli, T. D.; Gavriilidou, A.; Pitta, P. (2018). Low-dose addition of silver nanoparticles stresses marine plankton communities. *Environmental Science: Nano*, 5(8), 1965–1980. <https://doi.org/10.1039/c8en00195b>
2. Toncelli, C.; Mylona, K.; Tsapakis, M.; Pergantis, S. A. (2016). Flow injection with on-line dilution and single particle inductively coupled plasma-mass spectrometry for monitoring silver nanoparticles in seawater and in marine microorganisms. *Journal of Analytical Atomic Spectrometry*, 31(7), 1430–1439. <https://doi.org/10.1039/c6ja00011h>