

## ICP - Mass Spectrometry

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## Rapid Measurement of Nanoparticles in Seawater using Single Particle ICP-MS with All Matrix Solution

### Introduction

Single particle ICP-MS (SP-ICP-MS) has become an essential tool for the analysis of nanoparticles (NPs) in various environmental matrices.<sup>1-3</sup> It enables fast and accurate analysis of particle size, particle concentration, and ionic (dissolved) concentration in a single analysis, making

it the technique of choice for tracking nanoparticle transformations (dissolution and aggregation) in natural systems. Nevertheless, dissolution and aggregation of nanoparticles in environmental samples are matrix dependent and greatly influenced by the sample matrix composition, such as dissolved organic matter (DOM) and ionic strength.<sup>4</sup> As a result, diluting the sample prior to analysis might potentially affect the nanoparticles' state in the sample.

Achieving accurate measurements in SP-ICP-MS requires precise measurement of transport efficiency (TE), sample flow rate, and a close matrix matching between the standards used to calibrate the instrument and the sample matrix.

Transport efficiency and sample flow rate are very dependent on the sample matrix composition. Samples with high dissolved organic matter tend to increase the transport efficiency, while samples with high total dissolved solids tend to decrease TE and yield a lower flow rate. Using non-matrix-matched standards to measure particles in environmental matrix suspensions will cause signal suppression during ionization, which may result in underestimating the particle size. Preparing standards in a matrix-matched solution to the environmental samples is not trivial as ionic standards may precipitate and NP standards may aggregate, making accurate TE measurements and calibration curves difficult to acquire.

Generally, in ICP-MS analyses, samples with a heavy matrix are diluted prior to analysis. However, when dealing with nanoparticles, dilution may trigger transformations, meaning that obtained results may not accurately reflect the initial state of NPs in the sample.

A way to avoid dilution of heavy-matrix samples is to perform analyses using the NexION® ICP-MS' All Matrix Solution (AMS), providing on-line gas dilution of the sample aerosol that occurs between the spray chamber and the plasma.<sup>5</sup> This dilution mechanism alleviates the sample matrix without affecting the state of the NPs in the sample and eliminates signal suppression, allowing ionic and NP standards to be prepared without the need for matrix-matching the sample. In this work, we will explore the analysis of gold NPs in simulated seawater without any liquid dilution using AMS, discussing the importance of instrument setup and its effect on precise and accurate particle analysis using single particle ICP-MS.

## Experimental

### Samples and Sample Preparation

Ionic gold (Au<sup>+</sup>) standards were prepared at 1, 2 and 3 ppb in ultra-high purity (UHP) water, and a 60 nm Au nanoparticle standard (NIST 8013) was prepared at 60,000 part/mL in UHP water. Seawater samples were prepared using a standard reference material (CASS-6, National Research Council, Canada) and were spiked with 60,000 part/mL of the 60 nm Au NIST NPs. No further sample preparation was carried out prior to analysis.

### Instrumental Parameters

All analyses were performed on a NexION 2000 ICP-MS using the sample introduction components and parameters shown in Table 1. The All Matrix Solution (AMS) flow was set to 0.4 L/min resulting in 10x dilution, allowing the undiluted seawater to be analyzed without any liquid dilution, thereby simplifying sample preparation and ensuring the integrity of the NPs in the sample matrix.

## Results and Discussion

With the use of AMS, the TE, intensity of ionic calibration standards, and particle number will be affected. As shown in Figure 1, all of these parameters decrease with increasing AMS

Table 1. NexION 2000 ICP-MS Parameters for NP Analysis in Seawater.

Parameter	Value
Nebulizer	PFA-ST
Spray Chamber	Glass baffled cyclonic
Injector	Quartz, 2 mm id
RF Power (W)	1600
Nebulizer Flow (L/min)	0.66
AMS Flow (L/min)	0.40
Sample Uptake Rate (mL/min)	0.11
Analyte	Au 197
Dwell Time (μs)	50
Sample Analysis Time (sec)	60

flow, as to be expected since AMS dilutes the sample aerosol after nebulization but prior to introduction into the plasma. In order to attain accurate results, the TE and ionic calibration standards must be measured at the same AMS flow as the samples.

As shown in Figure 2, the size of NIST 60 nm Au NPs is accurately determined at several different AMS flows, demonstrating that AMS does not affect the accuracy of particle size measurements, if corresponding ionic calibration was used.

With the effect of AMS characterized and accuracy established, Au NPs were added to seawater and measured. Figure 3 shows the particle size distribution of 60 nm NPs added to both seawater and deionized water. The corresponding particle size and particle concentration measurements are shown in Figures 4 and 5, respectively. Taken together, these results show equivalent particle size and size concentrations. The results demonstrate that proper instrument setup and AMS alleviate the matrix effect, thus enabling accurate and precise NP measurements in complex environmental matrices, like seawater, without the need to matrix match the ionic calibration standards. This ability results in simplified usability of the instrument functionality and, most importantly, accurate results for the NP in the analyzed sample since liquid dilution is eliminated.

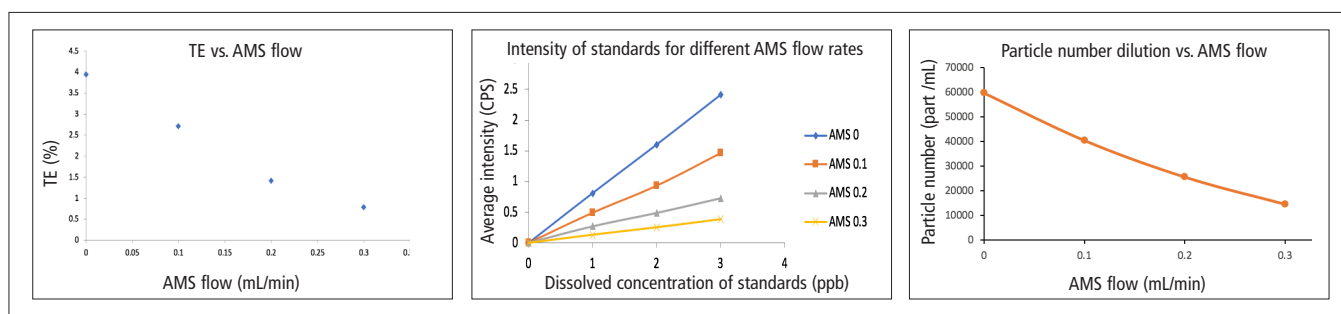


Figure 1. Effect of AMS flow on transport efficiency, intensity of dissolved standards, and particle number.

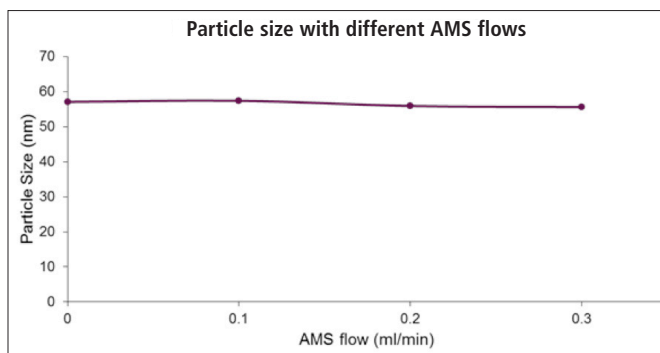


Figure 2. Effect of AMS flow on measured particle size of NIST 8013 60 nm Au NPs.

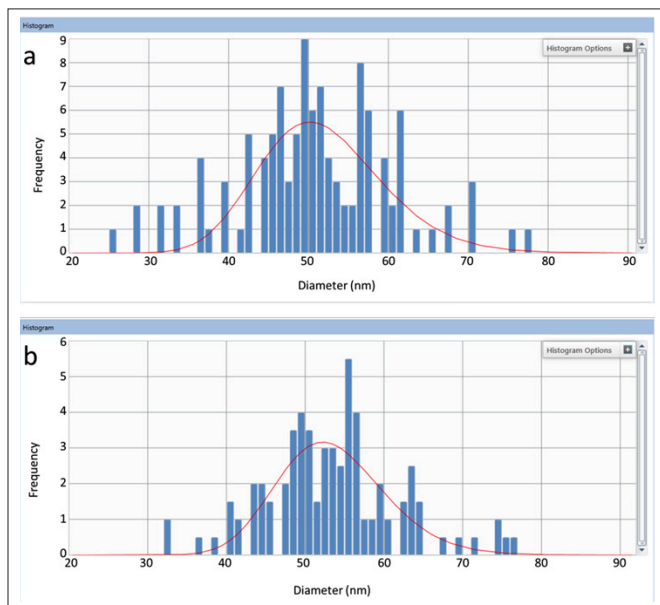


Figure 3. NIST 8013 60 nm Au NP particle size distributions in undiluted seawater (a) and deionized water (b).

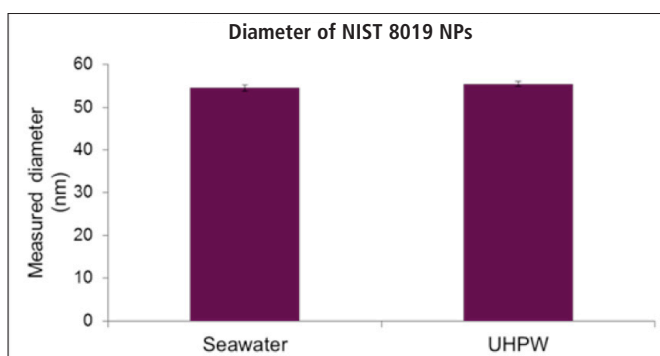


Figure 4. Particle size measurements of NIST 8013 60 nm Au NPs in both seawater and deionized water.

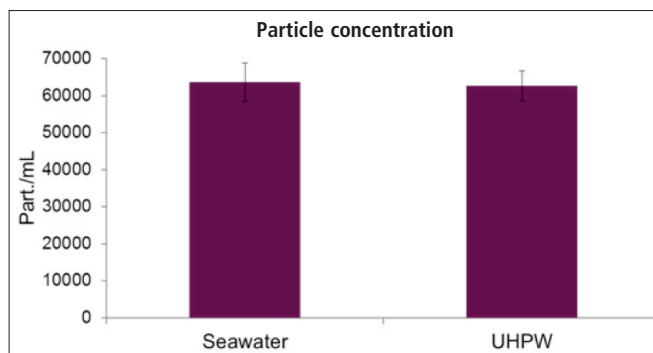


Figure 5. Particle concentration measurements of NIST 8013 60 nm Au NPs in both seawater and deionized water.

## Conclusion

This work has demonstrated the ability of SP-ICP-MS, using PerkinElmer's NexION 2000 ICP-MS, to accurately measure particle size and concentration in seawater (representative of a heavy matrix) without the need for sample dilution with water. These measurements were made possible through the use of All Matrix Solution (AMS), an on-line aerosol dilution technique which allows undiluted seawater to be aspirated directly. The ability to eliminate manual dilutions is important for NP measurements since dilution of the sample matrix prior to analysis can impact the NP state. AMS is an important tool for SP-ICP-MS analysis of heavy matrices as it provides a true measurement of the NP size and number in these suspensions, thus avoiding the need for speculation of the speed and type of NP transformations due to dilution with water.

## References

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