Characterization of Metal-Based Nanoparticles by Single Particle-ICP-MS in Various Matrices

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ABSTRACT

The use of nanoparticles in consumer products is showing a tremendous increase over time. The National Institute of Standards and Technologies reported that nanotechnology-based consumer products are currently entering the market at a rate of 3 to 4 per week, and it is estimated that $2.6 trillion in manufactured goods will contain nanotechnology by 2014[1].

In spite of their beneficial properties, possible risks for humans and the environment need to be thoroughly investigated, and multiple key characteristics need to be assessed. Detailed information about the quantity, shape, size, size distribution, structure, composition, surface charge and functionality need to be studied and addressed in order to perform an appropriate and reliable risk assessment.

This work presents Single Particle Inductively Coupled Plasma Mass Spectrometry (SP-ICP-MS) as a tool in assessing the fate of engineered nanoparticles in various matrices [2,3]. The technique allows for the differentiation between ionic and particulate signals, measurement of particle sizes and size distribution, and assists in monitoring agglomeration.

Keywords: Single Particle ICP-MS, Nanopartciles, Envenrimental Matrices,

1 INTRODUCTION

During the last decade, the production and use of engineered nanomaterials (ENMs) have experienced a drastic increase, resulting in a potential risk of their release into the environment. Therefore, the study of their impact on the environment becomes crucial. The appropriate ecological risk assessment and management of ENMs in the environment requires quantitative measurements of both exposure and effects [4] that should, ideally, be performed by in situ analysis and give physicochemical characterization. However, most analytical techniques are not suitable for environmental matrices since nanoparticle concentrations are typically very low [5].

Historically, particle size has been measured by dispersive light scatter (DLS) and tunneling electron microscopy (TEM), while dissolved content has been measured by ultrafiltration. These common techniques have known limitations for measuring low concentrations in the presence of colloidal species in complex waters.

Alternatively, single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has been found to be a promising technique for detecting and characterizing metal nanoparticles at very low concentrations. SP-ICP-MS is fast and efficient and can provide more information than other currently available techniques. It can lead to the determination of particle size, size distribution, particle number concentration, and the concentration of dissolved metal. Moreover, it can distinguish between particles of different elements.

The aim of this work is to investigate the efficiency of SP-ICP-MS for the detection and characterization of metal nanoparticles in environmental waters where they can be involved in various physicochemical processes as shown by Figure 1.

Figure 1 Possible fates of silver nanoparticles in surface waters: (A) Dissolution process leading to free ions release and smaller particles; (B) Aggregation into larger particles, which may settle out of the water, depending on the aggregate size; (C, D) Adsorption of released Ag+ and nAg, respectively, onto other solids present in the water; (E) Formation of soluble complexes; (F) Reaction with other components in the water, which may result in precipitation; (G) nAg remaining stable.

2 MATERIALS AND METHODS

A PerkinElmer NexION® 350X Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used for data acquisition using the Nano Application Module within Syngistix™ for ICP-MS software (SP-ICP-MS instrumental parameters are given in Table 1). The sample introduction system consisted of a quartz cyclonic spray chamber, type C0.5 concentric glass nebulizer and a 2 mm bore quartz injector. Commercially available suspensions of gold and silver nanoparticles were used in this work. A NIST reference material (RM 8013) consisting of a suspension of gold nanoparticles (60 nm nominal diameter, 50 mg/L total mass concentration and stabilized in a citrate buffer) was used to determine the nebulization efficiency. Suspensions of silver nanoparticles were purchased from Ted Pella Inc.: citrate coated (40 and 80 nm nominal diameter) and bare (80 nm nominal diameter) nanosilver

The surface water was sampled in Rivière des Prairies, Montreal, Canada and filtered with 0.2 μm filter paper prior to spiking with silver nanoparticles. Nano-Ag suspensions were added to water samples with concentrations ranging from 2.5 to 33.1 μg Ag L^{-1} and left to equilibrate under continuous and gentle shaking. Prior to SP-ICP-MS analysis, small aliquots of the samples were diluted to below 0.2 μg Ag L^{-1}. Data acquisition was performed in triplicate measurements for each sample, and deionized (DI) water was analyzed between replicates to check memory effects.

Table 1. Instrumental parameters for SP-ICP-MS data acquisition.

Parameter	Value
Instrument	NexION 350X ICP-MS
Nebulizer	Concentric
Spray Chamber	Cyclonic
Torch and Injector	Quartz Torch and Quartz 2.0 mm bore injector
Power (W)	1600
Plasma Gas (L/min)	18
Aux Gas (L/min)	1.2
Neb Gas (L/min)	0.97
Sample Uptake Rate (mL/min)	0.5
Sample Tubing	Black/Black
Dwell Time (μs)	100
Sampling Time (s)	60

3 RESULTS AND DISCUSSIONS

3.1 Fate of Silver Nanoparticles

Figures 2-4 show the evolution of the average particle diameter and the percentage of dissolved metal over time in both pure and river water. In all cases, the average particle size of the persistent nanoparticles remains substantially constant (Figures 2a, 3a and 4a). For suspensions of particles with a nominal diameter greater than 40 nm, between 50 and 80% of the particles persist for at least five days of equilibration in pure and surface water (Figures 2b and 3b). Under the experimental conditions of this work, the coating appears to have no significant effect on the dissolution of nanoparticles over time, as both citrate-coated and bare nAg (80 nm) suspensions showed a slight decrease of particulate silver by ca. 20% during five days. In the meantime, for the same size and equilibration time, the proportion of dissolved silver was found higher in the case of citrate-coated nAg. This does not necessarily mean that bare nanosilver is more stable than citrate-coated nAg. In fact, the release of silver ions may be due to oxidation and/or to residual Ag+ adsorbed on the surface of nAg or bonded to the coating. Thus, we believe that the stability and behavior of nanoparticles in any medium will depend on the synthesis procedure. According to Figure 4b, smaller particles with a nominal diameter below 40 nm tend to dissolve in greater quantities, but caution should be taken here due to the limitation of the technique to the detection of particles under 20 nm.
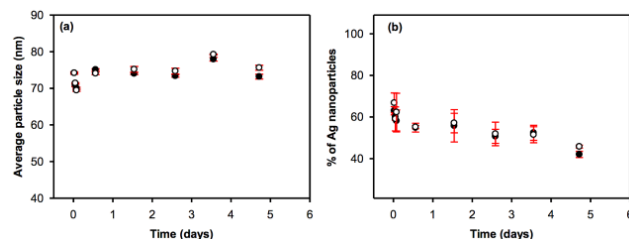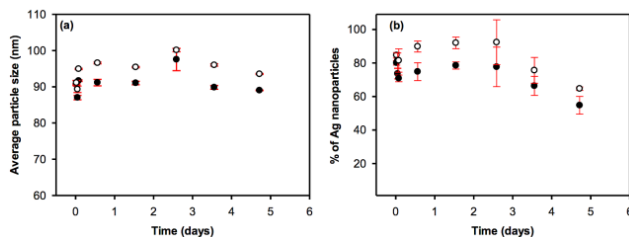

Figure 2. Evolution of (a) the average particle size and (b) the proportion of particulate silver as a function of equilibration time in pure (l) and surface (o) waters. Waters were spiked with 80 nm citrate-coated nAg, and the total metal concentrations were equal to 72.2 and 72.4 ng L^{-1} in DI water and surface water, respectively

Figure 3. Evolution of (a) the average particle size and (b) the proportion of particulate silver as a function of equilibration time in pure (l) and surface (o) waters. Waters were spiked with uncoated 80 nm nAg, and the total metal concentrations were equal to 196.4 and 200.8 ng L^{-1} in DI water and surface water, respectively.
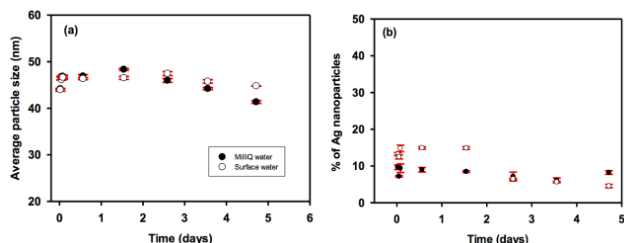

Figure 4. Evolution of (a) the average particle size and (b) the proportion of particulate silver as a function of equilibration time in pure (l) and surface (o) waters. Waters were spiked with 40 nm citrate-coated nAg, and the total metal concentrations were equal to 135.8 and 133.7 ng L^{-1} in DI water and surface water, respectively.

Indeed, the signal intensity of such small nanoparticles is very low and overlaps with the background noise – therefore, all particles smaller than ca. 15 nm will be erroneously counted as dissolved metal. In the case of bare 80 nm nAg, both average particle size and percentage of particles were found higher in surface water compared to DI water (Figure 3). In the case of citrate-coated nAg, no noticeable difference in behavior was found in either aqueous media. This can be explained by the fact that bare nanoparticles are more favorable to aggregation than citrate-stabilized ones. But overall, no significant aggregation was observed.

4   CONCLUSION

Using the Nano App Module in the Syngistix for ICP-MS software, it was possible to study the behaviour of silver nanoparticles in surface water without using any subsequent manual data processing. The technique has allowed the effective and selective measurement of changing particle size, aggregation and dissolution over time at low concentration. SP-ICP-MS is practically the only suitable technique that can provide such information on the fate of metal nanoparticles at very low concentrations in environmental waters. Although this study only showed the effectiveness of the technique in the particular case of nAg in river water, it is, without any doubt, applicable to other types of metal and metal oxide nanoparticles in a variety of complex matrices form wastewater, effluents to biological fluids and culture media.

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