APPLICATION NOTE

ICP - Mass Spectrometry

Authors:

Madjid Hadioui, Ph.D.
Université de Montréal

Kevin Wilkinson, Ph.D.
Université de Montréal

Chady Stephan, Ph.D.
PerkinElmer, Inc.

Assessing the Fate of Silver Nanoparticles in Surface Water using Single Particle ICP-MS

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[1] 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[2].

Some studies on the persistence, aggregation and dissolution of metal nanoparticles in natural freshwaters and synthetic complex waters were recently published[3-7]. 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[8-10]. 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 distribution, particle number concentration, and the proportion of dissolved metal. Moreover, it can distinguish between particles of different elements. The principle of SP-ICP-MS is based on the measurement of the signal intensity produced by a single particle. The suspension of nanoparticles must be sufficiently diluted to make sure that only a single particle reaches the plasma at a time, where it is atomized and ionized, producing a signal of relatively high intensity which is measured as one pulse. If the suspension contains dissolved metal of the same element as in the particles, a constant, continuous signal of that element will be produced as a result of its homogeneous distribution. The recorded signal intensity as a function of time can be processed using a theoretical approach first developed by Duegeldre et al.[11-15] for natural metal colloids and then supported by other authors such as Laborda et al.[16, 17].

Ag, ZnO and TiO_2 are among the most frequently studied nanoparticles[18]. In the case of Ag, this is most probably due to the fact that nanosilver is among the most common nanomaterials found in consumer products and tends to release free Ag^+, especially at low concentration[19]. 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. Dissolved silver, including released free ions (Figure 1C) and soluble complexes (Figure 1E), can easily and instantly be measured by SP-ICP-MS. These dissolved species can also be determined by ultrafiltration followed by total metal quantification using ICP-MS or AAS, but this procedure is time consuming since it requires the pre-equilibration of the membrane for at least three cycles of centrifugation, generally 20 min each[19]. Aggregates (Figure 1B) and remaining stable silver nanoparticles (Figure 1G) can be counted and measured by other commonly used techniques (DLS, NTA, TEM) but SP-ICP-MS is the only method that can distinguish between nAg and other colloids in surface water.

Experimental

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 suspensions (product numbers. 84050-40, 84050-80 and 15710-20SC, respectively).

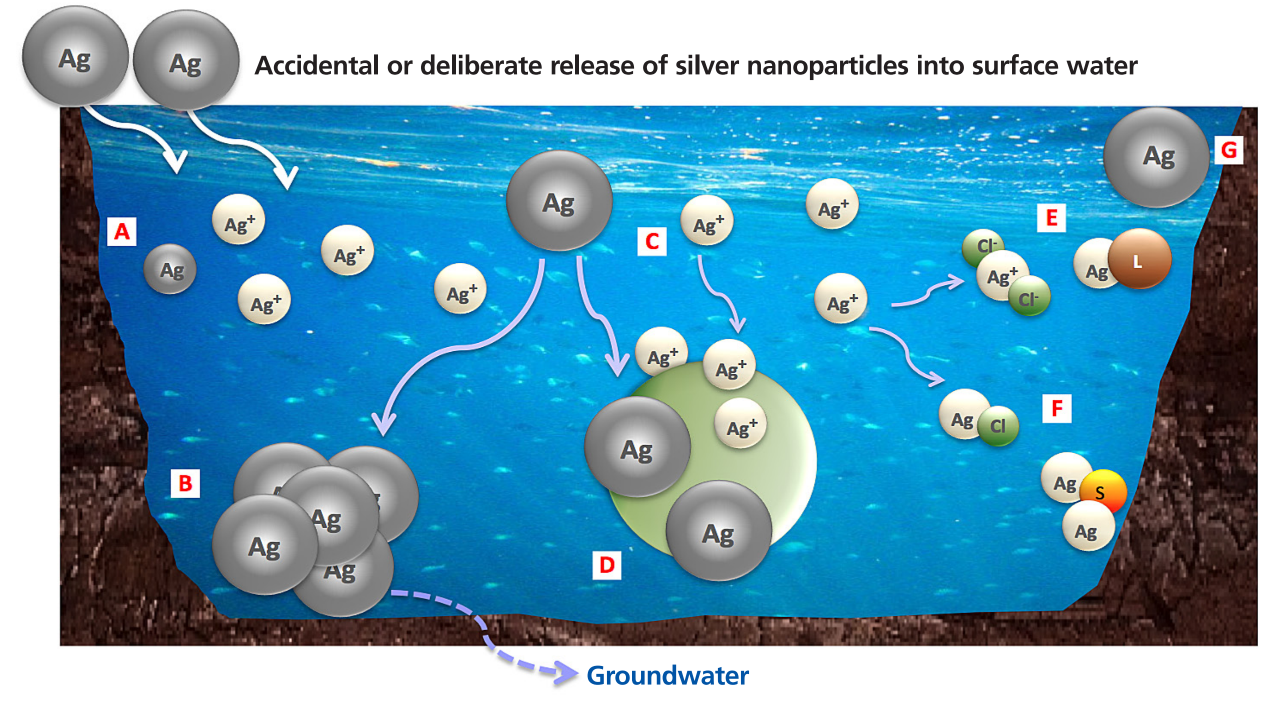

Figure 1. Possible fates of silver nanoparticles in surface waters: (A) Dissolution process leading to free ions release and smaller particles; (B) Aggregation into larger particles, which may settle out of the water, depending on the aggregate size; (C, D) Adsorption of released Ag^+ and nAg, respectively, 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.

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. As shown by Figure 2, Syngistix Nano App Module generates frequency vs. size (nm) plots with an interactive focusing window, eliminating the need for any subsequent data processing using theoretical equations[11-17].

SP-ICP-MS data processing is based on distinguishing between the signal of dissolved metal and that of nanoparticles, counting the pulses (or events) corresponding to individual nanoparticles and converting their intensities to particle size. Indeed, the frequency of the events (pulses) provides particle number concentration, and the intensity of each pulse is proportional to the mass of analyte. The latter was converted to volume and then into size knowing the density and the geometry of the particle using the Syngistix Nano Application Module, which provides automated data treatment, so no subsequent manual data processing is required.

Results

Even after filtration of surface waters at 0.2 µm, Nanoparticle Tracking Analysis (NTA), using an LM14 instrument (NanoSight Ltd. – Amesbury, Wiltshire, UK) with a green laser at 532 nm, showed the presence of non-negligible amounts of colloidal particles with an average diameter of ca. 110 nm. Thus, the addition of metal nanoparticles to this complex matrix will make their detection and characterization very difficult, if not impossible, with commonly used techniques (DLS, TEM, etc.).

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

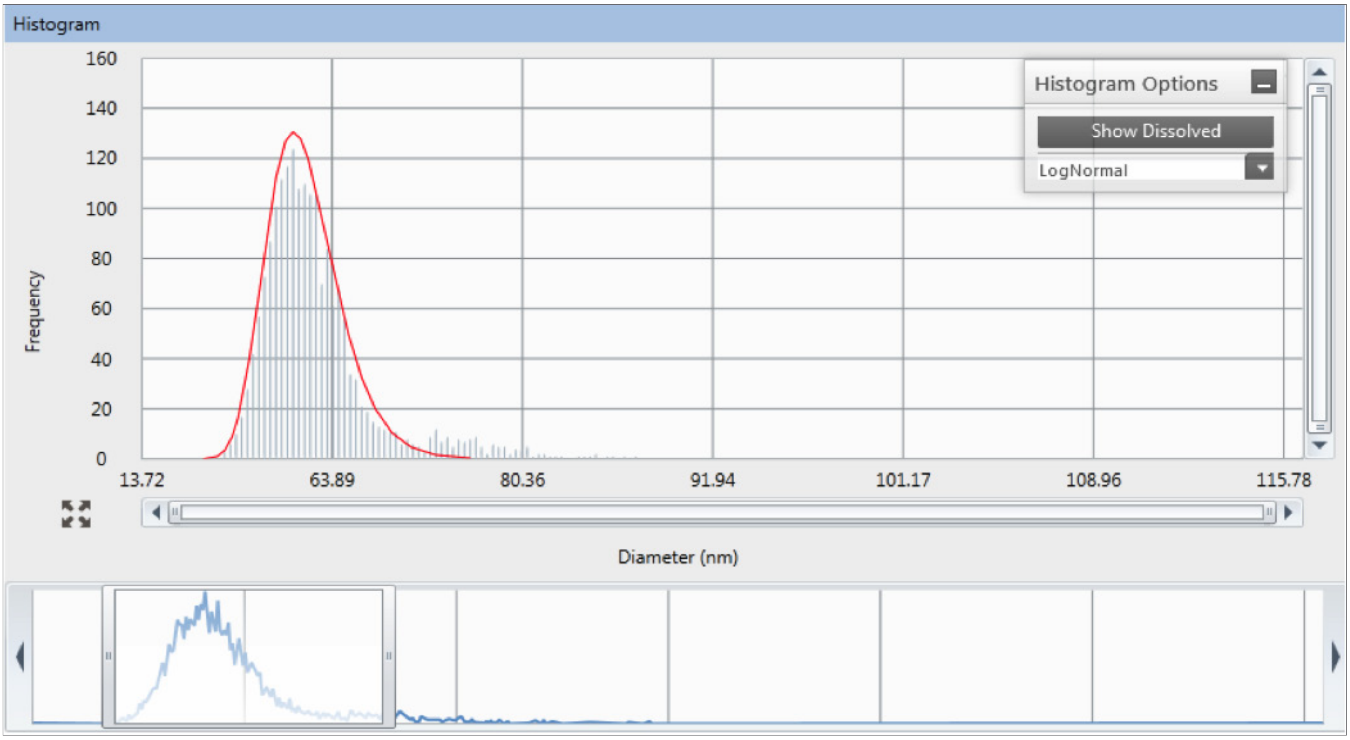

Figure 2. Interactive view of data acquisition with Syngistix for ICP-MS software: signal intensity as a function of acquisition time for silver nanoparticles (bare nAg, 60 nm nominal diameter, total metal concentration 200.8 ng/L) in surface water.

Furthermore, even the determination of the dissolved fraction that is usually performed by ultrafiltration may be inadequate because silver ions may adsorb on the surface of the colloids and, therefore, will be retained by the filtration membrane. Consequently, the proportion of dissolved metal will be underestimated. SP-ICP-MS measurements were found to be more effective and to have fewer limitations than other techniques. Indeed, the presence of other insoluble particles does not interfere with the analysis of silver nanoparticles, as the signal of Ag is recorded independently of the other constituent elements of the colloids.

Figures 3-5 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 3a, 4a and 5a). 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 3b and 4b). 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 5b, 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.

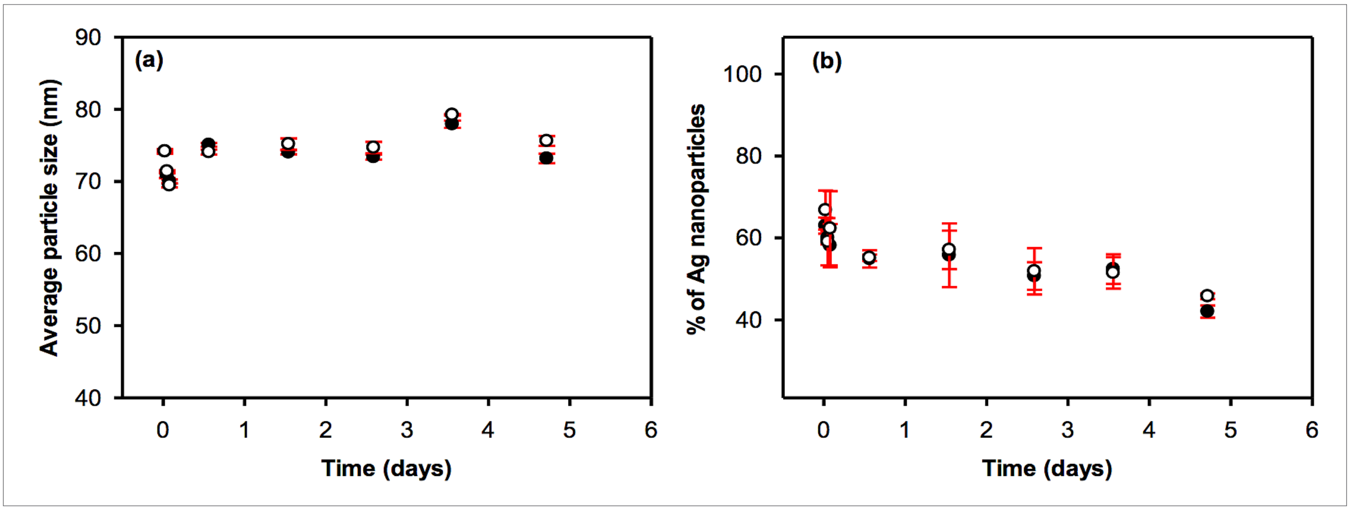

Figure 3. Evolution of (a) the average particle size and (b) the proportion of particulate silver as a function of equilibration time in pure (●) and surface (○) waters. Waters were spiked with 80 nm citrate-coated nAg, and the total metal concentrations were equal to 72.2 and 72.4 ng L^{-1} in DI water and surface water, respectively.

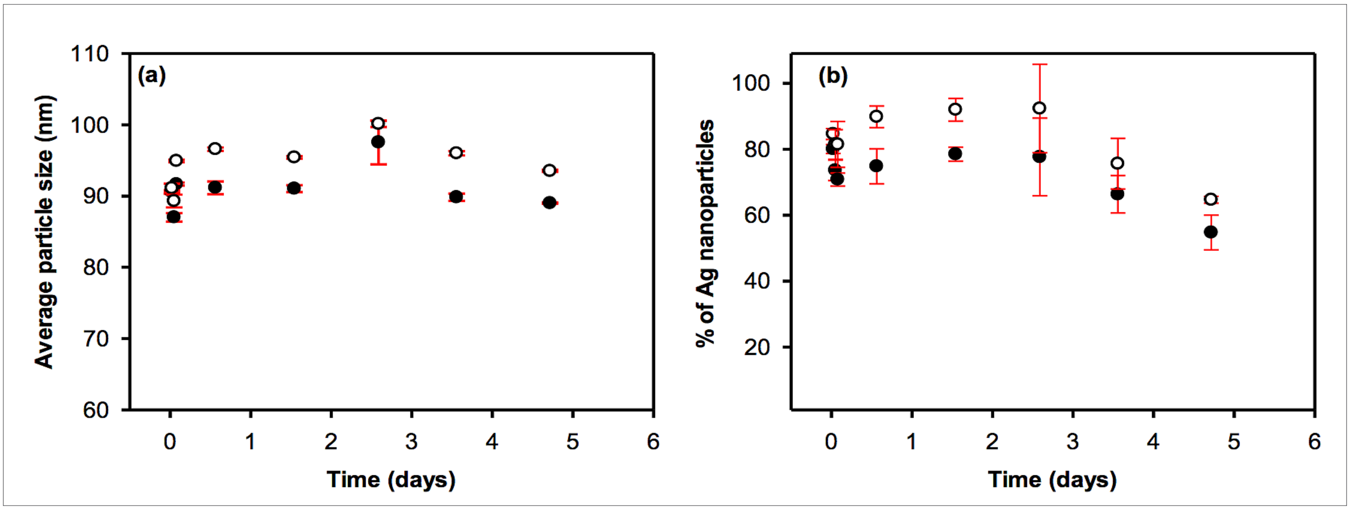

Figure 4. Evolution of (a) the average particle size and (b) the proportion of particulate silver as a function of equilibration time in pure (●) and surface (○) waters. Waters were spiked with uncoated 80 nm nAg, and the total metal concentrations were equal to 196.4 and 200.8 ng L^{-1} in DI water and surface water, respectively.

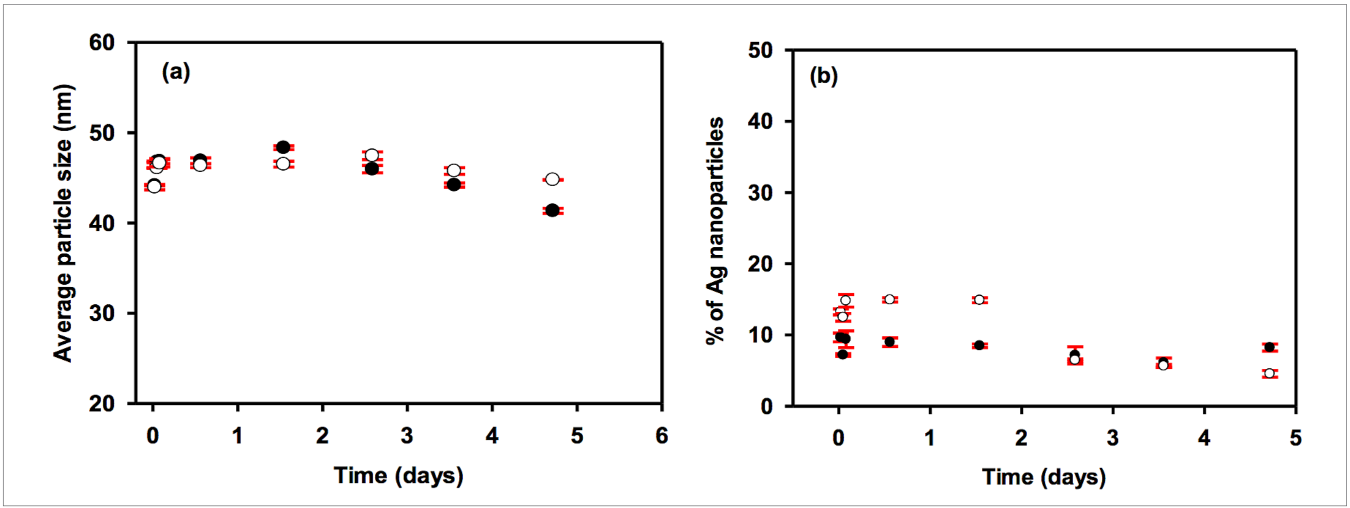

Figure 5. Evolution of (a) the average particle size and (b) the proportion of particulate silver as a function of equilibration time in pure (●) and surface (o) waters. Waters were spiked with 40 nm citrate-coated nAg, and the total metal concentrations were equal to 135.8 and 133.7 ng L^{-1} in DI 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 4). 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.

Conclusion

Using the Nano App Module in the Syngistix for ICP-MS software, it was possible to study the behavior 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.

References

1. Klaine, S.J., et al., N*anomaterials in the environment: Behavior, fate, bioavailability, and effects.* Environmental Toxicology and Chemistry, 2008. 27(9): p. 1825-1851.
2. Domingos, R.F., et al., *Characterizing Manufactured Nanoparticles in the Environment: Multimethod Determination of Particle Sizes.* Environmental Science & Technology, 2009. 43(19): p. 7277-7284.
3. Chinnapongse, S.L., R.I. MacCuspie, and V.A. Hackley, *Persistence of singly dispersed silver nanoparticles in natural freshwaters, synthetic seawater, and simulated estuarine waters.* Science of the Total Environment, 2011. 409(12): p. 2443-2450.
4. Weinberg, H., A. Galyean, and M. Leopold, *Evaluating engineered nanoparticles in natural waters.* Trac-Trends in Analytical Chemistry, 2011. 30(1): p. 72-83.
5. Van Hoecke, K., et al., *Aggregation and ecotoxicity of* CeO_2 *nanoparticles in synthetic and natural waters with variable pH, organic matter concentration and ionic strength.* Environmental Pollution, 2011. 159(4): p. 970-976.
6. Badireddy, A.R., M.R. Wiesner, and J. Liu, *Detection, Characterization, and Abundance of Engineered Nanoparticles in Complex Waters by Hyperspectral Imagery with Enhanced Darkfield Microscopy.* Environmental Science & Technology, 2012. 46(18): p. 10081-10088.
7. Li, X. and J.J. Lenhart, *Aggregation and Dissolution of Silver Nanoparticles in Natural Surface Water.* Environmental Science & Technology, 2012. 46(10): p. 5378-5386.
8. Krystek, P., et al., *Application of plasma spectrometry for the analysis of engineered nanoparticles in suspensions and products.* Journal of Analytical Atomic Spectrometry, 2011. 26(9): p. 1701-1721.
9. Tuoriniemi, J., G. Cornelis, and M. Hassellov, *Size Discrimination and Detection Capabilities of Single-Particle ICPMS for Environmental Analysis of Silver Nanoparticles.* Analytical Chemistry, 2012. 84(9): p. 3965-3972.
10. Pace, H.E., et al., *Single Particle Inductively Coupled Plasma-Mass Spectrometry: A Performance Evaluation and Method Comparison in the Determination of Nanoparticle Size.* Environmental Science & Technology, 2012. 46(22): p. 12272-12280.

11. Degueldre, C. and P.Y. Favarger, *Colloid analysis by single particle inductively coupled plasma-mass spectroscopy: a feasibility study.* Colloids and Surfaces a-Physicochemical and Engineering Aspects, 2003. 217(1-3): p. 137-142.
12. Degueldre, C., P.Y. Favarger, and S. Wold, *Gold colloid analysis by inductively coupled plasma-mass spectrometry in a single particle mode.* Analytica Chimica Acta, 2006. 555(2): p. 263-268.
13. Degueldre, C. and P.Y. Favarger, *Thorium colloid analysis by single particle inductively coupled plasma-mass spectrometry.* Talanta, 2004. 62(5): p. 1051-1054.
14. Degueldre, C., P.Y. Favarger, and C. Bitea, *Zirconia colloid analysis by single particle inductively coupled plasma-mass spectrometry.* Analytica Chimica Acta, 2004. 518(1-2): p. 137-142.
15. Degueldre, C., et al., *Uranium colloid analysis by single particle inductively coupled plasma-mass spectrometry.* Talanta, 2006. 68(3): p. 623-628.
16. Laborda, F., et al., *Selective identification, characterization and determination of dissolved silver(I) and silver nanoparticles based on single particle detection by inductively coupled plasma mass spectrometry.* Journal of Analytical Atomic Spectrometry, 2011. 26(7): p. 1362-1371.
17. Laborda, F., et al., *Critical considerations for the determination of nanoparticle number concentrations, size and number size distributions by single particle ICP-MS.* Journal of Analytical Atomic Spectrometry, 2013. 28(8): p. 1220-1232.
18. Baun, A., et al., *Setting the limits for engineered nanoparticles in European surface waters - are current approaches appropriate?* Journal of Environmental Monitoring, 2009. 11(10): p. 1774-1781.
19. Hadioui, M., S. Leclerc, and K.J. Wilkinson, *Multimethod quantification of Ag+ release from nanosilver.* Talanta, 2013. 105(0): p. 15-19.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs