APPLICATION NOTE

ICP – Mass Spectrometry

Authors:

Ariel R. Donovan[1,2], Honglan Shi[1,2], Craig Adams[2,3], Chady Stephan[4]

[1] Department of Chemistry and Environmental Resource Center, Missouri University of Science and Technology

[2] Center for Single Nanoparticle, Single Cell, and Single Molecule Monitoring (CS³M)

[3] Department of Civil and Environmental Engineering, Utah State University

[4] PerkinElmer, Inc.

Rapid Analysis of Silver, Gold, and Titanium Dioxide Nanoparticles in Drinking Water by Single Particle ICP-MS

Introduction

As the use of nanoparticles (NPs) in industrial processes and consumer products has increased, so has the likelihood that they will appear in the environment, both through the discharge of industrial waste and from discarded consumer products. Although the concentration of NPs is expected to be low in environmental systems, their impact on human health is unknown. Therefore, the need exists to determine NPs in drinking water systems.

Because of its unique ability for rapid, sensitive and element-specific analysis, single particle ICP-MS (SP-ICP-MS) is an ideal tool for measuring NPs in drinking water systems. This work will highlight the efficiency of drinking water treatment systems in removing silver (Ag), gold (Au), and titanium dioxide (TiO_2) nanoparticles using SP-ICP-MS as the sole analytical technique.

Experimental

Chemicals and Materials

Au and Ag nanoparticles were purchased from nanoComposix™ Inc. (San Diego, California, USA), and TiO_2 nanoparticles were acquired from US Research Nanomaterials, Inc. (Houston, Texas, USA). Table 1 shows the sizes and characteristics of the NPs used in this study. Intermediate suspensions were prepared in ultra-high purity water to disperse any agglomerated particle clusters.

Table 1. Nanoparticle Characteristics.

Material	Diameters (nm)	Characteristics
Gold (Au)	50, 80, 100	Capped with citrate
Silver (Ag)	40, 70, 100	Capped with citrate
Titanium dioxide (TiO_2)	100, 160	Uncapped

Water samples studied include ultra-pure water, source water (surface water from Missouri River), and the corresponding drinking water (post- treatment) from three water treatment plants.

Instrumental Conditions

All analyses were performed on a PerkinElmer NexION® 300D/350D ICP-MS using Syngistix™ software with the Syngistix Nano Application Module (PerkinElmer Part No. N8140309). Table 2 shows the instrumental and method parameters used. The sample uptake rate was measured gravimetrically, and the transport efficiency was determined with Au nanoparticles.

All measurements were made against external calibration curves in the Syngistix Nano Application Module. For the dissolved concentrations, calibration standards were made from serial dilutions of single-element stock solutions. Particle calibration standards were made by diluting the appropriate particles to concentrations of approximately 10^5 particles/mL or less to minimize the probability that multiple particles arrive at the plasma at the same time.

Table 2. Instrument and Method Parameters for Single Particle ICP-MS Analysis of Au, Ag, and TiO_2 in Single Particle Mode.

Instrument Parameter	Operation Setting
Nebulizer	Concentric
Spray Chamber	Cyclonic
Cones	Platinum
RF Power (W)	1400
Nebulizer Gas Flow (L/min)	1.02-1.06
RPq	0.5
Sample Uptake Rate (mL/min)	0.26-0.29
Dwell Time (μs)	100
Sample Time (s)	100
Transport Efficiency (%)	7.5-8.5

Method Parameters	Au	Ag	Ti
Isotope (amu)	196.967	106.905	46.9518
Density (g/cm^3)	19.3	10.49	4.23
Mass Fraction (%)	100	100	60
Ionization Efficiency (%)	100	100	100

Results and Discussion

Detection Limits

Both the dissolved and particle size detection limits in surface water are shown in Table 3 and were determined by preparing the nanoparticle suspension in filtered river water using SP-ICP-MS mode. The dissolved detection limits are higher than those obtained by conventional ICP-MS measurements due to the short integration times used: 100 μs in this work vs. 1 second or longer (typically) by conventional ICP-MS measurements. The particle size detection limit for TiO_2 is greater than that for Au and Ag due to the particle composition: while Au and Ag particles are pure metal, TiO_2 particles are only 60% Ti. Additionally, $^{47}Ti^+$ was used for titanium measurements, even though it is only 7.4% abundant. The reason for selecting this mass instead of the most abundant titanium isotope ($^{48}Ti^+$ = 73.8% abundant) is that Ca also has an isotope at m/z 48. Since Ca is present at elevated levels in drinking waters, it would interfere with Ti at this mass. Therefore, $^{47}Ti^+$ was chosen for analysis.

Table 3. Detection Limits.

Element	Dissolved (μg/L)	Particle (nm)
Ag	0.10	23-25
Au	0.10	28-30
TiO_2	0.75	65-70

To evaluate the effectiveness of the water treatment process in the treatment plants for Au, Ag, and TiO_2 nanoparticles, water samples were collected both pre- and post-treatment at three water treatment plants. None of the six waters contained measureable amounts of Ag or Au, either as particles or dissolved. However, all source water samples contained TiO_2, as shown in Table 4. Plants 1 and 2 effectively removed both dissolved Ti and TiO_2 particles, as evidenced by the lower amounts present in the post-treatment waters than the pre-treatment ones. The results from Plant 3 differed from the first two plants in that Ti-containing particles could still be detected after treatment, although significantly fewer than pre-treatment. However, all the dissolved Ti was removed.

Table 4. Effectiveness of Three Water Treatment Plants Removing TiO_2 Particles and Dissolved Ti.

Plant	Pre/ Post Treatment	Most Frequent Size (nm)	Particle Concentration (particles/mL)	Dissolved Concentration (µg/L)
1	Pre Post	170 < MDL	432,000 < MDL	17.9 1.21
2	Pre Post	156 < MDL	451,000 < MDL	11.7 1.17
3	Pre Post	153 76	425,000 17,237	10.6 < MDL

Table 5. Spike Recovery Studies in Drinking Waters.

Sample	Au			Ag			TiO_2		
	Most Freq Size (nm)	Part Conc. Spike Recovery	Diss Conc. Spike Recovery	Most Freq Size (nm)	Part Conc. Spike Recovery	Diss Conc. Spike Recovery	Most Freq Size (nm)	Part Conc. Spike Recovery	Diss Conc. Spike Recovery
1	98	97%	80%	98	97%	80%	102	9%	84%
2	97	88%	84%	97	88%	84%	87	6%	88%
3	101	94%	89%	101	94%	89%	87	6%	112%

To check the accuracy, spike recovery tests were performed for all metals, both as dissolved and nanoparticles. Three samples were spiked with 2 µg/L of the dissolved metals and 100 nm nanoparticles at a concentration ≈ 1×10^5 particles/mL. Table 5 shows the results of these spike recovery studies, which indicate accurate recoveries, except for the concentration of TiO_2 nanoparticles, which recovered below 10% for each sample. Low recovery for TiO_2 particles was due to aggregation in the standards and in the water matrix. Without the addition of a surfactant, these uncapped TiO_2 particles tended to aggregate, which resulted in particle loss between dilutions and in the water matrix where they had the opportunity to react and form new species and/or aggregate further and fall out of solution. The highest recovery obtained for these particles in ultra-pure water and in water matrix were 24% and 9%, respectively.

Conclusions

This work has demonstrated the ability of the NexION 350 ICP-MS running in Single Particle mode to accurately detect Au, Ag, and TiO_2 nanoparticles in drinking water systems. Real samples analyzed both pre- and post-treatment showed that drinking water treatment processes of the studied water treatment plants effectively remove both dissolved and Ti-containing nanoparticles. (Neither Au nor Ag were detected in these water samples.)

The use of the Syngistix Nano Application Module with the NexION 350 running in Single Particle mode is an ideal tool for nanoparticle analysis in real samples to be able to measure rapidly and continually, very important when analyzing samples with low particle concentrations.

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

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