APPLICATION NOTE

ICP - Mass Spectrometry

Authors:

Ariel R. Donovan[1,2]

Honglan Shi[1,2]

Craig D. Adams[2,3]

Chady Stephan[4]

[1]Department of Chemistry and Environmental Research Center, Missouri University of Science and Technology
Rolla, Missouri, 65409, United States

[2]Center for Single Nanoparticle, Single Cell, and Single Molecule Monitoring (CS^{3}M)
Rolla, Missouri 65409, United States

[3]Department of Civil and Environmental Engineering, Utah State University
Logan, Utah, 84321, United States

[4]PerkinElmer, Inc., 501 Rowntree Dairy Rd, Woodbridge, On, Canada, L4L 8H1

Monitoring Cerium Dioxide and Zinc Oxide Nanoparticles through Drinking Water Treatments using Single Particle ICP-MS

Introduction

With the increasing use of nanoparticles (NPs) in industrial processes and consumer products, it is inevitable that nanoparticles will make their way into environmental systems, including drinking water. As a result, removal of these nanoparticles from drinking water is important, and the effectiveness of various water treatment processes for removing the nanoparticles needs to be understood.

Two commonly and widely used nanoparticles are zinc oxide (ZnO) and cerium dioxide (CeO_2), which have a global production of 550 t/year and 55 t/year, respectively.[1] Both of these nanoparticles cause acute toxicity that results in oxidative stress and oxidative damage to mammalian cells.[2-5]

Although a variety of techniques are available to measure nanoparticles, single particle ICP-MS (SP-ICP-MS) has become increasingly important due to its speed and ability to measure environmentally relevant low nanoparticle concentrations, surpassing the limitations of light-based technologies.[6-7]

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This work focuses on the use of SP-ICP-MS to analyze samples simulating real-world systems to measure ZnO and CeO_2 NP size, size distribution, particle concentration, and ionic concentration in the various steps of drinking water treatment processes. Using SP-ICP-MS, the fate and transformation of ZnO and CeO_2 NPs was assessed without any laborious sample preparation steps or extensive data processing using PerkinElmer's NexION® 350D ICP-MS with Syngistix™ Nano Application Software Module. More detailed information about this work was recently published in *Analytical and Bioanalytical Chemistry.*[8]

Experimental

Standard and Sample Preparation

Water samples were collected from the Missouri River in polypropylene bottles. To understand the effects of the various processing steps, river water samples without added nanoparticles and river water spiked with ZnO (80-200 nm) and CeO_2 (30-50 nm) nanoparticles (US Research Nanomaterials, Inc., Houston, Texas, USA) were subjected to the various water treatment processes by simulating the general drinking water treatment process (Figure 1) using a six-gang stirrer system. Before treatment and after each process, the samples were collected and analyzed by SP-ICP-MS to understand the effect of treatment on the ZnO and CeO_2 nanoparticles.

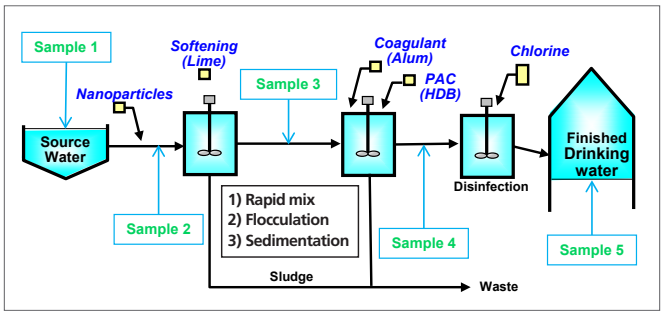

Figure 1. Diagram of simulated drinking water treatment process using the six-gang stirrer system.

Instrumentation and Methodology

All SP-ICP-MS measurements were carried out with a NexION 350D ICP-MS (PerkinElmer Inc., Shelton CT) using the parameters in Table 1. Although Zn at m/z 67 has a lower natural abundance than the other Zn isotopes, it has the fewest potential interferences, so was chosen for this work. In future work, Zn at m/z 66 will be examined in Reaction mode to remove interferences, allowing smaller particles to be measured. Nevertheless, Zn at m/z 67 proved adequate for this work.

Size calibration and transport efficiency studies were carried out with gold nanoparticles (citrate-capped; 50, 80, 100 nm) in 2 mM sodium citrate (nanoComposix™, San Diego, California, USA). Aqueous Ce and Zn calibration standards were made by dilution of 1000 mg/L stock standards (PerkinElmer Inc., Shelton CT).

Table 1. SP-ICP-MS Instrumental and Method Parameters.

Instrument Parameter	Value
Nebulizer	Glass Meinhard Type C
Spray Chamber	Glass Cyclonic
Sample & Skimmer Cones	Platinum
RF Power (W)	1600
Sample Uptake Rate (mL/min)	0.26 -0.29
Dwell Time (ms)	0.1
Sampling Time (s)	100
Transport Efficiency (%)	7.5-8.5

Method Parameter	Zn	Ce
Isotope (amu)	67	140
Density (g/cm^3)	5.61	7.13
Mass Fraction (%)	80.31	81.41
Ionization Efficiency (%)	100	100

Results and Discussion

Before measuring water samples, the CeO_2 and ZnO nanoparticles were first characterized in deionized water to gauge the performance of the methodology; the resulting size distributions are shown in Figures 2a and 2c. The ZnO size distribution is inconsistent, which reflects the wide range stated by the manufacturer (80-200 nm, measured by scanning electron microscopy [SEM] as indicated on the certificate of analysis). The CeO_2 size distribution has a clear maximum at about 25 nm with a wide distribution to larger sizes, which corresponds to the certificate value supplied with the particles. To confirm the inhomogeneity, we also examined these NPs with SEM. The resulting images are shown in Figures 2b and 2d and clearly illustrate the inhomogeneity of both particles, with the ZnO being much more inhomogeneous and irregularly shaped than the CeO_2 particles, which confirms the SP-ICP-MS results.

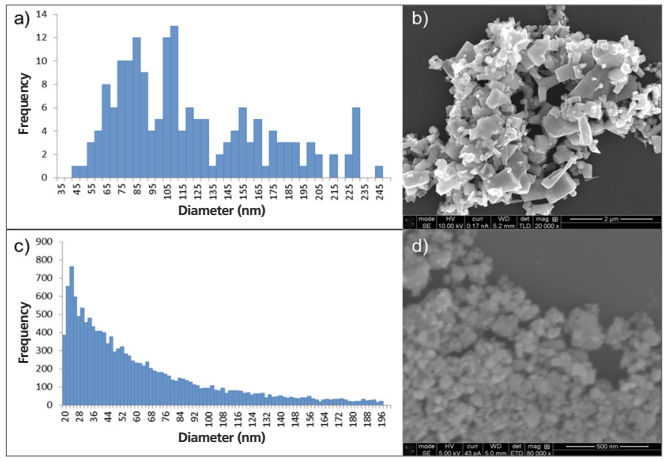

Figure 2. SP-ICP-MS and SEM characterization of ZnO (a and b) and CeO_2 (c and d) NPs.

The NP size detection limits were determined by five times the standard deviation above the background when measuring ultrapure water by SP-ICP-MS. The size detection limits are shown in Table 2. The larger ZnO detection limit is most likely due to the use of $^{67}Zn^{+}$ as the analyte; smaller particles could be detected using a more abundant Zn isotope, although the actual results may be less accurate due to potential interferences.

Table 2. CeO_2 and ZnO NP Size Detection Limits

Nanoparticle	Size Detection Limit (nm)	Dissolved Ion Detection Limit (µg/L)
CeO_2	18-20	0.10
ZnO	35-40	0.20

Next, an untreated river water sample was subjected to each of the treatment steps typically used in water treatment plants: lime softening, alum coagulation with PAC sorption, and disinfection with free chlorine, as shown in Figure 1. Prior to treatment and after each treatment step, the sample was analyzed for CeO_2 and ZnO NPs, as well as their dissolved ions. The same tests were also repeated after spiking the sample with CeO_2 and ZnO NPs at 1×10^6 particles/mL corresponding to mass concentration of 7 µg/L ZnO and 4 µg/L CeO_2.

Table 3 shows the results for ZnO particle size, particle concentration, and dissolved Zn concentration for both the unspiked and spiked sample after each stage of treatment. The results for the unspiked sample indicate that lime softening removes the large ZnO particles, reducing the average size from 75 to 35 nm, and decreases the particle number concentration by 38%. At such particle concentrations (10^6 particles/mL), monitoring the change in the dissolved Zn concentration will not reveal much about the fate of ZnO particles, as they are too small to cause a significant increase in the ionic fraction. Assuming an average particle size of 75 nm, 0.47 µg/L of ZnO would be removed during lime softening. Furthermore, the dissolved Zn concentration also decreased following the lime softening treatment/precipitation process that is causing Zn to drop out of solution. The subsequent water treatment steps did not affect the ZnO particle size or dissolved Zn concentration, but significantly decreased the particle concentration.

Next, the river water was spiked with ZnO NPs, and the same experimental steps were repeated. The results (Table 3) follow the same trends as the unspiked river water. Such observations may suggest that the Zn pulse signals detected in the unspiked river water are ZnO NPs. However, the size is at the detection limit of the NP.

Table 3. Effect of Treatment Steps on ZnO NPs in River Water.

Sample	Parameter	Untreated	Lime	Alum	Chlorine
River Water	Particle Size (nm)	75	35	35	35
	Change in Particle Conc	---	↓38%	↓74% (36%)	↓77% (3%)
	Dissolved Conc (µg/L)	1.11	0.43	0.48	0.52
River Water with ZnO NP Addition (1 x 10^6 parts/mL)	Particle Size (nm)	120	50	50	50
	Change in Particle Conc	---	↓53%	↓79% (26%)	79%
	Dissolved Conc (µg/L)	16.5	0.36	0.46	0.46

The same tests performed with ZnO NPs in the river water samples were repeated with CeO_2 NPs; the results are shown in Table 4. The obtained results demonstrate that the CeO_2 NPs were completely removed during the lime softening treatment, and that no further treatment is needed. It should also be pointed out that CeO_2 NPs are stable in environmental aqueous media and no signs of dissolution were noticed during an up-to-12-hour treatment process.

Table 4. Effect of Treatment Steps on CeO_2 NPs in River Water.

Sample	Parameter	Untreated	Lime	Alum	Chlorine
River Water	Particle Size (nm)	24	---	---	---
	Change in Particle Conc	---	↓> 99%	---	---
	Dissolved Conc (µg/L)	< DL	< DL	< DL	< DL
River Water with CeO_2 NP Addition (1 x 10^6 parts/mL)	Particle Size (nm)	38	---	---	---
	Change in Particle Conc	---	↓> 99%	---	---
	Dissolved Conc (µg/L)	< DL	< DL	< DL	< DL

DL = Detection Limit

A graphical representation of the results from all four sets of experiments appears in Figure 3.

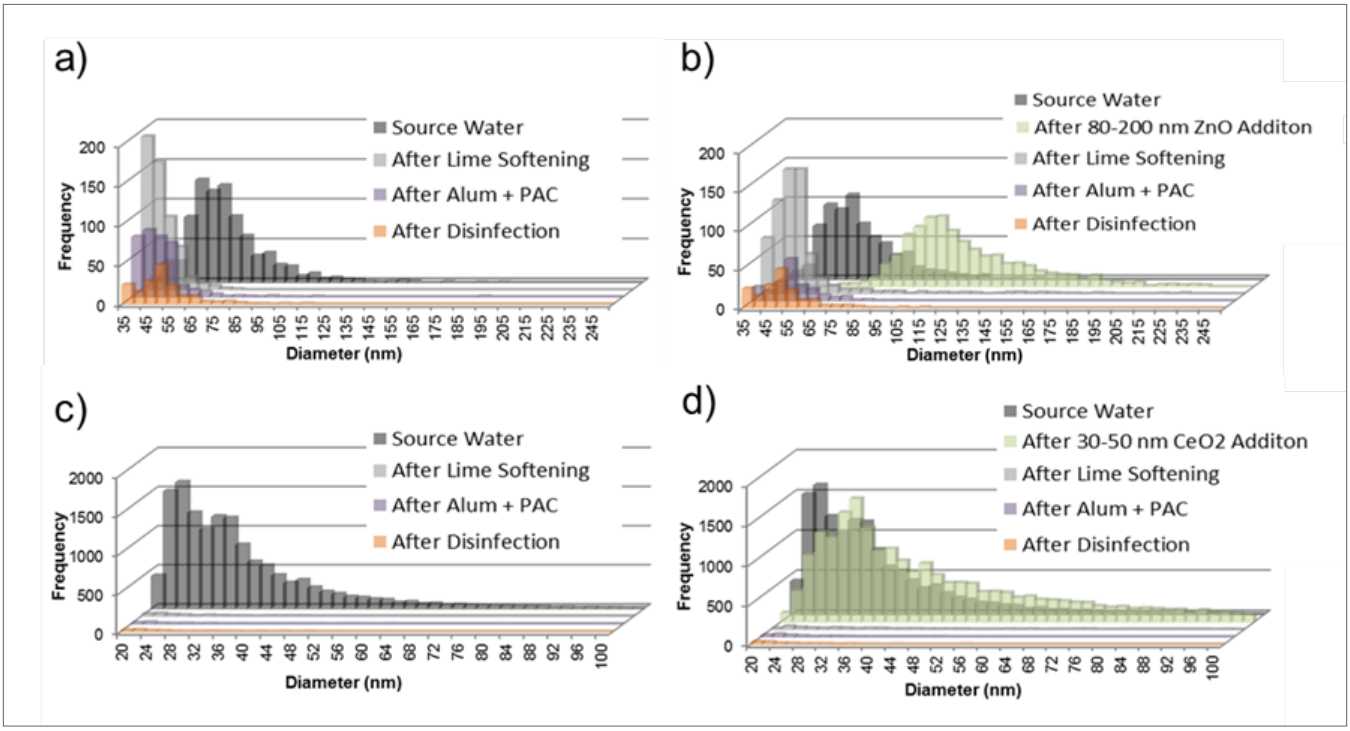

Figure 3. Change in size distribution histograms after sequential drinking water treatments for a) ZnO without NP addition (n=2), b) ZnO with 80-200 nm ZnO addition (n=2), c) CeO_2 without NP addition (n=2), and d) CeO_2 with 30-50 nm CeO_2 addition (n=2).

Conclusion

This work serves as a proof of concept demonstrating the applicability and superiority of SP-ICP-MS as a routine technique in monitoring the efficiency of drinking water treatment process for removal, transformation, and transportation of environmental relevant levels of ZnO and CeO_2 nanoparticles. The results show that the conventional drinking water treatment procedures can reduce up to 80% of ZnO particles and virtually eliminate the presence of CeO_2 nanoparticles. As more complex nanoparticles are being used and introduced in various consumer products, there is an increased need for pilot studies to further investigate the impact of these emerging chemicals on the environment and, subsequently, human health. SP-ICP-MS can serve not only for the pilot research, it may also serve as a rapid tracking technology as part of routine water quality testing for nanoparticles.

References

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Consumables Used

Component	Part Number
50 nm Gold Nanoparticles	N8142302
80 nm Gold Nanoparticles	N8142305
100 nm Gold Nanoparticles	N8142307
1000 ppm Cerium Standard	N9303765 (125 mL) N9300110 (500 mL)
1000 ppm Zinc Standard	N9300178 (125 mL) N9300168 (500 mL)
0.38 mm ID (Green/Green) Flared Peristaltic Pump Tubing for Sample Uptake	N0777042
1.30 mm ID (Gray/Gray) Santoprene Peristaltic Pump Tubing for Drain	N0777444

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

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