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Analysis of Cerium Dioxide Nanoparticles in Soil Using Single Particle ICP-MS

Introduction

Over the past few decades, engineered nanoparticles (ENPs) have been increasingly used in many commercial products.[1,2] As a result, more and more ENPs have been released into the environment, which raises concerns over their fate, toxicity and transport therein.[3] Cerium dioxide nanoparticles (CeO_2 NPs) are widely used in industry, and once they are released into the environment, soils are likely to be their primary repository. Nevertheless, given their relatively low concentrations and high natural background of Ce-containing minerals in the environment, it still remains a challenge to detect and characterize the CeO_2 NPs in environmental samples. Single particle ICP-MS (SP-ICP-MS) has proven to be a powerful technique to detect and characterize ENPs, especially at very low concentrations (as expected in environmental samples), owing to its capability to quickly provide information about particle size, size distribution and particle number concentration.[4-6] Since its development, SP-ICP-MS has been successfully utilized to investigate ENPs in various matrices.[7-16] This work demonstrates a robust method using SP-ICP-MS technology to detect CeO_2 NPs which were extracted from soil samples with tetrasodium pyrophosphate (TSPP).

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Experimental

Materials

CeO_2 NPs (30-50 nm) were purchased from US Research Nanomaterials (Houston, Texas, USA). Ultrapure water (18.2 MΩ) was prepared using a Simplicity 185 Millipore water purification system (Billerica, Massachusetts, USA). Citrate-coated Au NPs (40 nm, Nanocomposix, San Diego, California, USA) were employed to determine transport efficiency. A dissolved Ce standard was purchased from High-Purity Standards (Charleston, South Carolina, USA). Tetrasodium Pyrophosphate Decahydrate (TSPP) was purchased from Thermo Fisher Scientific (Pittsburgh, Pennsylvania, USA).

Soil Samples

The soil used in this work was collected from the upper 5 cm layer on the campus of Missouri University of Science and Technology. Prior to use, the soil was dried in an oven at 100 °C and subsequently ground into a fine powder with a porcelain mortar and pestle. The powdered samples were then stored in a plastic sample bag at room temperature for future use.

Soil Spiking and Extraction

The CeO_2-NP-dosed soil samples were prepared by adding 50 μL of 100 mg/L of CeO_2 NP dispersion into 0.15 g soil, followed by mixing on a vortex mixer. The dosed soil samples were then left at room temperature for 24h to age prior to analysis. Upon aging, the soil control (i.e. soil without CeO_2 NPs added) and CeO_2-NP-dosed soil were extracted with various concentrations of TSPP solutions (2.5 mM, 5 mM, and 10 mM) to investigate the effect of the concentration of TSPP on the extraction efficiency. The soil was mixed with 15 mL of TSPP solution to achieve a reagent-to-soil ratio of 100:1 (mL:g) and homogenized on a vertical rotator for 30 min at 30 rpm. The samples were then sonicated in a bath sonicator for 30 min, followed by an additional 30-min homogenization step on a rotatory mixer at 30 rpm. After extraction, the samples were left to settle overnight at room temperature to sediment out micrometer-sized particles. All samples were extracted in triplicate and diluted to a final TSPP concentration of 0.025 mM for SP-ICP-MS analysis.

SP-ICP-MS Method

All sample analyses were performed using a PerkinElmer NexION® ICP-MS (Shelton, Connecticut, USA) operated in single particle mode. Instrumental operating conditions, as shown in Table 1, were optimized for maximum sensitivity for ^{140}Ce, which is the most abundant cerium isotope and also free of interferences. The sample flow rate was measured by weighing the amount of MQ water aspirated for 3 min, and the transport efficiency was determined by using 40 nm AuNPs. The particle sizes of CeO_2 NPs and dissolved Ce concentrations were calculated based on the calibration curves generated from dissolved Ce standards prepared in 0.025 mM TSPP solution. All data was acquired and processed using the Syngistix™ Nano Application Module within Syngistix for ICP-MS software.

Table 1. NexION ICP-MS instrumental and method details.

SP-ICP-MS Instrument Conditions and Settings	
Nebulizer	MEINHARD® Type C, Glass
Spray Chamber	Cyclonic, Glass
Sample Flow Rate	0.28-0.35 mL/min
Nebulizer Gas Flow	1.02 L/min
RF Power	1600 W
SP-ICP-MS Method Parameters	
Element Monitored	^{140}Ce
CeO_2 Density	7.13 g/cm³
Ce Mass Fraction in CeO_2 NPs	81.39%
Dwell Time	50 μs
Sample Analysis Duration	100 s
Sample Introduction	Manual

Results and Discussion

In order to obtain reliable results for particle analysis via SP-ICP-MS, the estimation of the particle number concentration detection limit of CeO_2 NPs is very important. Therefore, to determine the method detection limit (MDL) for CeO_2 NPs, various particle concentrations of CeO_2 NP standards in 0.025 mM TSPP solutions prepared by a series of dilutions of 0.5 mg/L CeO_2 NPs ranging from 500 to 256,000 NPs/mL were analyzed. As shown in Figure 1, the measured particle concentrations show a linear trend in the particle concentration range from 0.0078 μg/L to 1 μg/L. However, when the prepared particle concentration was further decreased to less than 0.0078 μg/L, deviations from linearity were noticed. This suggests that the current established SP-ICP-MS method is able to precisely detect CeO_2 NPs as low as 1700 NPs/mL, which is extremely sensitive. The particle number concentration detection limit is dependent on the analysis time: a lower particle number concentration detection limit could be achieved with longer sample acquisition times and/or a higher transport efficiency.
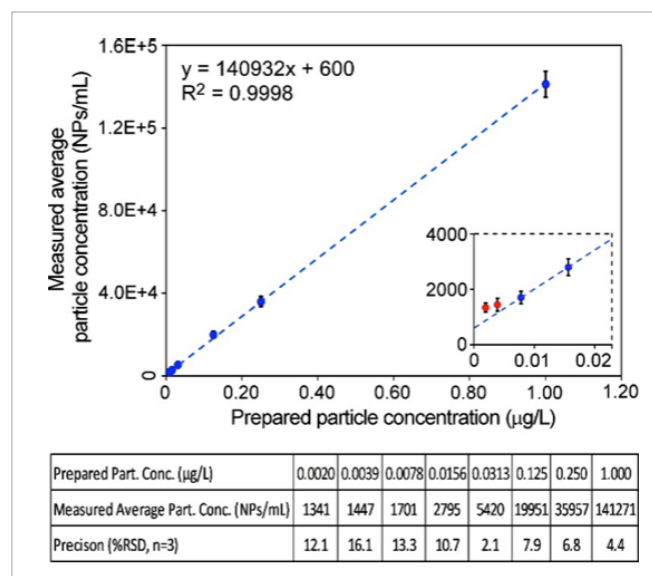

Prepared Part. Conc. (μg/L)	0.0020	0.0039	0.0078	0.0156	0.0313	0.125	0.250	1.000
Measured Average Part. Conc. (NPs/mL)	1341	1447	1701	2795	5420	19951	35957	141271
Precison (%RSD, n=3)	12.1	16.1	13.3	10.7	2.1	7.9	6.8	4.4

Figure 1. Estimation of the concentration detection limit of SP-ICP-MS for CeO_2 NPs.

To estimate the particle size detection limit of CeO_2 NPs, 0.025 mM TSPP reagent blanks, which did not contain any CeO_2 NPs, were analyzed by SP-ICP-MS. The intensity of the majority of pulse signals observed from the blanks was employed to determine the particle detection threshold which was then utilized to define the particle size detection limit. Signal intensities above the threshold were considered to be particle events, whereas those lower than or equal to the threshold were treated as dissolved Ce. The results showed that the majority of the highest signal intensities from the reagent blanks were two counts. Therefore, to minimize false positives, the intensity of three counts was chosen as the threshold, which led to a particle size detection limit of ~24 nm.

To evaluate whether the TSPP extraction has any influence on the CeO_2 NPs, a CeO_2 NP solution (in water) was extracted using a high concentration TSPP solution (10 mM) and characterized via SP-ICP-MS. As a control, another CeO_2 NP solution was analyzed immediately without extraction. Figure 2 shows that no significant differences in particle concentration and particle size were observed, suggesting that TSPP is suitable for extracting CeO_2 NPs from soil without leading to changes in the physiochemical behavior of CeO_2 NPs.
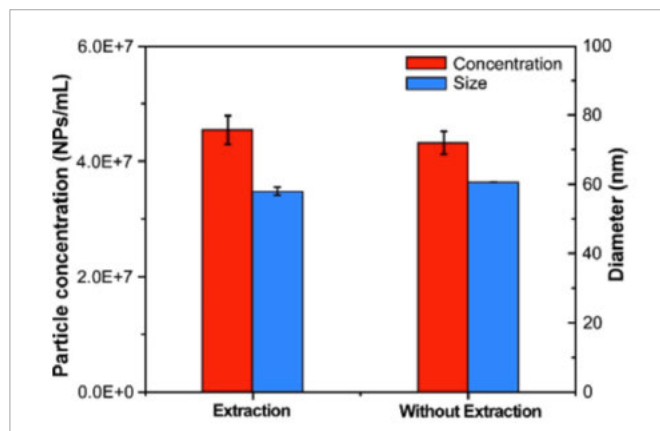

Figure 2. Comparison of particle concentrations and measured size distributions of CeO_2 NPs with and without going through the TSPP extraction process. All samples were analyzed in three replicates.

To investigate whether the CeO_2 NPs can be quantitatively extracted from soil, both dosed and un-dosed soils were extracted with 2.5 mM TSPP and subsequently analyzed by SP-ICP-MS. Figure 3 shows the resulting raw data for both samples. It can be seen that continuous and pulse signals appeared in both cases, indicating that dissolved and particulate Ce exists in both soil samples. It is worth noting that only a few low-intensity pulse

signals appeared in the raw SP-ICP-MS data of the un-dosed soil (i.e. control, Figure 3A), compared with the raw data for the reagent blank (0.025 mM TSPP). This suggests that the control soil is relatively clean of particulate Ce. By comparing Figure 3A with 3B, one can see that the frequency and the intensity of the pulse signals detected in the CeO_2 NP-exposed soil are much higher than those in the control soil (with the same dilution factor). This indicates that the dosing and extraction procedure are realistic.
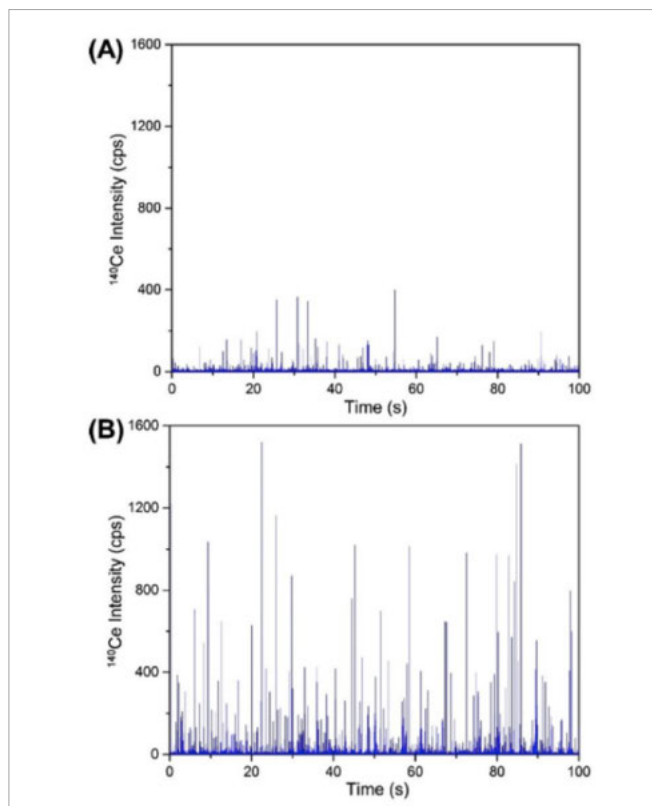

Figure 3. (A) Raw data for un-dosed soil (control). (B) Raw data for CeO_2-NP-dosed soil.

To explore the influence of the TSPP concentration on the extraction efficiency of CeO_2 NPs from soil, three different concentrations of TSPP solutions (2.5 mM, 5 mM, and 10 mM) were employed to extract the CeO_2-NP-dosed soil samples, and the extraction yields were compared. Table 2 shows that 2.5 mM and 5 mM of TSPP could efficiently extract both particulate Ce and dissolved Ce (including particles smaller than the size detection limit) from soil. However, 10 mM TSPP resulted in a high recovery. Thus, the concentration of TSPP should be used in the range of 2.5 to 5 mM for CeO_2 NPs analysis in soil by this SP-ICP-MS method.

Table 2. Comparison of TSPP extraction efficiency.

TSPP Conc. (mM)	Sample	Most Freq. Size (nm)	Mean Particle Size (nm)	CeO₂ NPs Concentration (parts/mL)	CeO₂ NPs Concentration (µg/L)	Dissolved Ce Concentration (µg/L)
2.5	Soil control	44	54	34080592	20.2	121
	CeO₂ NP spiked soil	50	75	88757313	138	131
	NP extraction recovery yield (%)			112		
5	Soil control	45	57	30224127	21.2	138
	CeO₂ NP spiked soil	49	73	77356625	111	139
	NP extraction recovery yield (%)			97		
10	Soil control	47	58	24458120	17.6	159
	CeO₂ NP spiked soil	49	73	90422555	134	191
	NP extraction recovery yield (%)			135		
	CeO₂ NP standard	61	99	48739336	179	8.58

Conclusion

This work has demonstrated the application of SP-ICP-MS to accurately detect CeO₂ NPs in soil samples, leveraging PerkinElmer's NexION ICP-MS with Syngistix Nano Application Software Module. By using the extraction and the detection method demonstrated in this study, the particle number concentration, particle size and size distribution of CeO₂ dosed into natural soil samples could be successfully determined without changing the physio-chemical characteristics of the particles.

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