**Fate of Cerium Dioxide Nanoparticles in Soil Monitored by Single Particle ICP-MS**

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**Abstract**

With the rapid development of nanotechnology and the corresponding growing applications, the possibility of releasing engineered nanoparticles (ENPs) into the environment is increasing. The risk of nanorelease from consumer products prompts the need of investigating of the fate, transportation, transformation, and environmental toxicity of released ENPs. Cerium dioxide nanoparticles (CeO2 NPs) are one type of widely used ENPs due to their unique oxidative/reductive and catalytic properties. Once the CeO2 NPs are released into the environment, soils are likely to be their primary repository. However, detection and characterization of CeO2 NPs in soil is a challenge because of their low predicted environmental concentrations and the high natural background of Ce-containing minerals, leading to the fate of the CeO2 NPs after released into soils is largely unknown. In this study, we demonstrated the development and validation of a method for the extraction and determination of particle size and concentration of CeO2 NPs and dissolved Ce in soils. The method is composed of extracting CeO2 NPs from soils using tetrasodium pyrophosphate (TSPP) aqueous solution and detection of aqueous extracts through single particle ICP-MS. The efficacy of the extraction was assessed by varying the concentration of TSPP solutions. Our results demonstrated that the optimal method employed 5 mM TSPP (1:100 soil-to-reagent ratio), with ultra-sonication to enhance particle dispersion, could efficiently extract CeO2 particles from both non-aged and aged CeO2 NP-dosed soil samples with ~100% recovery yield. The aging study showed the size and the particle recovery yield of the dosed CeO2 NPs in aged soil samples got slightly increased, in comparison with that in the non-aged soil. Overall, the developed method was capable of extracting and accurately measuring the size and concentration of CeO2 NP in soils.

**Keywords:** Single particle (SP)- ICP-MS, CeO2 nanoparticles, Tetrasodium pyrophosphate, Soil, Extraction

**Introduction**

With the rapid development of nanotechnology and the corresponding growing applications of engineered nanoparticles (ENPs) in various industrial, commercial, and medicinal products [1, 2], more and more ENPs have been released into the environment, triggering concerns on their environmental toxicity, fate, and transport[3]. As a result, the ability to effectively detect and quantify the ENPs in complex environmental matrices is in high demand. Cerium dioxide nanoparticle (CeO2 NP) is one of these ENPs increasingly widely used in industrial applications such as fuel additives, nanomedicine, coating materials and sunscreens due to their unique oxidative, catalytic, and reductive properties[4, 5]. Consequently, these broad applications inevitably cause their release into the environment. Once the CeO2 NPs are released into the environment, soils are likely to be their primary repository. Therefore, given the uncertainty of the impacts of CeO2 NPs on humans and the environment, it is critical to study their fate and transport through soil. However, the detection and characterization of CeO2 NPs in soils remains a challenge due to their low predicted environmental concentrations and the high natural background of Ce-containing minerals in the complex soil system. To date, some methodologies have been employed to detect and characterize nanoparticles in environment samples, such as field flow fractionation coupled with inductively coupled plasma mass spectrometry (ICP-MS), scanning electron microscopy, transmission electronic microscopy, dynamic light scattering, etc. [6-10]. However, these techniques encountered more or fewer limitations in environmental analysis, such as low sensitivity for environmental-type study and tedious sample preparation. Therefore, a robust, reliable, and sensitive method is highly desired. Most recently, single particle (sp) ICP-MS has been proved to be a promising technique to identify and characterize ENPs, especially at very low concentrations as expected in environmental samples [11-14]. This new emerging technique offers highly sensitive and selective ability to detect and quantify nanoparticles at very low concentration (ng/L), as compared to other methods. It is not only capable of providing information rapidly about particle size (based on the spherical geometry), size distribution and particle number concentration, but able to simultaneously determine the dissolve analyte concentrations in a sample. Hence, the sp-ICP-MS has been utilized characterize and quantify ENMs in various matrices, including the analysis of TiO2 NPs in sunscreens, gold nanoparticles (AuNPs), silver nanoparticles (AgNPs) and copper NPs in the soil, AuNPs and CeO2 NPs in Plant tissues, and AgNPs in the aquatic environment[15-22].

To investigate effectively and reliably ENPs in the soil by sp-ICP-MS the development of a method enabling efficient extraction of ENPs from soil while preserving their physical properties is critical. Various extraction reagents have been reported in the literature for use in extracting ENPs from soils [18-20, 23-25]. Among them, alkaline extracting reagents are commonly used owing to their ability of dispersion/dissolution soil organic matters which play a major role in the formation and stability of hetero-aggregates (including metal nanoparticles) in soils [26]. For example, tetrasodium pyrophosphate (TSPP) has been employed to extract AgNPs and Fe(hydr) oxide nanoparticles from soils[19, 20, 23].

The objectives of this work were (1) to investigate a robust method using TSPP as extracting regent to efficiently extract CeO2 NPs out from soils which dosed with CeO2 NPs; (2) to develop and optimize the sp-ICP-MS analysis method for the characterization of particle size including size distribution and particle number concentration of CeO2 NPs in soils; (3) to apply the approach to analyze the impact of aging on the physical properties of the CeO2 NPs.

**Material and methods**

**1. Chemicals**

An aqueous dispersion of CeO2 NPs (40 wt.%) with a particle diameter range of 30-50 nm was purchased from US Research Nanomaterials (Houston, TX, USA). Ultrapure water (18.2 M.Ω) for preparation/dilution of standards and samples was generated by a Simplicity 185 Millipore water purification system (Billerica, MA, USA). Citrate-coated AuNP standard (40 nm) used in determining the nebulization transport efficiency was purchased from Nanocomposix (San Diego, CA, USA), and the AuNP suspension was sonicated for 15 min prior to use. Dissolved Ce standard solution (1000mg/L in 2% HNO3) was purchased from High-Purity Standards (Charleston, SC, USA). Tetrasodium pyrophosphate decahydrate (TSPP) serving as extraction reagent was purchased from Fisher Scientific (Pittsburgh, PA, USA).

**2. Instrument and Analysis**

All sample analysis was carried out on a PerkinElmer NexION 300D ICP-MS (Shelton, CT, USA) running in single particle mode under the conditions listed in **Table 1**. In this study, 139.9Ce was selected for monitoring all sample measurements because it is the most abundant isotope of Cerium and is interference-free, which endows the highest instrument response. The dwell time, one of the most critical parameters in sp-ICP-MS, was set at 0.1 ms to improve the sizing accuracy and particle concentration dynamic range, and the total sampling time was set to 100 s. At the beginning of each series of analysis, the sample flow rate of the nebulizer was determined by weighing the amount of MQ water aspirated for 3 min, and the transport efficiency of the system was measured in triplicates via particle number concentration method[27], using a well-characterized 40 nm gold nanoparticle standard. Particle sizes and dissolved Ce concentrations were determined based on calibration with dissolved Ce standards, which were prepared in 0.025 mM TSPP solution, with concentrations in the range from 0.1 µg/L to 10 µg/L. All samples were sonicated in an ultrasonic bath for at least 15min before analysis.

The data were acquired and processed by Syngistix Nano Application module. The critical challenge in the sp-ICP-MS data processing is to distinguish particle signals from the dissolved ion signals. Therefore, setting a proper threshold is very important. Here, the threshold was set to the value equal to the intensity of most of highest pulse signals observed from the blank solution (0.025 mM TSPP) to minimize false positives detected from the blanks. Only the signals above the threshold are particle events, while the signals below the threshold are treated as dissolved ions. Considering the fact that soils are complicated systems where Ce-bearing materials exist in various forms (such as CeO2 NPs, Ce ions adsorbed on undigested soil colloids, or a combination of both), therefore, during the sp-ICP-MS method development, we assumed that Ce-bearing particulates in soil are CeO2 NPs with a spherical geometry, and the particle mass, and thus size was calculated based on a mass fraction of 81.39% and a density of 7.13 g/cm3. The mean and most frequent particle sizes were derived by fitting particle size distributions with a Gaussian curve. All the measurements were performed in at least two replicates.

**Table 1. Settings and parameters for** NexION 300D ICP-MS

|  |  |
| --- | --- |
| 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 |
| Transport Efficiency | Particle concentration method, using 40 nm AuNP standard |
| Nebulizer gas flow | 1.02 L/min |
| RF power | 1600 W |
| Cones | Platinum |
| sp-ICP-MS method parameters | |
| Analyte Monitored | 139.9Ce |
| CeO2 Density | 7.13 g/cm3 |
| Ce Mass Fraction in CeO2NPs | 81.39% |
| Dwell Time | 0.1 ms |
| Sample analysis duration | 100 s |
| Sample Introduction method | Manual |

**3. Evaluation on detection limits of particle size and particle concentration**

The size detection limit of CeO2 NPs was determined by analyzing 0.025 mM TSPP blank solution which did not contain any CeO2 NPs. The intensity of the main pulse signals observed from the blank solution was used to establish the particle detection threshold which was used to calculate the NP size detection limit via dissolved Ce calibration curve. Signal intensities above the detection threshold are particle events, while those below the detection threshold are treated as dissolved Ce. The detection limit for the concentration for CeO2NPs was estimated by analyzing different particle concentrations of CeO2 NP standards in 0.025 mM TSPP blank solution prepared by a series of dilutions of 0.5 mg/L CeO2 NPs ranging from 500 to 128000.

**4. Effect of dispersant agent tetrasodium pyrophosphate (TSPP) on CeO2 NPs**

TSPP, an alkaline extracting reagent, has been employed to disperse soil during particle analysis due to its ability to disperse and dissolve soil organic matter which is a major agent responsible for formation and stability of hetero-aggregates in soil, including metal nanoparticles [26]. To evaluate whether the TSPP extraction has any impact on the physiochemical properties of the CeO2 NPs, we prepared two samples of CeO2 NP using 0.025 mM TSPP solution. One sample underwent the extraction process as described in soil spiking and extraction experiments section, and another did not. The samples were then analyzed using the developed sp-ICP-MS method and the results obtained were compared.

**5. Soil samples**

The soil used in this research was collected from the upper 5 cm of the campus top-soil Missouri University of Science and Technology, Rolla, MO. Prior to use, the soil was dried in an oven at 100 °C for three days until completely dry, then grounded into fine powder using a porcelain mortar and pestle, and further passed through a 75 µm – aperture sieve to remove larger lumps. Portions of the sample was split for analysis of the mineral and organic fractions, and dispersion of minerals. The powdered soil was stored in a clean ziplock plastic bag.

**6. Soil Aging**

Two sets of soil samples (150 g each) were prepared. One functioning as a control was mixed with 50 mL of Ultrapure water, and the other was spiked with 50 mL of 100 ppm CeO2 NP solution in a 250-mL beaker, respectively, and then the soils were homogenized using a spatula. Upon mixing, the soils were left at room temperature and humidity under growing light (light intensity: 4280 Lux) with 16 h light/8 h dark cycles to allow the soils age for 30 days. Soil moisture content was monitored by weighing the containers, and maintained by wetting with ultrapure water every four days, and at the same time, the room temperature and relative humidity were measured.

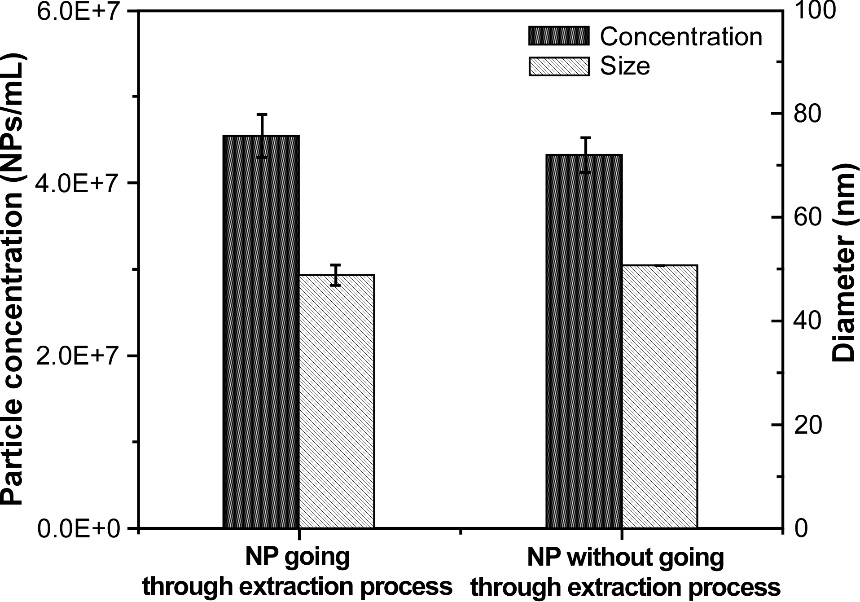
**7. Soil spiking and extraction experiments**

The spiked soil samples were prepared by adding 50 µL of 100 mg/L of CeO2 NP suspensions, which were sonicated for 15 min before use, to 0.15 g of soil, followed by aging for one day at room temperature in 19 mL polypropylene tubes. The soil and CeO2 NP dosed soil were extracted by following the extraction approach previously reported with slight modifications[19]. Briefly, to evaluate the effect of the concentration of TSPP on the extraction efficiency, 15-mL of various concentrations of TSPP (2.5 mM, 5 mM, and 10 mM) were added into a 19-mL polypropylene tube containing 0.15 g of soil, giving a reagent to soil ratio of 100: 1 (mL: g). The samples were mixed on a vertical rotator for 30 min at 30 rpm, then sonicated for 30 min in an ultrasound bath, followed by another 30 min of mixing on the rotatory mixer at 30 rpm. After that, the mixtures were allowed to settle overnight at room temperature to sediment out micrometer-sized particles. To prevent the introduction of the large particle (e.g., > 1µm) into the sp-ICP-MS system, subsamples were taken from depths of 0.5 cm -1 cm below sample surface. All samples were extracted in triplicate, and during sp-ICP-MS analysis, the samples were diluted to a final TSPP concentration of 0.025 mM.

**Results and Discussion**

1. **Effect of TSPP on CeO2 NPs**

**Figure 1** shows the comparison of particle concentrations and measured sizes of CeO2 NPs with and without going through the TSPP extraction process. There was no apparent difference in particle concentration and particle size of CeO2 NPs observed between samples being carried through the extraction process and without through the extraction process. This indicates the TSPP is suitable for extracting CeO2 NPs from soil without leading to significant changes in physiochemical behavior (e.g., dissolution and aggregation) of CeO2 NPs.



**Figure 1**. Comparison of particle concentrations and measured size distributions of CeO2 NPs with and without going through the TSPP extraction process. All samples are analyzed in three replicates.

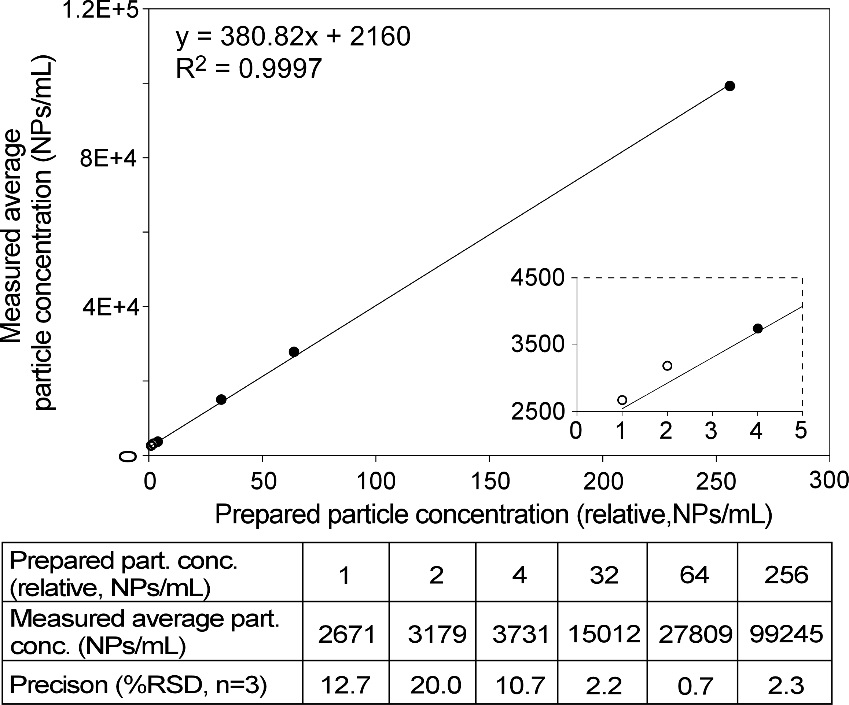
1. **Particle size detection limit**

It is critical to determine a reasonable threshold to distinguish the particle signals from background noise to obtain reliable results for particle analysis via sp-ICP-MS. The particle size derived from the intensity threshold value based on the calibration curve is the basis for the reported particle size detection limit. In the literature, an iterative approach was employed to determine the intensity threshold. The basic principle of this method lies in repeatedly calculating the intensity threshold is reported on the sample mean (µ) and corresponding standard deviation of the blank (σ) following the relationship *µ* + (n×*σ)* (where µ and σ correspond to the average and standard deviation of the blank, and n corresponds to the multiplicator of the standard deviation) until there is no more particle signals higher than *µ* + (n×*σ)* can be differentiated. However, this approach is suitable for obtaining the particle size detection limit from continuous signals, but not from pulse (discontinuous) signals generated by particles during the sp-ICP-MS analysis. **Figure 3A** shows the raw sp-ICP-MS data of 0.025 mM TSPP solution (blank). As can be seen, most pulse signals lie between 1 and 3 counts with the majority of highest pulse signals being 2 counts. Based on this data, the Syngistix software automatically derived an intensity threshold of about 0.2 counts using the iterative method of µ +3σ. However, this threshold is below the smallest intensity (1 count) the sp-ICP-MS can detect, thus, leading to the unpractical particle size detection limit.

Given all sp-ICP-MS analysis, in this work, was performed in the 0.025 mM TSPP solution which in most cases exhibited the highest signals with an intensity of 2 counts, the signal intensity of CeO2 nanoparticles in the samples equal or below 2 counts cannot be distinguished. Therefore, we chose 3 counts as the intensity threshold, and as a result, this led to a particle size detection limit of about 24 nm, based on the dissolved Ce calibration curve.

1. **Particle concentration detection limit**

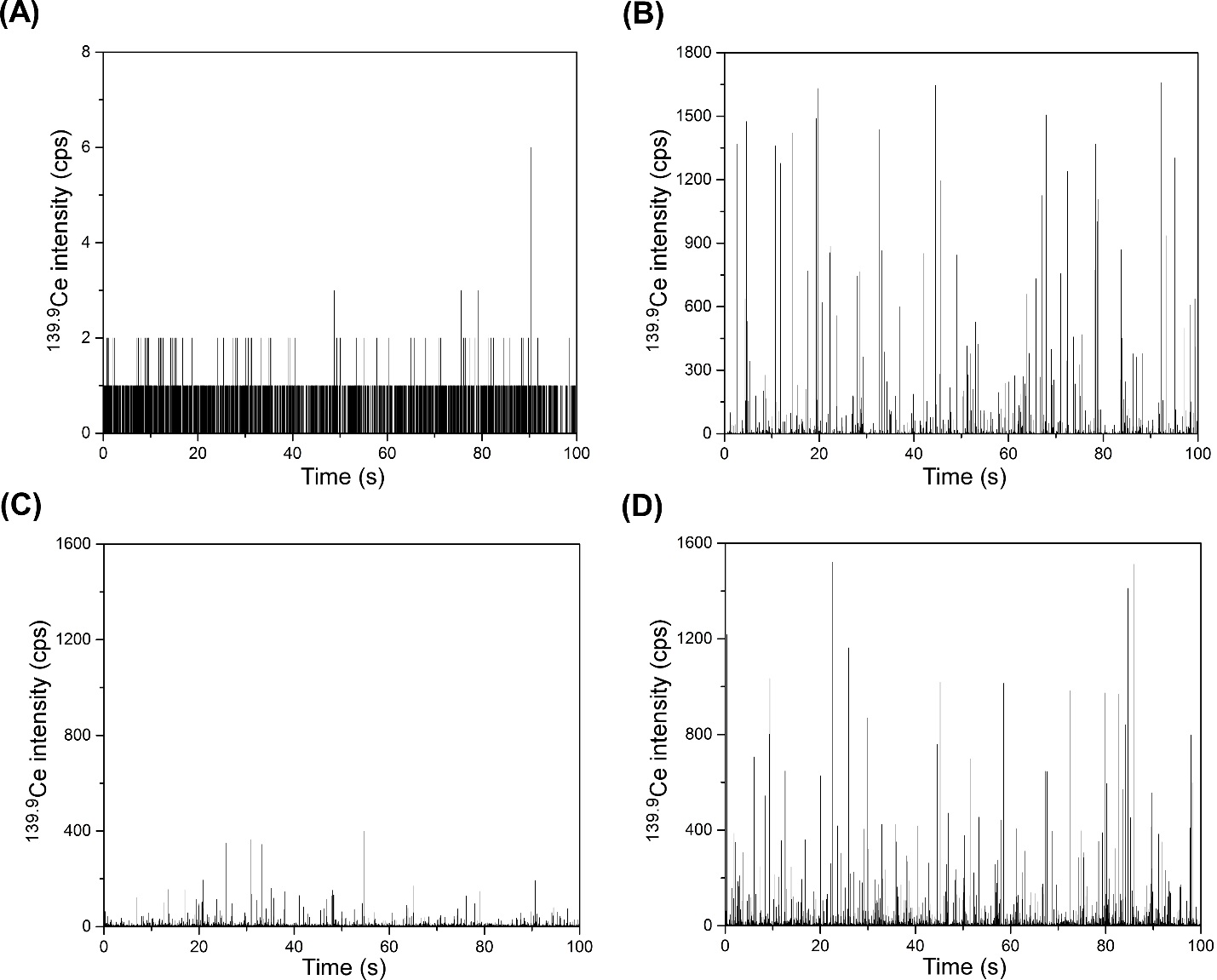
**Figure 2** shows the results of the particle concentration detection limit of CeO2 NP standard analyzed in extraction solution (0.025 mM TSPP). Since the particle number concentration of CeO2 NP standard is unknown, relative concentrations were used for the prepared CeO2 NP concentrations, where the lowest concentration tested was defined as 1 NPs/mL. As can be seen, in the prepared particle concentration range from 4 NPs/mL to 256 NPs/mL, the measured particle concentrations exhibit a corresponding linear trend. As the prepared particle concentration was further decreased to lower than 4 NPs/mL, however, deviations from linearity was observed (red dots are shown in Figure 2). Moreover, the precision of the particle concentrations dropped significantly (RSD: 20.0% and 12.7 % of the measured particle concentrations of 3179 NPs/mL and 2671 NPs/mL, respectively). This suggests the current sp-ICP-MS method has a particle concentration quantitative detection limit of ~ 3700 NPs/mL for CeO2 NPs. The result indicate the method is highly sensitive to CeO2 NPs, and is capable of direct and quantitative detection of the very low concentration of CeO2 NPs in environmental matrices.



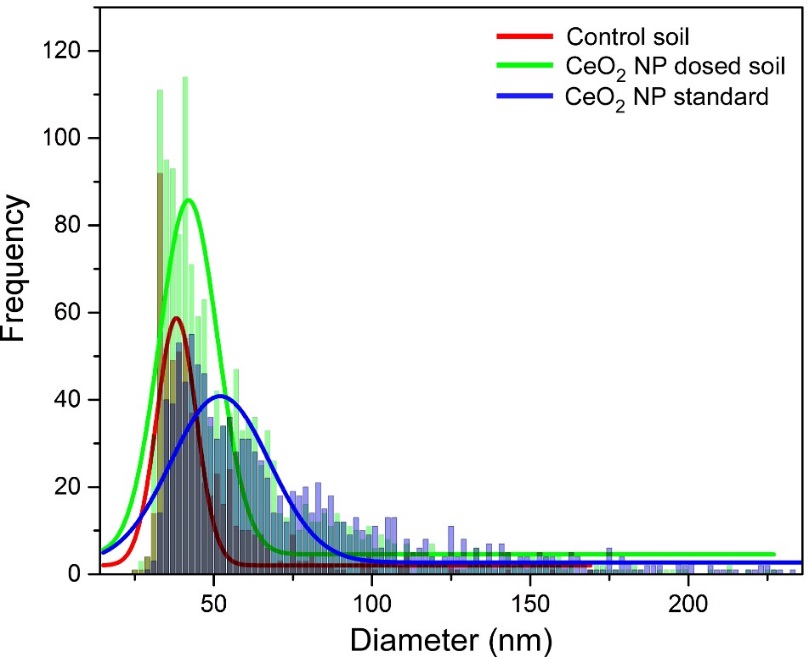
**Figure 2**. Estimation of the concentration detection limit of sp-ICP-MS for CeO2 NPs.

1. **sp-ICP-MS analysis of TSPP extraction of CeO2 NPs in soil**

To determine if CeO2NPs can be extracted out from the soil, both dosed and un-dosed soil have been extracted with 2.5 mM TSPP and subsequently analyzed by sp-ICP-MS. **Figure 3C and 3D** display the resulting raw data for the un-dosed soil and the soil dosed with 30-50 nm CeO2 NPs, respectively. Continuous and pulse signals appear in both cases. Given the continuous signals corresponds to the ionic form of the Ce (include NPs with a size smaller than the size detection limits) and distinct pulse signals represent particulate Ce, this indicates that both dissolved Ce and particulate exist in soil samples. As a comparison to the raw data for the reagent blank (0.025 mM TSPP) shown in **Figure 3A**, only a few low-intensity pulse signals appeared in the raw sp-ICP-MS data of the un-dosed soil sample (**Figure 3C**). This indicates the soil is relatively clean of CeO2NPs, although containing specific types of Ce-bearing particles likely originated from CeO2NPs, Ce ions adsorbed on undigested soil colloids, or a combination of both. A comparison between **Figure 3D** and **3C** shows the frequency and the intensity of the pulse signals detected in the soil exposed to CeO2 NPs are higher than those of the undoped soil. This suggests the dosing and extraction procedure are realistic. **Figure 4** shows the histogram of the particle size distributions generated from **Figure 3B-D**. After CeO2 NPs spike the average particle size observed in dosed soil increased significantly, where the value was between the sizes obtained from the un-dosed soil and the CeO2 NP standard. This size shift is likely due to the deposition of dissolved Ce on the Ce-bearing NPs or the overlap of the particle size distributions of dosed CeO2 NPs and Ce-bearing particles initially present in the soil.



**Figure 3**. Comparison of raw data obtained from soil without dosing CeO2 NPs and CeO2 NP dosed soil. (A) Raw data for reagent blank (0.025 mM TSPP solution). (B) Raw data for CeO2 NP standard. (C) Raw data for un-dosed soil. (D) Raw data for CeO2 NP dosed soil.

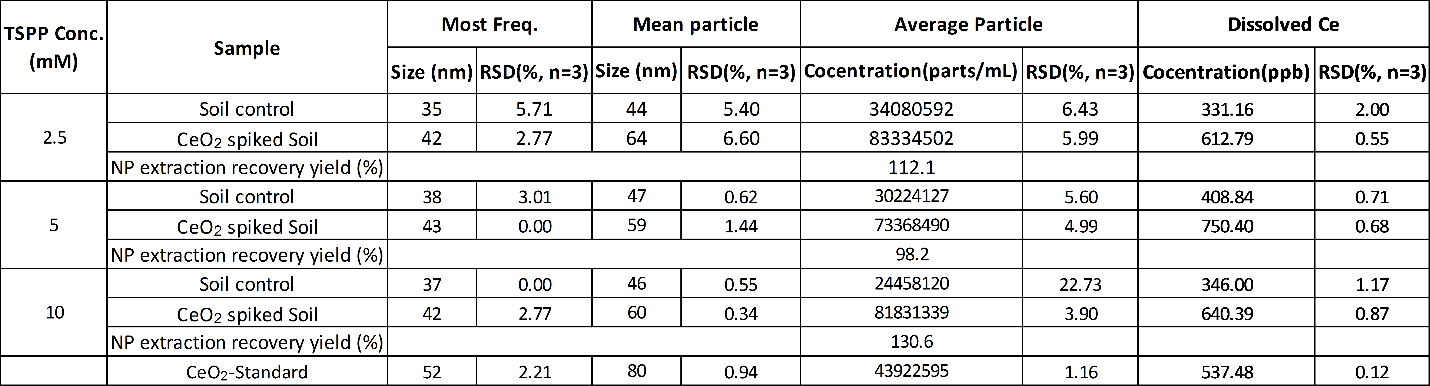


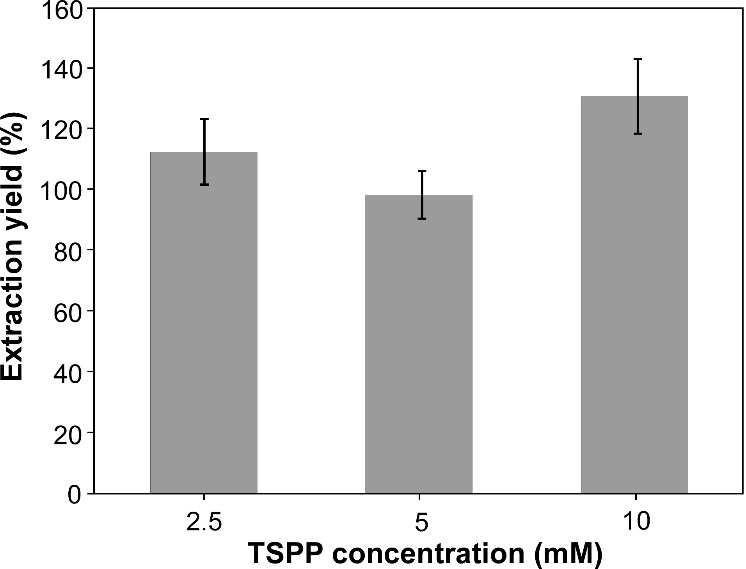
**Figure 4**. Comparison of particle size distributions of CeO2 in soil samples. Red: control soil; green: CeO2 NP dosed soil; and blue: CeO2 NP standard.

1. **Effect of the concentration of TSPP on the extraction efficiency**

To assess the effect of the TSPP concentration on the extraction efficiency of CeO2 NPs from soil, the CeO2 NP-dosed the soil samples were extracted with three different concentrations of TSPP solutions (2.5 mM, 5 mM, and 10 mM), and the extraction efficiency was compared. **Table 2** illustrates the sp-ICP-MS results for the corresponding soil extracts. It is evident the extraction yield was similar for 2.5 mM, 5 mM TSPP concentrations with good recovery (close to 100%), and further increasing the TSPP concentration resulted lower extracted particle concentration and high recovery (130%) (see **Figure 5**). This suggests that the TSPP concentrations tested from 2.5 to 5 mM are appropriate for efficient extraction of CeO2 NPs from the soil. Therefore, 5 mM TSPP was chose for the soil aging study.

**Table 2. Comparison of TSPP extraction efficiency**





**Figure 5**. Effect of TSPP concentration on the CeO2 NP extraction yield. All samples are analyzed in 3 replicates.

1. **Effect of aging on the fate of CeO2 NPs in soil**

To evaluate the influence of soil aging on the CeO2 NPs, the CeO2 NP dosed soil was aged for one month before the TSPP extraction and sp-ICP-MS analysis, as described in the material and methods section, and the results were compared with those obtained from a fresh CeO2 NP-dosed soil sample. As can be seen in **Table 3**, the average particle number concentration, the most frequent particle size, and the particle recovery obtained from the aged soil are greater than those from the fresh soil sample, while the dissolved Ce concentration decreased after aging. This phenomenon may suggest that the aging could cause the dissolved Ce to transfer into particulate forms, possibly by the deposition on the surface of clutters in soil.

**Table 3. Comparison of the particle size and the particle concentration of CeO2 NPs extracted from aged and non-aged soils**



**Conclusion**

In this study, we have successfully demonstrated the development of an analytical method for the extraction, detection, and characterization of CeO2 NPs in the soil. The method is composed of the extraction of the CeO2 NPs from soils using tetrasodium pyrophosphate (TSDP) aqueous solution and the subsequent characterization of aqueous soil extracts via sp-ICP-MS. The results showed that the optimal extraction approach employed 2.5 to 5 mM TSPP at 1:100 soil-to-solvent ratio, with ultra-sonication to enhance particle dispersion. TSPP solution can efficiently extract CeO2 NPs out from the CeO2NP-dosed soil samples, without changing the physicochemical properties of the CeO2NPs; the particle number concentration, particle size as well as size distribution of CeO2 NPs in soil could be reliably determined via sp-ICP-MS analysis. Moreover, the results showed that the aging process could cause the dissolved Ce to convert into particulate forms. Overall, the developed method provides a promising way to monitor the fate of CeO2 NPs in the natural soil.

**Disclaimer**

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