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Practical limitations of single particle ICP-MS in the determination of nanoparticle size distributions and dissolution: case of rare earth oxides

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ABSTRACT

The applicability of single particle ICP-MS (SP-ICP-MS) for the analysis of nanoparticle size distributions and the determination of particle numbers was evaluated using the rare earth oxide, La_2O_3, as a model particle. The composition of the storage containers, as well as the ICP-MS sample introduction system were found to significantly impact SP-ICP-MS analysis. While La_2O_3 nanoparticles (La_2O_3 NP) did not appear to interact strongly with sample containers, adsorptive losses of La^{3+}(over 24 h) were substantial (> 72%) for fluorinated ethylene propylene bottles as opposed to polypropylene (< 10%). Furthermore, each part of the sample introduction system (nebulizers made of perfluoroalkoxy alkane (PFA) or glass, PFA capillary tubing, and polyvinyl chloride (PVC) peristaltic pump tubing) contributed to La^{3+} adsorptive losses. On the other hand, the presence of natural organic matter in the nanoparticle suspensions led to a decreased adsorptive loss in both the sample containers and the introduction system, suggesting that SP-ICP-MS may nonetheless be appropriate for NP analysis in environmental matrices. Coupling of an ion-exchange resin to the SP-ICP-MS led to more accurate determinations of the La_2O_3 NP size distributions.

1. Introduction

Over the past decade, single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has rapidly evolved into a powerful technique to measure particle size distributions and particle numbers for metallic or metal oxide nanoparticles (NP) and natural colloids [1,2]. SP-ICP-MS has been used for a variety of matrices including simple aqueous media, surface and waste waters [3,4], food containers [5] in addition to animal tissues [6–8] and plants [9], following enzymatic extraction. Much of the success of SP-ICP-MS comes from its ability to provide detailed information on the composition and particle size distributions of nanoparticles, generally faster and at much lower concentrations than other commonly used techniques such as transmission electron microscopy (TEM) or dynamic light scattering (DLS) [10]. Nonetheless, silver and gold NP remain by far, the most analyzed nanomaterials using SP-ICP-MS [7,8,11–14], often because experimental difficulties are much greater for other NP. For example, for particles that dissolve extensively, the background signal resulting from the dissolved metal can mask that of the smallest particles, significantly increasing size detection limits [4,15]. In addition, since SP-ICP-MS analyses are necessarily performed on non-acidified samples, adsorptive losses of the ions and particles to various components of the instrument can be important. To date, these effects have generally not been well studied, largely because: (i) stabilized Ag NP and Ag^+ are not significantly adsorbed by the ICP-MS sample introduction system; and (ii) Au NP generally undergoes little dissolution.

In an effort to extend the applicability of SP-ICP-MS to nanoparticles other than Ag and Au, the goal of this paper was to evaluate the feasibility of SP-ICP-MS for the analysis of a rare earth oxide NP. The production of these NP is increasing substantially [16,17]. For example, La_2O_3 NP are used to improve the performance of piezoelectric materials; as catalysts in light-converting/emitting materials and for the manufacturing of precision optical glass and high-refraction optical fiber [18–21]. In spite of a growing industrial importance and the potential for increasing environmental release [22–27], the utility of SP-ICP-MS has not yet been established for the analysis of NP of the rare earth oxides (with the possible exception of CeO_2 [2,28]). In this paper, some of the constraints associated with analyses of this type of NP have been examined. Special attention has been paid to the effects of adsorption on determinations of NP numbers and particle size distributions.

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2. Experimental section

2.1. Chemicals

Suspensions of lanthanum oxide nanoparticles (hereby referred to as La_2O_3 NP) were prepared from a commercially available nanopowder (99.99%, 10–100 nm, US Research Nanomaterials Inc., #: US3265) with an initial particle size distribution that was provided by the manufacturer (based upon a sample analyzed by transmission electron microscopy, TEM), which was confirmed by our own TEM analysis (Fig. S1). Three mg of the La_2O_3 NP powder were suspended in 50 mL of ultrapure water (Milli-Q, R > 18.2 MΩ cm; total organic carbon < 2 μg L^{-1}); vortexed for 30 s; sonicated in an ultrasonic bath for 10 min and finally centrifuged for 5 min at 3000 rpm (1872 g) to remove large agglomerates. The supernatant was sonicated an additional 10 min and then diluted in Milli-Q water to a concentration range of 0.64–0.94 μg L^{-1} (based on an ICP-MS quantification of total La in acid digested samples). To facilitate comparison of the different experimental parameters, a single freshly prepared supernatant was used for each series of the same experiment. Dilutions were performed on an analytical balance using sample containers made of either polypropylene (PP) or fluorinated ethylene propylene (FEP). Lanthanum calibration solutions (La ranging from 0.5 to 4 μg L^{-1}) were prepared by diluting ICP-MS standards (Inorganic Ventures) in 1% v/v ultrapure nitric acid (65%, Aristar Ultra, BDH). A fulvic acid standard (aquatic fulvic acid, 1S101F) was purchased from the International Humic Substances Society.

In some experiments, nanoparticle samples were passed over an analytical grade Chelex 100 cation exchange resin (50–100 mesh, Sigma-Aldrich) with a binding capacity of 0.7 meq mL^{-1}. The resin was first washed with 1.5 M HNO_3, rinsed with Milli-Q water, converted to its Na^+ form using 0.1 M NaOH (≥98%, Sigma-Aldrich) then rinsed with Milli-Q water. The wet and swollen resin was used to fill a small column (1 mL Rezorian solid phase extraction kit with polyethylene frits, Sigma-Aldrich).

2.2. SP-ICP-MS

A Perkin-Elmer NexION 300x ICP-MS was used for data acquisition in single particle mode. The sample introduction system consisted of a quartz cyclonic spray chamber, a quartz injector (2 mm internal diameter) and a nebulizer: either a Micro-Flow PFA-100 self-aspirating nebulizer (90–150 μL/min, SN 100–9178, ESI) or a Meinhard type C0.5 concentric glass nebulizer (0.5 mL min^{-1}, PerkinElmer). Time resolved signals were acquired in fast scan mode using the Syngistix nano application module integrated into the NexION software (version 1.1.4624). For verification purposes, raw data were also reprocessed manually (using Excel) as described previously [29] or using the NuQuant software (Nu Instruments). All concentrations and particle diameters were determined from triplicate samples. Sample flow rates were measured prior to analysis. Transport efficiencies were determined using a NIST reference NP (RM 8013) that consisted of 50 mg L^{-1} of citrate stabilized gold NP with a nominal diameter of 60 nm. For measurements presented here, data were acquired over 50 s using a dwell time of 500 μs and no settling time. In spite of the ability of the instrument to acquire data at very short dwell times (often leading to lower background noise and improved data quality [30,31]), a dwell time of 500 μs, in concert with an appropriate particle number concentration, was more suitable for this work (details on the justification of the dwell time are provided in the Supporting information, Fig. S2). In order to perform mass balances, several different La concentrations were measured and compared (Table 1).

Table 1
La measurements for mass balance calculations.

Measured form of La	Analytical method	Sample treatment
(i) Total La	ICP-MS	Digested sample with HNO_3
(ii) Non-adsorbed La	ICP-MS	Sample transferred to clean tube, and acidified with 1% HNO_3
(iii) La_2O_3 NP	SP-ICP-MS	Non-acidified sample
(iv) Dissolved La	SP-ICP-MS	Non-acidified sample

3. Results and discussion

3.1. Adsorption by sample containers

Suspensions of La_2O_3 NP (0.64–0.94 μg La L^{-1}) were studied over 22 days of storage at room temperature (23 ± 2 °C) in two types of containers: polypropylene (PP) tubes and fluorinated ethylene propylene (FEP) bottles. For each examined time point, an aliquot of the suspension was sampled and acidified in a new container. After 22 days, the remaining solution was acidified in the initial container for mass balance calculations. Adsorption occurred for both container materials, but it was substantially greater for the FEP bottles. For example, after 1 day of equilibration, only ca. 28% of the added La was recovered from the FEP tubes, whereas recoveries for PP, while variable, were in the vicinity of 90%. Nonetheless, for both container types, relatively high relative standard deviations (RSDs) were observed for replicate (n=3) samples measured on acidified aliquots of the solutions (Fig. S3). The high standard deviations illustrate clearly one of the main problems found when working with NP in non-acidified working solutions- adsorptive losses to the container surfaces and indeed, to the pipette tips (made of polypropylene) used to remove the sample aliquots are likely to contribute to high sample-to-sample variability.

SP-ICP-MS performed directly on non-acidified samples confirmed that the sample storage conditions influenced both the partitioning between the NP and dissolved metal fractions and the particle sizes (Figs. 1 and 2). For instance, average particle diameters in the PP tubes appeared to be consistently larger than those determined in the FEP tubes, which were relatively constant at 36 nm (Fig. 1). Nonetheless, particle sizes in the PP tubes eventually decreased and converged with those in the FEP tubes, giving an average particle diameter of 35 ± 3 nm after two weeks of equilibration. Dissolved La was notably lower for the dispersions stored in the FEP, with values of 23 ± 9 ng L^{-1} (corresponding to 3 ± 1% of total La) being measured after 24 h of equilibration. In the PP tubes, dissolved concentrations of 84 ±

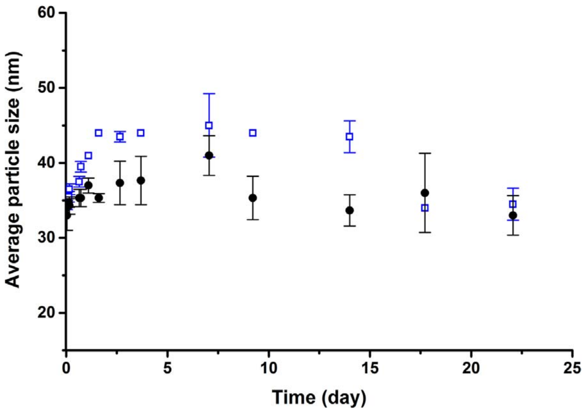

Fig. 1. Effect of time and container material on average particle size for a suspension of La_2O_3 NP stored in (□) polypropylene (PP) tubes and (•) fluorinated ethylene propylene (FEP) bottles. Error bars correspond to standard deviations determined from triplicate samples.