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Size determination and quantification of engineered cerium oxide nanoparticles by Flow Field-Flow Fractionation coupled to inductively coupled plasma mass spectrometry

L. Sánchez-García^{a,*}, E. Bolea^a, F. Laborda^a, C. Cubel^a, P. Ferrer^b, D. Gianolio^b, I. da Silva^c, J.R. Castillo^a

^a Group of Analytical Spectroscopy and Sensors (GEAS), Institute of Environmental Sciences (IUCA), University of Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

^b Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Chilton OX11 0DE, UK

^c ISIS Facility, Rutherford Appleton Laboratory, Chilton, Oxfordshire OX11 0QX, UK

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ABSTRACT

Facing the lack of studies on characterization and quantification of cerium oxide nanoparticles (CeO₂ NPs), whose consumption and release is greatly increasing, this work proposes a method for their sizing and quantification by Flow Field-Flow Fractionation (FFFF) coupled to Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Two modalities of FFFF (Asymmetric Flow- and Hollow Fiber-Flow Field Flow Fractionation, AF4 and HF5, respectively) are compared, and their advantages and limitations discussed. Experimental conditions (carrier composition, pH, ionic strength, crossflow and carrier flow rates) are studied in detail in terms of NP separation, recovery, and repeatability. Size characterization of CeO₂ NPs was addressed by different approaches. In the absence of feasible size standards of CeO₂ NPs, suspensions of Ag, Au, and SiO₂ NPs of known size were investigated. Ag and Au NPs failed to show a comparable behavior to that of the CeO₂ NPs, whereas the use of SiO₂ NPs provided size estimations in agreement to those predicted by the theory. The latter approach was thus used for characterizing the size of CeO₂ NPs in a commercial suspension. Results were in adequate concordance with those achieved by transmission electron microscopy, X-ray diffraction and dynamic light scattering. The quantification of CeO₂ NPs in the commercial suspension by AF4-ICP-MS required the use of a CeO₂ NPs standards, since the use of ionic cerium resulted in low recoveries (99 ± 9% vs. 73 ± 7%, respectively). A limit of detection of 0.9 μg L⁻¹ CeO₂ corresponding to a number concentration of 1.8 × 10¹² L⁻¹ for NPs of 5 nm was achieved for an injection volume of 100 μL.

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1. Introduction

Nanotechnology is developing rapidly in numerous industries such as chemistry, medicine, energy, computer sciences, or optics, with the consequent increase in the manufacturing of synthetic nanoparticles (NPs). Great part of the NPs interest derives from their size (1–100 nm) [1], which provides them with interesting properties such as high specific surface area, rapid diffusion or high reactivity in liquid and gas phase. It is indeed owed to their size and the resulting particular properties that questions about their potential toxicity and environmental impact also emerge [2], given the

high mobility and rapid transport they exhibit in the environment and inside the body. While the consumption of engineered nanomaterials grows, the release of NPs, their evolution and interaction with the natural media and organisms is insufficiently understood. Nanomaterials may pose new risks as a result of their novel properties. In view of this potential hazard, regulatory and scientific assessment requires an understanding of exposure to both humans and the environment. Characterizing and tracking NPs in the environment is a priority for the responsible-sustainable development of nanotechnology.

Cerium oxide nanoparticles (CeO₂ NPs) have different applications in multiple fields (polishing, catalysis, UV blocker, electronics, environmental remediation, sensing, biomedicine, etc.) [3], as a consequence of their interesting mechanical, spectroscopic, catalytic and oxidant/antioxidant properties [4,5]. Most of the uses of

* Corresponding author. Fax: +34 976 761 292.

E-mail addresses: laurasg@unizar.es, laura.biomarkers@gmail.com (L. Sánchez-García).

CeO₂ NPs are related to their catalytic and sorption properties. For instance, the automotive industry uses the oxygen buffering capacity of the CeO₂ NPs to catalyze the fuel oxidation in diesel engines, where combustion tends to be incomplete. This results into lower consumption of fuel and lower emission of soot particles and toxic gases [6,7]. Beyond the positive effects on air quality, little is known about the intrinsic toxicity of the CeO₂ NPs released to the environment. At the time nanotoxicology deals with the CeO₂ NPs hazards, efforts should be also devoted to determine the physicochemical properties responsible for their potential toxic effect.

The physicochemical characterization of CeO₂ NPs entails a series of analytical challenges related to their size, nature, and physicochemistry in aqueous phases, as well as to the expected low concentration in environmental samples. Although little information is available to date on the likely concentrations of CeO₂ NPs that end up in the environment, estimations for aquatic environments are in the range of 0.005–1.0 µg/L of CeO₂ [8], where the highest value predicted based on current usage of ceria as a fuel additive in the UK is 0.37 µg/L of CeO₂ [9]. Ecotoxicological studies use diverse analytical techniques for characterizing NPs, to understand the mechanisms and extent of toxicity of the CeO₂ NPs in relation to their properties [10–14]. Among all, particle size has been pointed as a key property for determining the toxicity of CeO₂ NPs [e.g., [12,13]] in relation to differences in the surface area. The complexity of the CeO₂-NPs suspensions and the limitations of the analytical techniques lead to diverse operative problems. For instance, Microscopy-based techniques such as Transmission Electronic Microscopy (TEM) or Atomic Force Microscopy (AFM) show limitations for measuring individual sizes in samples of inherent instability and sample-preparation protocols promoting agglomeration [15]. Similarly, Dynamic Light Scattering (DLS), ideally developed for monodisperse populations, present inconveniences for measuring unknown, polydisperse samples. This technique, requiring concentrations of NPs in the range of mg L⁻¹, may not be very useful for characterizing NPs in natural environments or biological media, where typically neutral pH values promote the CeO₂ NPs agglomeration [15]. Brunauer–Emmett–Teller (BET) surface-area measurements assuming spherical shape of the NPs may underestimate the surface area, thus leading to the overestimation of particle size [16]. Size measures from X-ray diffraction (XRD) have limited value in the case of polydisperse samples with amorphous components. While size determinations by XRD and BET are not directly relevant in aqueous media (i.e., done on solid samples), they provide relevant information for understanding the effect of the medium on NP properties [15]. All in all, the instability of CeO₂ NPs in common environmental medium (i.e., aqueous suspension) and the multiple analytical limitations described above reveals the necessity for developing novel analytical tools and sample preparation protocols to standardize the characterization of CeO₂ NPs, where robust and sensitive methods providing low limits of detection are required.

The present study proposes the use of Flow Field-Flow Fractionation (FFFF) coupled to Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for the size characterization and quantification of CeO₂ NPs. Despite FFFF is a family of powerful techniques for size characterization of NPs of diverse nature [17], there is a lack of studies dealing with the quantification of CeO₂ NPs, largely due to the lack of certified size standards of CeO₂ NPs and the poor stability of these NPs in suspension. We have investigated different conditions and separation factors affecting the stability of the CeO₂ NPs in suspension, and discussed different size-calibration strategies. We pose the FFFF-ICP-MS tandem as an alternative to other commonly used techniques, where results are limited by sample amount requirements or hydrodynamic stability. The performance of two FFFF separation modes (Asymmetric Flow Field-Flow Fractionation and Hollow Fiber-Flow Field-Flow Fractionation) is evaluated

here in the search of the best response in terms of resolution and recovery. This study constitutes the first application of size characterization of CeO₂ NPs by FFFF techniques and aims at exploring the capabilities of this analytical tool for quantifying CeO₂ NPs at environmental relevant concentrations, given the good sensitivity of ICP-MS for metal-containing NPs.

2. Experimental

2.1. Chemicals

Two different carriers were studied, one containing an ionic surfactant (sodium dodecyl sulfate, SDS) and the other consisting of a commercial mixture of nonionic and ionic detergents (mixed surfactant). The carriers were prepared by dissolving the corresponding mass of SDS (Merk, Darmstadt, Germany) and mixed surfactant (Novachem Surfactant 100, Postnova Analytics) in ultrapure water obtained from a Milli-Q Advantage system (Millipore, Bedford, MA, USA). Diluted solutions of sodium hydroxide (Merck, analytical grade) and nitric acid (J.T. Baker, trace metal analysis, 69–70%) were used to adjust the carrier pH. Nylon 0.2 µm filters (Millipore, USA) were used for filtering the carrier.

2.2. CeO₂ nanoparticles

Two commercial suspensions of cerium oxide NPs were used for method optimization. STD-4 (5 wt. % aqueous suspension 0.01 M HNO₃) had a nominal average size of 4 nm and was purchased from PlasmaChem (Berlin, Germany). STD-10 (20 wt. % aqueous suspension, 2.5% acetic acid), with nominal average size of 10–20 nm, was obtained from Sigma–Aldrich (Saint Louis, USA).

A commercial suspension (NanoArc[®], CAS: 1306-38-3) supplied by Alfa Aesar (Karlsruhe, Germany) for polishing purposes (e.g., in ultrafine acid side polishing slurries) was used as sample for testing the size characterization and quantification methods. The product is provided by the manufacturer as colloidal suspension of ceria NPs (25 wt. % in H₂O, pH 3.5), with a nominal BET size of 30 nm for the dry powder.

Diluted suspensions of CeO₂ NPs (10 or 50 mg L⁻¹) were prepared by further dilution of the commercial products with the corresponding carrier. These dilutions were prepared from suspensions of intermediate concentration of CeO₂ NPs (ca. 2000 mg L⁻¹), in similar conditions as provided by the manufacturers (i.e., HNO₃ 0.01 M). The CeO₂ NPs were stable in the acidic conditions for at least one month. Dilutions with carriers were freshly prepared prior to each measurement and subsequently analyzed within the next hour since preparation, where the risk for aggregation was observed to be minimum. Stability of bulk and intermediate suspensions, as well as suspensions diluted with carriers, was periodically checked by UV–vis absorption spectrophotometry.

2.3. Flow Field-Flow Fractionation-Inductively Coupled Plasma Mass Spectrometry (FFFF-ICP-MS)

The FFFF system used was an AF2000 (Postnova Analytics, Landsberg, Germany), run in two modes: (a) Asymmetric Flow Field-Flow Fractionation (AF4), and (b) Hollow Fiber-Flow Field-Flow Fractionation (HF5). In AF4 mode, separation is achieved by applying a transverse, unidirectional cross-flow towards a flat membrane. This system used a trapezoidal channel of 27.5 cm in length and from 2 to 0.5 cm in width, with spacers of 190 µm or 350 µm. The channel thicknesses were determined experimentally for each spacer used by injecting NaN₃ (Sigma–Aldrich, Saint Louis, USA; 100 µL, 0.1% (w/v) in carrier) [18]. The eluting peak was detected by the UV–vis detector (at 254 nm) at a fixed channel flow rate of 0.5 mL min⁻¹ and a minimum crossflow of 0.01 mL min⁻¹.

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