Frontier article

Determination of metal oxide nanoparticles and their ionic counterparts in environmental waters by size exclusion chromatography coupled to ICP-MS

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ARTICLE INFO

ABSTRACT

Analysis of metal oxide nanoparticles (MO NPs) and their released metal ions (M^{n+}) is essential for understanding their environmental effects and biological toxicity. For the first time, size exclusion chromatography (SEC) was coupled with inductively coupled plasma mass spectrometry (ICP-MS) for speciation analysis of MO NPs and their corresponding M^{n+}. By using a 1000 Å poresize silica column, and an acetate buffer (pH 7.0, 10 mM) containing 10 mM sodium dodecyl sulfate (SDS) as a mobile phase at a flow rate of 0.5 mL/min, M^{n+} and MO NPs with sizes smaller than the column poresize were baseline separated within 10 min, whereas MO NPs with sizes larger than the exclusion limit were filtered off by the column. More importantly, this mobile phase is able to avoid the dissolution of MO NPs during the SEC separation. The high recoveries (>97%) of M^{n+} from the SEC column ensured their accurate quantification directly with the online coupled SEC-ICP-MS, while the quantification of MO NPs by subtracting the M^{n+} content from the total metal content, which was determined with ICP-MS after digestion without SEC separation, efficiently eliminating the influence of retention of large MO NPs in the column. MO NPs with different sizes and compositions including NiO, CoO, ZnO, CuO and CeO_2 NPs were analyzed with this proposed method, with low detection limits (0.016–0.390 μg/L for both M^{n+} and MO NPs) and relative standard deviations (<0.4% for retention time and <2.2% for peak area at 50 μg/L M^{n+}). The proposed method was verified by analyzing Ni^{2+}, Ce^{4+}, NiO and CeO_2 NPs in various environmental waters, with spiked recoveries in the range of 80.8–105.1%. Our method has great potential for speciation analysis of MO NPs and their corresponding M^{n+} in the environmental waters.

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1. Introduction

The unique chemical and physical properties make metal oxide nanoparticles (MO NPs) predominated nanomaterials applied in consumer and industrial products (Kastner et al., 2008; Li and Shang, 2010; Jassby et al., 2012; Applerot et al., 2012). The increasing production and widespread usage of MO NPs resulted in their increasing release into the environment during the production, application, recycling and disposal, and therefore enhanced exposure and risk to environment and ecosystems (Gottschalk and Nowack, 2011; Horie et al., 2012; Gottschalk et al., 2013; Jarvis et al., 2013; Zheng et al., 2014; Kaweeteerawat et al., 2015). As toxicology studies show that MO NPs can cause physiological and genetic damage (Atha et al., 2012; Feng et al., 2013; Wang et al., 2013; Ge et al., 2014), risk assessment of MO NPs has received increased attention. Although there are many studies on the toxicity of MO NPs, the toxicity

mechanisms of MO NPs are still not yet fully understood, which could partly be attributed to the coexistence of MO NPs and their released metal ions (M^{n+}) (Ji et al., 2012; Shen et al., 2013; Poynton et al., 2013; Ma et al., 2014; Djurisic et al., 2015). A study on 19 kinds of MO NPs showed that the released M^{n+} played important roles in the toxicity of MO NPs (Horie et al., 2012). While the toxicity of NiO and CuO NPs was reported to be mainly caused by their released ionic counterparts (Horie et al., 2009; Misra et al., 2014), the toxicity of MO NPs cannot be simply explained by the release of M^{n+}. For example, it was also found that in the case of CuO NPs, the toxicity was induced by reactive oxygen species (ROS) generated by the CuO NPs attached to cells, whereas the released Cu^{2+} showed no significant toxicity (Applerot et al., 2012). Therefore, accurate determination of MO NPs and their released M^{n+} in different matrices are essential to understand their toxicological role and evaluate the risk of MO NPs.

Currently, a few methods have been developed for speciation analysis of MO NPs and M^{n+}. The commonly used approach is the separation of MO NPs and M^{n+} via centrifugation (Horie et al., 2012; Yang et al., 2015), ultrafiltration (James et al., 2013; Majedi et al., 2013), dialysis

(Shen et al., 2013; Odzak et al., 2014; Fabricius et al., 2014) or diffusive gradient in thin films (DGT) (Odzak et al., 2014; Pouran et al., 2014), followed by determination with inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma optical emission spectrometer (ICP-OES). However, these size-based separation techniques are unable to distinguish small sized MO NPs (e.g. <5 nm) from M^{n+}. Another challenge is that the detection limits are too high to satisfy the determination of MO NPs at environmental level or the expected exposure concentration. While the superior sensitivity makes single particle ICP-MS an ideal approach for environmental NP analysis in the range of low to medium ng/L, the size limit of NP identification is of >10 nm for most MO NPs limited its application (Laborda et al., 2011; Pace et al., 2012). Cloud point extraction (CPE) is another approach for separating MO NPs and the corresponding M^{n+} (Majedi et al., 2013; Majedi et al., 2014), in which the MO NPs were concentrated into the Triton X-114-rich phase while the M^{n+} remained in the aqueous phase as hydrophilic complexes formed with the added M^{n+} masking agents. However, the addition of M^{n+} masking agents such as ethylene diamine tetraacetic acid (EDTA) might induce the partial dissolution of MO NPs (Han et al., 2010) and therefore artifacts. Thus, rapid and sensitive speciation of MO NPs and M^{n+} remains a great challenge.

Chromatography techniques, such as field flow fraction (FFF) (Hagendorfer et al., 2012; Pettibone et al., 2013; Gigault et al., 2014; Tan et al., 2015), size exclusion chromatography (SEC) (Huve et al., 1994; Wei et al., 1999; Wei and Liu, 1999; Wilcoxon et al., 2001; Song et al., 2004; Helfrich et al., 2006; Helfrich and Bettmer, 2011; Soto-Alvaredo et al., 2013; Zhou et al., 2014), hydrodynamic chromatography (HDC) (Tiede et al., 2009), and capillary electrophoresis (CE) (Franze et al., 2014; Liu et al., 2014) showed excellent performance in size and shape separation of NPs. To our knowledge, however, only SEC has been successfully applied to separate metal ions from small sized NPs (e.g. <5 nm). Soto-Alvaredo et al. (2013) reported the separation of Ag(I) from >7 nm Ag NPs with detection limits in the low and medium ng/L range, which was correlated to the Ag speciation and size of the particular nanoparticle fraction. However, because the Ag NP sensitivities differed with the particle size (Soto-Alvaredo et al., 2013) and NPs with diameter larger than exclusion limit of LC column were easily filtered off by the column (Fischer et al., 1994), simultaneous determination of Ag(I) and Ag NPs with unknown sizes remained problematic. Very recently, we developed a rapid and sensitive method for speciation analysis of dissoluble Ag(I) and silver-containing NPs covering 1–100 nm, in which the soluble Ag(I) was eluted as a baseline separated peak and quantified with SEC-ICP-MS, whereas the nanoparticulate Ag concentration cannot be obtained directly from SEC-ICP-MS peak for the size-dependent recoveries of NPs, which was calculated by subtracting soluble Ag(I) from the total Ag content determined with ICP-MS after digestion of the sample without SEC separation (Zhou et al., 2014). However, SEC-ICP-MS has been only reported for speciation analysis of noble metal NPs and their ionic counterparts, and still not been applied to speciation analysis of MO NPs and their metal ionic counterparts. The main challenge in SEC separation of MO NPs and M^{n+} is that MO NPs are very sensitive to the organic ligands in the mobile phase. While addition of organic ligands into the mobile phase is essential to elute M^{n+}, this usually induces the partial dissolution of MO NPs (Pace et al., 2012) and therefore artifacts.

The objective of this work was to establish a rapid and sensitive platform for speciation analysis of MO NPs and M^{n+} in complex matrices. Conditions for SEC separation of MO NPs and M^{n+} were optimized by using six commercially available MO NPs with different compositions and particle sizes, including NiO, CoO, ZnO, CuO and CeO_2 NPs. The M^{n+} was quantified directly by SEC-ICP-MS by external calibration with ICP-MS standards, while the MO NPs were calculated by subtracting M^{n+} content from the total metal concentration which was determined after microwave digestion without SEC separation. Special attention was paid to avoid the dissolution of MO NPs during the SEC separation. The developed method was applied to speciation analysis of Ni^{2+}, Ce^{4+}, NiO and CeO_2 NPs in environmental waters.

2. Materials and methods

2.1. Chemicals and reagents

Among the six MO NPs (with nominal sizes in the parenthesis) used, CoO (30–50 nm), NiO (30 nm) and CeO_2 NPs-1 (<25 nm) were purchased from Sigma-Aldrich (St. Louis, MO, USA), while CuO (40 nm), ZnO (30 nm) and CeO_2 NPs-2 (50 nm) were obtained from Aladdin Chemistry Co. Ltd. (Shanghai, China). The MO NPs were dispersed with water under sonication for 20 min and the supernatants was collected as stock solutions. $Co(NO_3)_2$, $Ce(NO_3)_4$ and $Ni(NO_3)_2$ were from Aladdin Chemistry Co. Ltd. (Shanghai, China), while $Zn(NO_3)_2$ and $Cu(NO_3)_2$ were purchased from Sinopharm Chemical Reagent Co. (Beijing, China). Sodium dodecyl sulfate (SDS, 98.5%) of guaranteed reagent grade was obtained from Sinopharm Chemical Reagent Co. (Beijing, China). High purity nitric acid (65%) was obtained from Merck (Darmstadt, Germany). The other reagents were purchased from Beijing Chemicals (Beijing, China). All the reagents were used as obtained without further purification. Ultrapure water (18.3 MΩ) produced with a Milli-Q Gradient system (Millipore, Billerica, MA, USA) was used throughout the experiments. All the columns (Venusil Durashell, 1000 Å pore size, 5 μm particle size, 250 × 4.6 mm) were purchased from Bonna-Agela Technologies Inc. (Tianjin, China).

2.2. Characterization of MO NPs

The MO NPs were dispersed, respectively, with water under sonication (240 W, 25 °C water bath) for 20 min, and the supernatants were collected for characterization. The hydrodynamic diameters and zeta potential of MO NPs in ultrapure water were measured by dynamic light scattering (DLS) with a Malvern Nano ZS (Malvern Instruments, UK). Transmission electron microscopy (TEM) was carried out on an H-7500 (Hitachi, Japan) at 80 kV, and the samples were prepared by placing 5 μL aliquots of MO NP aqueous sample onto a carbon-coated grid and drying at room temperature under vacuum.

2.3. SEC-ICP-MS instrumentation

A LC system (Agilent 1200 series, Agilent Technologies, Palo Alto, CA) was coupled to the ICP-MS instrument (Agilent 7700cs) by directly connecting the column outlet to the cross-flow nebulizer of ICP-MS through a commercial polytetrafluoroethylene (PTFE) connector. All the connections and injection loop were of polyetheretherketone (PEEK). The relevant parameters of ICP-MS were daily tuned by introducing a multielement tuning solution according to manufacturer's instructions. Typical experimental parameters of the SEC-ICP-MS setup are summarized in Table 1. No cell gas was needed due to the slight interference to the determination of the M^{n+} in this study.

Table 1
Instrumental parameters of the SEC-ICP-MS system.

ICP-MS parameters	
Instrument	Agilent 7700cs ICP-MS
RF power	1500 W
Sampling depth	8 mm
Carrier gas	1.0 L/min
Integration time	0.5 s
Monitored isotopes (m/z)	$^{60}Ni^+$, $^{65}Cu^+$, $^{68}Zn^+$, $^{59}Co^+$, $^{142}Ce^+$
SEC parameters	
Column	Venusil Durashell-Silica, 1000 Å poresize, 250 × 4.6 mm
Column temperature	25 °C
Flow rate	0.5 mL/min
Injection volume	20 μL
Mobile phase	10 mM acetate buffer, pH 7.0, 10 mmol/L SDS