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Single particle ICP-MS characterization of titanium dioxide, silver, and gold nanoparticles during drinking water treatment

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HIGHLIGHTS

- Single particle-ICP-MS methods for analysis for TiO_2, Ag, and Au nanoparticles.
- Rapid tracking of nanoparticles during simulated drinking water treatment.
- Nanoparticles are removed during lime softening and alum coagulation.
- Ti-containing particles present in source water were removed by water treatment.

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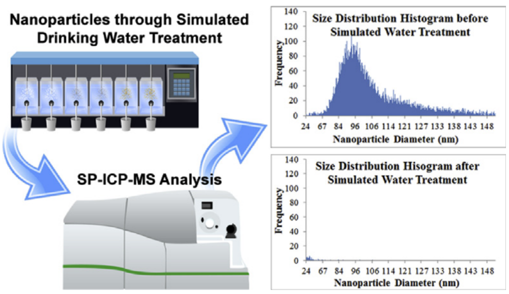
GRAPHICAL ABSTRACT



ABSTRACT

One of the most direct means for human exposure to nanoparticles (NPs) released into the environment is drinking water. Therefore, it is critical to understand the occurrence and fate of NPs in drinking water systems. The objectives of this study were to develop rapid and reliable analytical methods and apply them to investigate the fate and transportation of NPs during drinking water treatments. Rapid single particle ICP-MS (SP-ICP-MS) methods were developed to characterize and quantify titanium-containing, titanium dioxide, silver, and gold NP concentration, size, size distribution, and dissolved metal element concentration in surface water and treated drinking water. The effectiveness of conventional drinking water treatments (including lime softening, alum coagulation, filtration, and disinfection) to remove NPs from surface water was evaluated using six-gang stirrer jar test simulations. The selected NPs were nearly completely (97 ± 3%) removed after lime softening and alum coagulation/activated carbon adsorption treatments. Additionally, source and drinking waters from three large drinking water treatment facilities utilizing similar treatments with the simulation test were collected and analyzed by the SP-ICP-MS methods. Ti-containing particles and dissolved Ti were present in the river water samples, but Ag and Au were not present. Treatments used at each drinking water treatment facility effectively removed over 93% of the Ti-containing particles and dissolved Ti from the source water.

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1. Introduction

Nanoparticles (NPs) are used in many commercial products that, during use or after disposal, can lead to their release into waste and natural waters (Benn and Westerhoff, 2008; Kaegi et al., 2008, 2010; Nowack et al., 2012; Windler et al., 2012). It is estimated that TiO_2 and Ag NP concentrations in the environment will be in the ng/L-μg/L range (Mueller and Nowack, 2008; Gottschalk et al., 2009) and are expected to increase as NP production increases. Therefore, assessing NP behavior under environmental conditions is critical as NPs in source water for drinking water may present a direct exposure route for human ingestion of NPs. It has been reported that uncoated NPs tend to aggregate slowly with time in natural waters but remain in suspension (Keller et al., 2010; Tso et al., 2010) possibly due to the stabilizing effect of natural organic material (NOM) (Zhang et al., 2009; Thio et al., 2011).

Water treatment is the primary means to remove contaminants from drinking water, including organic compounds and suspended matter. Coagulation processes are well-known and used to remove these contaminants, but their ability to remove NPs from water has not been well established. Several studies have been conducted to determine TiO_2 and/or Ag NPs removal during alum or ferric based coagulation (Zhang et al., 2008; Chalew et al., 2013; Wang et al., 2013; Zhang, 2013). TiO_2 and Ag NP breakthrough were reported between 3–60% and 2–20%, respectively, depending on the complexity of the water (synthetic versus natural water) and treatment optimization. One study determined that microfiltration, an advanced drinking water treatment, resulted in only 0–4% and 0–2% of TiO_2 and Ag NP breakthrough, respectively (Chalew et al., 2013). However, due to the lack of analytical methods to characterize and quantify NPs at environmentally relevant concentrations, acid digestion was used during sample preparation of analysis in each study; the state of the particles during and after treatment was unidentified. It is imperative to develop analytical methods and to conduct future studies using methodologies that can directly monitor NPs during conventional drinking water treatment processes. Single particle – inductively coupled plasma – mass spectrometry (SP-ICP-MS) is an evolving tool for NP analysis in environmental matrices. SP-ICP-MS can characterize and quantify NPs at predicted environmental concentrations directly while simultaneously measuring dissolved metal element content (Loeschner et al., 2013; Lee et al., 2014; Mitrano et al., 2014; Montano et al., 2014; Cascio et al., 2015; Dan et al., 2015b), making the rapid tracking the fate of NPs during drinking water treatment process possible. The theory of SP-ICP-MS analysis has been well described elsewhere (Degueldre and Favarger, 2003; Mitrano et al., 2012; Laborda et al., 2014) and will not be discussed here.

The objectives of this study were: 1) to develop rapid SP-ICP-MS methods for detecting Au-, Ag-, and Ti-containing NPs in surface and drinking water; 2) to simulate conventional drinking water treatments for tracking fate of NPs during each water treatment step; and 3) to screen for the occurrence of NPs and the corresponding dissolved metal elements in source and drinking water from drinking water treatment facilities (DWTFs).

2. Materials and methods

2.1. Materials and instrumentation

Citrate-capped Au NPs (at 50, 80, and 100 nm diameter) and Ag NPs (at 40, 70, 100 nm diameter) suspended in 2 mM sodium citrate were acquired from nanoComposix, Inc. (San Diego, CA). TiO_2 particles of 100 nm and 160 nm diameter were obtained from US Research Nanomaterials, Inc. (Houston, TX). TiO_2, Ag, and Au NPs used in the drinking water treatment simulations were characterized by both SEM (160 nm TiO_2 particles only) and SP-ICP-MS. A representative SEM image obtained for TiO_2 particles and SP-ICP-MS measurements for each NP suspended in ultra-pure water can be found in Appendix A: Supporting material. Dissolved Ag and Ti standards (PerkinElmer, Waltham, MA) and dissolved Au standard (High-Purity Standards, Charleston, SC) were used for dissolved element calibrations. Sodium hydroxide (caustic), trace metal grade nitric acid, and aluminum sulfate ($Al_2(SO_4)_3 \cdot 14.3H_2O$) were purchased from Thermo Fisher Scientific Inc. (Pittsburgh, PA). Trace metal grade sulfuric acid and sodium hypochlorite were purchased from Sigma–Aldrich (St. Louis, MO). Hydrodarco B (HDB) powdered activated carbon (PAC) was purchased from Cabot (Marshall, TX). Ultra-pure water was generated by a Simplicity185 water purification system from Millipore. Whatman #40 filter paper was purchased from GE Healthcare Biosciences (Pittsburgh, PA). A PerkinElmer (Shelton, CT) NexION 300/350D ICP-MS with Syngistix Nano Application module was used for SP-ICP-MS analysis. Dissolved organic carbon (DOC) was monitored using a TOC-L analyzer with ASI-L liquid autosampler from Shimadzu Scientific Instruments (Columbia, MD). Turbidity was measured using a TB200 Portable Turbidimeter from Orbeco-Hellige (Sarasota, FL). UV_{254} absorbance was monitored using a Cary 50 Conc Scanning UV/Vis Spectrophotometer from Agilent (Santa Clara, CA). A Hitachi (Tokyo, Japan) S-4700 model field emission scanning electron microscope (FESEM) with energy-dispersive X-ray spectroscopy (EDS) capability was used to image and confirm elemental composition of NPs used during drinking water treatment simulations.

2.2. SP-ICP-MS analysis and data processing

Masses of ^{47}Ti (7.3% abundance, used to avoid calcium interference at 48 amu), ^{107}Ag, and ^{197}Au were monitored by SP-ICP-MS methods developed. Previous studies have shown that a single NP results in a signal duration between 0.3 and 0.5 ms and that using sub ms dwell times allow for peak profiling (Laborda et al., 2011; Montaño et al., 2014). Therefore, the dwell time used was 0.1 ms with data collected over 100 s. Dissolved element calibrations were prepared for Au, Ag, and Ti in 0.45 μm nylon membrane filtered river water to matrix match. Citrate-capped Au NPs and Ag NPs were used as particle calibration standards to prevent dissolution or aggregation.

2.3. Drinking water treatment simulation by six-gang stirrer jar test

A programmable six-gang stirrer (Phipps & Bird, Richmond, VA) was used to sequentially simulate lime softening, alum coagulation with PAC sorption, and disinfection. Missouri River water was collected and refrigerated unfiltered in pre-cleaned polypropylene bottles for use in jar tests. The river water was analyzed for Au, Ag, Ti NPs, and corresponding dissolved ions, DOC, UV_{254} absorbance, turbidity and pH before use in jar tests and after each treatment step during the simulation. NPs (100 nm Au, 100 nm Ag, or 160 nm TiO_2) were added to 2-L of Missouri River water at 1×10^6 particles/mL and dispersed by stirring for 1 min at 100 rpm before a sample was taken. Excess lime softening was conducted with a dose of 260 mg/L as $Ca(OH)_2$ to reach pH 11. The water was mixed rapidly at 300 rpm for 30 s, mixed slowly to form floc for 10 min each at 58, 42, and 28 rpm, and allowed to settle for 180 min before another sample was taken for analysis. The water was then decanted into a new 2-L square beaker, leaving only solids behind. Alum (60 mg/L as $Al_2(SO_4)_3 \cdot 14.3H_2O$, Zone 4 coagulation at pH 7–8) and PAC (HDB, 20 mg/L) were added to the softened water and mixed using the same stirring parameters as softening. The pH was quickly adjusted to 8 using trace metal grade sulfuric acid during flocculation. After settling, another sample was taken for analysis and 1-L of the water