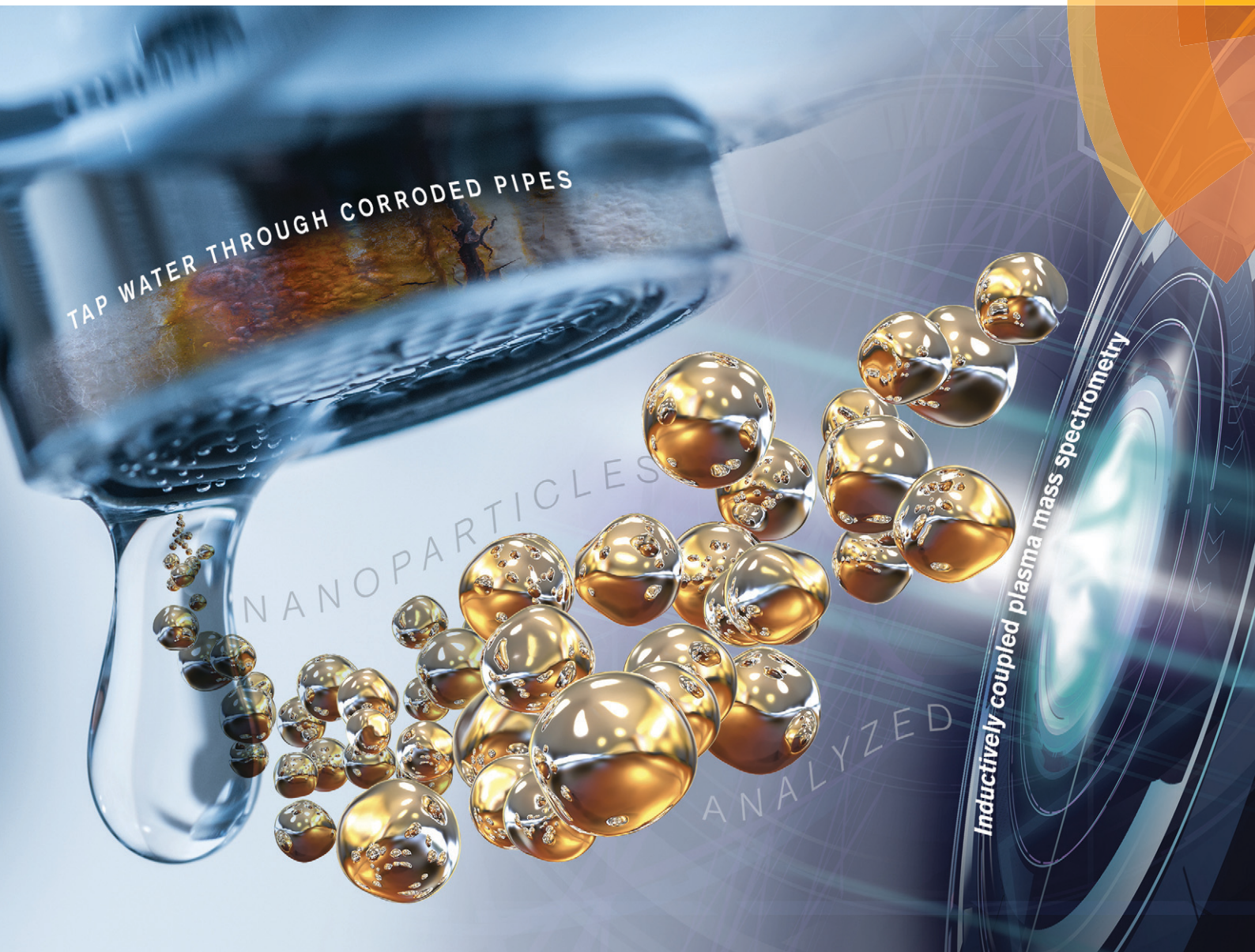


Environmental Science Water Research & Technology

rsc.li/es-water



ISSN 2053-1400



PAPER

Arjun K. Venkatesan *et al.*

Using single-particle ICP-MS for monitoring metal-containing particles in tap water

PAPER



Cite this: *Environ. Sci.: Water Res. Technol.*, 2018, 4, 1923

Using single-particle ICP-MS for monitoring metal-containing particles in tap water†

Arjun K. Venkatesan,^a Blanca T. Rodríguez,^c Aurelie R. Marcotte,^c Xiangyu Bi,^b Jared Schoepf,^b James F. Ranville,^d Pierre Herckes^c and Paul Westerhoff^b

Engineered, natural or incidental colloidal-sized materials in tap water may originate from source water or be generated in distribution systems (e.g., corrosion-related). An optimized single-particle (sp)-ICP-MS technique was applied to tap water samples ($n = 50$) collected from three buildings to analyze for Pb, Fe, Sn, Cu, Ag and Ti-containing particles. The Pb, Sn and Fe-containing particles were detected at an average concentration (ng L^{-1}) of 1.2 (range: 0.06–4.8), 1.8 (range: 0.11–14), and 88 (range: 26–890), respectively, representing the corresponding total dissolved metal concentrations at a minimum of 0.4%, 10%, and 15%. No particulate Ti and Ag were observed in the samples. The Pb concentrations in the first 125 mL fraction collected were on average three times higher than those in the subsequent samples. Detection of the Cu particles required modification of the sample introduction system (direct self-aspiration into the nebulizer) to reduce matrix interaction with the auto-sampler tubing. The Cu particles were detected in 50% of the analyzed samples at an average concentration of 69 (range: 15–136) ng L^{-1} . While all the metal concentrations were below the health advisory levels, this study showcases the feasibility and first application of spICP-MS to monitor metal-containing particles in tap waters, and the results suggest that the particulate forms of the studied elements may represent a significant fraction of the bulk elemental concentration in tap water.

Received 12th July 2018,
Accepted 12th September 2018

DOI: 10.1039/c8ew00478a

rsc.li/es-water

Water impact

Engineered nanomaterials (ENMs) are used extensively in a variety of commercial products and applications. ENMs in tap water may originate from contaminated source water or be generated in distribution systems (e.g., corrosion related), and hence it is essential to monitor the presence of metal-containing particles in drinking water to understand their life cycle and associated human exposure risks.

Introduction

Engineered nanomaterials (ENMs) are reported to be present in common consumer products such as cosmetics, toothpastes, and sunscreens¹ and they may pose unintended consequences upon release into the environment. As a consequence, there have been advances in analytical techniques to differentiate nano-sized particles from dissolved ions or

micron to larger-sized particles in water. Resulting from the focus on human exposure to ENMs, there is recognition that ENMs exist as a relatively small fraction of natural (and incidental) colloidal or nano-sized particles.² Nanoparticle concentrations in environmental waters are expected to be at the parts-per-trillion (ng L^{-1}) level.³ It is challenging to detect such low concentrations of nanoparticles using analytical methods such as dynamic light scattering (DLS), differential centrifugal sedimentation (DCS), and nanoparticle tracking analysis (NTA), because the minimum concentration required to obtain a feasible particle size distribution is in the parts-per-billion ($\mu\text{g L}^{-1}$) range for these techniques.⁴ Unlike DLS, DCS and NTA, a single-particle inductively coupled plasma mass spectrometry (spICP-MS) method is capable of detecting and sizing nanoparticles at environmentally relevant concentrations (e.g., ng L^{-1}) in addition to providing chemical information.^{4–6} Previous work has primarily focused on developing a spICP-MS technique and comparing it to other methods capable of sizing and quantifying nanoparticles in environmentally relevant levels.^{4,7–10}

^a Center for Clean Water Technology, Department of Civil Engineering, Stony Brook University, Stony Brook, New York, 11794, USA.

E-mail: Arjun.Venkatesan@stonybrook.edu; Tel: +1 631 632 1998

^b Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment, Arizona State University, School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, Arizona, 85287-3005, USA

^c School of Molecular Sciences, Arizona State University, Tempe, Arizona, 85287-1604, USA

^d Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado, 80401, USA

† Electronic supplementary information (ESI) available: As figures, (i) comparison of metal-containing particles between the AM and PM samples and (ii) the instrumental set-up for spICP-MS of tap water samples. See DOI: 10.1039/c8ew00478a

Single-particle ICP-MS is a time-resolved analysis that detects particles as pulses above the background elemental signal.^{4,11,12} Dissolved ionic species are homogeneously dispersed in a sample and determines the intensity of the background signal. Hence, the sensitivity and accuracy of spICP-MS to determine and size nanoparticles depend largely on the dissolved concentration since nanoparticle “pulses” are typically considered to be those with counts greater than three or four times the standard deviation (3σ or 4σ) of the background signal. For particles to be accurately sized, background dissolved concentrations would ideally be low so a clear distinction between background and small particle ‘pulse’ can be made. The size is determined from the intensity of each nanoparticle event and is binned in a particle size distribution (PSD) histogram to determine the average size of the particles and their polydispersity.^{4,13} Several studies have applied the spICP-MS technique to study the fate of nanoparticles in fortified water samples,^{14,15} with a few recent works featuring its application in monitoring non-fortified natural waters.^{6,16} Nano- and colloidal particles in tap water, to the best of our knowledge, have not been monitored using spICP-MS and remain unregulated because of the lack of data confirming their presence and toxicity. In cities’ distribution systems, metal-containing particles may occur from either the survival of particles through water treatment systems and/or particle generation from the treatment process. The distribution system may additionally contribute to the particles in tap water since piping is likely to corrode and/or solder could be freed by shearing.^{17–19} Pb, Fe and Sn particulates from distribution pipelines, solders, and fixtures have been reported to occur in tap and drinking waters.^{19–22} Nanosized iron oxide particles released from the distribution system can further adsorb hazardous chemicals such as Pb and As, and hence the presence of such particles in distribution pipelines can become a health hazard.^{21,22} Prior research has used various analytical methods including filtration,²³ magnetic measurements,²² and size-exclusion chromatography with ICP-MS²¹ to detect and characterize such particles.

The aim of this study was to develop the capability to apply spICP-MS to tap water. Tap water samples from different buildings, collected over time, were analyzed using spICP-MS to detect and size Pb, Fe, Sn, Cu, Ag and Ti-containing particles. Ag and Ti-containing particles were thought to be potentially related to ENMs that may have entered the distribution system after treatment.²⁴ Ti-containing particles also exist naturally and may originate from the source water. The other metals were likely to be related to corrosion and scaling by-products in the distribution pipelines.^{18,25} It was necessary to implement careful equipment operating conditions to successfully avoid matrix interferences and apply spICP-MS for routine monitoring of metal-containing particles in tap water.

Experimental

Reagents

The ionic elemental standards were purchased from VHG Laboratories (Manchester, UK). Trace metal grade nitric acid

(70%) and hydrochloric acid (33–36%) were purchased from EMD Chemicals (OmniTrace, EMD Chemicals, Gibbstown, NJ, USA) and J. T. Baker (Ultrex II, JT Baker Inc., NJ, USA), respectively. The tannic acid-stabilized Au reference nanomaterial (80 nm) was purchased from NanoComposix (CA, USA). All the other chemicals were obtained from Sigma-Aldrich (MO, USA) unless specifically stated. Deionized water (18.3 M Ω cm, NANOpure Infinity, LA, USA) was used to dilute samples.

Sample collection

The tap (drinking) water samples were obtained from sink faucets over the course of 4 days at 3 different sites in Phoenix, Arizona: (i) an apartment complex in Tempe, AZ (building 1); (ii) a new Arizona State University (ASU) building with a 2012 Leadership in Energy and Environmental Design (LEED) certification (referred to as building 2); and (iii) an older ASU classroom/office structure built in 1976 (building 3). All the three locations have the same source water and are served by the same drinking water treatment plant. At each location and day, two sets of the samples were collected: one during the morning (AM) and one during the afternoon (PM) to understand the impact on stagnant water overnight and during peak usage. For each sampling period, an aliquot of 125 mL (referred to as F125) was obtained immediately when the faucet was turned on. This was done to investigate the possible build-up of metal particles in the pipes over time. The faucet was then run for a full minute before obtaining a bulk sample of 500 mL (referred to as bulk). For Cu analysis, 14 additional tap water samples were collected from building 2 for analysis using a modified spICP-MS method (see the Results section). A total of 50 tap water samples were collected (36 + 14), stored in a refrigerator and analyzed within seven days after collection.

spICP-MS instrumentation and data analysis

Analysis by spICP-MS was performed using a Thermo Scientific (Waltham, MA) X-Series II ICP-MS in time-resolved analysis (TRA) mode.^{6,13} The TRA mode provides an output signal as intensity (counts per second – cps) *versus* time. An 80 nm Au reference nanoparticle standard at 200 ng L⁻¹ was analyzed to determine transport efficiency using the particle mass method described elsewhere.^{13,26} Calibration standards were prepared in 2% HNO₃ for ²⁰⁸Pb, ⁵⁶Fe, ¹¹⁸Sn, ⁶⁵Cu, ⁴⁹Ti, and ¹⁰⁷Ag, and 2% HCl for ¹⁹⁷Au. All the elements, except ⁵⁶Fe, were measured in the normal mode using argon as the carrier gas. ⁵⁶Fe was measured in the collision cell technology (CCT) mode. The calibration standards were analyzed for 70 seconds and the tap water samples were analyzed for 180 seconds. The instrument was tuned prior to each sample batch using a solution containing Li, In, Ce and U at a concentration of 10 μ g L⁻¹ and by monitoring for minimum oxide levels (CeO/Ce < 2%). A dwell time of 10 ms was used. The sample flow rate was measured by weighing the water mass pumped in one

minute (mL min^{-1}), which was used to calculate the fraction of sample reaching the plasma (*i.e.* transport efficiency).²⁶

The most commonly used approach for sizing particles is to measure the average and standard deviation of the background signal through an iterative analysis, considering anything above a chosen cut-off ($\text{mean} + x \times \sigma$) as a particle detection event. Particulate pulses with an instrument response greater than 4 standard deviations (4σ) from the background signal were counted as particle events in the present study. The pulse intensity above background was then converted to mass *via* a dissolved calibration curve, and to diameter *via* particle density and spherical geometry. We assumed that all the metal-containing particles are composed of single element, and used the density of the corresponding element to obtain particle size distributions. To calculate particulate mass concentrations, the elemental mass corresponding to all the pulse signals from a given run was divided by the sample volume analyzed, which was known based on the instrument flow rate and analysis time.^{4,13} The average background/baseline signal of the elements in spICP-MS for the samples (*i.e.*, $<4\sigma$) was used to determine ionic elemental concentrations and concentrations of particles less than the size detection limit (SDL) of the instrument. In this paper, the 'background' concentration is defined as the ionic elemental concentration plus metal-containing particles below the SDL. The SDL for the particles will vary depending on both the instrument sensitivity and the standard deviation of the background signal (sample matrix). The instrument's minimum detectable sizes determined for Pb, Fe, Sn, Cu, Ti and Ag were 11.3, 55, 26, 40, 75 and 13 nm, respectively.¹³

Transmission electron microscopy

About 50 mL of the tap water sample was sonicated for five minutes to suspend the particles. A Ted Pella carbon type-B transmission electron microscopy (TEM) grid was placed at the bottom of the tap water sample in a centrifuge tube. The sample was centrifuged at 4600g for 4 hours to settle any metal-containing particles present on to the surface of the TEM grid. Microscopy was performed on a JEOL 2010F TEM (Peabody, MA, USA) with energy-dispersive X-ray spectroscopy (EDS). The EDS data is reported in a counts *vs.* energy (keV) graph. The copper peaks are a result of the copper TEM grids used for analysis. The mean particle diameter was measured manually with ImageJ™ software.

Results and discussion

Metal-containing particle detection and quantification in tap water by spICP-MS

For each sample, time-resolved spICP-MS data were obtained for Pb, Fe, Sn, Cu, Ti, and Ag. The Pb, Fe, and Sn particles were detected in all the samples with varying concentrations, with Fe being the most abundantly detected particles in the tap water samples at an average concentration of 88 (range: 26–890) ng L^{-1} (Fig. 1). The Pb and Sn particles were detected

at an average concentration of 1.2 ng L^{-1} (range: 0.06–4.8) and 1.8 ng L^{-1} (range: 0.11–14.1), respectively. Though the particles (pulses) were detected in all the samples, the particle concentrations for Pb (53%) and Sn (44%) were low ($<1 \text{ ng L}^{-1}$) in about half of the samples analyzed. No particulate Ti and Ag were observed in any of the samples analyzed. The Cu-containing particles were detected after method modification and the results are discussed in the section below.

Pb-Containing particles. The concentration of particulate Pb was <1 ppt in buildings 1 and 2, but higher in building 3 with an average concentration of 2.6 (range: 0.45–4.8) ng L^{-1} . The average background Pb concentration ($<4\sigma$) in buildings 1, 2, and 3 was 125 (range: 34–476), 441 (range: 181–690), and 876 (range: 177–2059) ng L^{-1} , respectively. To the best of our knowledge, there are no lead pipes in the buildings that we sampled; but older homes in the metro-Phoenix region might contain lead. Before enforcement of the Federal Lead Ban in 1988, solders were typically made of 40 to 50% lead.²⁷ Hence, the elevated Pb concentration in building 3 compared to those in other buildings could be attributed to the age of the structure (built in 1976), which could contain a piping system leaching Pb (Pb-based solder shearing off). The Environmental Protection Agency drinking water action level for lead is 15 $\mu\text{g L}^{-1}$,²⁷ and all Pb measurements in the drinking water samples in this study were below this level. The background and particulate-Pb concentrations were higher in the initial 125 mL samples compared to those of their secondary bulk samples; this observation was especially pronounced in building 3 for background Pb concentration ($F_{125} = 1.53 \pm 0.49 \mu\text{g L}^{-1}$ and bulk = $0.22 \pm 0.04 \mu\text{g L}^{-1}$) (Fig. 1a and b). The mean background Pb concentrations in the AM samples from the three buildings were generally higher than the PM samples (see the ESI† Fig. S1b); whereas no significant difference was observed for the particulate Pb form between the AM and PM samples. These data are indicative of the dissolved Pb and/or Pb particles smaller than the SDL building up in pipes close to the faucet over short time scales. The particulate Pb fraction detected in the present study was low at only 0.4 (range: 0.09–1.8) % of the total bulk Pb by mass (Fig. 2). Prior research indicates that particulate Pb may enter the distribution lines from corrosion of lead bearing elements in the premise plumbing and/or *via* adsorption of dissolved Pb onto suspended solids.^{19,20,25}

Fe-Containing particles. Buildings 1, 2 and 3 have an average Fe-containing particle mass concentration of 40.8 (range: 26–237), 65.1 (range: 51–890), and 63.0 (range: 34–213) ng L^{-1} as Fe, and a corresponding background concentration of 615 (range: 595–1738), 703 (range: 336–1289), and 105 (range: 501–1088) ng L^{-1} as Fe, respectively. The average particulate fraction of Fe in the tap water samples was calculated to be 10 (range: 2–71) % (by mass) of the total bulk Fe, with one sample from building 2 featuring as high as 71% particulate Fe in the initial 125 mL fraction (F_{125}) collected during the morning of the first sampling day. An elevated particulate Fe content was detected in the F_{125} (Fig. 1c) and most of the morning (AM) samples collected immediately after turning

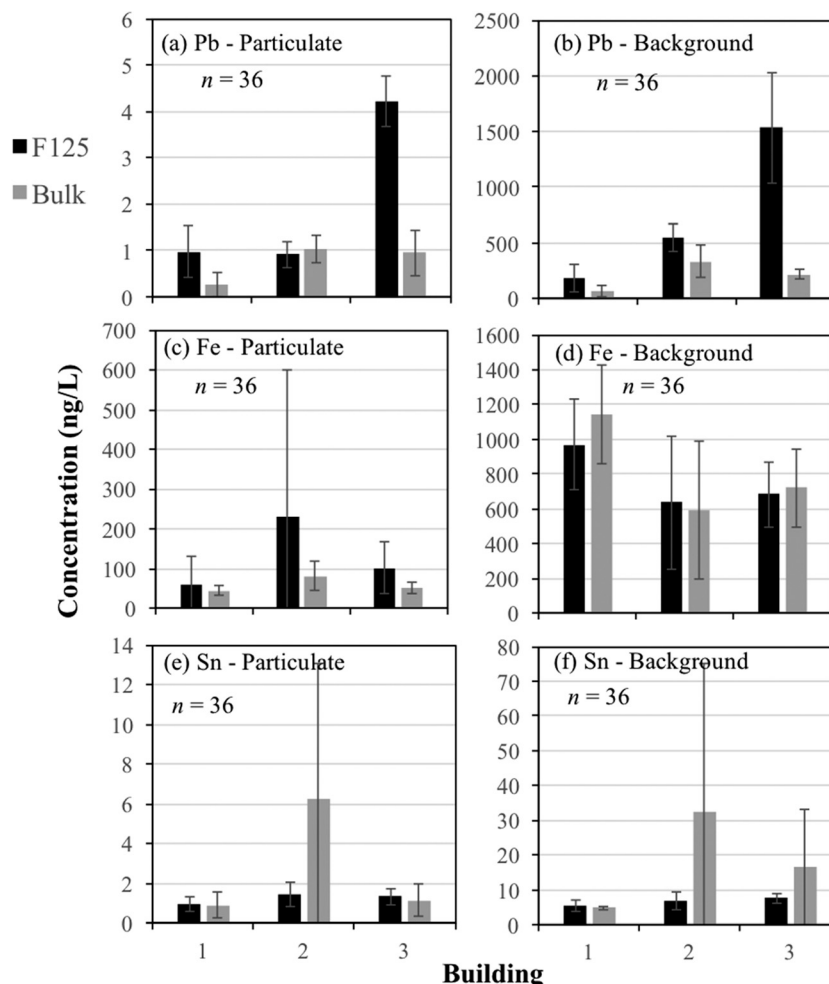


Fig. 1 Average particulate (a – Pb; c – Fe; e – Sn) and background (b – Pb; d – Fe; f – Sn) elemental concentrations determined by spICP-MS in the initial 125 mL fractions (black bar) and secondary 500 mL fractions (bulk; grey bar) of tap water collected from the three buildings. ‘n’ represents the number of tap water samples analyzed. Error bars represent plus/minus one standard deviation.

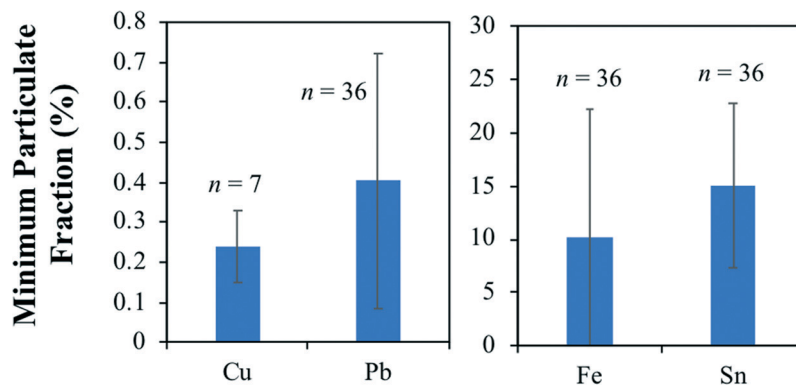


Fig. 2 Minimum fraction of metal-containing particles detected in tap waters. ‘n’ represents the number of samples analyzed. Error bars represent plus/minus one standard deviation.

on the tap (ESI† Fig. S1c). This can be likely attributed to stagnant water leaching Fe particles from the distribution pipes.¹⁸ The background Fe concentration, however, was mostly similar between the various sample fractions.

Sn-Containing particles. The particulate Sn concentration was low and detected near or less than 1 ng L⁻¹ concentra-

tion in buildings 1 and 3. Building 2 featured a relatively higher average concentration of 3.9 (range: 0.8–14) ng L⁻¹. The average background Sn concentration (<4σ) in buildings 1, 2, and 3 was 5.2 (range: 2.7–7.9), 19.5 (range: 3.1–106), and 12.1 (range: 4.2–45) ng L⁻¹, respectively. No observable trends occurred in either dissolved or particulate Sn concentrations

between F125 and bulk fractions. However, build-up of the Sn particles overnight was noticed for building 2, but not for buildings 1 and 3 (ESI† Fig. S1e). We expected similar results for Sn in building 3, since the Pb levels were high and the presence of both Sn and Pb could then be associated with leaching from the solder material in pipes. It is not clear what the sources are for these particles in tap water and further research is needed. One study evaluated the presence of contaminants in scales collected from pipe specimens across the U.S. and categorized Sn as a ‘moderate contaminant’ based on the concentration detected in scale samples.²⁵ Sn was detected in 55% of the samples analyzed in that study at an average concentration of 1129 mg kg⁻¹. Hence, scaling in the pipelines in addition to leaching from solder materials^{19,20} could likely be the source for the detected particles

and is supported by the high particulate fraction observed for Sn in the present study (15 (range: 2.2–33) % of the total bulk Sn concentration; Fig. 2).

Method modification for detection of Cu-containing particles

Detection of the Cu particles was initially challenging due to the fluctuation of the baseline observed in all the tap water samples (Fig. 3a). We measured the elevated Cu concentrations using conventional ICP-MS to be between 0.2 and ~1 mg L⁻¹ in building 2, a LEED certified building built in 2012. The building facility managers were able to reduce the Cu levels in the building through daily flushing of the entire six-story building plumbing system. LEED certified buildings are designed to reduce water consumption (>60%), but it

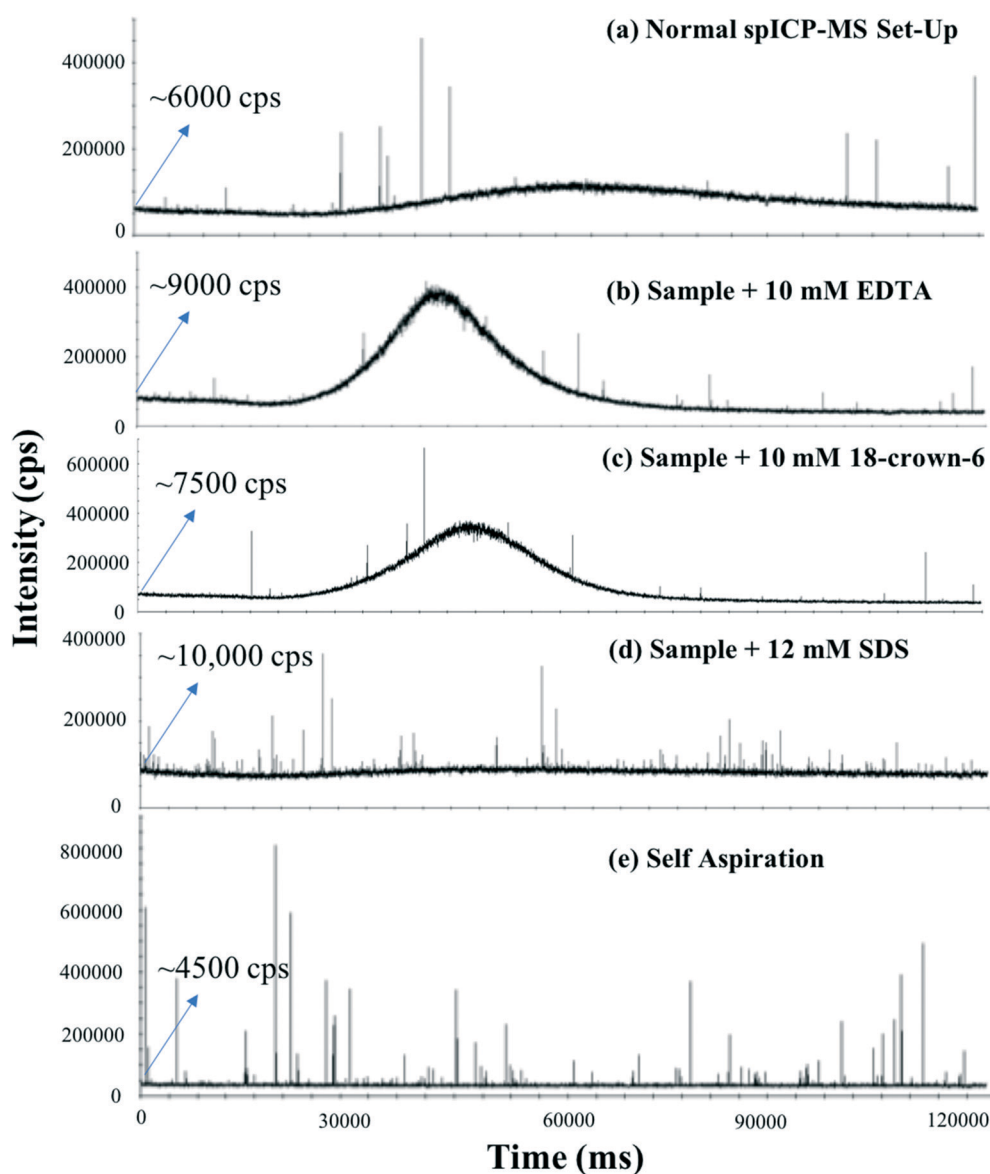


Fig. 3 Raw signal spectra of Cu in tap water using (a) the normal spICP-MS set-up; (b) the normal set-up plus the addition of 10 mM EDTA to the sample; (c) the normal set-up plus the addition of 10 mM 18-crown-6 to the sample; (d) the normal set-up plus the addition of 12 mM SDS to the sample; and (e) the self-aspiration technique.

appears that building and plumbing codes do not require downsizing pipe diameters. As a result, long retention time in the pipes depletes chlorine residuals and influences copper corrosion.²⁸

To identify the cause for baseline interferences, we performed controlled experiments using CuO₂ as a model nanoparticle spiked into nanopure water. We were able to point out that the baseline interference was due to the interaction of background Cu (-complexes) with the sample introduction system (SIS) tubing of the ICP-MS instrument. However, we were not able to identify what the tap water constituent was that caused this interference. Multiple spICP-MS runs were performed using the model nanoparticle (~ppt range) in the presence of common tap water constituents (carbonates, bicarbonates, NOM, *etc.*), but none of these contributed to the interference observed. In order to reduce the sample interaction with SIS tubing, we evaluated two modifications to the spICP-MS method: (i) addition of surfactant/complexing agents to the sample; and (ii) reducing the length of sample tubing. For the first modification, we tested the addition of sodium dodecyl sulfate (SDS), EDTA and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) to tap water and nanopure water spiked with CuO₂ particles. The justification for using these compounds are as follows: EDTA and 18-crown-6 were used in order to complex with Cu to eliminate the background Cu interacting with tubing; whereas, SDS was used in order to keep the particles in suspension and thus reducing particle interaction with the tubing. EDTA, crown ethers, and SDS have been used for ICP-MS analysis in the past for preservation, speciation and separation purposes.^{29–31} The complexation with EDTA and 18-crown-6 approach did not work, and the interference persisted in spICP-MS analysis (Fig. 3b and c). The use of SDS at ~12 mM concentration in the samples helped with stabilizing the baseline spectrum of Cu in tap water samples (Fig. 3d). However, we observed an increase in the intensity of the baseline spectrum, thus significantly affecting the resolution and SDL of Cu particles. In the second modification approach, to reduce the sample interaction with SIS tubing, we bypassed the auto-sampler and introduced the sample directly into the ICP-MS nebulizer through a short tubing (ESI† Fig. S2); *i.e.* the sample was allowed to 'self-aspirate' into the nebulizer. This modification stabilized the background signal for Cu and allowed us to detect and quantify Cu-containing particles in tap water (Fig. 3e). Additionally, this modification did not alter the background intensity of the spICP-MS spectrum and thus did not have any impact on the resolution of the method.

The self-aspiration technique was used to determine the Cu-containing particle concentration in samples. A new set of samples ($n = 14$) was collected from building 2 (after the pipelines were flushed and Cu concentrations were reduced) and analyzed using the modified method for the Cu particles in tap waters (transport efficiency was calculated for self-aspiration using ionic calibration and the reference Au stan-

dard). The Cu-containing particles were detected in 50% of the samples analyzed at an average concentration of 69 (range: 15–136) ng L⁻¹. We also noticed that there were no substantial differences between F125 and bulk, and between the AM and PM samples for Cu concentrations. This could be a result of the very high background Cu concentration ($34 \pm 28 \mu\text{g L}^{-1}$) present in the water samples, that might have masked the instrument's ability to distinguish particulate events from dissolved Cu (see the next section).

Sizing of metal-containing particles in tap water and confirmation by TEM

In spICP-MS, detection of particles is primarily affected by the intensity of the baseline signal caused by ionic/background fraction of the element analyzed. The background concentration, as determined by the spICP-MS baseline spectrum (*i.e.* $<4\sigma$), was in the ng L⁻¹ range for Sn (11 ng L⁻¹; range: 2.7–106), Pb (421 ng L⁻¹; range: 34–2059), and Fe (836 ng L⁻¹; range: 336–1738). This enabled us to detect true nanoparticles (<100 nm diameter) of these elements in the tap water samples as seen in the PSD plots (Fig. 4a–c). The minimum particle sizes detected for Sn, Pb and Fe in the present study were roughly 45, 60, and 90 nm, respectively. The minimum size detected in the present study was higher than the minimum particle size (D_{min}) calculated previously for these elements using the same instrument at 26, 13, and 55 nm, respectively.¹³ This was expected since the calculated D_{min} values in the latter study represented lower end sensitivity of the instrument under the best conditions, and the difference is very likely due to tap water matrix interferences. In the case of Cu, the average background Cu concentration in the samples analyzed was $34 \pm 28 \mu\text{g L}^{-1}$ and was almost two orders of magnitude higher than the other elements monitored. Hence, the minimum particle size detected in tap water was ~140 nm, which is not a nanoparticle by definition (Fig. 4d). This was expected because with increasing ionic/background elemental concentration, the minimum particle size detected by the instrument increases linearly.⁶ Hence it is very much possible that smaller Cu particles may have been present in the tap water samples which were binned along with ionic Cu as the background concentration ($<4\sigma$).

To confirm the presence of the particles detected in the present study, selected samples were subjected to TEM and EDS. We used a Cu TEM grid and hence we were not able to identify the Cu particles in the samples. The Sn and Pb particle concentrations were low in all the samples as discussed above, and hence we couldn't identify those particles *via* TEM even after multiple attempts. However, the Fe-containing particles were successfully detected and confirmed using TEM (Fig. 5). Elemental analysis by EDS found Fe nanoparticles in the tap water, along with C and O, Cu from the TEM grid, and trace amounts of other elements. The image revealed spherical particles with an average diameter of 8 ± 2 nm, which was an order of magnitude lower than what was determined by spICP-MS sizing. This

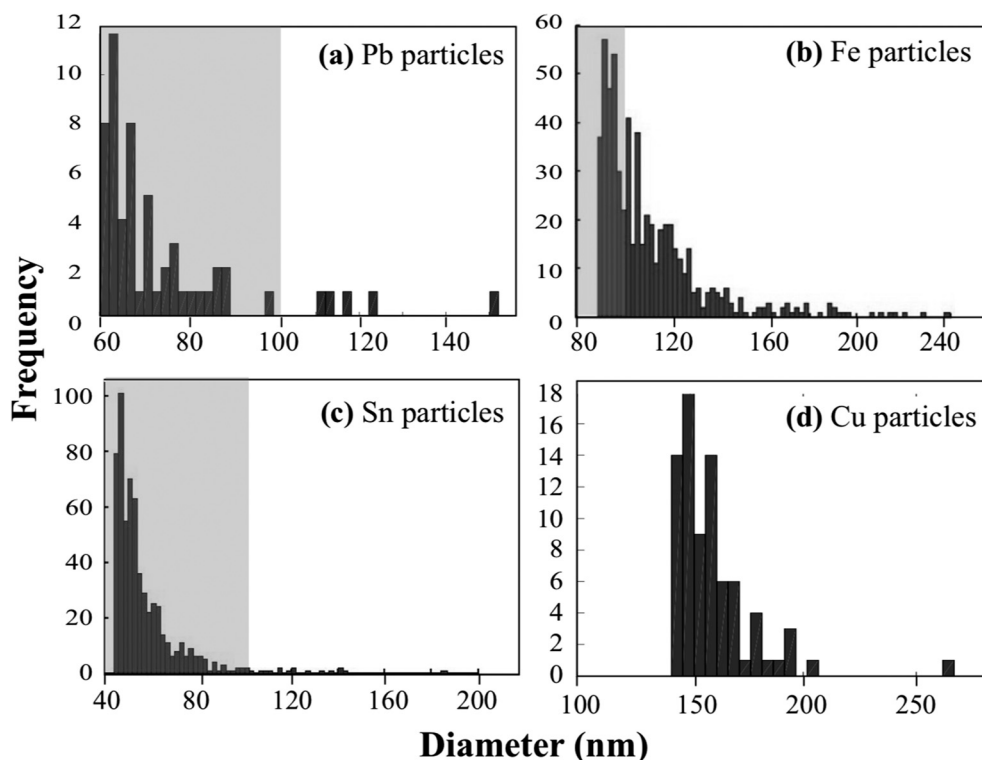


Fig. 4 Size distribution of (a) Pb, (b) Fe, (c) Sn, and (d) Cu-containing particles detected in tap water samples collected from Phoenix, AZ. Shaded region represents particles at <100 nm (*i.e.* nanoparticles by definition).

difference could be due to the fact that spICP-MS was able to detect only particle aggregates and the size detection could have been affected by the presence of high Fe background concentration (836 ng L^{-1}). The Fe particle size determined by TEM in this study is comparable to the previously reported particle size of corrosion-related Fe particles (3.2–5.6 nm) in tap water samples.²²

Study limitations and future work

Several studies list the criteria and requirements to obtain accurate size distributions of particles *via* spICP-MS.^{13,32,33} The selection of instrument dwell time and a critical nanoparticle number concentration in samples are important considerations to control precision associated with the counting of particle events and in the generation of size distributions. In this study, we used a 10 ms dwell time and the number of particle events for Pb and Sn was low. By increasing the analysis time to >3 minutes, we were able to capture sufficient particle events for Pb and Sn. The displayed PSD histograms (Fig. 4) are from the selected samples that featured the highest number of corresponding particles in the samples analyzed. However, the background levels for the Fe and Cu particles were relatively high and hence the 10 ms dwell time used in this study might have not been ideal for the detection of smaller particles. This effect can be observed in the PSD histograms, especially for Cu particles. Recent work has shown that extremely short

dwell time (as low as 0.1 ms) can significantly improve instrument resolution enabling the detection of particles even at high background concentrations.³³ It was our goal to test the feasibility of using spICP-MS to detect common metal-containing particles in tap water samples and though we achieved successful detection, further modifications such as removal of interfering dissolved elemental forms (*e.g. via* ion-exchange³⁴) may be needed for accurate sizing of nanoparticles in tap water. Additionally, spiking experiments (similar to CuO_2 used in this study) with other model nanoparticles will provide quantitative information about tap water matrix effects and nanoparticle recoveries for various elements.

Conclusions

We successfully demonstrated the feasibility of using spICP-MS for routine monitoring of common metal-containing particles in tap water. The results show that the particulate forms of Sn and Fe represent a significant fraction of the corresponding total bulk elemental mass (>10%). Pb and Cu particles were also detected in the tap water samples, likely due to leaching from pipelines. Method modification (self-aspiration) was necessary for successful detection of Cu particles in tap water. To the best of our knowledge, this is the first application of the ‘self-aspiration’ technique for spICP-MS that may be extended to other challenging matrices showing similar interferences with the instrument SIS. Future

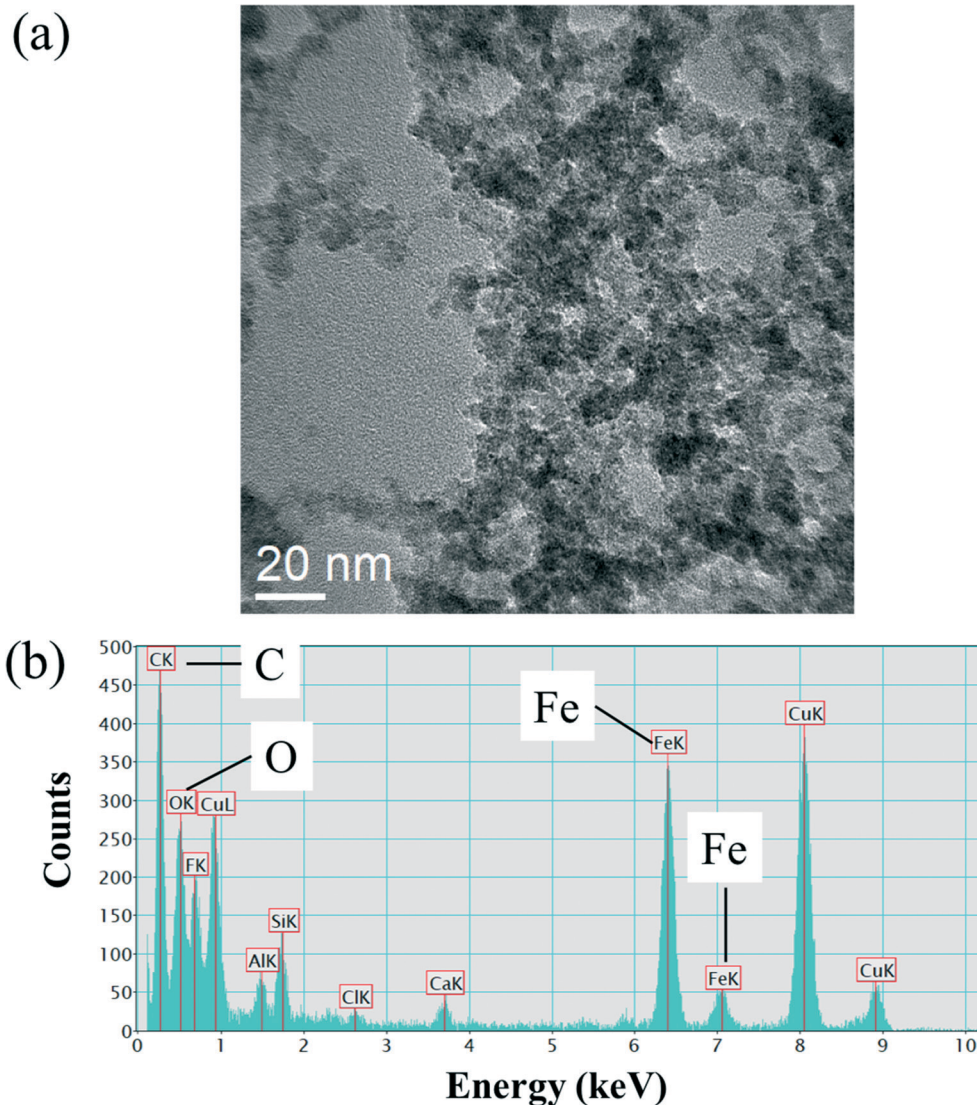


Fig. 5 Identification by (a) TEM and (b) elemental analysis (EDX) of Fe-containing nanoparticles in tap water. Note: Cu detected is from the TEM grid.

improvements to further reduce nanoparticle size detection limits, potentially through shorter instrument dwell times and removal of interfering background ionic forms, will make it possible to resolve and monitor even smaller metal-containing particles in drinking water. All the metal concentrations detected were lower than the regulatory limits in drinking water, but the presence of particulate forms in tap water will require additional research to evaluate possible human exposure risks. It is well known that toxic species such as Pb and As can adsorb onto Fe nanoparticles leading to elevated levels in water at the point of use.^{19,22,35} An Fe-containing particle concentration of up to 890 ng L⁻¹ in tap water was detected in the present study. Hence, it is particularly important to evaluate the risks of such incidental nanoparticles (*e.g.* corrosion by-products) released from distribution pipes, since the concentrations of ENMs are typically low in tap water.³⁶

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partially funded by the Western Alliance to Expand Student Opportunity, the National Science Foundation Nanosystems Engineering Research Center on Nano-Enabled Water Treatment (EEC-1449500; CBET 0847710) and the US Environmental Protection Agency through the STAR program (RD83558001). Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the NSF and USEPA. We gratefully acknowledge the use of facilities of the LeRoy Eyring Center for Solid State Science at Arizona State University.

References

- 1 K. Gibson and D. Pula, *Nanoparticles: Environmental risk and regulation*, Environmental Quality Management, 2009, vol. 18, pp. 1–7.
- 2 M. Baalousha and J. Lead, *Characterization of nanomaterials in complex environmental and biological media*, Elsevier, 2015.
- 3 N. C. Mueller and B. Nowack, Exposure modeling of engineered nanoparticles in the environment, *Environ. Sci. Technol.*, 2008, 42, 4447–4453.
- 4 H. E. Pace, N. J. Rogers, C. Jarolimek, V. A. Coleman, E. P. Gray, C. P. Higgins and J. F. Ranville, Single particle inductively coupled plasma-mass spectrometry: a performance evaluation and method comparison in the determination of nanoparticle size, *Environ. Sci. Technol.*, 2012, 46, 12272–12280.
- 5 A. P. Gondikas, F. v. d. Kammer, R. B. Reed, S. Wagner, J. F. Ranville and T. Hofmann, Release of TiO₂ nanoparticles from sunscreens into surface waters: a one-year survey at the old Danube recreational Lake, *Environ. Sci. Technol.*, 2014, 48, 5415–5422.
- 6 A. K. Venkatesan, R. B. Reed, S. Lee, X. Bi, D. Hanigan, Y. Yang, J. F. Ranville, P. Herckes and P. Westerhoff, Detection and Sizing of Ti-Containing Particles in Recreational Waters Using Single Particle ICP-MS, *Bull. Environ. Contam. Toxicol.*, 2018, 100, 120–126.
- 7 C. Degueldre and P.-Y. Favarger, Colloid analysis by single particle inductively coupled plasma-mass spectroscopy: a feasibility study, *Colloids Surf., A*, 2003, 217, 137–142.
- 8 D. M. Mitrano, E. K. Lesher, A. Bednar, J. Monserud, C. P. Higgins and J. F. Ranville, Detecting nanoparticulate silver using single-particle inductively coupled plasma-mass spectrometry, *Environ. Toxicol. Chem.*, 2012, 31, 115–121.
- 9 F. Laborda, J. Jiménez-Lamana, E. Bolea and J. R. Castillo, Selective identification, characterization and determination of dissolved silver (I) and silver nanoparticles based on single particle detection by inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.*, 2011, 26, 1362–1371.
- 10 R. B. Reed, C. P. Higgins, P. Westerhoff, S. Tadjiki and J. F. Ranville, Overcoming challenges in analysis of polydisperse metal-containing nanoparticles by single particle inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.*, 2012, 27, 1093–1100.
- 11 M. D. Montaña, J. W. Olesik, A. G. Barber, K. Challis and J. F. Ranville, Single particle ICP-MS: advances toward routine analysis of nanomaterials, *Anal. Bioanal. Chem.*, 2016, 408, 5053–5074.
- 12 R. Peters, Z. Herrera-Rivera, A. Undas, M. van der Lee, H. Marvin, H. Bouwmeester and S. Weigel, Single particle ICP-MS combined with a data evaluation tool as a routine technique for the analysis of nanoparticles in complex matrices, *J. Anal. At. Spectrom.*, 2015, 30, 1274–1285.
- 13 S. Lee, X. Bi, R. B. Reed, J. F. Ranville, P. Herckes and P. Westerhoff, Nanoparticle size detection limits by single particle ICP-MS for 40 elements, *Environ. Sci. Technol.*, 2014, 48, 10291–10300.
- 14 A. R. Donovan, C. D. Adams, Y. Ma, C. Stephan, T. Eichholz and H. Shi, Detection of zinc oxide and cerium dioxide nanoparticles during drinking water treatment by rapid single particle ICP-MS methods, *Anal. Bioanal. Chem.*, 2016, 408, 5137–5145.
- 15 A. R. Donovan, C. D. Adams, Y. Ma, C. Stephan, T. Eichholz and H. Shi, Single particle ICP-MS characterization of titanium dioxide, silver, and gold nanoparticles during drinking water treatment, *Chemosphere*, 2016, 144, 148–153.
- 16 R. Reed, D. Martin, A. Bednar, M. Montaña, P. Westerhoff and J. Ranville, Multi-day diurnal measurements of Ti-containing nanoparticle and organic sunscreen chemical release during recreational use of a natural surface water, *Environ. Sci.: Nano*, 2017, 4, 69–77.
- 17 N. S. Wigginton, K. L. Haus and M. F. Hochella Jr, Aquatic environmental nanoparticles, *J. Environ. Monit.*, 2007, 9, 1306–1316.
- 18 S. Gonzalez, R. Lopez-Roldan and J.-L. Cortina, Presence of metals in drinking water distribution networks due to pipe material leaching: a review, *Toxicol. Environ. Chem.*, 2013, 95, 870–889.
- 19 E. Deshommes, L. Laroche, S. Nour, C. Cartier and M. Prévost, Source and occurrence of particulate lead in tap water, *Water Res.*, 2010, 44, 3734–3744.
- 20 E. Deshommes and M. L. Prévost, Pb particles from tap water: bioaccessibility and contribution to child exposure, *Environ. Sci. Technol.*, 2012, 46, 6269–6277.
- 21 B. F. Trueman and G. A. Gagnon, A new analytical approach to understanding nanoscale lead-iron interactions in drinking water distribution systems, *J. Hazard. Mater.*, 2016, 311, 151–157.
- 22 F. E. Senftle, A. N. Thorpe, J. R. Grant and A. Barkatt, Superparamagnetic nanoparticles in tap water, *Water Res.*, 2007, 41, 3005–3011.
- 23 S. De Mora, R. M. Harrison and S. Wilson, The effect of water treatment on the speciation and concentration of lead in domestic tap water derived from a soft upland source, *Water Res.*, 1987, 21, 83–94.
- 24 T. E. A. Chalew, G. S. Ajmani, H. Huang and K. J. Schwab, Evaluating nanoparticle breakthrough during drinking water treatment, *Environ. Health Perspect.*, 2013, 121, 1161.
- 25 M. R. Schock, R. N. Hyland and M. M. Welch, Occurrence of contaminant accumulation in lead pipe scales from domestic drinking-water distribution systems, *Environ. Sci. Technol.*, 2008, 42, 4285–4291.
- 26 H. E. Pace, N. J. Rogers, C. Jarolimek, V. A. Coleman, C. P. Higgins and J. F. Ranville, Determining transport efficiency for the purpose of counting and sizing nanoparticles via single particle inductively coupled plasma mass spectrometry, *Anal. Chem.*, 2011, 83, 9361–9369.
- 27 R. P. Maas, S. C. Patch, D. M. Morgan and T. J. Pandolfo, Reducing lead exposure from drinking water: recent history and current status, *Public Health Rep.*, 2005, 120, 316–321.
- 28 W. J. Rhoads, A. Pruden and M. A. Edwards, Survey of green building water systems reveals elevated water age and water quality concerns, *Environ. Sci.: Water Res. Technol.*, 2016, 2, 164–173.

- 29 P. A. Gallagher, C. A. Schwegel, X. Wei and J. T. Creed, Speciation and preservation of inorganic arsenic in drinking water sources using EDTA with IC separation and ICP-MS detection, *J. Environ. Monit.*, 2001, **3**, 371–376.
- 30 S. Londesborough, J. Mattusch and R. Wennrich, Separation of organic and inorganic arsenic species by HPLC-ICP-MS, *Fresenius' J. Anal. Chem.*, 1999, **363**, 577–581.
- 31 B. Gammelgaard, O. Jøns and L. Bendahl, Selenium speciation in pretreated human urine by ion-exchange chromatography and ICP-MS detection, *J. Anal. At. Spectrom.*, 2001, **16**, 339–344.
- 32 F. Laborda, J. Jiménez-Lamana, E. Bolea and J. R. Castillo, Critical considerations for the determination of nanoparticle number concentrations, size and number size distributions by single particle ICP-MS, *J. Anal. At. Spectrom.*, 2013, **28**, 1220–1232.
- 33 M. Montano, H. Badiei, S. Bazargan and J. Ranville, Improvements in the detection and characterization of engineered nanoparticles using spICP-MS with microsecond dwell times, *Environ. Sci.: Nano*, 2014, **1**, 338–346.
- 34 M. Hadioui, C. Peyrot and K. J. Wilkinson, Improvements to single particle ICPMS by the online coupling of ion exchange resins, *Anal. Chem.*, 2014, **86**, 4668–4674.
- 35 A. D. Knowles, C. K. Nguyen, M. A. Edwards, A. Stoddart, B. McIlwain and G. A. Gagnon, Role of iron and aluminum coagulant metal residuals and lead release from drinking water pipe materials, *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.*, 2015, **50**, 414–423.
- 36 P. Westerhoff, A. Atkinson, J. Fortner, M. S. Wong, J. Zimmerman, J. Gardea-Torresdey, J. Ranville and P. Herckes, Low risk posed by engineered and incidental nanoparticles in drinking water, *Nat. Nanotechnol.*, 2018, **13**, 661.