



Single-particle inductively coupled plasma mass spectroscopy analysis of size and number concentration in mixtures of monometallic and bimetallic (core-shell) nanoparticles



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ABSTRACT

It is challenging to separate and measure the physical and chemical properties of monometallic and bimetallic engineered nanoparticles (NPs), especially when mixtures are similar in size and at low concentration. We report that single particle inductively coupled mass spectroscopy (SP-ICP-MS), alongside field flow fractionation (FFF), has allowed for the accurate measurement of size and particle number concentrations of mixed metallic nanoparticles (NPs) containing monometallic NPs of gold (Au) and silver (Ag) and a bimetallic core-shell structured NP (Au@Ag) of equivalent size. Two sets of these NPs were measured. The first contained only 60 nm particles, where the Au@Ag NP had a 30 nm core and 15 nm shell to make a total diameter of 60 nm. The second contained only 80 nm particles (Au@Ag NP core particle of 50 nm with a 15 nm shell). FFF separation was used here as a sizing technique rather than a separation technique. It was used to confirm that suspensions containing either individual or mixtures of the Au 60 nm, Ag 60 nm and AuAg 60 nm suspensions eluted together and were of the same size. Similarly, FFF was used to show that suspensions containing individual or mixtures of the equivalent 80 nm, eluted together and were of the same size. Although the 60 nm and 80 nm suspensions did not elute at the same time they were not run together. SP-ICP-MS is then used to identify the size and concentration of the particles within the suspension. Successful separation of the NPs was effected and the limits of the instrument were obtained.

1. Introduction

Nanoparticles (NP) are widely used in an array of applications [1,2] due to their unique physical-chemical properties. These properties can be tuned by changing the size, shape and composition of the NP [3,4]. It has always been a challenge to fully characterize suspensions of monometallic NPs, where a multimethod approach will yield the most reliable results [5,6]. This process becomes increasingly difficult for more complex bimetallic NPs, or mixtures thereof, used in some applications or for those that require a mixture of different NPs. There are a variety of techniques that have been used for the determination of particle diameter, composition and particle number concentration (part. mL⁻¹) of engineered NPs; including dynamic light scattering (DLS), field flow fractionation (FFF) [7,8], ultraviolet–visible spectroscopy (UV–vis) [9], multi-angle light scattering (MALS) [10] and transmission electron microscopy (TEM) [11]. More recently single-particle inductively coupled mass spectroscopy (SP-ICP-MS) [12,13] has been applied although it has not been fully developed in

this area. All these techniques have their own strengths and weaknesses as well as measuring size and/or composition in different ways. One of the most difficult properties to routinely measure in a NP suspension is particle number concentration [12,14]. This property can be measured Nanosight [15], although its accuracy is questionable [16,17]. In fact all current methods are arduous and inaccurate with limitations in measurement; for instance, bimetallic (core-shell) NPs cannot be measured. DLS can be used to quantify size for some systems, as can FFF, which must be used with a detector, such as UV–vis. Coupling FFF to an ICP-MS provides a lower detection limit compared with other methods [18]. However all these detection techniques are unable to discriminate mixtures of monometallic and/or bimetallic particles.

SP-ICP-MS is an excellent technique for the detection of metallic NPs providing data on size, size distribution, particle number concentration and other parameters [13] and giving such data at low concentrations, which are important for many applications such as environmental measurements [19,20]. Advances in the measurement within shorter dwell times have led to improvements in detection by

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SP-ICP-MS and have also enabled for the qualitative measurement of two elements within the same NP [21]. FFF separates NPs by their hydrodynamic diameters. However FFF is unable to distinguish between mixtures of NPs with the same diameter but different compositions. Here we use FFF to establish whether mixtures of particles are nominally of the same size. This enables us to conclude that if we measure two elements with SP-ICP-MS together in that fraction that are smaller than the FFF size, and the particle number concentrations of both metals are equal then they will be from a bimetallic particles. If the sizes of the 2 elements are comparable to the FFF size and the particle number concentrations are different then the suspension will contain a mixture of monometallic NPs. We are able to show that a sizing and particle number counting method using SP-ICP-MS can be used to measure more complex suspensions of NPs within these fractions, and can discriminate between mixtures of monometallic Au and Ag NPs and bimetallic Au@Ag (core shell) NPs, yielding particle sizes and particle numbers concentrations for each constituent. The limitations to such resolution are described.

2. Experimental

2.1. Nanoparticles (NPs)

NP suspensions for this study were purchased from Nanocomposix (San Diego, CA, USA) and the National Institute of Standards Technology (NIST, Gaithersburg MD, USA). Particles with several sizes and compositions were used including 60 nm Ag, 60 nm Au, 60 nm Au@Ag (core size 30 nm, shell thickness 15 nm), 80 nm Ag, 80 nm Au and 80 nm Au@Ag (core size 50 nm, shell thickness 15 nm), purchased from Nanocomposix, were used either as single particle suspensions or mixtures. In addition, Au 30 nm and Au 60 nm NPs from NIST were used as certified reference materials. NP concentrations and other parameters were provided by the supplier (See [supporting information S1 Table 1](#)) and were diluted to between 10,000 and 100,000 part. mL⁻¹ for SP-ICP-MS analysis, based on manufacturers data. For FFF analysis, NPs were used at concentrations of either the nominal concentrations of the stocks (See [supporting information S1 Table 1](#)) or diluted to 1,000,000 part. mL⁻¹, depending on detector and injection volumes used. It was found that the given particle concentrations and sizes were not always as the manufacturer stated and in some cases the particle numbers were higher or lower than what was expected.

2.2. Field flow fractionation (FFF)

An eclipse DualTech hollow fiber flow field-flow fractionation separation system (Wyatt technology, Santa Barbara, CA, USA) FFF was used in combination with a Agilent 1260 Infinity LC pump and auto sampler introduction system and an online UV detector (Agilent 1260 infinity, Agilent technologies, Santa Clara, Ca, USA).

A 10 kDa PES hollow fiber was used as a separation channel with a diameter of 0.8 mm and length of 17 cm (purchased from Wyatt). The detector flow was 0.5 mL min⁻¹, focus flow of 0.2 mL min⁻¹ for 10 min, and a ramped cross flow of 0.15–0 mL min⁻¹ over a 10 min period the particles eluted between 0.1 and 0.6 mL min⁻¹ cross flow) and injection volumes of 2–20 µL. The carrier solution was a sodium citrate solution at a concentration of 0.2 mM.

2.3. Inductively coupled plasma mass spectroscopy (ICP-MS)

A PerkinElmer NexION 350D ICP-MS was used with a Meinhard nebulizer, cyclonic (standard) spray chamber, a 2 mm ID injector and a glass torch. A RF power of 1600 W, auxiliary gas flow of 1.2 mL min⁻¹ and nebulizer gas flow of 1.12 mL min⁻¹ was used for measurements. The sample uptake was 0.49 mL min⁻¹. For single particle measurements (SP-ICP-MS) a dwell time of 50 µs was used with 30–

60 s second sampling times.

2.4. Standards

1, 2, 3 and 4 ppb ionic Au and Ag standards were used as ionic calibrations. NIST Au standards of 30 nm and 60 nm were used for Au particle calibrations at concentrations of 100,000 part. mL⁻¹. The NIST 60 nm Au particles were used to determine transport efficiency.

3. Results and discussion

NIST standards of nominally 30 and 60 nm certified reference materials were used to quantify the accuracy of the SP-ICP-MS system (Data in [Fig. S2](#)). The diameter and size distribution measured by TEM and quoted by NIST for the nominally 30 and 60 nm standards are slightly smaller than the nominal value: 27.6 (± 2.1) and 56.3 (± 1.5) nm respectively. Diameters of the same NPs measured in this study were 26.9 (± 0.3) nm and 57.3 (± 0.1), in excellent agreement with the stated values from NIST. The 60 nm CRM were measured over the course of the experiment, and the particle number concentrations for these suspensions were consistently within 1% of those originally measured for the TE. This along with the consistency of the size showed gave confidence in the stability of the machine throughout the experiment. Additionally, the particle number concentrations of the 30 nm certified reference materials were within 3% of the values stated by NIST, showing that the particle number counting and particle sizing by SP-ICP-MS was in good agreement with well characterized NPs.

Six test NP suspensions purchased from commercial sources (Ag, Au and Au@Ag; all at 60 and 80 nominal sizes) were analyzed by SP-ICP-MS to derive the particle size and concentration of each individual suspension for later reference. The size histograms of the NIST samples ([Fig. S2A and B](#)) very monodisperse samples, while the Nanocomposix NPs have a higher degree of polydispersity, sometimes showing bimodal distributions (examples shown in [Figs. S3, S4 and S5](#)). For instance, peaks at 60.9 (± 0.1) nm and 47.5 (± 0.1) nm for the nominally Au-60 nm NPs (S3-B), 73.5 (± 0.1) nm and 59.6 (± 0.4) nm for the Ag signal of the Au@Ag-80 nm particles (S4-C) and 78.1 (± 0.1) nm and 60.4 (± 0.1) nm for the nominally Au-80 nm NPs (S4-B) were all observed by SP-ICP-MS. In all cases, the larger peak is closest to the manufacturer supplied data ([Table S5-1](#)). It is also evident that the secondary peak contains a substantial number of the particles: 65.8%, 65.6% and 54.2% of the particles are related to the larger diameter NP peak in the above examples. To simplify data analysis, we fitted a Gaussian curve to the size distributions and used these fits for data interpretation (seen in [Figs. S3 and S4](#)).

[Fig. 1A and B](#) show the measured particle diameters ([Fig. 1A](#)) and measured particle number concentrations ([Fig. 1B](#)) for the individual NP suspensions. The total particle diameters for the separate Ag or Au NPs are 73.5 (3.9) nm, 76.2 (0.2) nm, 54.7 (0.2) and 55.5 (0.3) nm for the nominally Au-80 nm, Ag-80 nm, Au-60 nm and Ag-60 nm particles respectively. The actual stated values from the manufacturers are 81.2 (10.5), 78.9 (10.5), 60.6 (5.9) and 59.6 (5.8), respectively. In general, the data is different, but not significantly so, largely due to the poor precision in the manufacturer's data.

SP-ICP-MS measures total number of ions generated from individual NP and does not account for geometry of the NP. Thus for bimetallic (core-shell) particles, two sizes are measured that assume a solid Au and a solid Ag NP (Discussion in [supporting information S6](#)). Accounting for the geometry (calculations can be found in Merrifield and Lead 2016 [22]), the number of ions for the Au and Ag solid NPs translate into a larger core-shell structured NP of 57.8 (± 0.3) and 74.3 (± 0.5) for the Au@Ag-60 nm and Au@Ag-80 nm respectively. These calculated sizes can be directly compared to the manufactures (TEM) measurements of 60.8 (± 6.3) and 78.2 (± 8.8), showing good agreement. In this case we knew the composition of the NP to have an Au core and Ag shell, however calculations can be made for the total size if

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