



# Improving accuracy in single particle inductively coupled plasma mass spectrometry based on conventional standard solution calibration

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## ABSTRACT

Single particle inductively coupled plasma mass spectrometry (spICPMS) has emerged as a useful tool for the characterization of metal-containing nanoparticles (NPs). However, if no NP standard is available for the measurement of the transport efficiency and standard solutions are used to this end, erroneous NP mass (and thus size) may result. This is the case when the ICPMS instrument exhibits a significant settling time during which no data is collected between dwell times, such as in this work, where the dwell time was 5 ms and the settling time was around 27 ms. A correction must be applied to the transport efficiency when the latter is obtained by dividing the mass of solution measured at the exit of the spray chamber to that nebulized. Indeed, when the settling time is significant, the transport efficiency is effectively reduced, as the mass exiting the chamber would only be measured during the fraction of the total measurement time that is actually spent collecting data. The effect of this correction was assessed by measuring a standard material of Au NPs. The results show that omission of this correction leads to a significant overestimation of the size of Au NPs, whereas results in good agreement with the certificate are obtained upon its application.

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## 1. Introduction

Due a large surface-to-volume ratio, nanoparticles (NPs) often behave differently than bulk materials, being usually more reactive towards both desired and undesired reactions. Their reactivity and behavior depend on their chemical composition, shape, size, etc. [1–3]. Because NPs are widely used in medicine, cosmetics, food processing, catalysis, energy production and storage, as well as electronics and textiles [1], they are increasingly found in the environment [4]. Sensitive analytical techniques are required to characterize NPs under exposure conditions in order to examine their impact on the human health and the environment [5].

Single particle inductively coupled plasma mass spectrometry (spICPMS) has emerged as a useful analytical tool for characterizing inorganic NPs in aqueous suspensions [6]. Indeed, the excellent sensitivity and element specificity of spICPMS compared to other material characterization techniques may overcome the challenges of NPs measurements at extremely low concentrations and in the presence of complex matrices in environmental samples [7]. Furthermore, spICPMS allows the concurrent detection of both soluble and particulate species,

while enabling mass (and size for NPs of known shape, density and composition) distribution analysis for polydisperse NPs.

The theoretical aspects of spICPMS were discussed by Degueldre et al. for aqueous suspensions of colloids [8–11]. Individual NPs can be detected as singular spikes in the monitored analyte signal if data acquisition is done in the time-resolved analysis mode [12]. If the dwell time is short enough and the suspension has a sufficiently low particle number concentration, then each intensity spike represents a single particle event. The frequency of such spikes is proportional to their number concentration, while the spike intensities are proportional to the number of atoms in each detected NP, which is then related to the mass of each particle [6]. Ideally, an external calibration of analyte signal versus analyte mass must be performed using monodisperse NP standards. To this end, the transport efficiency and NP chemical composition must be known [13].

The two main methods used to measure transport efficiency, based on the particle frequency and the particle size [14], both require well characterized monodisperse NP standards, which are not available for many elements. In their absence, aqueous standard solutions must be used, under the assumption that the transport efficiency of solutions is the same as that of NP suspensions [14]. However, the signal arising from a solution directly depends on the sample introduction efficiency, which is not the case of the signal generated by a NP [14]. Indeed, only the number of NPs detected depends on the transport efficiency [14].

When only solutions are available, the transport efficiency is obtained as the mass of solution collected at the exit of the spray chamber divided by the mass of solution nebulized [15]. The indirect method based

Abbreviations: spICPMS, single particle inductively coupled plasma mass spectrometry; DDW, doubly deionized water; NP, nanoparticle.

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on waste collection is less accurate, as the mass introduced in the ICP is obtained by a difference between two large numbers and does not take into account any leftover in the spray chamber, fluctuations in drainage rate, etc. [14].

With sequential MS instruments, such as quadrupoles, the electronics may require a settling time after each measurement dwell time (even when monitoring a single isotope) for overhead and processing before proceeding to the next measurement [16]. During this time, signals from neither NPs nor dissolved analyte are measured [17]. It also limits multi-element detection of NPs and explains why the majority of spICPMS analyses involve the measurement of a single isotope. In contrast, time-of-flight ICPMS allows quasi-simultaneous multi-element detection during 33- $\mu$ s dwell times [18].

In this work, not only was the settling time significantly larger than the dwell time but some scanning irregularities were frequently observed, where the settling time varied during nebulization of a NP suspension, further jeopardizing the accuracy of NP mass measurement and thus the particle size. A correction factor that corresponds to the fraction of time actually spent measuring is proposed to correct the transport efficiency for the settling time. To the best of the authors' knowledge, such correction has never been described in the literature on spICPMS.

## 2. Experimental

### 2.1. Chemicals

A 50 mg L<sup>-1</sup> suspension of standard monodisperse Au NPs (coated and stabilized with 2 mM citrate) with a particle number concentration of  $2.3 \times 10^{10}$  particles mL<sup>-1</sup> from nanoComposix (San Diego, CA, USA, 99.99% Au purity) was used to validate the proposed approach. The Au NPs have a near spherical shape and a diameter of  $60.6 \pm 5.9$  nm. Aqueous standard solutions of Au of 1–10  $\mu$ g L<sup>-1</sup> were prepared in 2% HCl from 1000 mg L<sup>-1</sup> mono-element Au standard solution (SCP Science, Baie d'Urfé, Québec, Canada) and doubly deionized water (DDW; 18 M $\Omega$  cm in resistivity, Arium Pro UV|DI water purification system, Sartorius Stedim Biotech, Göttingen, Germany).

### 2.2. Sample preparation

The standard Au NPs suspension was diluted to 50, 100, 150 and 500 ng L<sup>-1</sup> with DDW in polypropylene vials on the day of the analysis and placed in an ultrasonic bath (Branson 5800, MI, USA; 40 kHz frequency) for 10 min to ensure that the NPs were fully dispersed immediately prior to analysis. A few small ice cubes were added to the ultrasonic bath to prevent a rise in temperature that might facilitate the dissolution of NPs, as the Au NPs are only stable in the 4–25 °C range according to the certificate provided by the manufacturer.

### 2.3. Instrumentation

A Varian 820MS (Varian Inc., Australia) quadrupole-based ICPMS instrument, with Ni sampler and skimmer cones having respectively 0.9- and 0.4-mm diameter orifices, was used. The collision-reaction interface was not used to maximize sensitivity. The sample introduction system consisted of a MicroMist concentric nebulizer (Glass Expansion, Victoria, Australia) fitted into a Peltier-cooled Scott double-pass spray chamber (SCP Science, Quebec, Canada) maintained at 0 °C. Data acquisition was carried out in the time-resolved analysis mode during 1 min. Optimization of the instrument's operating conditions, including torch alignment, was performed daily for a compromise between optimal sensitivity and minimum oxide and double-charged ions levels using a solution containing 5  $\mu$ g L<sup>-1</sup> of Be, Mg, Co, In, Ce, Pb and Ba in 2% (v/v) HNO<sub>3</sub> (prepared by dilution of a 10 mg L<sup>-1</sup> Varian tuning solution). The ensuing operating conditions are summarized in Table 1. With the instrument's expert software (version 1.65), the settling time was

**Table 1**  
Instrumental operating conditions for spICPMS.

Parameter	Setting
Ar plasma gas flow rate (L min <sup>-1</sup> )	18
Ar auxiliary gas flow rate (L min <sup>-1</sup> )	1.80
Ar sheath gas flow rate (L min <sup>-1</sup> )	0.06
Nebulizer gas flow rate (mL min <sup>-1</sup> )	1.01
Sample uptake rate (mL min <sup>-1</sup> )	0.30
Sampling position (mm)	5.5
RF power (kW)	1.40
Dwell time (ms)	5
Monitored signal	<sup>197</sup> Au <sup>+</sup>

supposedly fixed at 27 ms, which was much longer than the 3-ms dwell time used to measure NPs.

### 2.4. Measurement of sample uptake rate

The sample uptake rate was checked daily in triplicate by measuring the change in weight of a vial containing DDW following 2 min of aspiration. Similarly, a mass-based direct method was used to determine the transport efficiency. The tip of a 1-mL micropipette tip was cut so as to match the inner diameter of the torch injector and was then loaded with a known mass of dry silica gel (placed between two glass wool plugs) before being attached to the aerosol outlet of the spray chamber to trap exiting aerosol [19]. The ratio of the mass of 1  $\mu$ g L<sup>-1</sup> Au solution absorbed over that aspirated, measured in triplicate, yielded the transport efficiency.

### 2.5. Correction to the transport efficiency

The transport efficiency  $\eta_n$  measured above inherently assumes that everything exiting the spray chamber is being measured. However, with a significant settling time, only a fraction of the solution exiting the spray chamber during the actual measurement time would be monitored. A correction is thus required, which is described as follows:

$$\eta'_n = \eta_n \times \frac{t_{dt} \times N_{dp}}{t_{at}} \quad (1)$$

where  $\eta'_n$  is the corrected transport efficiency,  $N_{dp}$  is the number of data points collected for dwell time  $t_{dt}$  during the total acquisition time  $t_{at}$ . This correction assumes that signal differences between the standard solutions and the dilute NPs suspensions are mainly dependent on the sample introduction system. This assumption is supported by the wide linear dynamic range of ICPMS in a given matrix, which indicates that the efficiencies of atomization and ionization in the plasma, and of ion extraction, transmission and detection in the mass spectrometer are essentially independent of the quantity of analyte over several orders of magnitude, as long as the matrix remains the same.

### 2.6. Data processing

Because the Varian 820MS instrument does not include spICPMS signal processing software, all data processing was done manually using a Microsoft Excel spreadsheet. The raw counts s<sup>-1</sup> data collected were converted to counts event<sup>-1</sup> by multiplying each signal by the dwell time. Particle events were discriminated from the background based on three times the standard deviation ( $3\sigma$ ) criterion proposed by Pace et al. [20]. The average intensity ( $\mu$ ) and  $\sigma$  were calculated for the whole data set, with any data greater than  $\mu + 3\sigma$  being collected as NP events and removed from the data set. This process was repeated by calculating a new  $\mu + 3\sigma$  for the remaining data and collecting data points until no more points could be distinguished as NP events. The remaining data set constituted the background signal corresponding to dissolved Au and unresolved particles.

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