Challenge

Determining AuNPs in water by spICP-MS per ISO/TS 19590:2016 involves overcoming low detection limits, interferences, aggregation, and ensuring accurate sample preparation.

Solution

PlasmaQuant MS Elite offers precise nanoparticle analysis, detailing elemental composition, concentration, size, and distribution, while overcoming matrix interferences.

Intended audience

Academia, research, pharma, environment, electronics, biotech, and regulation entities.

Determination of Gold Nanoparticles in Drinking Water by Single Particle ICP-MS (spICP-MS) according with ISO/TS 19590:2016

Introduction

ICP-MS is a highly versatile elemental technique, known for its rapid multielement analysis and low detection limits across a wide range of samples, primarily in liquid form. However, when samples contain nanoparticles (NPs), their unique characteristics challenges traditional analysis methods. Nebulizing a dilute suspension of NPs into the plasma generates transient signals lasting less than 0.5 ms, necessitating time-based recording for accurate measurement (Figure 1). These time scans reveal spikes representing individual NPs against a steady baseline, enabling the quantification and sizing of nanomaterials. While still emerging, single-particle ICP-MS (spICP-MS) has found applications in environmental research, including the detection of environmentally relevant concentrations of NPs, sizing and distribution studies, and investigations into NP stability and migration[1,2] The aim of this work is to provide insight into the AuNPs characterization in mineral water samples and their detection using the PlasmaQuant MS Elite according with ISO/TS 19590:2016[3].
Additionally, raw time scans were processed to obtain histograms, revealing distinct distributions corresponding to background signals and NP signals (Figure 2). The results revealed that the PlasmaQuant MS Elite is capable to achieve detection of particles as small as 10 nm.

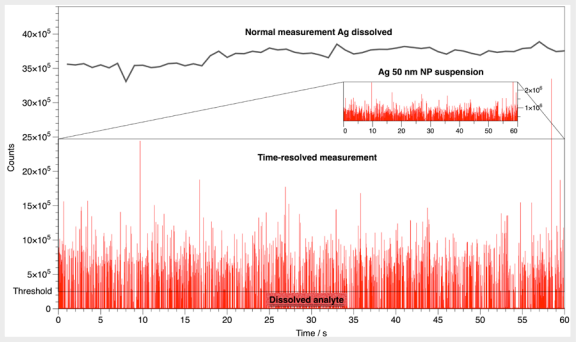

Figure 1: Steady state signal of a "normal" ICP-MS measurement of Au solution (above) versus time-resolved measurement (below) of an Au 50 nm NP suspension

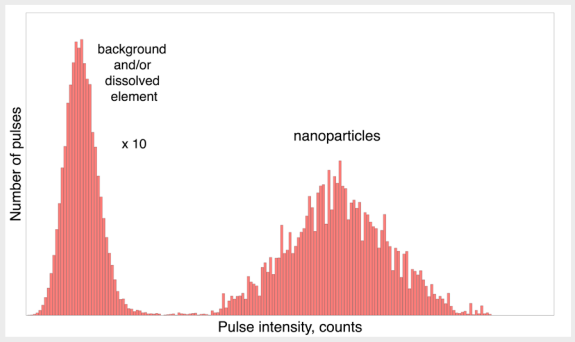

Figure 2: Pulse intensity frequency histogram of time scan data from Figure 1

Materials and Methods

Chemicals, reference materials and reagents

- Deionized water (>18.2 MΩ/cm, Millipore MiliQ)
- Nitric acid sub-boiled 69% (Analytik Jena GmbH+Co. KG)
- Rinsing solution of 3% (v/v) HNO_3

AuNps standards of three different particle sizes (10, 20, and 50 nm) from nanoComposix (San Diego, CA, USA) were considered. The 50 nm AuNP reference material was employed for determining transport efficiency and calibration, while 10 nm and 20 nm particles were utilized for quality control purposes and to assess the size determination capabilities of the PlasmaQuant Elite instrument. Table 2 provides details on the sizes and characteristics of the nanoparticles used in this study. For size determination, a single-element ionic Au standard (CertiPUR® 1000 mg/L in 2-3% HNO_3) was employed.

Instrumentation

Inductively coupled plasma mass spectrometry

The determination of AuNPs in drinking water samples was conducted using a PlasmaQuant MS Elite ICP-MS. Instrumental set up involved the use of nickel sampler and skimmer cones, along with a Peltier-cooled Scott-type spray chamber and MicroMistTM nebulizer. The PlasmaQuant MS Elite was tuned to best possible sensitivity for Au by optimizing nebulizer gas flow, RF power, and ion lens voltages to maximize the detected intensity of 1 µg/L of Au in 1% (v/v) HNO_3. Instrumental settings and method parameters are detailed in Table 1. Sample introduction was performed manually via self-aspiration.

Table 1: Optimized ICP-MS operating parameters

Parameter	Specification
Plasma gas flow	9.0 L/min
Auxiliary gas flow	1.35 L/min
Sheath gas flow	0.00 L/min
Nebulizer gas flow	1.05 L/min
Plasma RF power	1.40 kW
Nebulizer type	MicroMist™ 0.4 mL/min (quartz concentric)
Cones	Nickel
Torch	Fassel torch with 2.4 mm injector
Spray chamber type	Glass Scott with Peltier chiller (3 °C)
Rump rate	Self-aspiration
Dwell time	3 ms
Scan per replicate	1 (peak hopping, 1 pt/peak)
No. of replicates	1
Acquisition time	60 s
Isotope (amu)	197

Table 2: Au Nanoparticles standards specification

Material	Lot Number	Diameter (nm)	Mass Concentration (mg/mL)	Particle Concentration (particles/mL)
10 nm Gold Nanospheres, Citrate, NanoXact™	ECP1624	11.6 ± 1	0.053	3.3E+12
20 nm Gold Nanospheres, Citrate, NanoXact™	JRC0053	18.9 ± 1.5	0.053	7.8E+11
50 nm Gold Nanospheres, Citrate, NanoXact™	JRC0010	52 ± 5	0.053	3.7E+10

Standards, samples, and sequence

A stock standard solution of nominal 50 nm nanoparticles (53 µg/L) was prepared by diluting the appropriate volume of the stock solution in purified water in a 50 mL polypropylene (PP) vial. The solution was thoroughly mixed and stored at room temperature. Prior to further dilution, the stock standard was sonicated for 10 minutes. A daily working standard solution of nominal 50 nm Au nanoparticles (53 ng/L) was then prepared by diluting the appropriate volume of the stock standard with purified water.

Ionic Au working standards with concentrations ranging from 0.2 to 5 µg/L were prepared in purified water from the stock Au 1000 mg/L single standard in 50 mL PP vials.

Three commercially available Portuguese drinking waters (L, P and M) were chosen as mineral water samples for this study. Due to the absence of information on nanoparticle concentrations and the expectation of no nanoparticles in these samples, no initial dilution was performed. Additionally, no further dilution was employed based on the observed number of pulses during the analysis of the non-diluted samples. Two samples were spiked (L and P) with 10 and 20 nm AuNPs, respectively, and the dilutions were adjusted to maintain a particle number concentration in the range from 2.0E+6 to 2.0E+8 particles/L. The sample M was also spiked with a mixture of two sizes (10 and 50 nm) of AuNPs.

Before dilution of the standards/samples, and again prior to analysis, all solutions underwent 10 minutes of ultrasonication to ensure full homogenization in accordance with ISO/TS 19590:2016.

A sequence analysis was conducted to assess instrument performance and ensure quality control. This included the analysis of blanks, ionic calibration standards, and nanoparticle standards at the beginning, after every 10 samples, and at the end of the sequence. Drinking water samples were analyzed both with and without spikes. The calibration curve for the ionic standards was established only at the beginning of the sequence, as fewer than 10 samples were analyzed. Following each sample analysis, purified water blanks were measured to detect any memory effects.

Results and Discussion

Transport efficiency

Understanding the transport efficiency term of the sample/analyte introduced into the plasma during analysis is crucial for an accurate calculation of results. As per ISO/TS 19590:2016, this efficiency is determined using a known nanoparticle standard, such as the 50 nm Au reference standard employed in this study. To enhance precision, transport efficiency was experimentally calculated based on measured particle frequency, as follows:

$$\eta_n = \frac{6.10^4 q_p}{C_p V} x100\%$$

where
η_n is the transport efficiency (%);
q_p is the particle flux in the plasma (particles/s);
C_p is the particle number concentration (particles/L);
V is the sample flow (mL/min);
6.10^4 is the conversion factor from min to s and from mL to L.

After self-aspiration of 50 nm Au NP working standard with a nebulizer flow of 1.05 L/min, we observed an average flow rate of 0.3107 mL/min (n=5). This yielded a transport efficiency of 12.01%, calculated using the provided formula, falling within the typical expected range of 5% to 25%.

In terms of data processing, the ASpectNP software can also automatically calculates the transport efficiency and provides particle concentration (in #/L), particle size (in nm), mass concentration (in ng/L), and ionic concentration (in ng/L) for all measured samples (Figure 3).

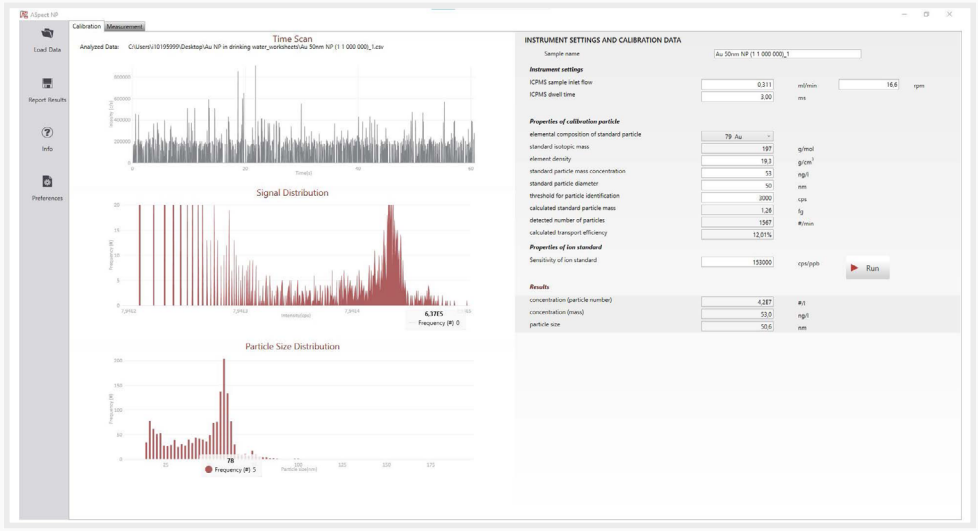

Figure 3: Transport efficiency calculation by the Aspect NP software based on measured particles frequency of the working 50nm AuNP standard

Particle concentration detection limit

The number-based detection limit (LOD_{NP}) was determined from the number of particles in the blank control samples and calculated using the formula specified in ISO/TS 19590:2016. Several control blanks (n=14) were considered throughout the two hours sequence to establish the Limit of Detection for Nanoparticles (LOD_{NP}). The LOD_{NP} obtained was 5.1E+3 particles/L accordingly to the following formula:

$$LOD_{NP} = \frac{(\bar{N}_p + 3 \times SD_p) \times 1000}{\eta_n \times \mathcal{V} \times t_a}$$

Where

LOD_{NP} is the number-based concentration detection limits (particles/L);

N_p is the average number of particles pulses observed in the blank control samples;

SD_p is the standard deviation of the number of particles pulses observed in the blank control samples;

η_n is the transport efficiency;

V is the sample flow (mL/min);

t_a is the duration of the time scan (min).

Particle size detection limit

According to ISO/TS 19590:2016, the size detection limit (LOD_S) is determined by the signal intensity of a pulse that can just be distinguished from the background. In this study, the LOD_S was determined graphically from the frequency distribution using the ASpectNP software (Figure 4). The estimated LOD_S was 10 nm.

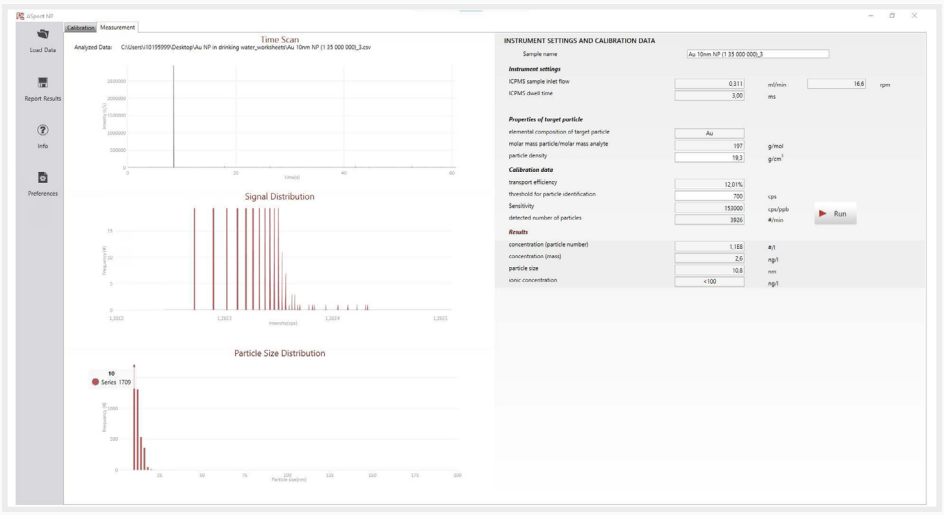

Figure 4: Particle size detection limit graphically determined using the 10nm Au NP standard

Particle concentration, size, and mass concentration

Table 3 presents results for three commercial Portuguese drinking water samples (L, P, and M) where nanoparticles were detected. The detected nanoparticles ranged from 4.9E+5 to 3.0E+7 particles/L across all samples. Sample M showed a significantly higher particle count and larger size. Spike recovery tests were conducted on two samples spiked with 10 nm and 20 nm nanoparticles, yielding accurate recovery rates between 94% and 115% for both particle concentration and size. Additionally, non-spiked drinking water contained Au nanoparticles sized between 11.8 and 15.5 nm. However, their detection approached the lower limit of detection (10 nm), with signal distribution near the background measured by ICP-MS.

Table 3: Results for Au NPs obtained in three Portuguese mineral waters (n=3) and recovery rates of spiked samples

Sample	Particle Concentration (particles/L)	Mass Concentration (ng/L)	Particle Size (nm) (mean ± 3SD)
L	2.1E+6	<LOD	11.8 ± 0.6
L spiked with 10nm	3.1E+15	58	12.7 ± 0.3
Rec. (%)	94	-	109
P	4.9E+5	<LOD	12.1 ± 0.3
P spiked with 20nm	8.0E+14	48	21.7 ± 0.1
REC. (%)	102	-	115
M	3.0E+7	<LOD	15.5 ± 2.7

Quality control

The suitability of the ICP-MS method was evaluated using three different AuNP standards with sizes of 10, 20, and 50 nm. Table 4 demonstrates that the measured sizes of each NP standard closely matched the reference values. Precision within the range of 0.5% to 11.4% indicated the excellent repeatability of the PlasmaQuant MS Elite spICP-MS method, even for low particle size of 10 nm, while accuracy within the range of 87-112% was observed for all three certified parameters.

Table 4: Results obtained for nine replicate analyses of 10, 20 and 50 nm Au NP standards over two hours sequence

Parameter	Certified Values	Experimental Values (mean +3SD)	%RSD	%REC
10 nm Gold Nanospheres, Citrate, NanoXact™				
Diameter (nm)	11.6 ± 1	10.9 ± 0.1	0.5	94
Mass concentration (mg/mL)	0.053	0.053 ± 0.017	10.5	101
Particle concentration (particles/mL)	3.3E+12	3.3E+12	11.4	101
20 nm Gold Nanospheres, Citrate, NanoXact™				
Diameter (nm)	18.9 ± 1.5	21.2 ± 1.2	1.9	112
Mass concentration (mg/mL)	0.053	0.046 ± 0.010	7.4	87
Particle concentration (particles/mL)	7.8E+11	8.3E+11	10.4	106
50 nm Gold Nanospheres, Citrate, NanoXact™				
Diameter (nm)	52 ± 5	55 ± 3	2.0	106
Mass concentration (mg/mL)	0.053	0.057 ± 0.007	4.0	108
Particleconcentration (particles/mL)	3.7E+10	3.8E+10	5.6	102

The absence of NPs outside the expected size range for each standard suggests that the final diluted samples provided a homogeneous distribution of NPs rather than particle agglomeration. Additionally, the chosen acquisition parameters ensured that no more than one NP event occurred during each Total Run Acquisition (TRA) integration period. Consequently, the dwell time selected in the method was appropriate for the discrete analysis of each individual NP introduced into the system.

The developed method was applied to a mixture of different-sized AuNPs, including 10 nm and 50 nm, to demonstrate its capability to distinguish between NPs of varying sizes (Figure 5). The results clearly indicate two distinct populations of NP sizes with no overlap between them. Therefore, the method exhibits sufficient resolution to detect and discriminate between mixtures of different sizes within a single sample.

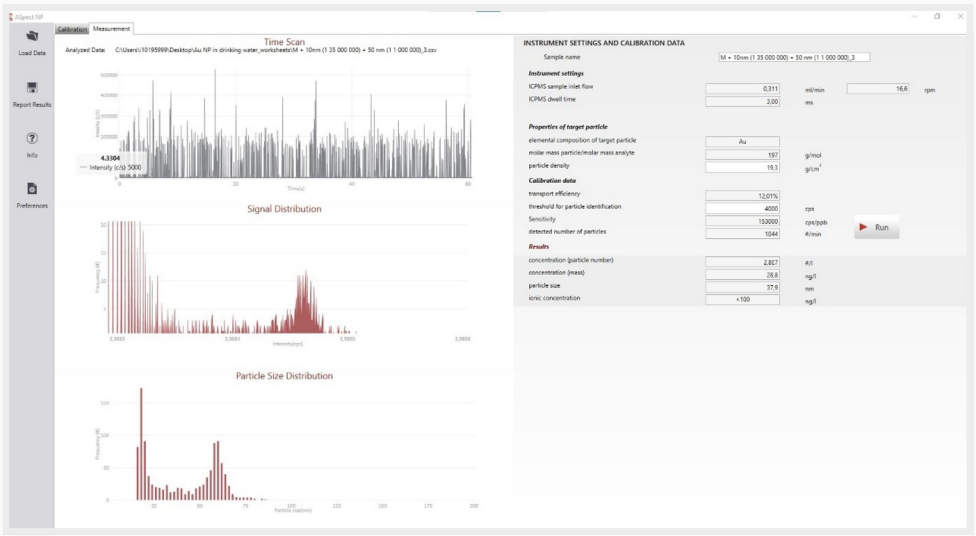

Figure 5: Particle size distribution for a mixture of 10 nm and 50 nm Au NPs standards spiked into sample M using ASpectNP software

Summary

In summary, the PlasmaQuant MS Elite has proven to be highly effective in measuring Au nanoparticles (NPs) by spICP-MS. Its advanced detector, improved sensitivity, and low instrumental background distinguish it from other less sensitive ICP-MS instruments. The study confirms the PlasmaQuant MS' capability to precisely characterize individual AuNPs ranging from 10 to 100 nm. Additionally, for research purposes, it might be possible to enhance data acquisition by reducing integration time to 50 µs.
This research demonstrates the PlasmaQuant MS Elite's ability to accurately detect AuNPs in drinking water samples, even amidst real-world matrix interferences, within the 10 to 50 nm size range. Future challenges in spICP-MS analysis involve extending the method to complex samples which may introduce spectral interferences on elements of interest like titanium, iron, or zinc. Furthermore, coupling ICP-MS with separation techniques like Field Flow Fractionation (FFF) or Hydrodynamic Chromatography (HDC) may provide additional precision in particle characterization.

Figure 6: PlasmaQuant MS Elite

Recommended device configuration

Table 5: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant MS Elite - ultimate sensitivity for targeted research applications	818-08021-2	The PlasmaQuant MS Elite excels in ultra-trace and isotope analysis

References

[1] Laborda, F.; Bolea, E and Jiménez-Lamana, J.; SINGLE PARTICLE INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY: A POWERFUL TOOL FOR NANOANALYSIS. Anal. Chem. 2014, 86, pages 2270-2278

[2]. Pace, H.E., Rogers, N.J., Jarolimek, C., Coleman, V.A., Higgins, C.P. and Ranville, J.F.; DETERMINING TRANSPORT EFFICIENCY FOR THE PURPOSE OF COUNTING AND SIZING NANOPARTICLES VIA SINGLE PARTICLES INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. Anal. Chem., 2011, 83, pages 9361-9369

[3]. ISO/TS 19590:2016: NANOTECHNOLOGIES – SIZE DISTRIBUTION AND CONCENTRATION OF INORGANIC NANOPARTICLES IN AQUEOUS MEDIA VIA SINGLE PARTICLE INDUCTIVELY COUPLED PLASMA SPECTROMETRY, published by International Organization for Standardization (ISO), 2016, Geneva, Switzerland

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