## Supporting Information:

## The accurate determination of number concentration of inorganic nanoparticles using spICP-MS with the dynamic mass flow approach

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Figure S1. Transmission electron microscope (TEM) image of bipyramidal  $TiO_2$  nanoparticle suspensions. Scale bar: 200 nm. A Morgagni 268 TEM (FEI, Hillsboro, OR) was used.

Instrumental parameters	
RF power	1550 W
Argon gas flow rate	
Plasma	15 L min <sup>-1</sup>
Auxiliary	0.90 L min <sup>-1</sup>
Nebuliser	1.05 - 1.15 L min <sup>-1</sup>
Nebuliser type	MicroMist DC Nebuliser 0.4 mL min <sup>-1</sup>
Spray chamber type	Scott
Spray chamber temperature	2 °C
Sample uptake rate	0.35 g min <sup>-1</sup>
Ti cell gas conditions	
Oxygen flow rate	20%
Hydrogen flow rate	4.5 mL min <sup>-1</sup>
Axial acceleration	1.5 V (only for $TiO_2 NP$ )
Data acquisition parameters	
Acquisition mode	SQ (Au), MS/MS (TiO <sub>2</sub> )
Dwell time	100 µs
Readings per replicate	600000
Settling time	-
Total acquisition time	60 s
Isotopes monitored	<sup>197</sup> Au, <sup>48</sup> Ti <sup>16</sup> O [MS/MS (Q1: 48, Q2:64)]

Table S1. Typical operating parameters for measurements of Au and  $TiO_2$  NP by spICP-MS.



**Figure S2.** Theoretical (broken line) and experimental (solid line) particle number concentration calibration at  $t_{dwell}$ =100 µs obtained for NIST RM 8012 30 nm Au NP. Total acquisition time: 60 s.



Figure S3. Signal distribution of 30 nm Au NP with dwell time of (a) 100 µs and (b) 3 ms.



Figure S4. Variation of the detection threshold using  $3-10\sigma$  critera, as applied for 30 nm Au NP.



**Figure S5.** Signal distribution histograms of  $TiO_2$  NP (a) without axial acceleration and dwell time of 100 µs and with axial acceleration and dwell time of 3 ms (b) and of 100 µs (c).

		Uncertainty contribution (%)				
Sample	Method of TE calculation	Number of particles detected in time scan	Dilution factor	Transport efficiency	Sample mass flow	Batch-to- batch variability
Au 30 nm		64.8	0.7	12.3	< 0.1	22.2
Au 60 nm (8013 NIST)	Dynamic mass flow	65.6	0.7	11.4	0.1	22.2
Au 100 nm		64.9	0.3	7.4	< 0.1	27.4
Au 30 nm	Fraguancy	26.6	0.3	63.9	<0.1	9.2
Au 100 nm	requency	28.6	0.2	61.3	<0.1	9.9

**Table S2.** Uncertainty budget for the determination of the number concentration of Au NP by DMF and particle frequency methods.

**Table S3.** Further breakdown of uncertainty contribution for the number of particles detected and the TE, using 30 nm Au as an example.

NP detected in time scan (N <sub>NP</sub> )	Contribution (%)	
Variability in particle counts	99.89	
Variability in background counts	0.11	
Detection threshold	<0.1	
Transport efficiency (TE)	Contribution (%)	
Variability of TE within day:	98.94:	
• Slope 1 (mass flow of sample reaching the plasma):	98.28	
• Slope 2 (mass flow of sample uptake)	1.72	
Time reading	1.06	
Weighing	<0.1	