Supporting information for: Particle generated spectral interferences in single particle ICP-MS: A roadblock to accurate nanometrology

Aaron J Goodman¹, Sandra Kanapilly², Anthony J Bednar³, and James F Ranville¹

Affiliations:

- 1. Department of Chemistry, Colorado School of Mines, United States of America
- 2. Perkin Elmer, United States of America
- 3. US Army Corps of Engineers, Engineer Research and Development Center, United States of America

Table of contents:

Equation S1: Mass flux calibration for spICP-MS data – 2 Equation S2: Particle mass calculation for spICP-MS data – 2 Equation S3: Particle sizing for spICP-MS data - 2 Table S1: Particle numbers and sizes for neat suspensions– 2 Figure S1: Raw data for Y-NP suspension – 3 Table S2: Interference ratios for solution and single particle mode - 6 Table S3: Particle numbers and sizes for mixed suspensions of Y and Pd NPs – 3 Figure S2: Instrument sensitivities for Pd in standard and DRC mode - 4 Figure S3: Pd-NP peak widths – 4 Figure S4: Raw data for Nd-NP suspension – 5 Table S4: Particle numbers in blank samples – 5

Table S5: Interference magnitude with variation of nebulizer gas flow rate

$$m_{mf} = \frac{m_{diss}}{q * t_{dt} * \eta}$$

Equation S1: The slope of the dissolved calibration curve (m_{diss}) is converted to the mass flux slope (m_{mf}) by correcting for flow rate (q), dwell time (t_{dt}), and transport efficiency (η , fraction of solution that enters the plasma).

$$M_p = \frac{\left(I_P - I_B\right)}{m_{mf}}$$

Equation S2: Peaks corresponding to particle events are individually integrated, and the peak area in counts is converted to a mass of the element of interest. M_p is the mass of the particle, I_p is the signal intensity of the particle in counts, I_B is the background intensity, and m_{mf} is the slope of the mass flux calibration curve (see Equation S1).

$$d = \sqrt[3]{\left[\frac{6*M_p}{\pi*\rho}\right]}$$

Equation S3: Particles are sized by assuming a spherical shape, and pure composition. ρ is the density, and d is the spherical diameter.

Particle Suspension	Mean Particle Diameter (nm)	Particle Number	Interference	Interference Diameter (nm)	Interference Particle Number
Nd	99	7100	⁷⁵ As (¹⁵⁰ Nd ²⁺)	60	30
			⁷² Ge (¹⁴⁴ Nd ²⁺)	70	900
Y	91	13,100	¹⁰⁵ Pd	40	2500
			¹⁰⁵ Pd (DRC)	50	2
Pd	82	6100	N/A		
Pd (DRC)	97	2200			

Table S1: Particle numbers and sizes for suspensions of each nano powder analyzed by spICP-MS (60s analysis). Size and number of the false NP reading are also provided.



Figure S1: Time resolved spICP-MS data for a suspension of Y nanoparticles; monitored isotopes are ⁸⁹Y (a), ¹⁰⁶Pd (b), ¹⁰⁵Pd with no cell gas (c), and ¹⁰⁵Pd with NH_3 used in the dynamic reaction cell (d). Scales are different on the x axis to preserve the resolution of the figures; space is too limited to plot the full 60s analysis for (a) and (c).

Analyte	Interference	spICP-MS Interference (%)	Solution ICP-MS Interference (%	
⁷² Ge	¹⁴⁴ Nd ²⁺	1.03 ± 0.08	1.12 ± 0.02	
⁷³ Ge	¹⁴⁶ Nd ²⁺	0.93 ± 0.35	0.78 ± 0.04	
¹⁵⁸ Gd	¹⁴² NdO ⁺	2.04 ± 0.08	1.61 ± 0.01	
¹⁶⁰ Gd	¹⁴⁴ NdO ⁺	2.17 ± 0.24	1.45 ± 0.03	
¹⁰⁵ Pd	⁸⁹ YO ⁺	1.12 ± 0.21	0.68 ± 0.02	
¹⁰⁶ Pd	⁸⁹ YOH⁺	0.34 ± 0.03	0.07 ± 0.01	

Table S2: Magnitude of interferences (%) for the isotopes monitored in single particle mode and solution mode. Percentages were calculated by dividing the counts recorded on the monitored isotope by the counts recorded on the interfering isotope. In solution mode, counts per second were used, and for sp mode, the sum of counts for a 60s analysis was used.

Mixture	Pd Dilution	Y Dilution	Pd Particle Number (DRC)	Pd Particle Number (Standard)	Y Particle Number
А	1,000	100,000	2100 ± 70	5890 ± 190	70 ± 10
В	1,000	10,000	2070 ± 30	5700 ± 60	430 ± 10
С	1,000	1,000	2100 ± 70	5880 ± 120	4100 ± 240
D	1,000	200	2130 ± 50	7440 ± 210	14,500 ± 1600

Table S3: Particle numbers for mixtures of Y- and Pd-NPs. Dilution factor refers to the dilution performed from the stock suspension, prepared by suspending a mg quantity of nano powder in 50mL 0.1% SDS. DRC refers to the dynamic reaction cell with NH_3 used. Standard refers to standard mode of operation, without cell gas.



Figure S2: Calibration curves for dissolved Pd with and without the Dynamic Reaction Cell (DRC), showing a 27% loss of sensitivity between the two modes of operation.



Figure S3: A 10ms example of time resolved data for the Pd NP suspension analyzed in standard mode (a) and DRC mode (b). In DRC mode the ion cloud from a single particle lasts nearly 10ms, while in standard mode, particles typically last <1ms.



Figure S4: Time resolved spICP-MS data for a suspension of Nd nanoparticles. Isotopes monitored were ¹⁴⁴Nd (a), ¹⁵⁰Nd (b), ⁷²Ge (c), ⁷⁰Ge (d), ¹⁶⁰Gd (e), ¹⁵⁵Gd (f), and ⁷⁵As (g). (h) presents ⁷⁵As data for a blank sample; As is monoisotopic, and does not have a clean isotope to compare.

Isotope Monitored	Peaks detected
¹⁴⁴ Nd	10
¹⁵⁰ Nd	0
⁸⁹ γ	0
⁷⁰ Ge	0
⁷² Ge	0
¹⁵⁵ Gd	0
¹⁶⁰ Gd	0
¹⁰⁵ Pd	1
¹⁰⁵ Pd (DRC)	1
¹⁰⁶ Pd	0
⁷⁵ As	1

Table S4: Number of peaks detected in blank samples (0.1% SDS). All blank samples contained peaks with low counts (peak area <5) which were eliminated after application of the particle detection threshold (set at 2 counts per dwell time).

Nebulizer flow rate (L min ⁻¹)	¹⁴⁴ Nd (Counts)	¹⁶⁰ Gd (Counts)	⁷² Ge (Counts)	% Oxide interference	% Doubly charged interference
0.7	3784548 ± 59216	66846 ± 1819	110152 ± 894	1.77 ± 0.03	2.91 ± 0.06
0.74	6670421 ± 142276	116422 ± 4599	141452 ± 1894	1.75 ± 0.08	2.12 ± 0.05
0.78	9537818 ± 234449	190934 ± 5675	217867 ± 403	2.00 ± 0.09	2.29 ± 0.06
0.82	13597323 ± 217644	353048 ± 4732	262706 ± 2009	2.60 ± 0.02	1.93 ± 0.04
0.86	15724330 ± 885156	831288 ± 60718	292280 ± 602	5.31 ± 0.54	1.93 ± 0.06

Table S5: Count rates and interference magnitudes measured for triplicate suspensions of Nd_2O_3 nanoparticles. Counts refers to the summed counts over the 60s analysis.