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Supplemental Information for Particle Signal Considerations for Isotope Ratio Analysis with Single Particle Multi-Collector Inductively Coupled Plasma Mass Spectrometry

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Figure S1 Time traces showing microextraction of 100 nm (diameter) Au particles using a cyclonic spray chamber (top) and CytoSpray chamber (bottom) with a lower flow rate. Using the CytoSpray, the particles are distributed more evenly through the sample run, rather than most particles being detected within the first ~3 seconds.

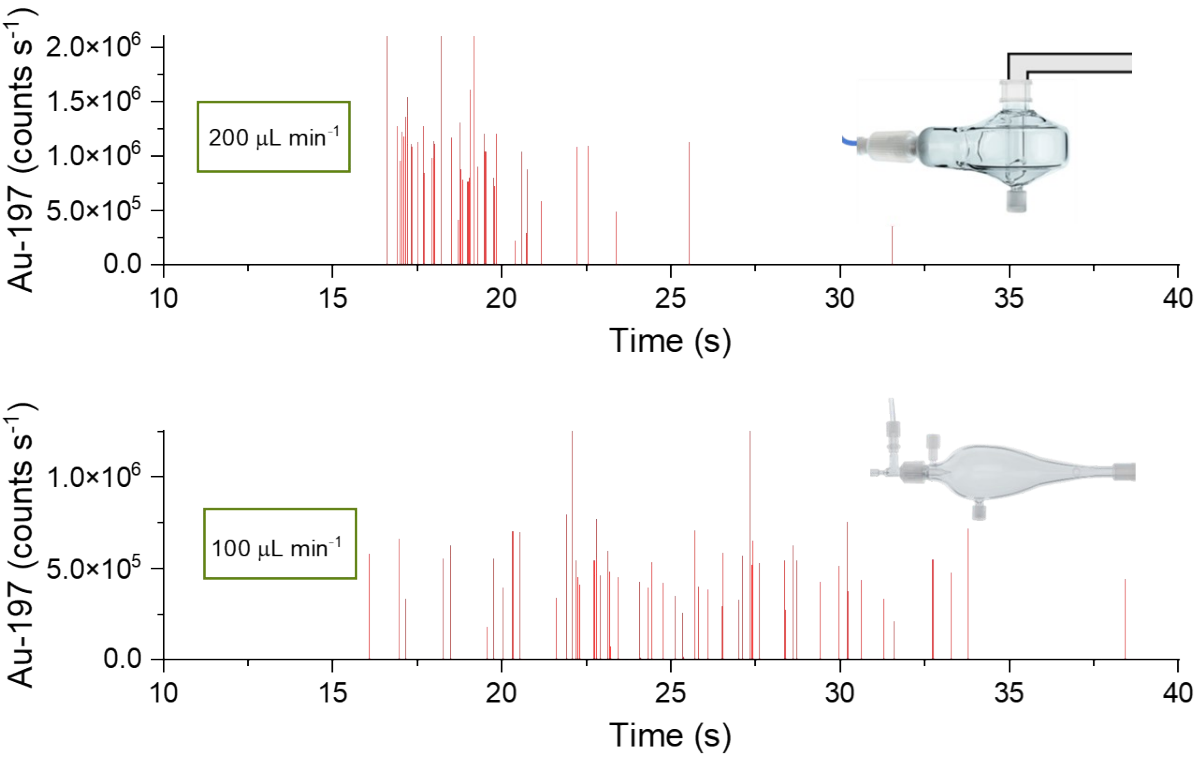
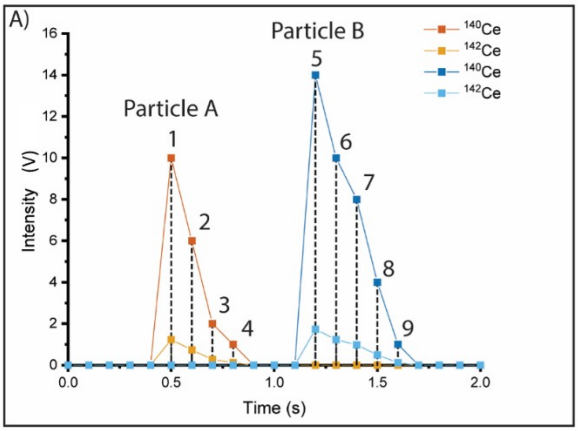
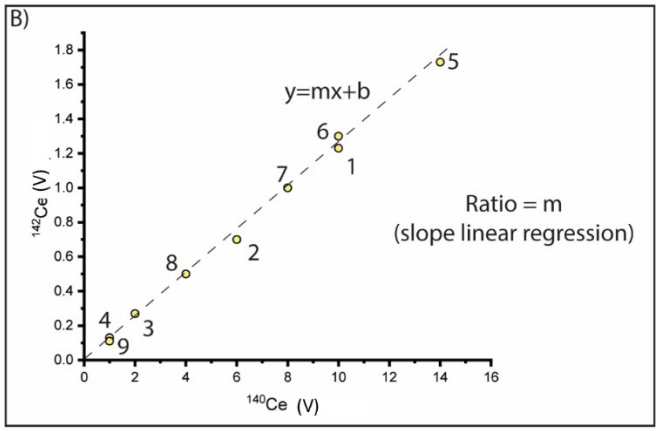
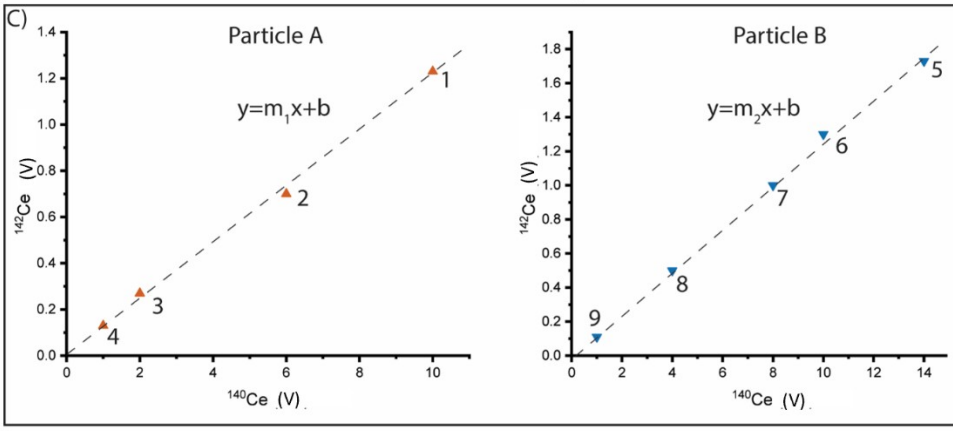


Figure S2 A graphical depiction of how the particle data was treated to determine isotopic ratios of ^{142}Ce to ^{140}Ce. A) The time trace of two particles detected (Particle A and Particle B) are shown, with each data point labeled 1-9. The first method used to determine particle isotope ratios was linear regression (LRS_{global}), as shown in B), where all data points are plotted together, and linear regression is performed. The slope obtained is the reported isotope ratio. The second method (LRS_{event}) in C) shows how the particles from A) are plotted on individual plots, and linear regression is performed. The slopes from each

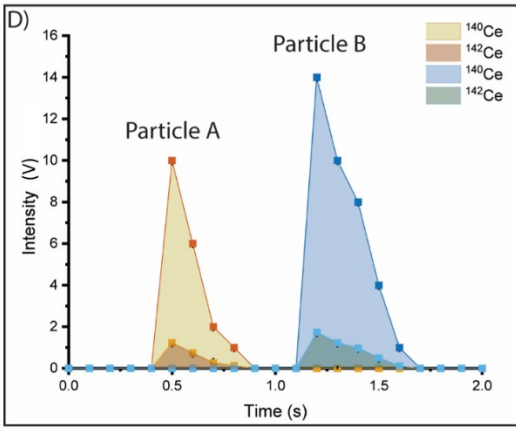
particle are then averaged, and that is the reported isotopic ratio. Event by event area ratio analysis (AR) is shown in D), where the particle signal 'spike' is integrated, and the ratio is obtained by dividing the area of ^{142}Ce by ^{140}Ce. The average ratio from all particles' areas is reported at the isotopic ratio. Finally, in E) the methods using the maximum (MAX) signal within a particle and using the split event correction (SEC - where all signal is summed into one data point), are shown. For MAX and SEC particle signal processing techniques, ratios were determined both using LRS (with all particles) and by taking the average ratio (AVG) from all particles (signal of ^{142}Ce over ^{140}Ce).







Ratio $= \frac{1}{n}\sum_i^n \mathrm{m}_i$

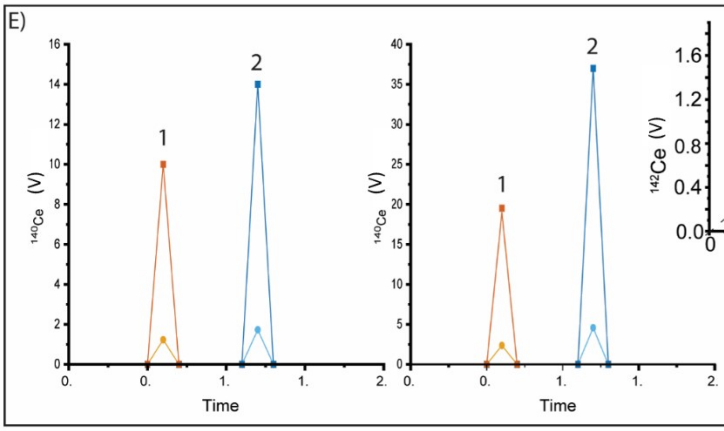


Integrate area under curve using

$Simpson's\ Rule \int_a^b f(x)dx = \cdots$

Ratio Particle n = $\int^{142}$Ce / $\int^{140}$Ce

Ratio $= \frac{1}{n}\sum_i^n \mathrm{m}_i$



Ratio = m

&

Ratio $= \frac{1}{n}\sum_i^n \frac{^{142}Ce_i}{^{140}Ce_i}$

Table S1 Uncorrected ratios for all cerium isotopes using all ratio methods with 50 ms integration time.

50 ms					
		slope	SE slope	mean	std
LRS_{global}	$^{136}Ce/^{140}Ce$	2.38E-03	1.73E-05		
	$^{138}Ce/^{140}Ce$	3.10E-03	1.40E-05		
	$^{142}Ce/^{140}Ce$	1.40E-01	4.07E-04		
LRS_{event}	$^{136}Ce/^{140}Ce$			2.52E-03	2.45E-04
	$^{138}Ce/^{140}Ce$			3.22E-03	3.04E-04
	$^{142}Ce/^{140}Ce$			1.44E-01	5.37E-03
AR	$^{136}Ce/^{140}Ce$			2.34E-03	1.84E-04
	$^{138}Ce/^{140}Ce$			2.93E-03	1.33E-04
	$^{142}Ce/^{140}Ce$			1.33E-01	2.39E-03
AVG_{SEC}	$^{136}Ce/^{140}Ce$			2.07E-03	1.42E-04
	$^{138}Ce/^{140}Ce$			2.68E-03	1.75E-04
	$^{142}Ce/^{140}Ce$			1.29E-01	1.85E-03
LRS_{SEC}	$^{136}Ce/^{140}Ce$	2.09E-03	1.09E-05		
	$^{138}Ce/^{140}Ce$	2.76E-03	1.04E-05		
	$^{142}Ce/^{140}Ce$	1.29E-01	1.30E-04		
AVG_{MAX}	$^{136}Ce/^{140}Ce$			2.46E-03	1.87E-04
	$^{138}Ce/^{140}Ce$			3.03E-03	1.46E-04
	$^{142}Ce/^{140}Ce$			1.37E-01	3.27E-03
LRS_{MAX}	$^{136}Ce/^{140}Ce$	2.34E-03	1.99E-05		
	$^{138}Ce/^{140}Ce$	3.07E-03	1.78E-05		
	$^{142}Ce/^{140}Ce$	1.40E-01	5.02E-04		

Table S2 Uncorrected ratios for all cerium isotopes using all ratio methods with 100 ms integration time.

100 ms					
		slope	SE slope	mean	std
LRS_{global}	$^{136}Ce/^{140}Ce$	2.28E-03	2.29E-05		
	$^{138}Ce/^{140}Ce$	3.00E-03	1.91E-05		
	$^{142}Ce/^{140}Ce$	1.36E-01	5.58E-04		
LRS_{event}	$^{136}Ce/^{140}Ce$			2.30E-03	5.32E-04
	$^{138}Ce/^{140}Ce$			3.06E-03	3.64E-04
	$^{142}Ce/^{140}Ce$			1.38E-01	1.43E-02
AR	$^{136}Ce/^{140}Ce$			2.29E-03	1.41E-04
	$^{138}Ce/^{140}Ce$			2.88E-03	9.66E-05
	$^{142}Ce/^{140}Ce$			1.32E-01	1.65E-03
AVG_{SEC}	$^{136}Ce/^{140}Ce$			2.13E-03	1.86E-04
	$^{138}Ce/^{140}Ce$			2.73E-03	1.43E-04
	$^{142}Ce/^{140}Ce$			1.29E-01	1.52E-03
LRS_{SEC}	$^{136}Ce/^{140}Ce$	1.71E-03	1.41E-05		
	$^{138}Ce/^{140}Ce$	2.26E-03	1.68E-05		
	$^{142}Ce/^{140}Ce$	1.29E-01	8.06E-05		
AVG_{MAX}	$^{136}Ce/^{140}Ce$			2.35E-03	1.86E-04
	$^{138}Ce/^{140}Ce$			2.97E-03	1.42E-04
	$^{142}Ce/^{140}Ce$			1.34E-01	4.05E-03
LRS_{MAX}	$^{136}Ce/^{140}Ce$	2.22E-03	2.75E-05		
	$^{138}Ce/^{140}Ce$	2.92E-03	2.42E-05		
	$^{142}Ce/^{140}Ce$	1.35E-01	7.03E-04		

Table S3 Uncorrected ratios for all cerium isotopes using all ratio methods with 250 ms integration time.

250 ms				
	slope	SE slope	mean	std

LRS_{global}	$^{136}Ce/^{140}Ce$	2.05E-03	1.92E-05		
	$^{138}Ce/^{140}Ce$	2.81E-03	1.59E-05		
	$^{142}Ce/^{140}Ce$	1.31E-01	4.33E-04		
LRS_{event}	$^{136}Ce/^{140}Ce$			2.07E-03	3.61E-04
	$^{138}Ce/^{140}Ce$			2.86E-03	3.76E-04
	$^{142}Ce/^{140}Ce$			1.33E-01	1.04E-02
AR	$^{136}Ce/^{140}Ce$			2.38E-03	1.69E-04
	$^{138}Ce/^{140}Ce$			2.85E-03	1.01E-04
	$^{142}Ce/^{140}Ce$			1.30E-01	1.41E-03
AVG_{SEC}	$^{136}Ce/^{140}Ce$			2.23E-03	2.46E-04
	$^{138}Ce/^{140}Ce$			2.79E-03	1.80E-04
	$^{142}Ce/^{140}Ce$			1.30E-01	2.61E-03
LRS_{SEC}	$^{136}Ce/^{140}Ce$	1.92E-03	3.16E-05		
	$^{138}Ce/^{140}Ce$	2.57E-03	2.48E-05		
	$^{142}Ce/^{140}Ce$	1.31E-01	2.81E-04		
AVG_{MAX}	$^{136}Ce/^{140}Ce$			2.36E-03	2.53E-04
	$^{138}Ce/^{140}Ce$			2.89E-03	1.67E-04
	$^{142}Ce/^{140}Ce$			1.32E-01	3.99E-03
LRS_{MAX}	$^{136}Ce/^{140}Ce$	2.03E-03	1.96E-05		
	$^{138}Ce/^{140}Ce$	2.78E-03	1.73E-05		
	$^{142}Ce/^{140}Ce$	1.30E-01	4.62E-04		

Table S4 Uncorrected ratios for all cerium isotopes using all ratio methods with 500 ms integration time.

500 ms					
		slope	SE slope	mean	std
LRS_{global}	$^{136}Ce/^{140}Ce$	2.05E-03	8.30E-05		

	$^{138}Ce/^{140}Ce$	2.81E-03	7.08E-05		
	$^{142}Ce/^{140}Ce$	1.28E-01	1.86E-03		
LRS_{event}	$^{136}Ce/^{140}Ce$			*	*
	$^{138}Ce/^{140}Ce$				
	$^{142}Ce/^{140}Ce$				
AR	$^{136}Ce/^{140}Ce$			2.21E-03	3.38E-05
	$^{138}Ce/^{140}Ce$			2.81E-03	8.98E-06
	$^{142}Ce/^{140}Ce$			1.30E-01	1.71E-04
AVG_{SEC}	$^{136}Ce/^{140}Ce$			2.26E-03	1.04E-04
	$^{138}Ce/^{140}Ce$			2.85E-03	8.31E-05
	$^{142}Ce/^{140}Ce$			1.31E-01	1.64E-03
LRS_{SEC}	$^{136}Ce/^{140}Ce$	2.13E-03	4.81E-05		
	$^{138}Ce/^{140}Ce$	2.79E-03	3.83E-05		
	$^{142}Ce/^{140}Ce$	1.29E-01	7.53E-04		
AVG_{MAX}	$^{136}Ce/^{140}Ce$			2.26E-03	1.06E-04
	$^{138}Ce/^{140}Ce$			2.85E-03	8.79E-05
	$^{142}Ce/^{140}Ce$			1.31E-01	1.96E-03
LRS_{MAX}	$^{136}Ce/^{140}Ce$	2.05E-03	7.74E-05		
	$^{138}Ce/^{140}Ce$	2.80E-03	6.88E-05		
	$^{142}Ce/^{140}Ce$	1.28E-01	1.65E-03		

*not enough data to report slope and error – in the 500 ms run, only 2 particles had enough intensity of minor cerium isotopes.

Figure S3 The signal from the Faraday cups on ^{136}Ce is shown to directly compare signal spread of the Faraday cups versus secondary electron multiplier detectors (shown in Figure 3 in the text).

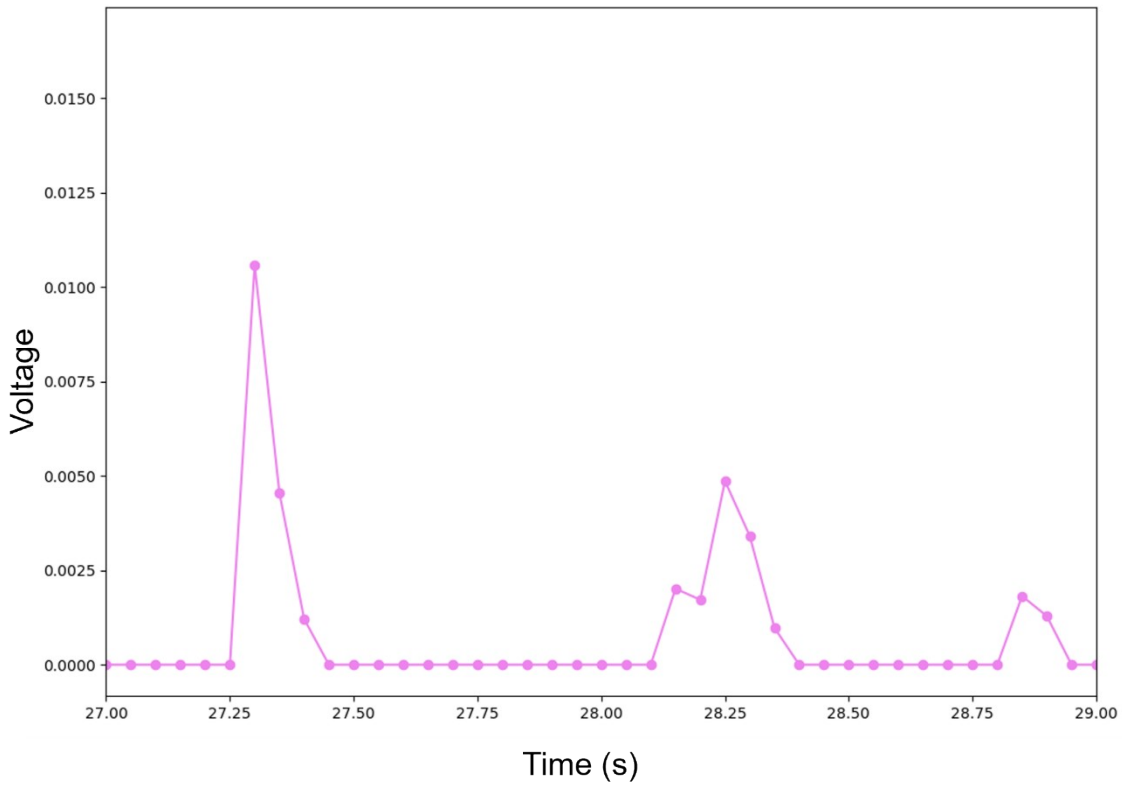


Figure S4 ANOVA testing for LRS_{event}, AR, AVG_{max}, and AVG_{sec} ratio analysis methods for each integration time are shown for the $^{142}Ce/^{140}Ce$ ratio. Ratios obtained via linear regression (slope) were not included in ANOVA testing for statistical significance.

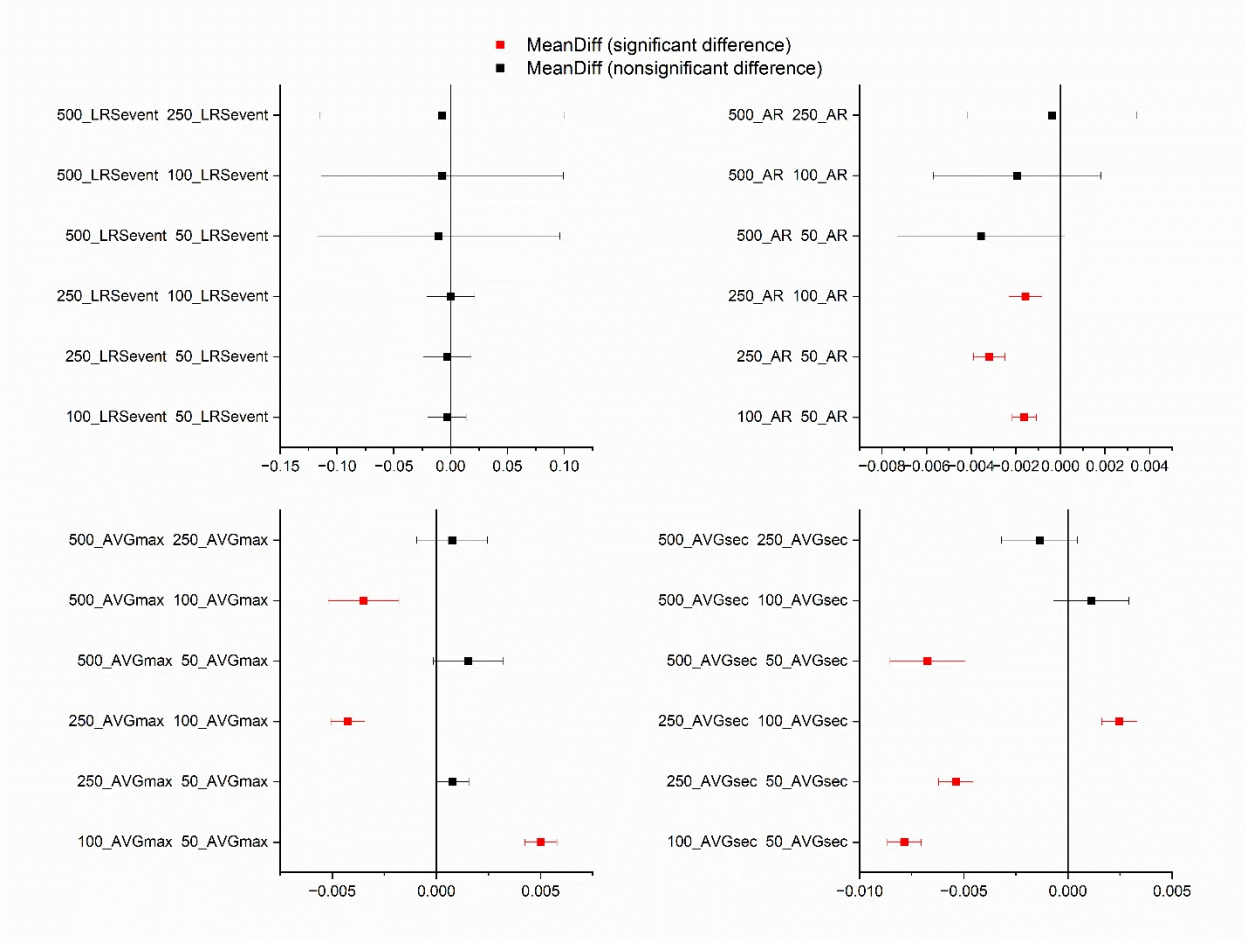


Figure S5 Time traces from all 20 microextractions for each integration time: a) 50 ms, b)100 ms, c) 250 ms, d) 500 ms.

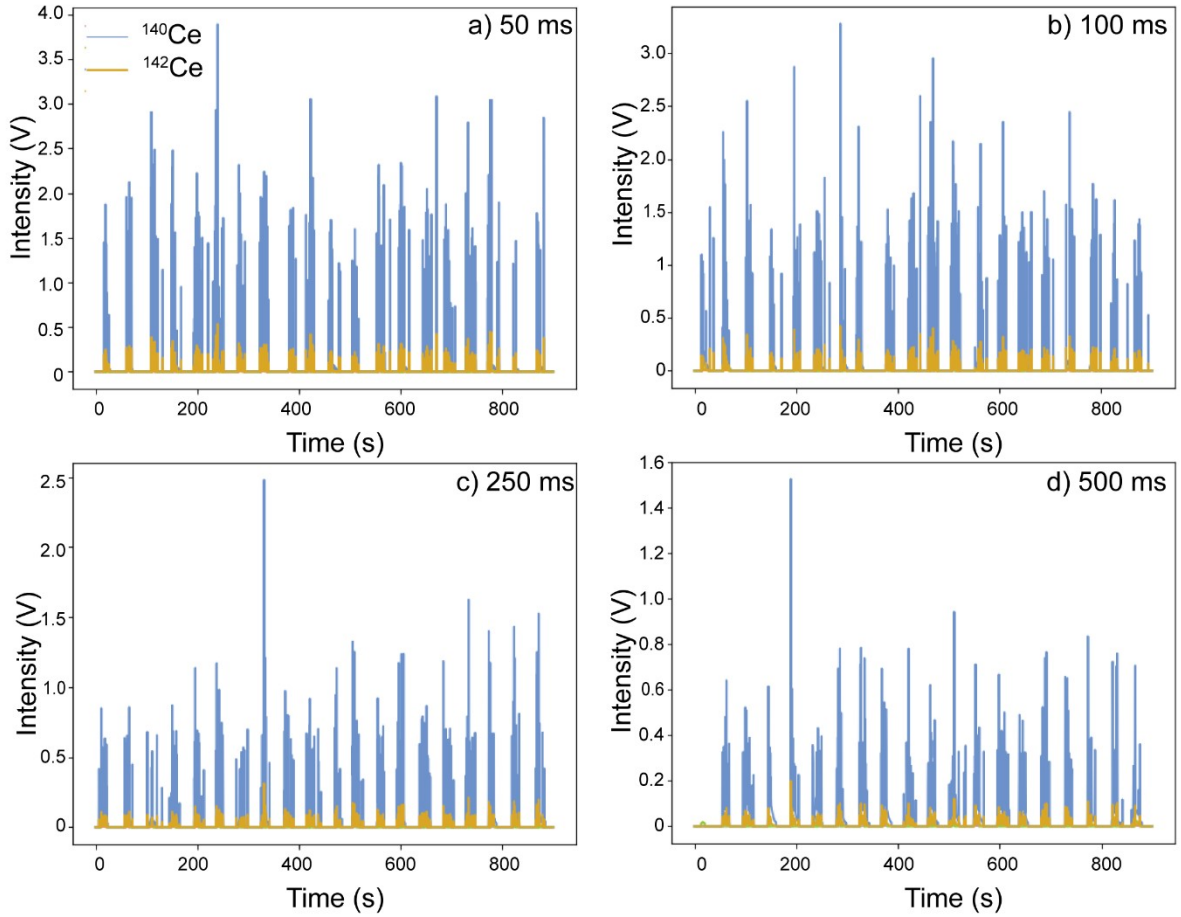


Table S5 Percent difference from 'true' ratio (0.125636) and the RSD for each $^{142}Ce/^{140}Ce$ ratio obtained via ME-spMC-ICP-MS.

	Int Time (ms)	% Difference	% RSD
LRS_{global}	50	3.85	0.08
	100	2.86	0.10
	250	0.74	0.11
	500	0.47	0.11
AR	50	0.26	2.26
	100	1.06	2.34
	250	0.15	0.62
	500	0.31	0.45
AVG_{SEC}	50	8.70	20.50
	100	3.39	12.11
	250	0.42	1.22
	500	0.20	1.09
LRS_{SEC}	50	0.13	0.05
	100	0.81	0.08
	250	0.15	0.04
	500	0.23	0.05