

ELECTRONIC SUPPLEMENTARY INFORMATION

Extending the application range of Hg isotopic analysis to sub- $\mu\text{g/L}$ levels using cold vapor generation multi-collector inductively coupled plasma-mass spectrometry with 10^{13} Ohm Faraday cup amplifiers.

Laura Suárez-Criado¹, Eduardo Bolea-Fernandez^{2,3}, Lana Abou-Zeid², Mathias Vandermeiren², Pablo Rodríguez-González¹, J. Ignacio García Alonso¹ and Frank Vanhaecke²

¹*Department of Physical and Analytical Chemistry, University of Oviedo, Julián Clavería, 8, 33006-Oviedo, Spain*

²*Department of Chemistry, Atomic & Mass Spectrometry – A&MS research unit, Ghent University, Campus Sterre, Krijgslaan 281 - S12, 9000 Ghent, Belgium*

³*University of Zaragoza, Aragón Institute of Engineering Research (I3A), Department of Analytical Chemistry, Zaragoza, Spain*

*Author for correspondence: Frank.Vanhaecke@UGent.be

Number of pages: 9

Number of Tables: 7

Table S1. Average $\delta^{202}\text{Hg}$ values (‰) for the IH standard (n=5) and two standard deviations obtained at different concentration levels, several cone configurations (Standard and Jet), plasma conditions (Wet and dry) and amplifier setups ((i) $10^{11} \Omega$ for each Faraday cup, (ii) $10^{11} \Omega$ for Faraday cups L2 (^{199}Hg), L1 (^{200}Hg), H1 (^{202}Hg) and $10^{13} \Omega$ for Faraday cups L3 (^{198}Hg) and C (^{201}Hg), and (iii) $10^{11} \Omega$ for Faraday cup L1 (^{200}Hg) and $10^{13} \Omega$ for Faraday cups L3 (^{198}Hg), L2 (^{199}Hg), C (^{201}Hg) and H1 (^{202}Hg)).

Cones	Plasma	Amplifiers	$\delta^{202}\text{Hg}$ (‰) \pm 2SD							
			$5 \mu\text{g L}^{-1}$	$2.5 \mu\text{g L}^{-1}$	$1 \mu\text{g L}^{-1}$	$0.5 \mu\text{g L}^{-1}$	$0.25 \mu\text{g L}^{-1}$	$0.1 \mu\text{g L}^{-1}$	$0.05 \mu\text{g L}^{-1}$	
IH (Literature value)⁶			-0.59 ± 0.15							
Standard	Wet	(i)	-0.56 ± 0.06	-0.49 ± 0.22	-0.48 ± 0.30	0.00 ± 0.68				
Standard	Wet	(ii)	-0.49 ± 0.26	-0.67 ± 0.10	-0.54 ± 0.28	-0.46 ± 0.08	-0.51 ± 1.05			
Jet	Wet	(i)	-0.51 ± 0.08	-0.61 ± 0.22	-0.53 ± 0.26	-0.32 ± 0.74	-0.37 ± 0.69			
Jet	Wet	(ii)		-0.63 ± 0.12	-0.65 ± 0.23	-0.43 ± 0.38				
Jet	Dry	(i)	-0.59 ± 0.06	-0.56 ± 0.06	-0.50 ± 0.15	-0.46 ± 0.36	-0.17 ± 0.82			
Jet	Dry	(ii)			-0.61 ± 0.10	-0.42 ± 0.35	-0.45 ± 0.43	-0.25 ± 0.63		
Jet	Wet	(iii)			-0.56 ± 0.10	-0.54 ± 0.18	-0.33 ± 0.27	-0.44 ± 0.45		
Jet	Dry	(iii)			-0.58 ± 0.23	-0.53 ± 0.10	-0.48 ± 0.28	-0.63 ± 0.42	-0.41 ± 0.54	

Table S2. Average $\delta^{201}\text{Hg}$ values (‰) for the IH standard (n=5) and two standard deviations obtained at different concentration levels, several cone configurations (Standard and Jet), plasma conditions (Wet and dry) and amplifier setups ((i) $10^{11} \Omega$ for each Faraday cup, (ii) $10^{11} \Omega$ for Faraday cups L2 (^{199}Hg), L1 (^{200}Hg), H1 (^{202}Hg) and $10^{13} \Omega$ for Faraday cups L3 (^{198}Hg) and C (^{201}Hg), and (iii) $10^{11} \Omega$ for Faraday cup L1 (^{200}Hg) and $10^{13} \Omega$ for Faraday cups L3 (^{198}Hg), L2 (^{199}Hg), C (^{201}Hg) and H1 (^{202}Hg)).

Cones	Plasma	Amplifiers	$\delta^{201}\text{Hg}$ (‰) \pm 2SD							
			$5 \mu\text{g L}^{-1}$	$2.5 \mu\text{g L}^{-1}$	$1 \mu\text{g L}^{-1}$	$0.5 \mu\text{g L}^{-1}$	$0.25 \mu\text{g L}^{-1}$	$0.1 \mu\text{g L}^{-1}$	$0.05 \mu\text{g L}^{-1}$	
IH (Literature value)⁶			-0.45 \pm 0.12							
Standard	Wet	(i)	-0.45 \pm 0.12	-0.28 \pm 0.28	-0.45 \pm 0.64	-0.09 \pm 0.99				
Standard	Wet	(ii)	-0.41 \pm 0.11	-0.44 \pm 0.12	-0.51 \pm 0.21	-0.32 \pm 0.29	0.44 \pm 0.46			
Jet	Wet	(i)	-0.39 \pm 0.08	-0.48 \pm 0.12	-0.36 \pm 0.29	-0.30 \pm 0.81	0.10 \pm 1.02			
Jet	Wet	(ii)		-0.48 \pm 0.13	-0.52 \pm 0.14	-0.40 \pm 0.15				
Jet	Dry	(i)	-0.48 \pm 0.07	-0.41 \pm 0.09	-0.36 \pm 0.12	-0.28 \pm 0.33	-0.24 \pm 1.07			
Jet	Dry	(ii)			-0.43 \pm 0.08	-0.39 \pm 0.06	-0.39 \pm 0.22	-0.37 \pm 0.78		
Jet	Wet	(iii)			-0.40 \pm 0.09	-0.44 \pm 0.23	-0.38 \pm 0.19	-0.25 \pm 0.26		
Jet	Dry	(iii)			-0.45 \pm 0.18	-0.43 \pm 0.08	-0.37 \pm 0.17	-0.39 \pm 0.54	-0.29 \pm 0.51	

Table S3. Average $\delta^{200}\text{Hg}$ values (‰) for the IH standard (n=5) and two standard deviations obtained at different concentration levels, several cone configurations (Standard and Jet), plasma conditions (Wet and dry) and amplifier setups ((i) $10^{11} \Omega$ for each Faraday cup, (ii) $10^{11} \Omega$ for Faraday cups L2 (^{199}Hg), L1 (^{200}Hg), H1 (^{202}Hg) and $10^{13} \Omega$ for Faraday cups L3 (^{198}Hg) and C (^{201}Hg), and (iii) $10^{11} \Omega$ for Faraday cup L1 (^{200}Hg) and $10^{13} \Omega$ for Faraday cups L3 (^{198}Hg), L2 (^{199}Hg), C (^{201}Hg) and H1 (^{202}Hg)).

Cones	Plasma	Amplifiers	$\delta^{200}\text{Hg} (\text{‰}) \pm 2\text{SD}$							
			$5 \mu\text{g L}^{-1}$	$2.5 \mu\text{g L}^{-1}$	$1 \mu\text{g L}^{-1}$	$0.5 \mu\text{g L}^{-1}$	$0.25 \mu\text{g L}^{-1}$	$0.1 \mu\text{g L}^{-1}$	$0.05 \mu\text{g L}^{-1}$	
IH (Literature value)⁶			- 0.30 ± 0.12							
Standard	Wet	(i)	-0.29 ± 0.08	-0.22 ± 0.24	-0.16 ± 0.38	0.10 ± 0.78				
Standard	Wet	(ii)	-0.21 ± 0.19	-0.32 ± 0.17	-0.38 ± 0.27	-0.20 ± 0.34	-0.05 ± 0.36			
Jet	Wet	(i)	-0.25 ± 0.03	-0.29 ± 0.11	-0.21 ± 0.39	-0.04 ± 0.50	0.23 ± 0.92			
Jet	Wet	(ii)		-0.33 ± 0.10	-0.41 ± 0.21	-0.13 ± 0.26				
Jet	Dry	(i)	-0.30 ± 0.08	-0.28 ± 0.07	-0.23 ± 0.11	-0.30 ± 0.47	-0.03 ± 1.03			
Jet	Dry	(ii)			-0.30 ± 0.14	-0.20 ± 0.43	-0.19 ± 0.24	-0.25 ± 0.60		
Jet	Wet	(iii)			-0.32 ± 0.17	-0.21 ± 0.28	-0.19 ± 0.36	-0.15 ± 0.64		
Jet	Dry	(iii)			-0.29 ± 0.35	-0.25 ± 0.16	-0.31 ± 0.24	-0.05 ± 0.52	-0.10 ± 0.30	

Table S4. Average $\delta^{199}\text{Hg}$ (‰) values for the IH standard (n=5) and two standard deviations obtained at different concentration levels, several cone configurations (Standard and Jet), plasma conditions (Wet and dry) and amplifier setups ((i) $10^{11} \Omega$ for each Faraday cup, (ii) $10^{11} \Omega$ for Faraday cups L2 (^{199}Hg), L1 (^{200}Hg), H1 (^{202}Hg) and $10^{13} \Omega$ for Faraday cups L3 (^{198}Hg) and C (^{201}Hg), and (iii) $10^{11} \Omega$ for Faraday cup L1 (^{200}Hg) and $10^{13} \Omega$ for Faraday cups L3 (^{198}Hg), L2 (^{199}Hg), C (^{201}Hg) and H1 (^{202}Hg)).

Cones	Plasma	Amplifiers	$\delta^{199}\text{Hg}$ (‰) \pm 2SD							
			5 $\mu\text{g L}^{-1}$	2.5 $\mu\text{g L}^{-1}$	1 $\mu\text{g L}^{-1}$	0.5 $\mu\text{g L}^{-1}$	0.25 $\mu\text{g L}^{-1}$	0.1 $\mu\text{g L}^{-1}$	0.05 $\mu\text{g L}^{-1}$	
IH (Literature value)⁶			-0.14 \pm 0.09							
Standard	Wet	(i)	-0.08 \pm 0.09	-0.07 \pm 0.17	0.04 \pm 0.72	-0.15 \pm 0.88				
Standard	Wet	(ii)	-0.02 \pm 0.27	-0.19 \pm 0.18	-0.09 \pm 0.40	0.00 \pm 0.51	0.48 \pm 0.66			
Jet	Wet	(i)	-0.09 \pm 0.07	-0.17 \pm 0.21	-0.05 \pm 0.50	0.12 \pm 0.77	0.29 \pm 0.70			
Jet	Wet	(ii)		-0.12 \pm 0.14	-0.23 \pm 0.18	-0.15 \pm 0.25				
Jet	Dry	(i)	-0.17 \pm 0.02	-0.11 \pm 0.06	-0.06 \pm 0.14	-0.07 \pm 0.51	-0.19 \pm 0.73			
Jet	Dry	(ii)			-0.09 \pm 0.15	-0.06 \pm 0.13	-0.33 \pm 0.68	0.30 \pm 1.33		
Jet	Wet	(iii)			-0.12 \pm 0.11	-0.15 \pm 0.09	-0.22 \pm 0.20	-0.10 \pm 0.65		
Jet	Dry	(iii)			-0.15 \pm 0.14	-0.12 \pm 0.08	-0.09 \pm 0.35	-0.15 \pm 0.39	-0.09 \pm 0.63	

Table S5. Average $\delta^{XX}\text{Hg}$ values (‰) for the IH standard (n=5) and standard deviation obtained with standard and Jet cones under wet plasma conditions and with $10^{11} \Omega$ amplifiers at different concentration levels.

Standard cones, wet plasma, $10^{11} \Omega$ amplifiers	$\delta^{199}\text{Hg} \pm \text{SD}$	$\delta^{200}\text{Hg} \pm \text{SD}$	$\delta^{201}\text{Hg} \pm \text{SD}$	$\delta^{202}\text{Hg} \pm \text{SD}$
5 $\mu\text{g L}^{-1}$ Without blank subtraction	-0.08 ± 0.05	-0.29 ± 0.04	-0.45 ± 0.06	-0.56 ± 0.03
5 $\mu\text{g L}^{-1}$ With blank subtraction	-0.10 ± 0.08	-0.30 ± 0.07	-0.47 ± 0.10	-0.58 ± 0.05
2.5 $\mu\text{g L}^{-1}$ Without blank subtraction	-0.07 ± 0.09	-0.22 ± 0.12	-0.28 ± 0.14	-0.49 ± 0.11
2.5 $\mu\text{g L}^{-1}$ With blank subtraction	0.01 ± 0.05	-0.21 ± 0.08	-0.22 ± 0.09	-0.44 ± 0.10
1 $\mu\text{g L}^{-1}$ Without blank subtraction	0.04 ± 0.36	-0.16 ± 0.19	-0.45 ± 0.32	-0.48 ± 0.15
1 $\mu\text{g L}^{-1}$ With blank subtraction	-0.01 ± 0.30	-0.10 ± 0.20	-0.46 ± 0.28	-0.45 ± 0.09
0.5 $\mu\text{g L}^{-1}$ Without blank subtraction	-0.15 ± 0.44	0.10 ± 0.39	-0.09 ± 0.50	0.00 ± 0.34
0.5 $\mu\text{g L}^{-1}$ With blank subtraction	-0.01 ± 0.73	0.52 ± 0.25	-0.11 ± 0.30	0.22 ± 0.17
Jet cones, wet plasma, $10^{11} \Omega$ amplifiers				
5 $\mu\text{g L}^{-1}$ Without blank subtraction	-0.09 ± 0.04	-0.25 ± 0.02	-0.39 ± 0.04	-0.51 ± 0.04
5 $\mu\text{g L}^{-1}$ With blank subtraction	-0.10 ± 0.06	-0.25 ± 0.05	-0.41 ± 0.09	-0.55 ± 0.09
2.5 $\mu\text{g L}^{-1}$ Without blank subtraction	-0.17 ± 0.11	-0.29 ± 0.06	-0.48 ± 0.06	-0.61 ± 0.11
2.5 $\mu\text{g L}^{-1}$ With blank subtraction	-0.18 ± 0.16	-0.31 ± 0.10	-0.54 ± 0.06	-0.66 ± 0.11
1 $\mu\text{g L}^{-1}$ Without blank subtraction	-0.05 ± 0.25	-0.21 ± 0.20	-0.36 ± 0.14	-0.53 ± 0.13
1 $\mu\text{g L}^{-1}$ With blank subtraction	0.07 ± 0.21	-0.09 ± 0.18	-0.28 ± 0.22	-0.45 ± 0.18
0.5 $\mu\text{g L}^{-1}$ Without blank subtraction	0.12 ± 0.38	-0.04 ± 0.25	-0.30 ± 0.40	-0.32 ± 0.37
0.5 $\mu\text{g L}^{-1}$ With blank subtraction	0.27 ± 0.71	-0.04 ± 0.56	-0.45 ± 0.60	-0.26 ± 0.69

Table S6. Average RSD values (%) and SD for the Hg isotope ratios of six measurements performed at decreasing concentration levels of a NIST SRM 3133 solution under several configurations: two cone configurations (Standard and Jet), two plasma conditions (Wet and dry) and three amplifier setups ((i) $10^{11} \Omega$ for each Faraday cup, (ii) $10^{11} \Omega$ for Faraday cups L2 (^{199}Hg), L1 (^{200}Hg), H1 (^{202}Hg) and $10^{13} \Omega$ for Faraday cups L3 (^{198}Hg) and C (^{201}Hg), and (iii) $10^{11} \Omega$ for Faraday cup L1 (^{200}Hg) and $10^{13} \Omega$ in Faraday cups for L3 (^{198}Hg), L2 (^{199}Hg), C (^{201}Hg) and H1 (^{202}Hg)).

Cones	Plasma	Amplifiers	5 $\mu\text{g L}^{-1}$		2.5 $\mu\text{g L}^{-1}$		1 $\mu\text{g L}^{-1}$		0.5 $\mu\text{g L}^{-1}$		0.25 $\mu\text{g L}^{-1}$		0.1 $\mu\text{g L}^{-1}$		0.05 $\mu\text{g L}^{-1}$													
			Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD												
Standard	Wet	(i)	$^{199}\text{Hg}/^{198}\text{Hg}$	0.0026	0.0003	0.0037	0.0005	0.0077	0.0002	0.0248	0.0317																	
			$^{200}\text{Hg}/^{198}\text{Hg}$	0.0026	0.0004	0.0040	0.0003	0.0080	0.0005	0.0196	0.0204																	
			$^{201}\text{Hg}/^{198}\text{Hg}$	0.0027	0.0002	0.0044	0.0006	0.0082	0.0004	0.0217	0.0216																	
			$^{202}\text{Hg}/^{198}\text{Hg}$	0.0026	0.0003	0.0037	0.0004	0.0074	0.0005	0.0195	0.0208																	
Standard	Wet	(ii)	$^{199}\text{Hg}/^{198}\text{Hg}$	0.0096	0.0017	0.0095	0.0020	0.0108	0.0020	0.0124	0.0007	0.0215	0.0010															
			$^{200}\text{Hg}/^{198}\text{Hg}$	0.0094	0.0019	0.0091	0.0016	0.0100	0.0012	0.0124	0.0007	0.0179	0.0024															
			$^{201}\text{Hg}/^{198}\text{Hg}$	0.0024	0.0003	0.0031	0.0005	0.0052	0.0006	0.0075	0.0006	0.0132	0.0016															
			$^{202}\text{Hg}/^{198}\text{Hg}$	0.0093	0.0020	0.0091	0.0020	0.0094	0.0016	0.0111	0.0009	0.0182	0.0040															
Jet	Wet	(i)	$^{199}\text{Hg}/^{198}\text{Hg}$	0.0020	0.0002	0.0029	0.0003	0.0055	0.0004	0.0089	0.0007																	
			$^{200}\text{Hg}/^{198}\text{Hg}$	0.0018	0.0002	0.0027	0.0003	0.0050	0.0003	0.0079	0.0005																	
			$^{201}\text{Hg}/^{198}\text{Hg}$	0.0022	0.0002	0.0030	0.0002	0.0055	0.0006	0.0097	0.0008																	
			$^{202}\text{Hg}/^{198}\text{Hg}$	0.0018	0.0001	0.0027	0.0003	0.0048	0.0004	0.0082	0.0007																	
Jet	Wet	(ii)	$^{199}\text{Hg}/^{198}\text{Hg}$			0.0061	0.0011	0.0075	0.0006	0.0101	0.0008																	
			$^{200}\text{Hg}/^{198}\text{Hg}$			0.0064	0.0013	0.0068	0.0007	0.0094	0.0016																	
			$^{201}\text{Hg}/^{198}\text{Hg}$			0.0027	0.0004	0.0041	0.0004	0.0060	0.0005																	
			$^{202}\text{Hg}/^{198}\text{Hg}$			0.0063	0.0014	0.0071	0.0007	0.0094	0.0013																	
Jet	Dry	(i)	$^{199}\text{Hg}/^{198}\text{Hg}$	0.0028	0.0031	0.0024	0.0003	0.0043	0.0002	0.0069	0.0009	0.0123	0.0014															
			$^{200}\text{Hg}/^{198}\text{Hg}$	0.0028	0.0032	0.0022	0.0002	0.0042	0.0005	0.0065	0.0008	0.0121	0.0022															
			$^{201}\text{Hg}/^{198}\text{Hg}$	0.0017	0.0004	0.0024	0.0003	0.0046	0.0003	0.0074	0.0009	0.0133	0.0016															
			$^{202}\text{Hg}/^{198}\text{Hg}$	0.0028	0.0034	0.0022	0.0004	0.0041	0.0005	0.0059	0.0006	0.0119	0.0020															
Jet	Dry	(ii)	$^{199}\text{Hg}/^{198}\text{Hg}$					0.0064	0.0015	0.0076	0.0017	0.0090	0.0007	0.0128	0.0024	0.0207	0.0030											
			$^{200}\text{Hg}/^{198}\text{Hg}$							0.0060	0.0011	0.0076	0.0016	0.0084	0.0013	0.0127	0.0030	0.0197	0.0029									
			$^{201}\text{Hg}/^{198}\text{Hg}$									0.0028	0.0003	0.0034	0.0002	0.0046	0.0005	0.0068	0.0007	0.0135	0.0009							
			$^{202}\text{Hg}/^{198}\text{Hg}$									0.0078	0.0016	0.0085	0.0011	0.0115	0.0022	0.0178	0.0019	0.0178	0.0019							
Jet	Wet	(iii)	$^{199}\text{Hg}/^{198}\text{Hg}$							0.0040	0.0005	0.0051	0.0005	0.0095	0.0011	0.0172	0.0013											
			$^{200}\text{Hg}/^{198}\text{Hg}$									0.0115	0.0015	0.0120	0.0013	0.0221	0.0016	0.0266	0.0029									
			$^{201}\text{Hg}/^{198}\text{Hg}$										0.0044	0.0010	0.0059	0.0008	0.0108	0.0012	0.0173	0.0012								
			$^{202}\text{Hg}/^{198}\text{Hg}$										0.0044	0.0003	0.0054	0.0006	0.0101	0.0012	0.0161	0.0022								
Jet	Dry	(iii)	$^{199}\text{Hg}/^{198}\text{Hg}$														0.0156	0.0014										
			$^{200}\text{Hg}/^{198}\text{Hg}$															0.0132	0.0037	0.0104	0.0007	0.0124	0.0017	0.0179	0.0027	0.0250	0.0041	
			$^{201}\text{Hg}/^{198}\text{Hg}$																0.0042	0.0008	0.0049	0.0003	0.0065	0.0004	0.0109	0.0014	0.0161	0.0013
			$^{202}\text{Hg}/^{198}\text{Hg}$																	0.0045	0.0007	0.0048	0.0006	0.0060	0.0007	0.0104	0.0018	0.0151

Table S7. Average $\delta^{XXX}\text{Hg}$ values (‰) for the IH standard (n=5) with corresponding SD and average RSD(%) values for Hg isotope ratio results for NIST SRM 3133 (n=6) and SD obtained at various concentration levels, with and without tau correction.

			$\delta^{199}\text{Hg}$	$\delta^{200}\text{Hg}$	$\delta^{201}\text{Hg}$	$\delta^{202}\text{Hg}$	$^{199}\text{Hg}/^{198}\text{Hg}$	$^{200}\text{Hg}/^{198}\text{Hg}$	$^{201}\text{Hg}/^{198}\text{Hg}$	$^{202}\text{Hg}/^{198}\text{Hg}$
							RSD (%)	RSD (%)	RSD (%)	RSD (%)
1.00 $\mu\text{g L}^{-1}$	with tau	Average	-0.130	-0.308	-0.423	-0.617	0.007	0.007	0.003	0.007
	correction	SD	0.105	0.056	0.036	0.041	0.001	0.002	0.000	0.001
	without tau	Average	-0.095	-0.296	-0.426	-0.606	0.008	0.008	0.003	0.008
	correction	SD	0.073	0.072	0.041	0.051	0.002	0.002	0.000	0.002
0.50 $\mu\text{g L}^{-1}$	with tau	Average	-0.129	-0.242	-0.383	-0.470	0.009	0.008	0.005	0.008
	correction	SD	0.046	0.146	0.038	0.119	0.001	0.001	0.001	0.001
	without tau	Average	-0.064	-0.197	-0.394	-0.418	0.009	0.008	0.005	0.008
	correction	SD	0.067	0.217	0.030	0.177	0.001	0.001	0.000	0.001
0.25 $\mu\text{g L}^{-1}$	with tau	Average	-0.270	-0.151	-0.393	-0.441	0.012	0.012	0.007	0.011
	correction	SD	0.322	0.182	0.105	0.194	0.001	0.002	0.001	0.001
	without tau	Average	-0.330	-0.193	-0.394	-0.452	0.013	0.013	0.007	0.012
	correction	SD	0.342	0.119	0.110	0.214	0.002	0.003	0.001	0.002
0.10 $\mu\text{g L}^{-1}$	with tau	Average	0.323	-0.187	-0.359	-0.229	0.021	0.019	0.014	0.017
	correction	SD	0.627	0.317	0.392	0.335	0.003	0.002	0.001	0.001
	without tau	Average	0.301	-0.247	-0.368	-0.254	0.021	0.020	0.013	0.018
	correction	SD	0.664	0.302	0.390	0.313	0.003	0.003	0.001	0.002