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SUPPLEMENTARY INFORMATION

MEASUREMENT OF COMPOUND-SPECIFIC Hg ISOTOPIC COMPOSITION IN NARROW TRANSIENT SIGNALS BY GAS CHROMATOGRAPHY COUPLED TO MULTICOLLECTOR ICP-MS

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Figure S1. Representation of the time-lag between Faraday Cup amplifiers. Cup L3 is taken as reference cup. V_1 and V_2 are the voltages measured for the isotope xxx by the delayed cup, at the beginning and at the end of the integration time. V_{corr} represents the voltage of the delayed cup after correction. The calculation of V_{corr} is done by linear interpolation between V_1 and V_2.

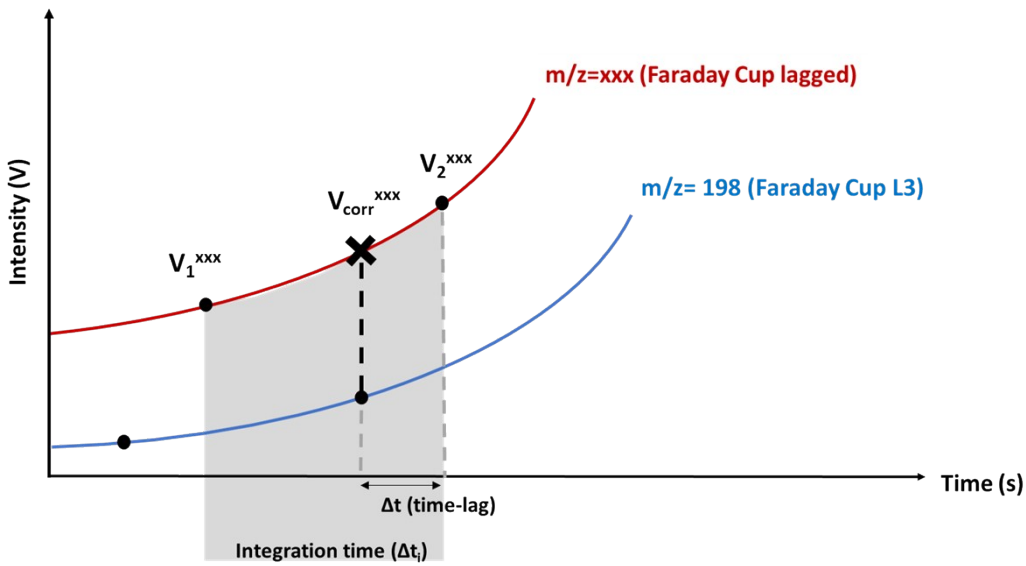


Figure S2. Determination of the time lag for cup H1 (202 m/z) by the linear regression procedure (LRS) using different optimisation criteria.

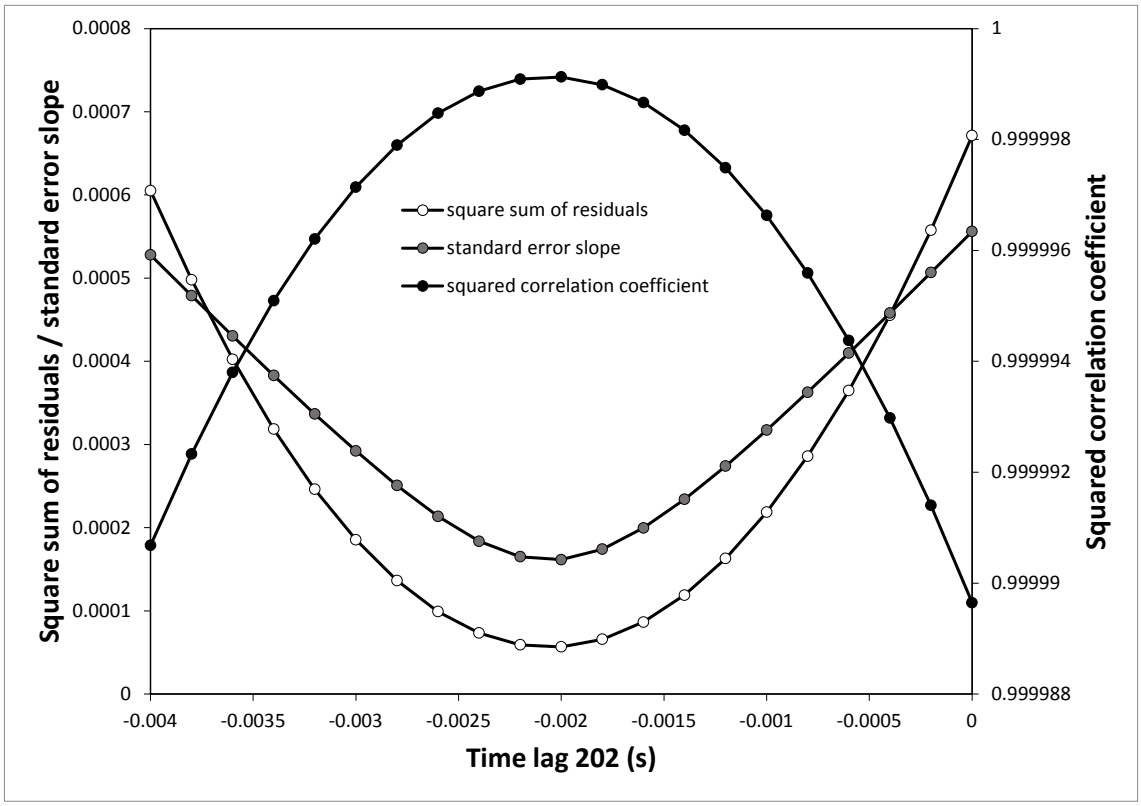


Figure S3. GC-MC-ICP-MS chromatogram for ^{202}Hg injecting 2 µL of a solution containing 250 ng g^{-1} of Hg(II) obtained with: a) T program 1 and b) T program 3. The continuous signals correspond to ^{203}Tl and ^{205}Tl, introduced by nebulization.

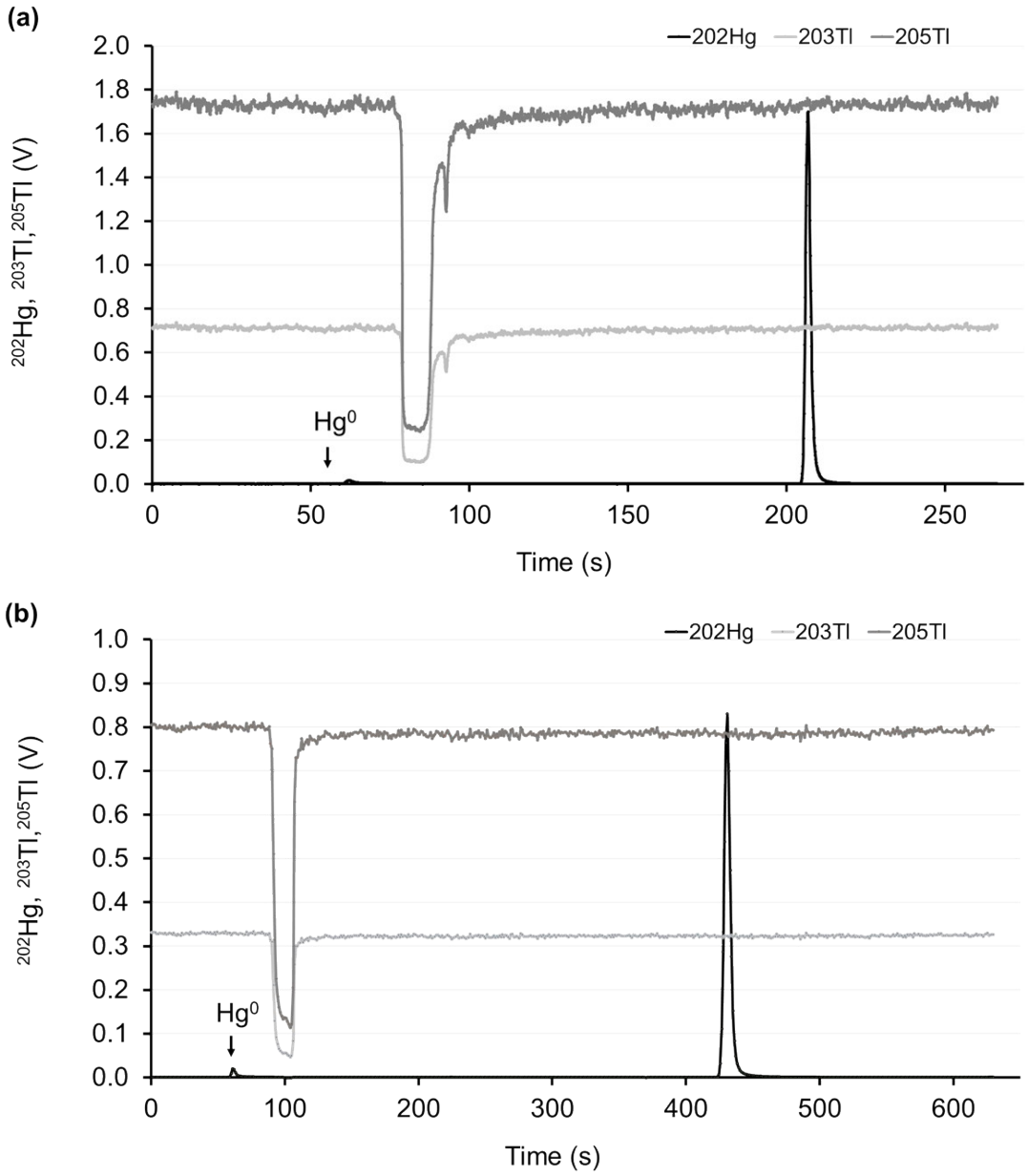


Table S1. Time-lag values (s) for Faraday cups L2, L1, C and H1 obtained in three independent analytical sessions of n=17 injections of 2 µL of a solution containing 250 ng g^{-1} of Hg(II).

Replicate	Δt L2 (m/z=199)			Δt L1 (m/z=200)			Δt C (m/z=201)			Δt H1 (m/z=202)		
	Session 1	Session 2	Session 3	Session 1	Session 2	Session 3	Session 1	Session 2	Session 3	Session 1	Session 2	Session 3
1	-0.0030	-0.0029	-0.0030	-0.0021	-0.0019	-0.0019	-0.0031	-0.0036	-0.0031	-0.0017	-0.0022	-0.0019
2	-0.0030	-0.0031	-0.0028	-0.0018	-0.0021	-0.0019	-0.0031	-0.0036	-0.0030	-0.0019	-0.0021	-0.0019
3	-0.0025	-0.0030	-0.0029	-0.0014	-0.0019	-0.0018	-0.0030	-0.0035	-0.0035	-0.0016	-0.0022	-0.0020
4	-0.0026	-0.0029	-0.0027	-0.0019	-0.0019	-0.0018	-0.0036	-0.0036	-0.0035	-0.0020	-0.0021	-0.0018
5	-0.0025	-0.0029	-0.0030	-0.0018	-0.0020	-0.0019	-0.0034	-0.0036	-0.0038	-0.0019	-0.0020	-0.0020
6	-0.0031	-0.0029	-0.0028	-0.0018	-0.0018	-0.0017	-0.0034	-0.0033	-0.0033	-0.0018	-0.0018	-0.0020
7	-0.0031	-0.0031	-0.0030	-0.0018	-0.0020	-0.0018	-0.0036	-0.0035	-0.0036	-0.0019	-0.0022	-0.0019
8	-0.0023	-0.0029	-0.0029	-0.0012	-0.0018	-0.0019	-0.0030	-0.0033	-0.0035	-0.0015	-0.0020	-0.0023
9	-0.0030	-0.0028	-0.0028	-0.0018	-0.0019	-0.0019	-0.0032	-0.0035	-0.0034	-0.0020	-0.0021	-0.0022
10	-0.0025	-0.0025	-0.0028	-0.0015	-0.0014	-0.0020	-0.0030	-0.0030	-0.0036	-0.0017	-0.0017	-0.0022
11	-0.0026	-0.0028	-0.0029	-0.0015	-0.0018	-0.0019	-0.0033	-0.0035	-0.0035	-0.0017	-0.0020	-0.0022
12	-0.0024	-0.0028	-0.0031	-0.0017	-0.0019	-0.0020	-0.0034	-0.0034	-0.0040	-0.0019	-0.0019	-0.0025
13	-0.0028	-0.0028	-0.0028	-0.0017	-0.0020	-0.0020	-0.0034	-0.0034	-0.0035	-0.0019	-0.0020	-0.0021
14	-0.0031	-0.0031	-0.0028	-0.0021	-0.0021	-0.0019	-0.0036	-0.0036	-0.0033	-0.0020	-0.0020	-0.0021
15	-0.0029	-0.0028	-0.0028	-0.0019	-0.0018	-0.0018	-0.0032	-0.0032	-0.0034	-0.0018	-0.0021	-0.0020
16	-0.0029	-0.0028	-0.0027	-0.0019	-0.0017	-0.0016	-0.0033	-0.0033	-0.0032	-0.0019	-0.0020	-0.0018
17	-0.0024	-0.0029	-0.0029	-0.0014	-0.0019	-0.0016	-0.0030	-0.0033	-0.0034	-0.0015	-0.0020	-0.0019
Average (sec) ± 1SD	-0.0028 ± 0.0002			-0.0018 ± 0.0002			-0.0034 ± 0.0002			-0.0020 ± 0.0002		

Table S2. $^{202/198}$Hg(II) isotope ratios and corresponding internal precisions (as 2SE) obtained by LRS under different experimental conditions (peak profiles and integration times) and calculation procedures (corrected and uncorrected isotope ratios and number of acquisition points) when analyzing NIST 3133.

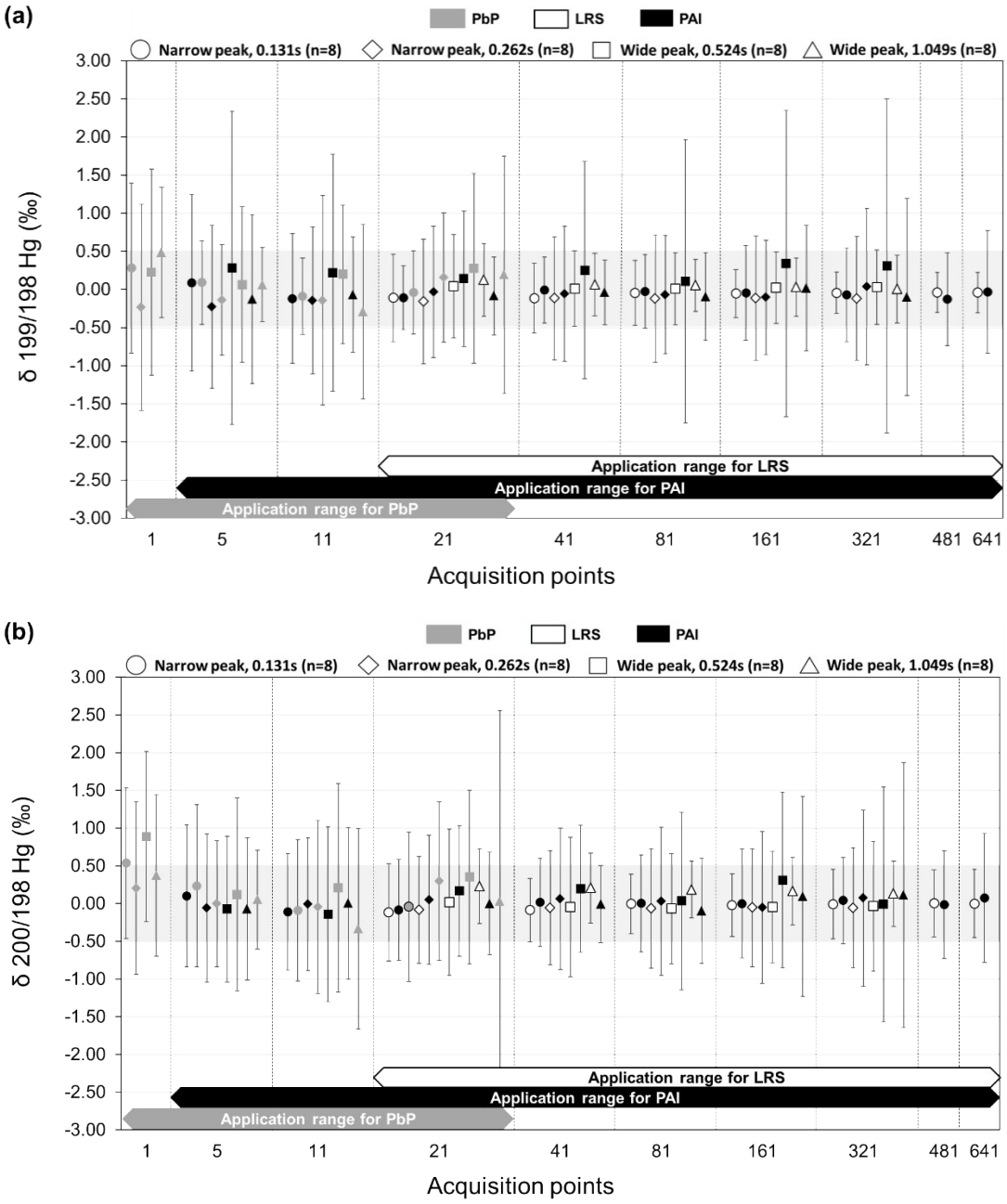
Narrow peak, 0.131 s integration time																												
	IR Drift corrected values														IR uncorrected values													
	21p		41p		81p		161p		321p		481p		641p		21p		41p		81p		161p		321p		481p		641p	
	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE
NIST 3133-1	2.9763	0.0006	2.9739	0.0003	2.9720	0.0002	2.9714	0.0002	2.9711	0.0002	2.9710	0.0002	2.9708	0.0002	2.9763	0.0029	2.9733	0.0012	2.9715	0.0007	2.9711	0.0005	2.9707	0.0003	2.9707	0.0003	2.9705	0.0003
NIST 3133-2	2.9746	0.0008	2.9738	0.0004	2.9725	0.0003	2.9715	0.0002	2.9712	0.0002	2.9710	0.0002	2.9709	0.0002	2.9746	0.0032	2.9732	0.0014	2.9720	0.0008	2.9711	0.0006	2.9708	0.0004	2.9706	0.0003	2.9705	0.0003
NIST 3133-3	2.9767	0.0013	2.9742	0.0006	2.9726	0.0004	2.9721	0.0003	2.9718	0.0002	2.9715	0.0002	2.9715	0.0002	2.9776	0.0032	2.9738	0.0014	2.9722	0.0008	2.9718	0.0006	2.9715	0.0004	2.9712	0.0003	2.9712	0.0003
NIST 3133-4	2.9746	0.0008	2.9730	0.0004	2.9728	0.0003	2.9716	0.0002	2.9712	0.0002	2.9712	0.0002	2.9711	0.0002	2.9754	0.0032	2.9724	0.0015	2.9723	0.0009	2.9712	0.0006	2.9708	0.0004	2.9708	0.0004	2.9708	0.0003
NIST 3133-5	2.9749	0.0009	2.9729	0.0005	2.9721	0.0003	2.9719	0.0002	2.9715	0.0002	2.9714	0.0002	2.9714	0.0002	2.9752	0.0030	2.9723	0.0014	2.9716	0.0008	2.9714	0.0005	2.9711	0.0004	2.9710	0.0003	2.9710	0.0003
NIST 3133-6	2.9740	0.0011	2.9726	0.0005	2.9717	0.0003	2.9712	0.0003	2.9709	0.0002	2.9710	0.0002	2.9710	0.0002	2.9747	0.0035	2.9721	0.0016	2.9713	0.0009	2.9708	0.0006	2.9706	0.0004	2.9706	0.0004	2.9706	0.0003
NIST 3133-7	2.9770	0.0008	2.9744	0.0004	2.9731	0.0003	2.9725	0.0002	2.9720	0.0002	2.9717	0.0002	2.9717	0.0002	2.9768	0.0031	2.9738	0.0013	2.9726	0.0008	2.9720	0.0005	2.9716	0.0004	2.9714	0.0003	2.9714	0.0003
NIST 3133-8	2.9791	0.0009	2.9763	0.0004	2.9746	0.0003	2.9736	0.0002	2.9733	0.0002	2.9732	0.0002	2.9731	0.0002	2.9797	0.0027	2.9759	0.0012	2.9743	0.0007	2.9733	0.0005	2.9730	0.0004	2.9729	0.0003	2.9729	0.0003
NIST 3133-9	2.9777	0.0009	2.9762	0.0004	2.9745	0.0003	2.9737	0.0002	2.9732	0.0002	2.9732	0.0002	2.9731	0.0002	2.9784	0.0034	2.9756	0.0014	2.9740	0.0008	2.9733	0.0005	2.9728	0.0004	2.9728	0.0003	2.9727	0.0003
NIST 3133-10	2.9767	0.0012	2.9743	0.0006	2.9726	0.0003	2.9721	0.0003	2.9719	0.0002	2.9715	0.0002	2.9715	0.0002	2.9776	0.0032	2.9738	0.0014	2.9722	0.0008	2.9718	0.0006	2.9715	0.0004	2.9712	0.0003	2.9712	0.0003
NIST 3133-11	2.9767	0.0012	2.9743	0.0005	2.9726	0.0003	2.9721	0.0003	2.9719	0.0002	2.9715	0.0002	2.9715	0.0002	2.9776	0.0032	2.9738	0.0014	2.9722	0.0008	2.9718	0.0006	2.9715	0.0004	2.9712	0.0003	2.9712	0.0003
NIST 3133-12	2.9748	0.0009	2.9734	0.0004	2.9728	0.0003	2.9722	0.0002	2.9721	0.0002	2.9719	0.0002	2.9719	0.0002	2.9749	0.0035	2.9728	0.0015	2.9723	0.0009	2.9718	0.0006	2.9717	0.0004	2.9715	0.0003	2.9716	0.0003
NIST 3133-13	2.9760	0.0014	2.9746	0.0006	2.9737	0.0004	2.9729	0.0003	2.9723	0.0002	2.9720	0.0002	2.9718	0.0002	2.9755	0.0036	2.9740	0.0015	2.9733	0.0008	2.9725	0.0006	2.9720	0.0004	2.9716	0.0003	2.9715	0.0003
NIST 3133-14	2.9721	0.0009	2.9717	0.0005	2.9716	0.0003	2.9713	0.0003	2.9709	0.0002	2.9709	0.0002	2.9708	0.0002	2.9721	0.0035	2.9711	0.0015	2.9710	0.0009	2.9708	0.0006	2.9705	0.0004	2.9705	0.0004	2.9704	0.0003
NIST 3133-15	2.9756	0.0009	2.9738	0.0004	2.9725	0.0003	2.9717	0.0002	2.9714	0.0002	2.9713	0.0002	2.9713	0.0002	2.9762	0.0032	2.9733	0.0014	2.9721	0.0008	2.9713	0.0005	2.9710	0.0004	2.9709	0.0003	2.9709	0.0003
NIST 3133-16	2.9764	0.0006	2.9741	0.0003	2.9732	0.0002	2.9725	0.0002	2.9723	0.0002	2.9719	0.0002	2.9718	0.0002	2.9766	0.0031	2.9735	0.0013	2.9727	0.0008	2.9721	0.0005	2.9719	0.0004	2.9715	0.0003	2.9715	0.0003
NIST 3133-17	2.9737	0.0010	2.9731	0.0005	2.9731	0.0003	2.9725	0.0002	2.9722	0.0002	2.9719	0.0002	2.9718	0.0002	2.9741	0.0027	2.9727	0.0012	2.9728	0.0007	2.9722	0.0005	2.9719	0.0003	2.9716	0.0003	2.9716	0.0003
	Narrow peak, 0.262 s integration time																											
NIST 3133-1	2.9748	0.0005	2.9724	0.0003	2.9713	0.0002	2.9708	0.0002	2.9707	0.0002					2.9736	0.0021	2.9715	0.0012	2.9706	0.0008	2.9701	0.0006	2.9701	0.0004				
NIST 3133-2	2.9757	0.0004	2.9747	0.0003	2.9735	0.0002	2.9731	0.0002	2.9732	0.0002					2.9746	0.0019	2.9738	0.0011	2.9728	0.0007	2.9724	0.0005	2.9725	0.0004				
NIST 3133-3	2.9754	0.0005	2.9738	0.0004	2.9729	0.0003	2.9722	0.0002	2.9722	0.0002					2.9742	0.0020	2.9729	0.0012	2.9721	0.0008	2.9715	0.0005	2.9715	0.0004				
NIST 3133-4	2.9754	0.0006	2.9732	0.0004	2.9726	0.0003	2.9718	0.0002	2.9717	0.0002					2.9742	0.0020	2.9722	0.0012	2.9718	0.0008	2.9711	0.0005	2.9710	0.0004				
NIST 3133-5	2.9761	0.0007	2.9738	0.0004	2.9731	0.0003	2.9728	0.0002	2.9726	0.0002					2.9745	0.0023	2.9725	0.0013	2.9720	0.0009	2.9718	0.0006	2.9716	0.0004				
NIST 3133-6	2.9746	0.0008	2.9732	0.0005	2.9724	0.0003	2.9721	0.0003	2.9718	0.0002					2.9728	0.0025	2.9719	0.0014	2.9713	0.0009	2.9710	0.0006	2.9708	0.0005				
NIST 3133-7	2.9743	0.0006	2.9733	0.0004	2.9724	0.0003	2.9718	0.0003	2.9713	0.0002					2.9731	0.0020	2.9724	0.0012	2.9716	0.0008	2.9711	0.0006	2.9706	0.0004				
NIST 3133-8	2.9753	0.0006	2.9737	0.0004	2.9730	0.0003	2.9724	0.0002	2.9719	0.0002					2.9741	0.0022	2.9728	0.0013	2.9722	0.0009	2.9717	0.0006	2.9712	0.0004				
NIST 3133-9	2.9763	0.0007	2.9741	0.0005	2.9733	0.0003	2.9728	0.0003	2.9726	0.0002					2.9751	0.0016	2.9732	0.0010	2.9726	0.0006	2.9721	0.0005	2.9719	0.0003				
NIST 3133-10	2.9759	0.0005	2.9740	0.0003	2.9730	0.0003	2.9726	0.0002	2.9723	0.0002					2.9747	0.0018	2.9731	0.0010	2.9722	0.0007	2.9720	0.0005	2.9717	0.0004				
NIST 3133-11	2.9750	0.0003	2.9737	0.0003	2.9731	0.0002	2.9724	0.0002	2.9717	0.0002					2.9738	0.0018	2.9728	0.0011	2.9723	0.0007	2.9716	0.0005	2.9710	0.0004				
NIST 3133-12	2.9735	0.0008	2.9724	0.0005	2.9713	0.0003	2.9709	0.0003	2.9706	0.0002					2.9722	0.0019	2.9714	0.0011	2.9704	0.0007	2.9701	0.0005	2.9698	0.0004				
NIST 3133-13	2.9742	0.0006	2.9732	0.0004	2.9725	0.0003	2.9722	0.0002	2.9720	0.0002					2.9730	0.0021	2.9723	0.0012	2.9718	0.0008	2.9715	0.0006	2.9713	0.0004				
NIST 3133-14	2.9744	0.0006	2.9731	0.0004	2.9721	0.0003	2.9716	0.0002	2.9714	0.0002					2.9731	0.0022	2.9722	0.0013	2.9713	0.0008	2.9708	0.0006	2.9706	0.0004				
NIST 3133-15	2.9753	0.0004	2.9737	0.0003	2.9730	0.0002	2.9726	0.0002	2.9724	0.0002					2.9740	0.0019	2.9728	0.0011	2.9722	0.0007	2.9718	0.0005	2.9717	0.0004				
NIST 3133-16	2.9732	0.0008	2.9715	0.0005	2.9706	0.0003	2.9704	0.0003	2.9701	0.0002					2.9718	0.0022	2.9704	0.0013	2.9697	0.0008	2.9695	0.0006	2.9693	0.0004				
NIST 3133-17	2.9748	0.0006	2.9737	0.0004	2.9731	0.0003	2.9727	0.0002	2.9726	0.0002					2.9736	0.0019	2.9728	0.0011	2.9723	0.0007	2.9720	0.0005	2.9719	0.0004				

	Wide peak, 0.524 s of integration time																									
	IR Drift corrected values														IR uncorrected values											
	21p		41p		81p		161p		321p		481p		641p		21p		41p		81p		161p		321p		481p		641p	
	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE	IR	2SE
NIST 3133-1	2.9759	0.0012	2.9754	0.0007	2.9751	0.0005	2.9751	0.0005	2.9750	0.0004	2.9751	0.0004			2.9812	0.0017	2.9793	0.0010	2.9776	0.0007	2.9771	0.0007	2.9766	0.0007	2.9766	0.0007		
NIST 3133-2	2.9774	0.0012	2.9766	0.0006	2.9761	0.0005	2.9754	0.0004	2.9754	0.0004	2.9755	0.0004			2.9759	0.0012	2.9755	0.0007	2.9752	0.0005	2.9752	0.0005	2.9751	0.0004	2.9752	0.0004		
NIST 3133-3	2.9783	0.0010	2.9771	0.0006	2.9760	0.0005	2.9755	0.0004	2.9751	0.0004	2.9752	0.0003			2.9775	0.0011	2.9767	0.0006	2.9762	0.0005	2.9755	0.0004	2.9755	0.0004	2.9756	0.0004		
NIST 3133-4	2.9757	0.0010	2.9751	0.0006	2.9751	0.0004	2.9749	0.0004	2.9745	0.0003	2.9747	0.0003			2.9783	0.0008	2.9773	0.0006	2.9761	0.0005	2.9756	0.0004	2.9752	0.0004	2.9753	0.0003		
NIST 3133-5	2.9781	0.0010	2.9767	0.0006	2.9754	0.0004	2.9753	0.0003	2.9749	0.0003	2.9748	0.0003			2.9756	0.0010	2.9753	0.0006	2.9752	0.0004	2.9750	0.0004	2.9746	0.0003	2.9747	0.0003		
NIST 3133-6	2.9788	0.0007	2.9758	0.0004	2.9749	0.0003	2.9742	0.0003	2.9741	0.0003	2.9741	0.0003			2.9781	0.0010	2.9768	0.0006	2.9755	0.0004	2.9754	0.0003	2.9750	0.0003	2.9749	0.0003		
NIST 3133-7	2.9764	0.0008	2.9749	0.0005	2.9748	0.0004	2.9745	0.0003	2.9744	0.0003	2.9746	0.0003			2.9788	0.0008	2.9759	0.0004	2.9750	0.0003	2.9743	0.0003	2.9742	0.0003	2.9742	0.0003		
NIST 3133-8	2.9767	0.0007	2.9750	0.0004	2.9742	0.0003	2.9739	0.0003	2.9736	0.0003	2.9737	0.0002			2.9764	0.0009	2.9750	0.0005	2.9749	0.0004	2.9746	0.0003	2.9744	0.0003	2.9747	0.0003		
NIST 3133-9	2.9786	0.0008	2.9755	0.0005	2.9744	0.0003	2.9741	0.0003	2.9740	0.0002	2.9734	0.0002			2.9766	0.0007	2.9751	0.0004	2.9743	0.0003	2.9740	0.0003	2.9736	0.0003	2.9738	0.0002		
NIST 3133-10	2.9783	0.0011	2.9786	0.0006	2.9780	0.0005	2.9772	0.0004	2.9773	0.0003	2.9770	0.0004			2.9785	0.0008	2.9756	0.0005	2.9745	0.0003	2.9742	0.0003	2.9741	0.0002	2.9735	0.0002		
NIST 3133-11	2.9799	0.0011	2.9771	0.0006	2.9756	0.0004	2.9755	0.0003	2.9758	0.0002	2.9743	0.0002			2.9783	0.0009	2.9788	0.0005	2.9781	0.0004	2.9773	0.0004	2.9774	0.0003	2.9770	0.0004		
NIST 3133-12	2.9794	0.0008	2.9768	0.0005	2.9750	0.0004	2.9745	0.0003	2.9746	0.0003	2.9743	0.0002			2.9799	0.0008	2.9772	0.0004	2.9757	0.0003	2.9756	0.0003	2.9759	0.0002	2.9744	0.0002		
NIST 3133-13	2.9788	0.0008	2.9761	0.0004	2.9742	0.0003	2.9732	0.0002	2.9722	0.0002	2.9725	0.0002			2.9793	0.0008	2.9769	0.0005	2.9751	0.0003	2.9746	0.0003	2.9747	0.0003	2.9744	0.0002		
NIST 3133-14	2.9773	0.0013	2.9753	0.0006	2.9743	0.0004	2.9738	0.0003	2.9729	0.0002	2.9738	0.0002			2.9789	0.0006	2.9762	0.0004	2.9743	0.0003	2.9733	0.0002	2.9722	0.0002	2.9726	0.0002		
NIST 3133-15	2.9802	0.0009	2.9769	0.0004	2.9749	0.0003	2.9746	0.0003	2.9750	0.0003	2.9736	0.0002			2.9772	0.0010	2.9754	0.0005	2.9744	0.0003	2.9739	0.0003	2.9730	0.0002	2.9739	0.0002		
NIST 3133-16	2.9789	0.0010	2.9762	0.0005	2.9753	0.0004	2.9734	0.0003	2.9722	0.0002	2.9731	0.0002			2.9800	0.0007	2.9770	0.0003	2.9750	0.0002	2.9747	0.0003	2.9751	0.0003	2.9736	0.0002		
NIST 3133-17	2.9775	0.0006	2.9747	0.0004	2.9733	0.0003	2.9722	0.0003	2.9705	0.0002	2.9728	0.0002			2.9788	0.0009	2.9763	0.0005	2.9754	0.0003	2.9735	0.0003	2.9723	0.0002	2.9732	0.0002		
	Wide peak, 1.049 s of integration time																											
NIST 3133-1	2.9777	0.0007	2.9768	0.0005	2.9767	0.0004	2.9767	0.0003	2.9770	0.0003					2.9780	0.0005	2.9771	0.0004	2.9769	0.0004	2.9769	0.0003	2.9772	0.0003				
NIST 3133-2	2.9763	0.0006	2.9762	0.0005	2.9763	0.0004	2.9760	0.0003	2.9760	0.0003					2.9766	0.0006	2.9764	0.0004	2.9766	0.0004	2.9762	0.0003	2.9762	0.0003				
NIST 3133-3	2.9755	0.0006	2.9757	0.0005	2.9761	0.0004	2.9760	0.0004	2.9766	0.0004					2.9758	0.0005	2.9759	0.0004	2.9763	0.0004	2.9762	0.0004	2.9768	0.0004				
NIST 3133-4	2.9771	0.0007	2.9771	0.0006	2.9771	0.0005	2.9770	0.0005	2.9772	0.0005					2.9774	0.0006	2.9773	0.0005	2.9773	0.0005	2.9772	0.0005	2.9773	0.0005				
NIST 3133-5	2.9793	0.0007	2.9793	0.0006	2.9791	0.0005	2.9793	0.0005	2.9792	0.0004					2.9796	0.0006	2.9796	0.0006	2.9793	0.0005	2.9795	0.0004	2.9794	0.0004				
NIST 3133-6	2.9800	0.0007	2.9793	0.0005	2.9793	0.0005	2.9792	0.0004	2.9794	0.0004					2.9803	0.0007	2.9796	0.0005	2.9795	0.0004	2.9793	0.0004	2.9796	0.0004				
NIST 3133-7	2.9763	0.0007	2.9762	0.0004	2.9764	0.0004	2.9762	0.0003	2.9764	0.0003					2.9766	0.0005	2.9764	0.0003	2.9766	0.0003	2.9764	0.0003	2.9765	0.0003				
NIST 3133-8	2.9777	0.0005	2.9770	0.0004	2.9770	0.0003	2.9772	0.0003	2.9774	0.0003					2.9780	0.0005	2.9773	0.0004	2.9772	0.0003	2.9774	0.0003	2.9775	0.0003				
NIST 3133-9	2.9757	0.0006	2.9750	0.0004	2.9752	0.0003	2.9750	0.0003	2.9760	0.0003					2.9760	0.0005	2.9752	0.0003	2.9754	0.0003	2.9752	0.0002	2.9762	0.0002				
NIST 3133-10	2.9772	0.0008	2.9777	0.0005	2.9776	0.0004	2.9778	0.0004	2.9779	0.0003					2.9775	0.0006	2.9779	0.0005	2.9778	0.0004	2.9780	0.0003	2.9781	0.0003				
NIST 3133-11	2.9752	0.0005	2.9754	0.0003	2.9758	0.0003	2.9758	0.0003	2.9760	0.0003					2.9755	0.0005	2.9756	0.0003	2.9760	0.0003	2.9760	0.0003	2.9761	0.0003				
NIST 3133-12	2.9779	0.0006	2.9779	0.0004	2.9769	0.0004	2.9769	0.0003	2.9770	0.0003					2.9782	0.0006	2.9781	0.0004	2.9771	0.0003	2.9770	0.0003	2.9772	0.0003				
NIST 3133-13	2.9776	0.0005	2.9776	0.0004	2.9773	0.0003	2.9770	0.0003	2.9772	0.0003					2.9779	0.0005	2.9778	0.0003	2.9775	0.0003	2.9771	0.0003	2.9774	0.0003				
NIST 3133-14	2.9765	0.0005	2.9763	0.0004	2.9763	0.0004	2.9763	0.0003	2.9763	0.0003					2.9767	0.0005	2.9766	0.0004	2.9765	0.0004	2.9765	0.0003	2.9765	0.0003				
NIST 3133-15	2.9755	0.0007	2.9749	0.0005	2.9747	0.0004	2.9752	0.0003	2.9754	0.0003					2.9758	0.0006	2.9751	0.0004	2.9749	0.0003	2.9754	0.0003	2.9755	0.0002				
NIST 3133-16	2.9767	0.0005	2.9754	0.0003	2.9756	0.0003	2.9756	0.0003	2.9760	0.0003					2.9769	0.0005	2.9756	0.0003	2.9758	0.0003	2.9758	0.0003	2.9762	0.0003				
NIST 3133-17	2.9751	0.0004	2.9746	0.0003	2.9744	0.0003	2.9748	0.0002	2.9745	0.0002					2.9754	0.0004	2.9748	0.0003	2.9746	0.0003	2.9750	0.0002	2.9746	0.0002				

Table S3. Hg(II) delta values obtained under different experimental conditions and calculation procedures when analyzing NIST 3133 versus NIST 3133. Uncertainty of the values correspond to the external precision (±2SD) for n=8 independent measurements

Method of Calculation	Nr points	Peak profile, integration time	$\delta^{199/198}$ Hg ± 2SD (‰)	$\delta^{200/198}$ Hg ± 2SD (‰)	$\delta^{201/198}$ Hg ± 2SD (‰)	$\delta^{202/198}$ Hg ± 2SD (‰)
PbP	1	Narrow peak, 0.131 s	0.280 ± 1.117	0.538 ± 0.997	0.692 ± 1.648	0.942 ± 2.042
		Narrow peak, 0.262 s	-0.234 ± 1.351	0.205 ± 1.144	0.145 ± 1.330	0.143 ± 1.778
		Wide peak, 0.524 s	0.227 ± 1.352	0.889 ± 1.127	0.743 ± 1.765	0.908 ± 2.027
		Wide peak, 1.049 s	0.483 ± 0.855	0.373 ± 1.072	0.451 ± 1.663	0.652 ± 2.205
	5	Narrow peak, 0.131 s	0.092 ± 0.547	0.236 ± 1.075	0.275 ± 1.526	0.433 ± 1.660
		Narrow peak, 0.262 s	-0.137 ± 0.727	-0.001 ± 0.836	-0.062 ± 0.830	-0.120 ± 1.180
		Wide peak, 0.524 s	0.064 ± 1.023	0.118 ± 1.281	0.184 ± 2.102	0.236 ± 1.893
		Wide peak, 1.049 s	0.065 ± 0.485	0.055 ± 0.655	0.146 ± 0.753	0.084 ± 0.885
	11	Narrow peak, 0.131 s	-0.088 ± 0.503	-0.090 ± 0.935	-0.178 ± 1.434	-0.250 ± 1.618
		Narrow peak, 0.262 s	-0.143 ± 1.377	-0.044 ± 1.148	0.066 ± 1.059	-0.088 ± 0.965
		Wide peak, 0.524 s	0.200 ± 0.908	0.209 ± 1.383	0.195 ± 1.977	0.262 ± 1.964
		Wide peak, 1.049 s	-0.292 ± 1.143	-0.333 ± 1.327	0.088 ± 1.779	-0.249 ± 1.741
	21	Narrow peak, 0.131 s	-0.040 ± 0.547	-0.042 ± 0.992	-0.247 ± 0.960	-0.136 ± 0.845
		Narrow peak, 0.262 s	0.159 ± 0.849	0.299 ± 1.050	0.200 ± 0.902	-0.048 ± 1.171
		Wide peak, 0.524 s	0.275 ± 1.245	0.354 ± 1.150	0.339 ± 1.117	0.369 ± 1.069
		Wide peak, 1.049 s	0.192 ± 1.560	0.031 ± 2.529	0.591 ± 2.201	0.189 ± 1.693
LRS	21	Narrow peak, 0.131 s	-0.111 ± 0.575	-0.117 ± 0.646	-0.142 ±1.291	-0.310 ± 1.260
		Narrow peak, 0.262 s	-0.159 ± 0.820	-0.081 ± 0.709	-0.116 ± 0.653	-0.139 ± 0.526
		Wide peak, 0.524 s	0.043 ± 0.679	0.019 ± 0.971	0.001 ± 1.910	0.113 ± 1.214
		Wide peak, 1.049 s	0.125 ± 0.478	0.231 ± 0.497	0.284 ± 0.435	0.310 ± 0.666
	41	Narrow peak, 0.131 s	-0.115 ± 0.456	-0.085 ± 0.420	-0.191 ± 0.874	-0.194 ± 0.746
		Narrow peak, 0.262 s	-0.117 ± 0.807	-0.056 ± 0.756	-0.088 ± 0.705	-0.122 ± 0.732
		Wide peak, 0.524 s	0.010 ± 0.497	-0.045 ± 0.928	-0.061 ± 1.389	-0.047 ± 0.907
		Wide peak, 1.049 s	0.065 ± 0.411	0.206 ± 0.464	0.240 ± 0.480	0.282 ± 0.660
	81	Narrow peak, 0.131 s	-0.047 ± 0.426	-0.003 ± 0.393	-0.073 ± 0.683	-0.066 ± 0.581
		Narrow peak, 0.262 s	-0.121 ± 0.836	-0.066 ± 0.792	-0.110 ± 0.689	-0.165 ± 0.766
		Wide peak, 0.524 s	0.012 ± 0.473	-0.067 ± 0.733	-0.101 ± 1.034	-0.142 ± 0.594
		Wide peak, 1.049 s	0.054 ± 0.341	0.185 ± 0.376	0.218 ± 0.478	0.244 ± 0.591
	161	Narrow peak, 0.131 s	-0.054 ± 0.313	-0.022 ± 0.417	-0.101 ± 0.601	-0.105 ± 0.399
		Narrow peak, 0.262 s	-0.115 ± 0.816	-0.052 ± 0.781	-0.092 ± 0.658	-0.151 ± 0.772
		Wide peak, 0.524 s	0.024 ± 0.469	-0.045 ± 0.744	-0.009 ± 1.048	-0.055 ± 0.628
		Wide peak, 1.049 s	0.028 ± 0.382	0.163 ± 0.446	0.199 ± 0.513	0.221 ± 0.659
	321	Narrow peak, 0.131 s	-0.043 ± 0.270	-0.007 ± 0.464	-0.082 ± 0.590	-0.072 ± 0.410
		Narrow peak, 0.262 s	-0.119 ± 0.815	-0.056 ± 0.793	-0.089 ± 0.684	-0.151 ± 0.802
		Wide peak, 0.524 s	0.031 ± 0.491	-0.035 ± 0.858	0.037 ± 1.109	-0.018 ± 0.886
		Wide peak, 1.049 s	0.005 ± 0.444	0.131 ± 0.433	0.172 ± 0.533	0.175 ± 0.687
	481	Narrow peak, 0.131 s	-0.038 ± 0.263	0.003 ± 0.447	-0.070 ± 0.543	-0.054 ± 0.361
	641	Narrow peak, 0.131 s	-0.041 ± 0.262	0.002 ± 0.449	-0.071 ± 0.536	0.002 ± 0.449
PAI	5	Narrow peak, 0.131 s	0.089 ± 1.158	0.102 ± 0.942	0.007 ± 1.625	0.042 ± 1.060
		Narrow peak, 0.262 s	-0.227 ± 1.067	-0.058 ± 0.979	-0.145 ± 1.047	-0.181 ± 0.980
		Wide peak, 0.524 s	0.285 ± 2.053	-0.072 ± 0.967	0.051 ± 1.614	-0.017 ± 1.082
		Wide peak, 1.049 s	-0.129 ± 1.106	-0.071 ± 0.941	-0.012 ± 0.810	0.009 ± 1.022
	11	Narrow peak, 0.131 s	-0.118 ± 0.849	-0.107 ± 0.772	-0.204 ± 1.282	-0.238 ± 0.909
		Narrow peak, 0.262 s	-0.143 ± 0.963	-0.007 ± 0.878	-0.024 ± 0.771	-0.134 ± 0.783
		Wide peak, 0.524 s	0.218 ± 1.554	-0.142 ± 1.159	-0.050 ± 1.428	-0.113 ± 1.055
		Wide peak, 1.049 s	-0.068 ± 0.756	0.005 ± 1.004	0.095 ± 1.057	0.120 ± 1.162
	21	Narrow peak, 0.131 s	-0.107 ± 0.422	-0.084 ± 0.673	-0.217 ± 0.802	-0.176 ± 0.584
		Narrow peak, 0.262 s	-0.032 ± 0.863	0.051 ± 0.856	0.075 ± 0.846	-0.072 ± 0.935
		Wide peak, 0.524 s	0.141 ± 0.887	0.169 ± 0.866	0.290 ± 1.103	0.136 ± 0.836
		Wide peak, 1.049 s	-0.085 ± 0.508	0.001 ± 0.679	0.043 ± 1.055	0.110 ± 1.107
	41	Narrow peak, 0.131 s	-0.007 ± 0.433	0.015 ± 0.587	-0.060 ± 0.639	-0.071 ± 0.493
		Narrow peak, 0.262 s	-0.058 ± 0.885	0.061 ± 0.937	0.097 ± 0.844	-0.089 ± 0.962
		Wide peak, 0.524 s	0.254 ± 1.425	0.194 ± 0.841	0.361 ± 0.810	0.143 ± 0.630
		Wide peak, 1.049 s	-0.039 ± 0.427	-0.010 ± 0.512	0.103 ± 1.023	0.129 ± 1.061
	81	Narrow peak, 0.131 s	-0.026 ± 0.481	0.003 ± 0.641	-0.080 ± 0.600	-0.076 ± 0.487
		Narrow peak, 0.262 s	-0.067 ± 0.774	0.029 ± 0.982	0.107 ± 0.936	-0.117 ± 0.982
		Wide peak, 0.524 s	0.109 ± 1.858	0.035 ± 1.174	0.271 ± 1.009	0.015 ± 0.902
		Wide peak, 1.049 s	-0.092 ± 0.572	-0.098 ± 0.695	0.009 ± 1.007	0.064 ± 1.392
	161	Narrow peak, 0.131 s	-0.046 ± 0.621	0.002 ± 0.722	-0.082 ± 0.662	-0.068 ± 0.581
		Narrow peak, 0.262 s	-0.104 ± 0.750	-0.053 ± 1.007	0.096 ± 1.019	-0.179 ± 0.964
		Wide peak, 0.524 s	0.340 ± 2.009	0.313 ± 1.165	0.392 ± 1.018	0.214 ± 0.926
		Wide peak, 1.049 s	0.017 ± 0.823	0.093 ± 1.325	0.255 ± 1.480	0.156 ± 1.863
	321	Narrow peak, 0.131 s	-0.069 ± 0.614	0.041 ± 0.572	0.015 ± 0.830	-0.032 ± 0.602
		Narrow peak, 0.262 s	0.038 ± 1.027	0.072 ± 1.173	0.233 ± 1.219	-0.135 ± 1.117
		Wide peak, 0.524 s	0.308 ± 2.190	-0.010 ± 1.558	0.221 ± 1.726	0.066 ± 1.152
		Wide peak, 1.049 s	-0.100 ± 1.291	0.114 ± 1.755	0.049 ± 1.861	0.229 ± 2.207
	481	Narrow peak, 0.131 s	-0.127 ± 0.610	-0.013 ± 0.716	-0.009 ± 0.923	-0.110 ± 0.703
	641	Narrow peak, 0.131 s	-0.033 ± 0.804	0.078 ± 0.855	0.175 ± 1.221	0.078 ± 0.855

Figure S4. (a) δ^{199}Hg(II), (b) δ^{200}Hg(II) and (c) δ^{201}Hg(II) (‰) obtained under different experimental conditions when analyzing NIST 3133 versus NIST 3133. Error bars represent the associated external precision (±2SD) for n=8 independent measurements. An optimal external precision interval of ±0.50 ‰ based on previous studies (Epov et al., 2010, 2008) is highlighted.



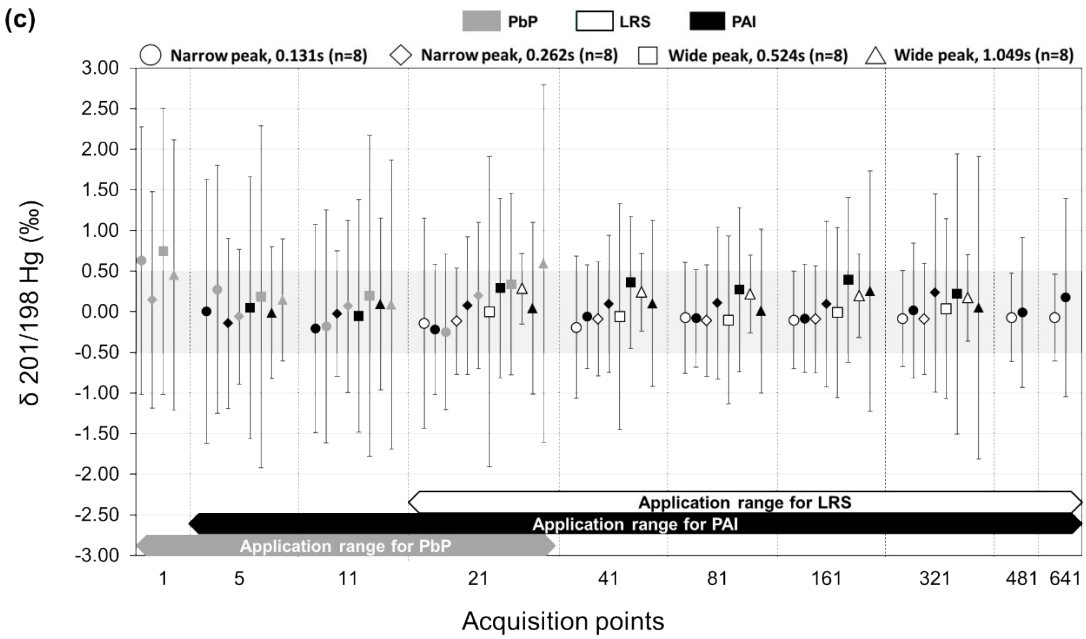
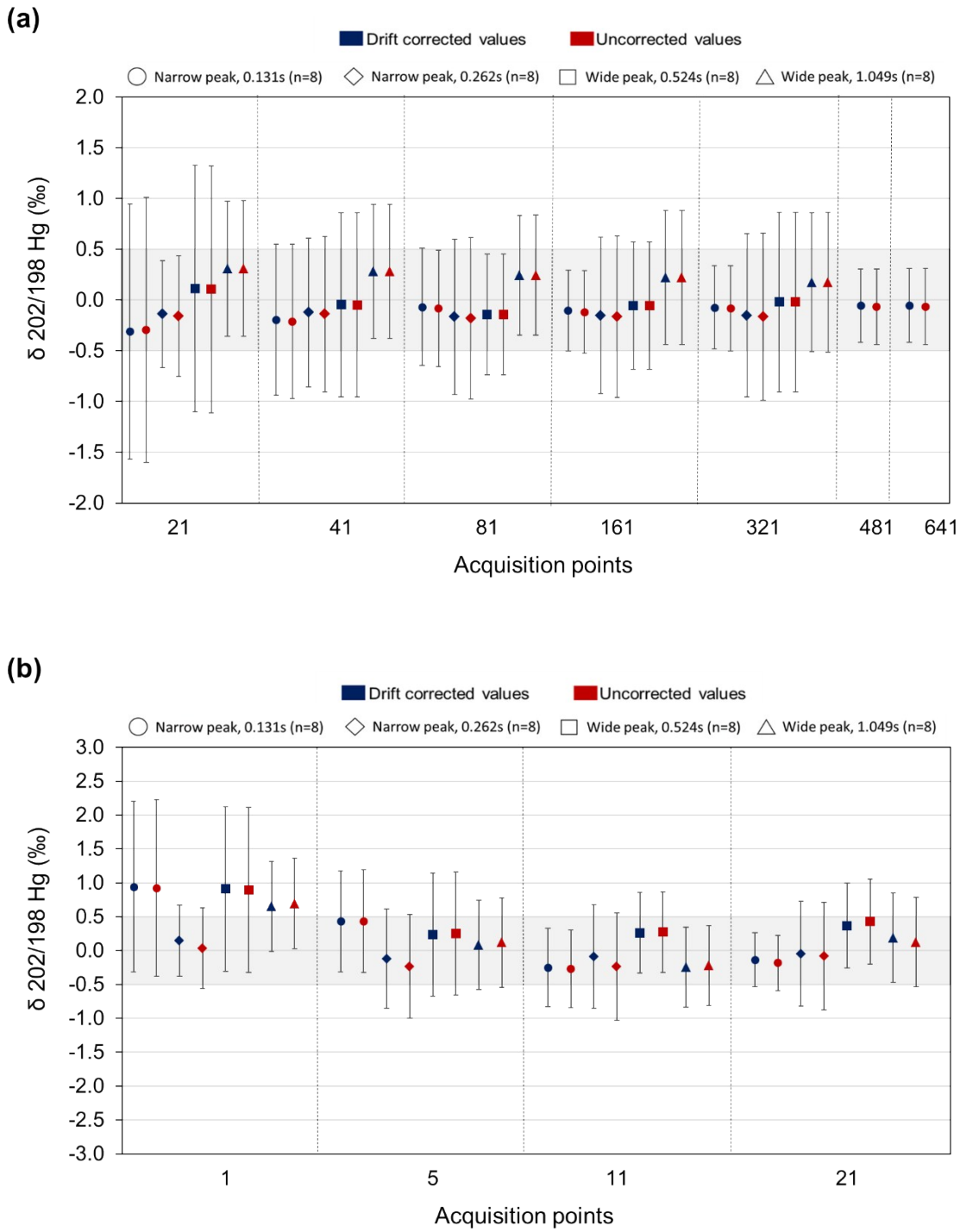

(c)
PbP
LRS
PAI
Narrow peak, 0.131s (n=8)
Narrow peak, 0.262s (n=8)
Wide peak, 0.524s (n=8)
Wide peak, 1.049s (n=8)
δ 201/198 Hg (‰)
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
Application range for LRS
Application range for PAI
Application range for PbP
1
5
11
21
41
81
161
321
481
641
Acquisition points

Figure S5. Influence of the time-lag correction of the Faraday cups in the external precision of δ^{202}Hg(II) when calculating the Hg(II)-specific isotope ratios by: (a) LRS and (b) PbP. Error bars represent the associated external precision (±2SD) for n=8 independent measurements. An optimal external precision interval of ±0.50 ‰ based on previous studies (Epov et al., 2010, 2008) is highlighted.



REFERENCES

Epov, V.N., Bérail, S., Jimenez-Moreno, M., Perrot, V., Pecheyran, C, Amouroux, D., Donard, O.F.X., 2010. Approach to measure isotopic ratios in species using multicollector-ICPMS coupled with chromatography. Anal. Chem. 82, 5652–62. https://doi.org/10.1021/ac100648f

Epov, V.N., Rodríguez-González, P., Sonke, J.E., Tessier, E., Amouroux, D., Bourgoin, L.M., Donard, O.F.X., 2008. Simultaneous determination of species-specific isotopic composition of Hg by gas chromatography coupled to multicollector ICPMS. Anal. Chem. 80, 3530–8. https://doi.org/10.1021/ac800384b