

ELECTRONIC SUPPLEMENTARY INFORMATION

COMPARISON OF DIFFERENT MASS BIAS CORRECTION PROCEDURES FOR THE MEASUREMENT OF MERCURY SPECIES-SPECIFIC ISOTOPIC COMPOSITION BY GAS CHROMATOGRAPHY COUPLED TO MULTICOLLECTOR ICP-MS

Laura Suárez-Criado, Silvia Queipo-Abad, Pablo Rodríguez-González*, José Ignacio García Alonso

Department of Physical and Analytical Chemistry, University of Oviedo, Julián Clavería, 8, 33006-Oviedo (Spain)

*Author for correspondence: rodriguezpablo@uniovi.es

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Table S1. GC-MC-ICP-MS operating conditions.

GC	Agilent 6890
Column	DB-5MS (5% diphenyl, 95% dimethylsiloxane, 30 m x 0.53 mm i.d. x 1µm)
Carrier gas	He
Injector temperature	250 °C
Volume of injection	2 µL
Injector purge time	1 min
GC-ICP-MS Interface T	270 °C
Initial temperature	60 °C
Initial time	1 min
Ramp	40 °C/min
Final temperature	250 °C
Final time	1 min
Total analysis time	6.8 min
MC-ICP-MS	Neptune Plus (Thermo Scientific)
RF power	1200 W
Resolution mode	Medium
Integration times	0.132 s
Cycles/Blocks	2500
Sample Ar gas flow	0.7 L/min
Nebulization Ar gas flow	0.5 L/min
Cooling Ar gas flow	15.2 L/min
Auxiliary Ar gas flow	0.8 L/min
Faraday Cups configuration	L4, L3 (¹⁹⁸ Hg), L2 (¹⁹⁹ Hg), L1 (²⁰⁰ Hg), C (²⁰¹ Hg), H1 (²⁰² Hg), H2 (²⁰³ Tl), H3 (²⁰⁵ Tl), H4

Figure S1. Schematic analytical setup of the GC-MC-ICPMS used in this work for the measurement of compound-specific Hg isotope ratios.

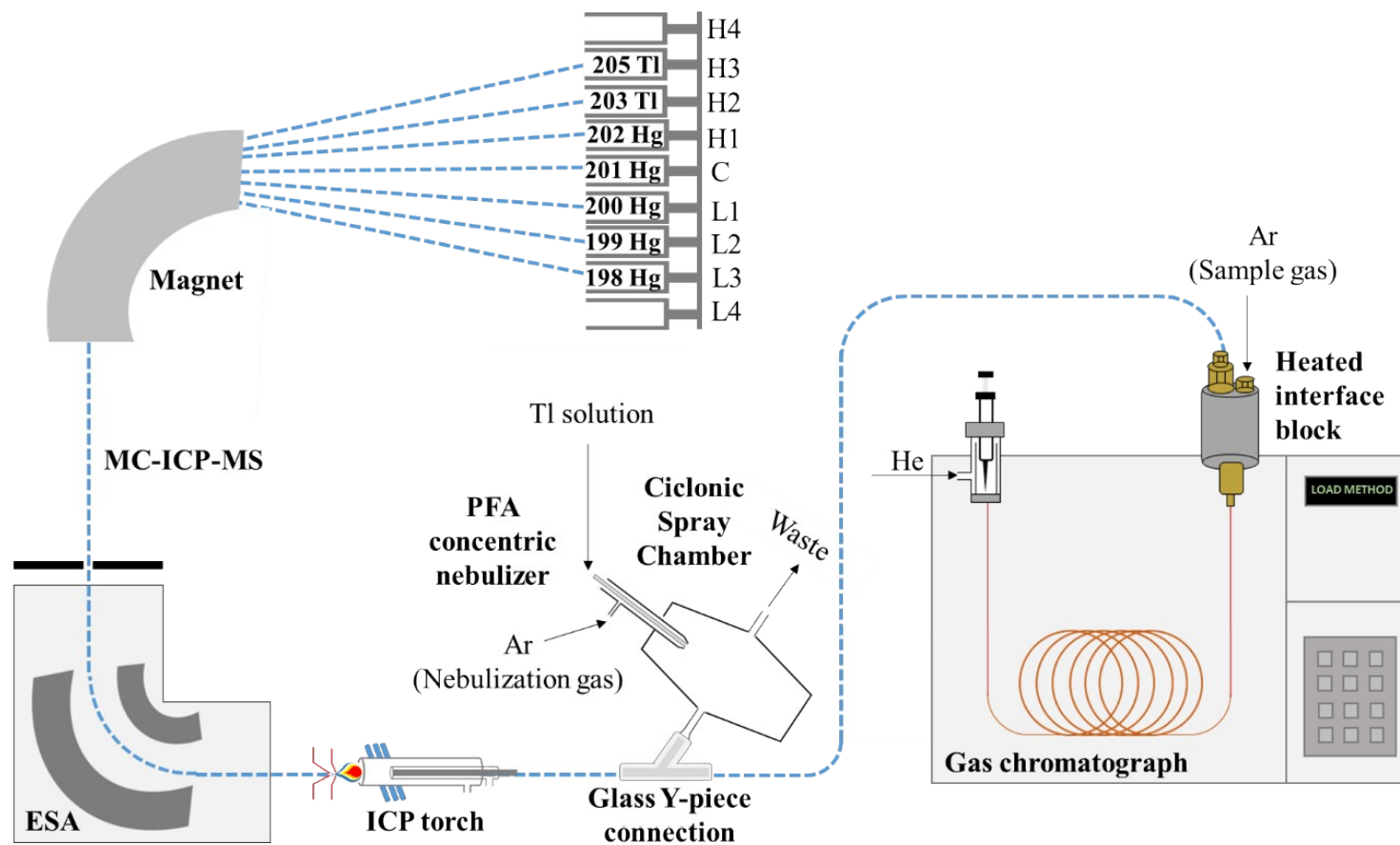


Figure S2. Process for the determination of mercury and thallium isotope ratios. 1) Signal profile for ^{198}Hg and ^{202}Hg for 321 consecutive data points (signal for ^{202}Hg shifted for clarity). 2) Measurement of the isotope ratio from the slope of the linear plot. 3) Correction for time-lag at ^{202}Hg and final isotope ratio. 4) Signal profile for ^{203}Tl and ^{205}Tl for 321 consecutive data points. 5) Calculation of the $^{205}\text{Tl}/^{203}\text{Tl}$ isotope ratio. 6) Determination of the residuals for thallium to check for mass bias alterations during the elution of the mercury peak.

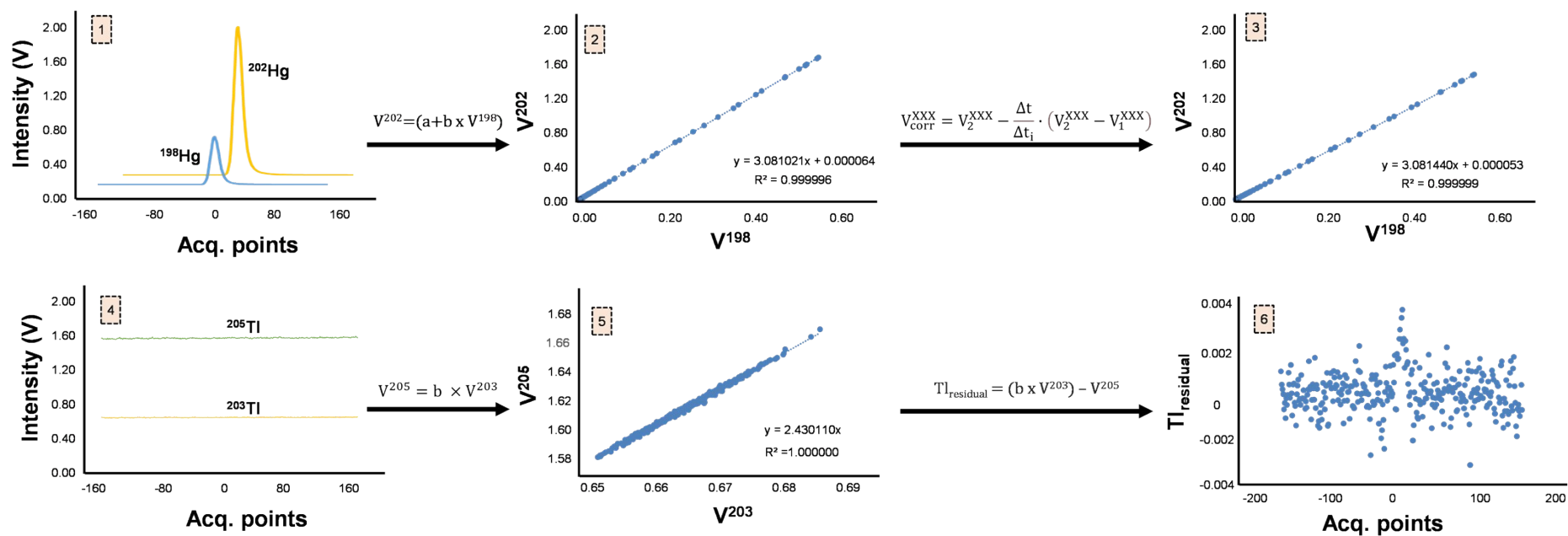


Figure S3. δ -values calculation. a) SSB and b) Baxter delta calculation model.

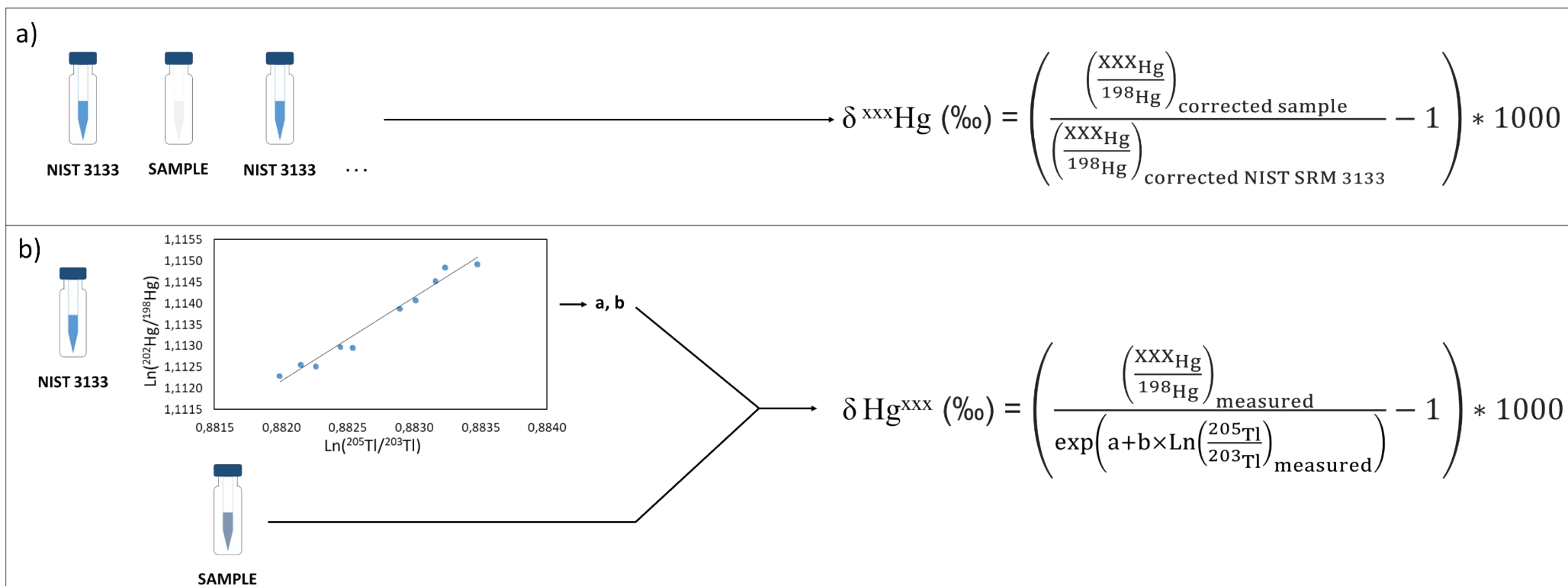


Table S2. Average NIST RM 8610 IR values and the internal precision expressed as $\pm 2SE$ calculated with Russell and Baxter for three independent measurement sessions with three different mass bias correction approaches: 1) 321 acquisition points of TI, 2) 27 acquisition points of TI and 3) point by point (Pbp).

Mass Bias Correction Model		Russell			Baxter	
Mass bias calculation procedure with TI		LRS-321 TI	LRS-27 TI	PbP – 321 TI	LRS-321 TI	LRS-27 TI
Session 1 NIST RM 8610 (n=8)	$^{199/198}\text{Hg}$	1.6871 ± 0.0005	1.6870 ± 0.0007	1.6869 ± 0.0008	1.6871 ± 0.0002	1.6871 ± 0.0003
	$^{200/198}\text{Hg}$	2.3042 ± 0.0008	2.3040 ± 0.0011	2.3037 ± 0.0014	2.3042 ± 0.0005	2.3042 ± 0.0005
	$^{201/198}\text{Hg}$	1.3114 ± 0.0005	1.3112 ± 0.0008	1.3109 ± 0.0013	1.3114 ± 0.0003	1.3111 ± 0.0005
	$^{202/198}\text{Hg}$	2.9611 ± 0.0008	2.9605 ± 0.0018	2.9597 ± 0.0033	2.9611 ± 0.0003	2.9608 ± 0.0009
Session 2 NIST RM 8610 (n=8)	$^{199/198}\text{Hg}$	1.6868 ± 0.0005	1.6869 ± 0.0005	1.6868 ± 0.0006	1.6868 ± 0.0002	1.6869 ± 0.0002
	$^{200/198}\text{Hg}$	2.3044 ± 0.0008	2.3045 ± 0.0012	2.3045 ± 0.0006	2.3044 ± 0.0003	2.3045 ± 0.0004
	$^{201/198}\text{Hg}$	1.3114 ± 0.0003	1.3115 ± 0.0006	1.3115 ± 0.0015	1.3114 ± 0.0001	1.3116 ± 0.0002
	$^{202/198}\text{Hg}$	2.9610 ± 0.0006	2.9613 ± 0.0015	2.9613 ± 0.0027	2.9610 ± 0.0002	2.9613 ± 0.0005
Session 3 NIST RM 8610 (n=8)	$^{199/198}\text{Hg}$	1.6871 ± 0.0008	1.6871 ± 0.0007	1.6871 ± 0.0007	1.6871 ± 0.0003	1.6871 ± 0.0003
	$^{200/198}\text{Hg}$	2.3044 ± 0.0010	2.3044 ± 0.0009	2.3043 ± 0.0012	2.3045 ± 0.0004	2.3044 ± 0.0003
	$^{201/198}\text{Hg}$	1.3114 ± 0.0005	1.3114 ± 0.0006	1.3113 ± 0.0012	1.3115 ± 0.0002	1.3115 ± 0.0002
	$^{202/198}\text{Hg}$	2.9612 ± 0.0014	2.9611 ± 0.0013	2.9608 ± 0.0032	2.9613 ± 0.0004	2.9611 ± 0.0005

Table S3. Average Hg(II)-NIST 3133 δ_{zero} (‰) and external precisions expressed as $\pm 2\text{SD}$ calculated with SSB and Baxter for three independent measurement sessions with three different mass bias correction calculation methods: 1) LRS for 321 acquisition points of Tl, 2) LRS for 27 acquisition points of Tl and 3) PbP approach.

Delta values calculation strategy		SSB			Baxter	
Mass Bias Correction Model		Russell	Russel	Russel	Baxter	Baxter
Mass bias calculation procedure with Tl		LRS-321 Tl	LRS-27 Tl	PbP – 321 Tl	LRS-321 Tl	LRS-27 Tl
NIST 3133 (n=26)	$\delta^{202}\text{Hg}$	0.07 \pm 0.41	0.11 \pm 0.70	0.14 \pm 1.26	0.06 \pm 0.46	-0.29 \pm 1.94
	$\delta^{201}\text{Hg}$	0.06 \pm 0.47	0.08 \pm 0.69	0.11 \pm 1.00	0.00 \pm 0.59	-0.13 \pm 0.97
	$\delta^{200}\text{Hg}$	0.02 \pm 0.43	0.03 \pm 0.50	0.05 \pm 0.77	0.00 \pm 0.50	-0.15 \pm 1.16
	$\delta^{199}\text{Hg}$	0.02 \pm 0.34	0.03 \pm 0.33	0.03 \pm 0.42	0.01 \pm 0.35	-0.14 \pm 0.87

Table S4. Average δ^{xxx} Hg(II) NIST RM 8610 (‰) and external precisions expressed as $\pm 2SD$ calculated with SSB and Baxter for three independent measurement sessions with three different mass bias correction calculation methods: 1) LRS for 321 acquisition points of Tl, 2) LRS for 27 acquisition points of Tl and 3) PbP approach.

Delta values calculation strategy		SSB			Baxter		Reference values
Mass Bias Correction Model		Russell	Russel	Russel	Baxter	Baxter	
Mass bias calculation procedure with Tl		LRS-321 Tl	LRS-27 Tl	PbP – 321 Tl	LRS-321 Tl	LRS-27 Tl	
NIST RM 8610 (n=24)	δ^{202} Hg	-0.59 ± 0.34	-0.61 ± 0.40	-0.77 ± 1.09	-0.60 ± 0.31	-0.60 ± 0.57	-0.56 ± 0.03
	δ^{201} Hg	-0.44 ± 0.35	-0.46 ± 0.46	-0.58 ± 0.92	-0.44 ± 0.44	-0.46 ± 0.74	-0.46 ± 0.02
	δ^{200} Hg	-0.27 ± 0.38	-0.28 ± 0.44	-0.36 ± 0.65	-0.27 ± 0.44	-0.25 ± 0.46	-0.27 ± 0.01
	δ^{199} Hg	-0.16 ± 0.40	-0.17 ± 0.38	-0.21 ± 0.43	-0.17 ± 0.44	-0.16 ± 0.45	-0.17 ± 0.01