Supplementary information

Applying standard addition to determine antimony isotopes in low-Sb samples using HG-MC-ICP-MS

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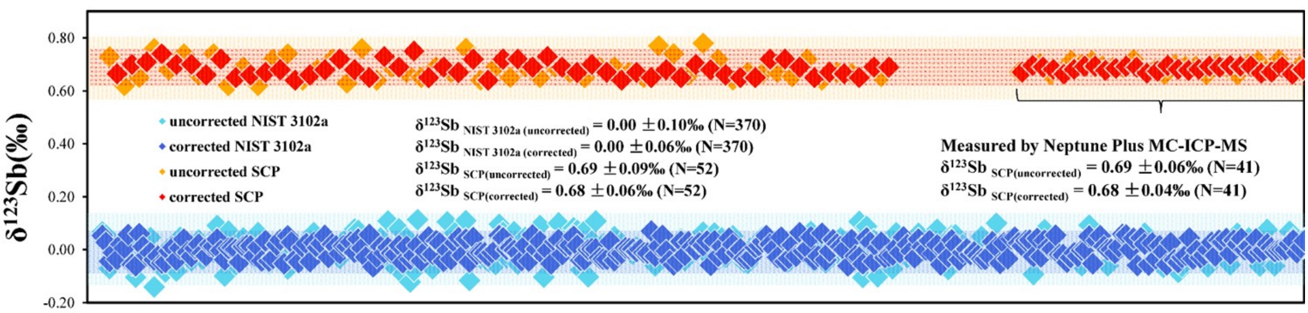
Revised version submitted to: JAAS
2024-10-25

Contents

Table S1. Operating parameters for Sb isotope measurement on HG-MC-ICP-MS

Parameters	Neptune plus	Nu plasma II
Cup configuration	L4 (^{111}Cd), L3 (^{112}Cd, ^{112}Sn), L2 (^{113}Cd), L1 (^{114}Cd, ^{114}Sn), C(^{117}Sn),H1(^{119}Sn),H2(^{121}Sb),H3 (^{123}Sb), H4 (^{126}Te)	L4(^{111}Cd),L3(^{112}Cd),L2(^{113}Cd), L1(^{114}Cd),Ax(^{115}In),H1(^{116}Cd), H2(^{117}Sn),H3(^{118}Sn),H6(^{121}Sb), H7(^{123}Sb),H8(^{125}Te)
Inlet system		
cool gas	15 L min^{-1}	13 L.min^{-1}
aux gas	0.80-1.15 L min^{-1}	0.85-0.9 L.min^{-1}
sample gas	0.85-1.10 L min^{-1}	0.90-1.30 L min^{-1}
RF power	1200W	1300W
sample cone	H type, Ni	Ni, 541b
skimmer cone	X type, Ni	Ni, 540
resolution mode	low	low
sample uptake	110 μL min^{-1}	110 μL min^{-1}
Aridus II		
spray chamber temperature	110°C	110°C
desolvator temperature	160°C	160°C
Ar sweep gas	2.0-2.5 L min^{-1}	1.8 L min^{-1}(adjusted daily)
nitrogen gas	1-6 mL min^{-1}	2-6 mL min^{-1}(adjusted daily)
Hydride generator		
Washing solution	1.5 M HCl	3 M HCl
$NaBH_4$	0.4 wt% $NaBH_4$ in 0.4 wt% NaOH	0.4 wt% $NaBH_4$ in 0.4 wt% NaOH
Sample media	1.5 M HCl	3 M HCl
Add Ar sweep gas	0.02-0.04 L min^{-1}	0.07~0.2 L min$_{-1}$
sensitivity	~2500V/ μg mL^{-1} for ^{123}Sb	~1500V/ μg mL^{-1} for ^{123}Sb
injecting concentration	3 ng mL^{-1}	6 ng mL^{-1}

Fig.S1 Long-term reproducibility of the corrected and uncorrected $\delta^{123}Sb$ value of NIST 3102a and SCP standard solutions.



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Text 1. The precision estimated by propagation error

The $\delta^{123}Sb_{spl}$ value is calculated from equation 10, and the precision can be estimated by error propagation[1,2], using the following equation:

$$\sigma_{spl} = \sqrt{(\frac{1}{f}\cdot\sigma_{mix})^2 + [(1-\frac{1}{f})\cdot\sigma_{std}]^2 + \left[\left(\frac{\delta^{123}Sb_{mix}}{-f^2} + \frac{\delta^{123}Sb_{std}}{f^2}\right)\cdot\sigma_f\right]^2} \quad (1)$$

where σ_{spl}, σ_{std} and σ_{mix} represent the two standard deviations (2SD) of $\delta^{123}Sb$ values of sample, standard solution, and mixed solution, respectively, and σ_f denote the 2SD of values of the relative proportions of sample and standard (***f***).

Eq 1 can be reduced to Eq 2:

$$\sigma_{spl} = \sqrt{(\frac{\sigma_{mix}}{f})^2 + (\frac{f-1}{f}\cdot\sigma_{std-3102a})^2 + \left[\left(\frac{\delta^{123}Sb_{std-3102a} - \delta^{123}Sb_{mix}}{f^2}\right)\cdot\sigma_f\right]^2} \quad (2)$$

In this study, two Sb standard solutions (NIST SRM 3102a and SCP) were used for SA method. So, the final calculated $\delta^{123}Sb_{spl}$ should be the mean value of the primary two $\delta^{123}Sb_{spl}$ using different Sb standard solutions:

$$\delta^{123}Sb_{spl}=1/2 \cdot (\delta^{123}Sb_{spl\ by\ 3102a}+\delta^{123}Sb_{spl\ by\ SCP}) \quad (3)$$

And the uncertainty can be estimated by error propagation:

$$\sigma_{spl} = \sqrt{(\frac{\sigma_{spl\ by\ 3102a}}{2})^2 + (\frac{\sigma_{spl\ by\ SCP}}{2})^2} \quad (4)$$

$\delta^{123}Sb_{spl\ by\ 3102a}$ and $\delta^{123}Sb_{spl\ by\ SCP}$ are the calculated $\delta^{123}Sb_{spl}$ using NIST 3102a and SCP as the standard addition solution. The $\sigma_{spl\ by\ 3102a}$ and $\sigma_{spl\ by\ SCP}$ represent their precision with 2SD.

As NIST 3102a was used as the isotope standard in this study, $\delta^{123}Sb$ should be zero; $\sigma_{std-3120a}$ in Eq 2 is 0.02‰, and $\sigma_{std-SCP}$ is 0.04‰ as shown in Fig 2. Hence, the calculated $\sigma_{spl\ by\ 3102a}$ is always less than $\sigma_{spl\ by\ SCP}$. To facilitate the assessment of propagation errors, we can substitute $\sigma_{spl\ by\ SCP}$ for $\sigma_{spl-3102a}$. Thus,

$$\sigma_{spl} \lesssim \sqrt{\frac{1}{2}}\cdot\sqrt{(\frac{\sigma_{mix}}{f})^2 + (\frac{f-1}{f}\cdot\sigma_{std-SCP})^2 + \left[\left(\frac{\delta^{123}Sb_{std-SCP} - \delta^{123}Sb_{mix}}{f^2}\right)\cdot\sigma_f\right]^2} \quad (5)$$