

Supplementary Information

A novel chemical purification method for accurate Sn isotope measurement by MC-ICP-MS

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Section 1 Evaporation and re-dissolution experiment

Six different types of acidic solutions were prepared for evaporation and re-dissolution experiments. These solutions comprised concentrated HCl, concentrated HNO₃, 3M HCl, 3M HCl + 0.5%HF, 2M HNO₃ and 2M HNO₃ + 0.5% HF, each with a volume of 20mL and containing ~100ng/mL of Sn. For each type of solution, three parallel samples and one blank were set up. Aliquots were taken

when the sample solvents were evaporated at 90°C for 6 hours, 12 hours and nearly drying out, respectively, as well as after re-dissolution with 5mL of the initial acidic solution for Sn yield check. Before taking the aliquots, the samples were cooled to room temperature, and their remaining solution was weighted. Aliquots were then taken from the sample solution, accounting for ~5% of the remaining solution volume. After taking the aliquots, the sample solution continued to evaporate. The aliquots were diluted to 4mL with 3% HNO₃ for Sn concentration measurement. By comparing the masses of the aliquot and remaining sample solution, the Sn yields during evaporation and re-dissolution process can be calculated.

Section 2 TBP extraction from the TRU-column elution

A poly-prep column charged with 2mL TRU resin was prepared for the TBP-bearing solution collection. According to the published elution scheme (Table 1), the resin was firstly conditioned and eluted with 18mL 0.5M HCl and 10mL 0.25M HCl in orderly. Following this, additional 10mL Milli-Q and 5mL 0.4M HNO₃ were respectively added to the column. This Milli-Q and HNO₃ mixed elution was collected for the subsequent TBP extraction.

To extract the potential TBP from the elution, the n-hexane was employed as the extractant. First, 0.5 mL n-hexane was added to the elution and the mixture was shaken vigorously for 1 minute. The solution was allowed to settle down until two distinct layers formed. The supernatant was collected into a 2 mL transparent screw chromatographic bottle and sealed. The above extraction was repeated three times, resulting in the acquisition of ~1.5 mL n-hexane extractants. Second, the extracted n-hexane was dehydrated by adding 0.2g NaSO₄ (c) into the chromatographic bottle and settled for 12 hours. The dehydrated n-hexane solution was then transferred into another chromatographic bottle and diluted 1000 times before GC-MS analysis.

Section 3 TBP identification by GC-MS

The TBP analysis was performed on the gas chromatography-mass spectrometry (Agilent 7200GC-QTOF, USA), at SESS of Tianjin University, China. The TBP analyzing protocol was summarized in Table S1.

Table S1 Protocol for TBP identification on GC-MS

Operating Condition	Parameters
Column	DB-5MS UI (Agilent)
Carrier gas	He
Injection mode	Split-less
Total flow	24.2mL/min
Sample injection volume	1μL
Oven heating	50°C for 1min increase to 240°C with a rate of 15°C/min, and keeping for 15min
EI temperature	230°C
EI energy	70.0V
MS flow rate	1.2mL/min

Table S2 Sn content variation during the solvent evaporation and re-dissolution using different acidic media

Acidic Media	Initial Sn content (ng)	Recovery* Evaporating for 6h	Recovery Evaporating for 12h	Recovery Drying out (~15h)	Recovery Re-dissolution	Blank (ng)
HCl (conc)	2250.96	96% (n=3)	99% (n=3)	99% (n=3)	90% (n=3)	2.39
3M HCl	2255.22	99% (n=3)	100% (n=3)	100% (n=2)	92% (n=3)	0.58
3M HCl +0.1M HF	2203.67	101% (n=3)	101% (n=3)	101% (n=3)	92% (n=3)	0.63
HNO ₃ (conc)	2280.03	101% (n=3)	102% (n=3)	86% (n=3)	86% (n=3)	0.10
2M HNO ₃	2242.99	98% (n=3)	99% (n=3)	99% (n=3)	93% (n=3)	0.00
2M HNO ₃ + 0.1M HF	2144.96	101% (n=3)	100% (n=3)	103% (n=3)	99% (n=3)	0.00

* All the recoveries above are calculated based on Sn content of the initial solutions

Table S3 Comparison of $\delta^{122}\text{Sn}$ ratios of previous study and this work

Reference Material	Tin isotope ratios (‰)	Literature
BHVO-2	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.18±0.04 (n=8)	Wang et al., 2017
	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.62±0.10 ^a (n=6)	Creech et al, 2017
	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.38±0.14 (n=6)	Wang et al., 2022
	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.35±0.02 (n=8)	She et al., 2023
	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.34±0.07 (n=12)	This study
AGV-2	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.48±0.20 ^a (n=1)	Creech et al, 2017
	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.26±0.06 (n=6)	Wang et al., 2022
	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.29±0.02 (n=6)	She et al., 2023
	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.27±0.07 (n=7)	This study
BCR-2	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.57±0.15 ^a (n=4)	Creech et al, 2017
	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.31±0.04 (n=9)	She et al., 2023
	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.27±0.04 (n=11)	This study
JG-2	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.44±0.10 (n=6)	Wang et al., 2022
	$\delta^{122}\text{Sn}_{\text{SRM}_3161a}$ 0.50±0.03 (n=3)	She et al., 2023

a $\Delta^{122/118}\text{Sn}_{\text{Sn}_{\text{IPGP-SRM}_3161\text{a}}} = 0.25 \pm 0.08\text{‰}$ (long-term precision 2s.d., by She et al., 2020)

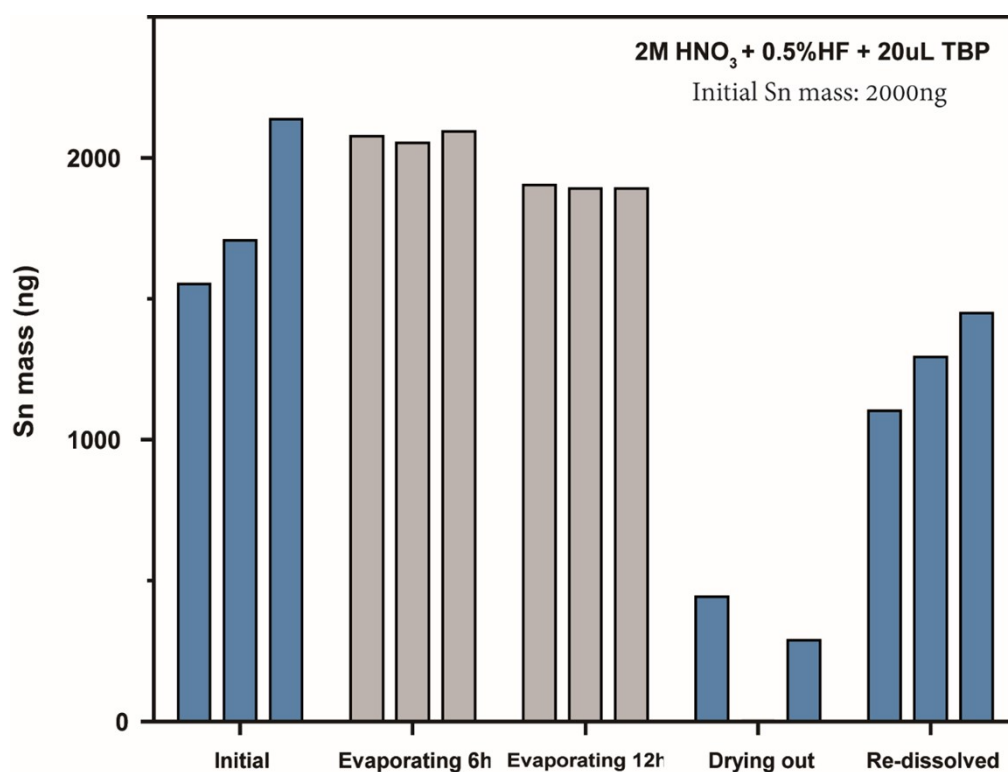


Figure S1 Sn content variation during solvent evaporation and re-dissolution. The solvent was prepared by 20 mL 2M HNO₃+0.5%HF and trace TBP (20uL). Approximately 2000ng Sn was doped into the solution, thus obtained a Sn concentration of ~100ppb. Three parallel samples were set for the experiment. Aliquots were taken when the sample solvent was evaporated for 6 hours, 12 hours, nearly drying out, as well as redissolved with 5mL 2M HNO₃+0.5%HF. The blue filled rectangular highlights the anomalous Sn loss.

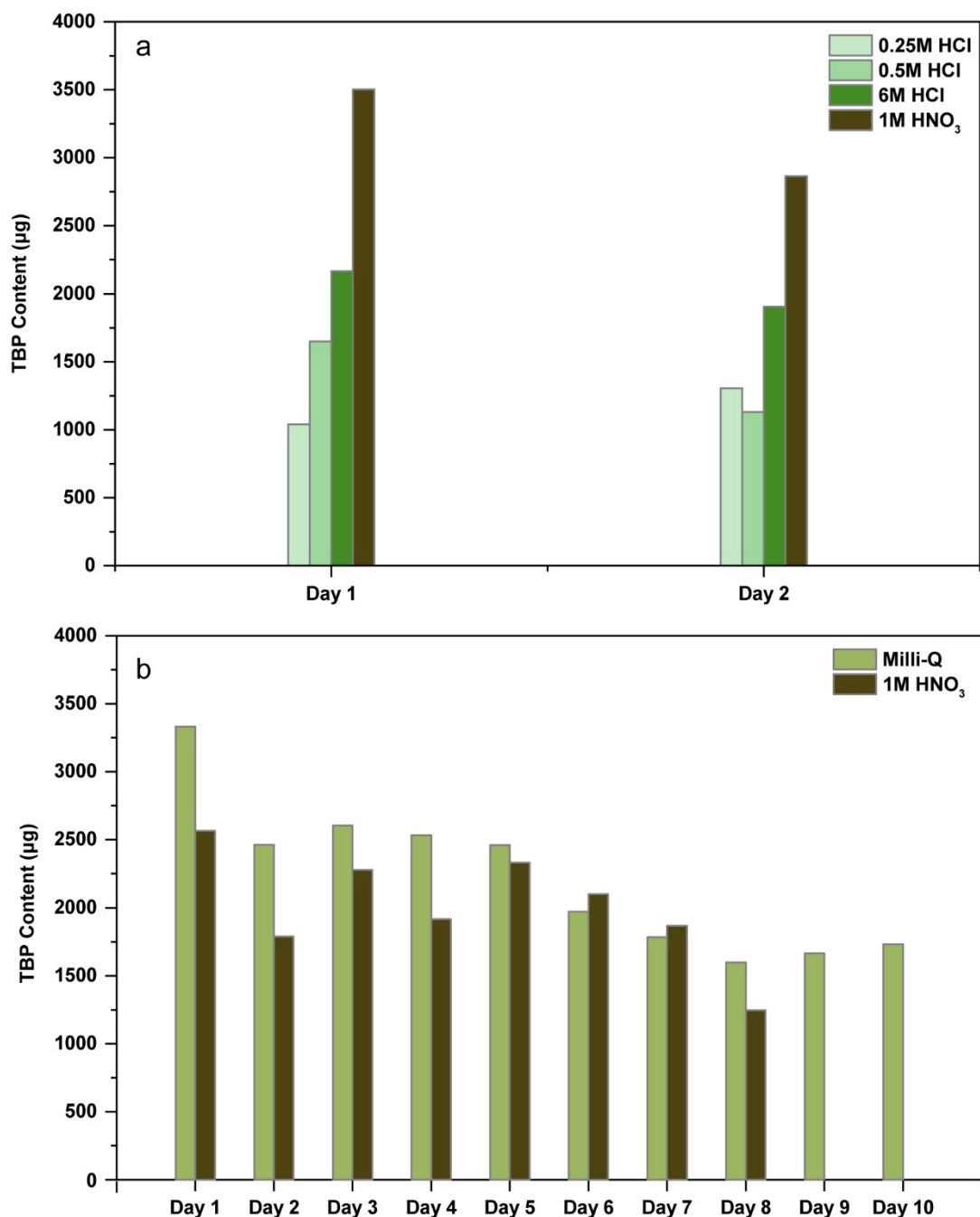


Figure S2 Efficiency of different wash solutions (Milli-Q, 0.25M HCl, 0.5M HCl, 6M HCl and 1M HNO₃) rinsing TBP from TRU resin. (a) TBP contents detected from the washing solutions of 0.25M HCl, 0.5M HCl, 6M HCl and 1M HNO₃ after soaking the TRU resin for two days. The washing solutions were replaced to fresh solutions every 24 hours. (b) TBP contents detected in the washing solutions of 1M HNO₃ and Milli-Q for respectively 8 days and 10 days' rinsing. The washing solutions were replaced to fresh solutions every 24 hours.

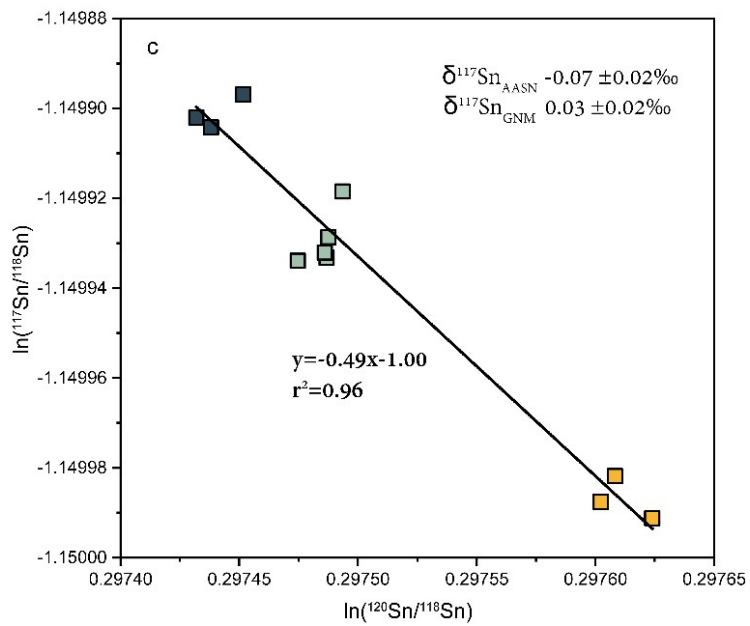
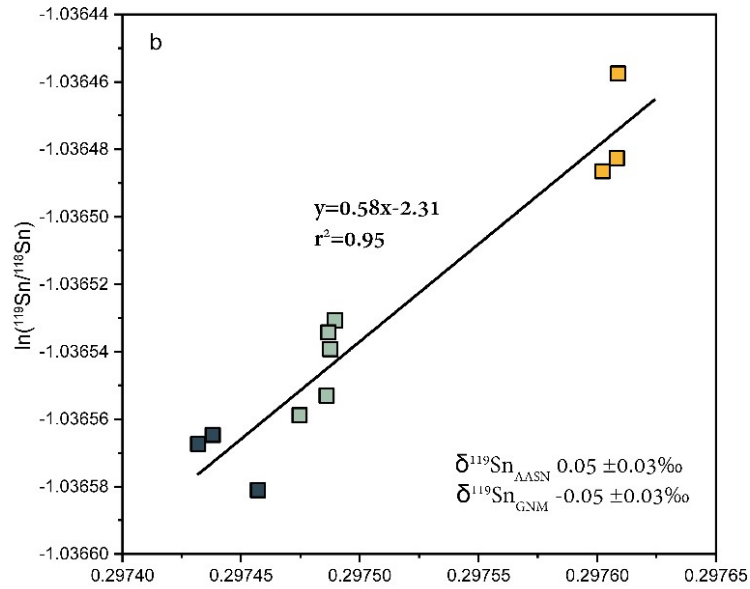
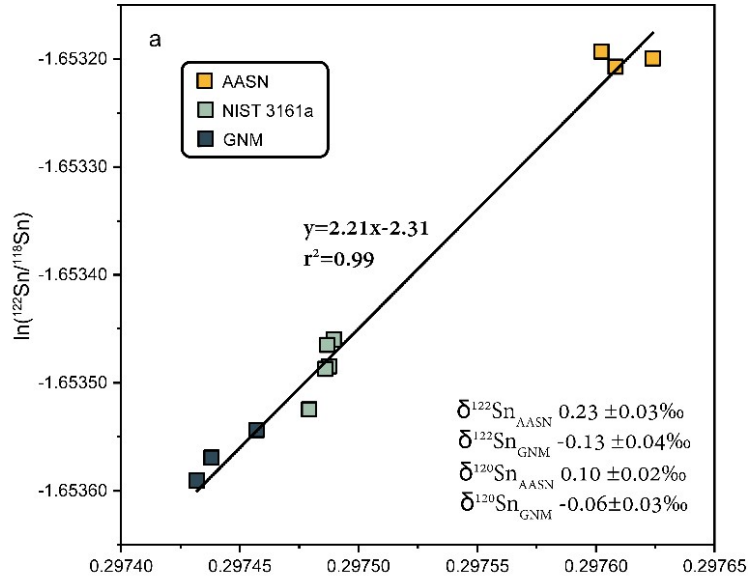


Figure S3 Sn isotopic composition of single-element standard solutions GNM (short for GNM-SSN-002-2013) and AASN (short for IV-AASN1) before the column purification (a) $\ln(^{120}\text{Sn}/^{118}\text{Sn})$ Vs $\ln(^{122}\text{Sn}/^{118}\text{Sn})$ (b) $\ln(^{120}\text{Sn}/^{118}\text{Sn})$ Vs $\ln(^{119}\text{Sn}/^{118}\text{Sn})$ (c) $\ln(^{120}\text{Sn}/^{118}\text{Sn})$ Vs $\ln(^{117}\text{Sn}/^{118}\text{Sn})$.