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A single-step purification method for the precise determination of antimony isotopic composition of environmental, geological and biological samples by HG-MC-ICP-MS

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Antimony isotopes have been recently used as geochemical tracers for archeological or environmental purposes. The purification of antimony in samples with a low Sb concentration and a complex matrix is a critical step to measure $^{123}\text{Sb}/^{121}\text{Sb}$ ratio by hydride generation coupled to a multi-collector inductively coupled plasma mass spectrometer (HG-MC-ICP-MS). A single-step purification method based on the use of Thiol-functionalized mesoporous Silica Powder (TSP) was developed to separate antimony from other elements. Low amount of Sb (40-100 ng) is required thanks to low procedural blanks (< 1 ng Sb) and an efficient removal (98.7% on average) of potential interfering elements (including As, Cd, Co, Cr, Cu, Fe, Ni, Pb, Se, Sn). The method was validated on fourteen Certified Reference Materials (CRM) including environmental materials (sediments, road dust, soils), biological materials (plants, human blood and urine), rocks and manufactured materials (fly ash, polyethylene). Antimony was recovered at $100 \pm 7\%$ and no isotopic fractionation occurred during the procedure. The isotopic composition of Sb ($\delta^{123}\text{Sb}$) in the CRM ranged between $-0.52 \pm 0.06\%$ (2 sd) and $0.40 \pm 0.03\%$ (2 sd) relative to an in-house isotopic standard solution (SPEX). The external reproducibility was evaluated at 0.05% (2 sd) for $\delta^{123}\text{Sb}$, based on replicated measurements of independently digested and purified CRM. CRM GSD-3, SDO-1 and BCR-176R exhibited $\delta^{123}\text{Sb}$ value similar to previous measurements by Rouxel et al. (2003)¹. In addition, three pure standard solutions of Sb were measured against the in-house isotopic standard solution. Two of them were isotopically similar ($\delta^{123}\text{Sb} = 0.00 \pm 0.05\%$, Sb Fisher Scientific[®] and PlasmaCAL-1, SCP Science[®]) while a $\delta^{123}\text{Sb}$ value of $0.62 \pm 0.02\%$ was measured for the third one (PlasmaCAL-2, SCP Science[®]). This raises the importance of choosing a common isotopic standard solution to compare already published and future Sb isotope data.

1. Introduction

Antimony is a pollutant of emerging concern due to recent increase of anthropogenic emissions from various sources (waste incineration, road traffic, mining and metallurgical activities)². Antimony is also a contaminant of natural origin, contaminated by ancient Sb mines varied over a wide range ($-0.06\% < \delta^{123}\text{Sb} < +0.83\%$) allowing to determine the contribution of two sub-watersheds to the total dissolved Sb load.

Antimony has two stable isotopes, ^{121}Sb (57.21%) and ^{123}Sb (42.79%)³. As for other trace metal contaminants, the isotopic composition of Sb might be used to track the sources of this element and investigate the processes involved in its transport in the environment^{4,5}. However, there is still a considerable amount of work before this new tool being validated for a broad range of applications. Pioneer work by Rouxel et al. (2003)¹ showed that natural Sb isotopic variation is wide enough to apply this tool as geochemical tracer. More recently, several studies focused on the application of Sb isotopes in archaeology and attempted to identify the provenance of antimony ores used to manufacture ancient Roman glass and bronze age artefacts and to trace ancient trade routes⁶⁻¹². Resongles et al. (2015)¹³ showed that Sb isotopic composition in surface waters (river water, groundwater)^{13,15,16} or for solid samples highly concentrated with Sb (stibnite)¹⁶. However, we faced major drawbacks using these materials such as extended processing times and clogging due to the low permeability of cotton fibres or cellulose, as well as uncomplete Sb recovery for geologic and

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

1 Table 1: Synthesis of existing strategies for Sb purification and Sb isotope analyses by MC-ICP-MS

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Sample type (number of samples)	Antimony pre-concentration and purification				Antimony isotope analysis by MC-ICP-MS		Reference
	Sorbent used for Sb purification Step 1	Sorbent used for Sb purification Step 2	Mass of Sb processed (ng)	Purification yield (%)	Sample introduction system	Concentration of the sample introduced in MC-ICP-MS	
Seawater (n=17), geological, environmental and anthropogenic samples (n=14)	Biorad AG50-X8 (cation removal)	Thiol cotton fiber (TCF)	50 - 100	n.s.	Dry plasma (Hydride Generation)	2 - 10 $\mu\text{g L}^{-1}$	Rouxel et al. (2003) ¹
River water (n=2)	Milled TCF		150 - 350	> 95	Wet plasma	n.s.	Asaoka et al. (2011) ¹⁵
Stibnite (n=2), mine drainage water (n=1)	TCF		150 - 350	> 95	Wet plasma	50 $\mu\text{g L}^{-1}$	Tanimizu et al. (2011) ¹⁶
Stibnite (n=10), ancient glass (n=69)	Dowex AG50-X8 (cation removal)	Amberlite IRA 743 (removal of S, Al and As)	100000	> 84	Wet plasma (Cyclonic/Scott dual spray chamber)	n.s.	Lobo et al. (2012, 2013, 2014) ⁶⁻⁸ , Degryse et al. (2015) ⁹
River waters (n=14)	Thiol-cellulose Powder (TCP)		100	96 \pm 2	Dry plasma (Hydride Generation)	1 $\mu\text{g L}^{-1}$	Resongles et al. (2015) ¹³
Stream sediment (n=1) and soil (n=1)	AG 1-X4 (Sb pre-concentration)	AG 50W-X8 (cation removal)	> 300	> 94.8	Wet plasma (Cyclonic/Scott dual spray chamber)	200 $\mu\text{g L}^{-1}$	Liu et al. (2020) ¹⁴
Contaminated river and groundwater samples (n=8)	Thiol-silica		1000 - 2000	> 95.2	Dry plasma (Desolvation system)	75 - 100 $\mu\text{g L}^{-1}$	Li et al. (2021) ¹⁷

n.s. not specified

3 environmental samples (unpublished data). Recently, Li et al.²⁵ generation separates Sb from the matrix; thus, hydride non-
4 (2021)¹⁷ proposed a new single-step purification method based²⁶ forming elements do not reach the plasma, avoiding to create
5 on thiol-functionalized silica. Antimony was successfully²⁷ potential non-spectral interferences.
6 purified (Sb recovery of 95.2%) from water samples²⁸ In the present study, we tested Thiol-functionalized mesoporous
7 contaminated by the Xikuangshan antimony mine (China) that²⁹ Silica Powder (TSP) for a single-step purification procedure of Sb in
8 presented extremely high Sb concentrations (up to 30 mg L^{-1}).³⁰ various environmental, geological and biological Certified Reference
9 However, thiol-functionalized silica has never been applied³¹ Materials (CRM) having a large range of Sb concentrations and matrix
10 to the separation of Sb from complex solid matrices with low Sb³² types. This material, synthesised by the French company Sikemia®, is
11 content using a single-step procedure.³³ a mesoporous material; it has a high porosity and is calibrated in size
12 Depending on the Sb concentration in purified samples,³⁴ and specific surface area, which is 10⁴ times larger than cellulose
13 different sample introduction techniques have been applied for³⁵ used in our previous study¹³. Thiol-functionalized silica has a high
14 MC-ICP-MS analysis (Table 1). For high Sb concentration (> 50³⁶ adsorption capacity for various metals (Pb, Pd, Hg, Cd...)²²⁻²⁵
15 $\mu\text{g L}^{-1}$), wet plasma conditions¹⁴⁻¹⁶ or a desolvation system¹⁷ can³⁷ including for Sb¹⁷. TSP can be easily packed in disposable cartridges
16 be used. For low Sb concentrations, Hydride Generation (HG)-³⁸ connected to a peristaltic pump to provide continuous flow
17 MC-ICP-MS is required. This technique, due to its highly efficient³⁹ processing at a constant rate. The purification procedure adapted
18 sample transport, has the advantage to increase sensitivity and⁴⁰ from previous studies^{1,13,26} was applied on fourteen geological (ore
19 thus decrease the Sb concentration required in analysed⁴¹ and rocks), environmental (soils, sediments, road dust, fly ash,
20 samples compared to other introduction systems (wet plasma,⁴² polyethylene) and biological (plants, human blood and urine)
21 desolvation) (Table 1). In addition, even though the purification⁴³ Certified Reference Materials. The reproducibility and efficiency of
22 step remains essential to remove hydride forming elements⁴⁴ the purification method were assessed and the Sb isotopic
23 (e.g. As, Pb, Se, Sn)¹⁸ and transition metals (e.g. Cd, Co, Cr, Cu,⁴⁵ composition of the CRM was determined by HG-MC-ICP-MS.
24 Fe, Ni) which may inhibit Sb hydride formation¹⁹⁻²¹, hydride

1 Table 2: Summary of the digestion procedures used for the different CRM types.

CRM type	CRM name	Amount of CRM digested	Acid mixture
Biological fluids	Clincheck® Urine control level II, Seronorm™ whole blood II	3 mL	Analpure HNO ₃ (3 mL)
Low-density polyethylene	ERM-EC680m	50 mg	
Soils	NIST 2711a	150 mg	Analpure HNO ₃ (3 mL) + Suprapur® HF (1 mL) + Suprapur® HCl (1 mL)
Plants	NCS-DC-73349, BCR-482	500 mg	
Sediments	NCS-DC-70317, PACS-3, GSD-3	50 mg	
Ore and rocks	GXR-4, SDO-1	50 mg	
Fly ash, road dust	BCR-176R, BCR-723	50 mg	

2. Material and methods

2.1. Chemical reagents and materials

Sample preparation was carried out in a class 10,000 cleanroom facility equipped with a class 100 laminar-flow clean bench. Ultrapure water (Milli-Q®, resistivity > 18.2 MΩ cm, Q-POP Element system, Millipore) was used for all experiments and reagent preparations. All material (e.g. sample bottles, tubes, SPE cartridges, pipette tips...) was soaked in 10% w/w analytical grade HCl for 48 h and rinsed three times with ultrapure water before use. Purification of antimony was carried out using 0.2 g (± 10%) of Thiol-functionalized Silica Powder (hereafter referred to as TSP) filled in 1 mL polypropylene SPE cartridges fitted with polyethylene frits (Supelco®). TSP was purchased from Sikémia® (Montpellier, France) after being prepared on special request from commercial silica powder (Geduran® Si 60, Merck, grain size 40–63 μm). Brunauer–Emmett–Teller (BET) analysis made by Sikémia® showed that TSP has a specific surface of 416 m² g⁻¹ versus 0.04 m² g⁻¹ for the thiol cellulose powder used previously¹³. The functionalisation rate was roughly estimated by Sikémia at one thiol function per nm² based on thermogravimetric analysis and assuming that the weight loss is due to grafted silanes. Both the grain size and specific surface area are similar with the thiol-functionalized silica used by Li and al. (2021)¹⁷.

Suprapur® 30% w/w HCl (Merck), Analpure 67% w/w HNO₃ (Analytika®), and Suprapur® 40% w/w HF (Merck®) were used for sample digestion, sample preparation, and analysis. A reducing solution was prepared daily by dissolving analytical grade ascorbic acid (Sigma-Aldrich®) and Suprapur potassium iodide (Merck®) at 10% w/v each in ultrapure water. A solution of sodium borohydride (1% w/v) stabilised with 0.05% w/v sodium hydroxide (both 99.99% trace metal basis, Sigma-Aldrich) was prepared daily by dissolving the appropriate amount of compounds in ultrapure water and filtrated. The pure Sb standard solution used as in-house isotopic standard was purchased from SPEX CertiPrep (Sb 1000 μg mL⁻¹ in 20% w/w HCl, batch number 24-175SBX, hereafter named “SPEX”).

This solution was preferred to previously used PlasmaCAL-1 (SCP Science®)¹³, chosen for its appropriate matrix for hydride generation (20% w/w HCl) and its promiscuity with the isotopic standard used in Resongles et al. (2015)¹³ ($\delta^{123}\text{Sb} = 0.04 \pm 0.08\%$, 2 sd, n=6). Three other pure Sb standard solutions were measured for their isotopic ratio and named “Fisher” (Sb 1001.2 μg mL⁻¹ in 20% w/w HCl, lot number 682785, Fisher Scientific®), “PlasmaCAL-1” and “PlasmaCAL-2” (PlasmaCAL ICP/ICPMS Standard-Antimony 1000 μg mL⁻¹ in 4% w/w HNO₃, lot number SC0108283 and S170206013, respectively, SCP Science®).

2.2. Certified Reference Materials

A series of fourteen Certified Reference Materials (CRM) was used to evaluate the quality of the Sb purification procedure for different types of environmental, geological, and biological materials of interest in environmental studies. Environmental CRM consisted of plants (NCS-DC-73349, BCR-482), soils (NIST SRM 2711a), river water (NIST 1643f), stream sediments (NCS-DC-70317, GSD-3), marine sediment (PACS-3) and anthropogenic materials including incinerator fly ash (BCR-176R), road dust (BCR-723), low-density polyethylene (ERM-EC680m). The geological CRM were composed of copper mill-head (GXR-4) and shale (SDO-1). Finally, biological fluids include human urine (Clincheck® Urine control level II) and human blood (Seronorm™ whole blood II).

NIST 2711a and NIST 1643f were bought from the National Institute of Standards and Technologies (NIST®, USA); BCR-176R, BCR-482, BCR-723 and ERM-EC680m were obtained from the European Institute for Reference Material and Measurements (IRMM, Belgium); NCS-DC-73349 and NCS-DC-70317 were bought to the NCS Testing Technologies Company (China); PACS-3 was purchased from the National Research Council of Canada (NRCC, Canada). Clincheck® Urine control level II was bought to Recipe company (Germany); Seronorm™ whole blood II was obtained from SERO AS (Norway). SDO-1, GXR-4 (USGS, USA) and GSD-3 (alias GBW07303, IGGE, China) are no longer marketed; they were kindly provided by the CRPG (Nancy, France).

1

2 **2.3. Sample digestion**

3 All CRM were digested using microwave-assisted acid
4 digestion (UltraWAVE, Milestone®) and with different acid
5 mixtures depending on their nature (Table 2). Three millilitres
6 of urine (Clincheck® Urine control level II) and blood
7 (Seronorm™ whole blood II), and 0.05 g of polyethylene (*ERM-*
8 *EC 680m*) were weighed in PTFE microwave tubes and digested
9 with 3 mL of concentrated HNO₃. Fifty milligrams of sediments
10 (*NCS-DC-70317*, *PACS-3*, and *GSD-3*), rocks (*GXR-4*, *SDO-1*), fly
11 ash (*BCR-176R*) and road dust (*BCR-723*), 150 mg of soil (*NIST*
12 *2711a*) and 500 mg of plants (*NCS-DC-73349*, *BCR-482*) were
13 weighed in PTFE microwave tubes and digested with 3 mL of
14 concentrated HNO₃, 1 mL of concentrated HF and 1 mL of
15 concentrated HCl. Triplicates were made for *GXR-4*, *GSD-3*, *BCR-*
16 *723*, and *BCR-482* to evaluate the reproducibility of the
17 digestion method. Digestion blanks for both digestion
18 procedures were performed as well.

19 The samples were heated from ambient temperature to
20 200 °C in 25 min and maintained at 200 °C for 10 min. Once the
21 samples had cooled, they were transferred in 30 mL PTFE vials.
22 Next, all samples were evaporated at 75 °C maximum to prevent
23 antimony volatilisation due to high temperature¹⁵. Finally, the
24 dry residue was re-dissolved in 5 mL of 1.5 M HNO₃, vials were
25 placed in an ultrasound bath for one hour and then heated
26 hermetically closed at 80 °C for one night.

27 Only *BCR-723* (road dust) showed dark particles in the final
28 digest solution probably consisting of black carbon. These
29 solutions were filtrated with 0.22 µm PVDF filters previously
30 rinsed with 1.5 M HNO₃. A filtration blank (1.5 M HNO₃) was
31 performed and showed that no significant amount of Sb was
32 released from the filter.

33 **2.4. Antimony purification**

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73 Table 3: Elution scheme for purification of Sb using Thiol-functionalized Silica Powder.

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Step	Volume (mL)	Eluent
1 Cleaning	10	Ultrapure water
Cleaning	5	6 M HCl
Cleaning	10	Ultrapure water
2 Conditioning	10	0.5 M HCl
3 Sample loading	10	0.5 M HCl, 0.5% w/v KI-AA
4 Washing	5	0.5 M HCl
5 Washing	6	2.5 M HCl
6 Sb elution (collection of purified sample)	6	6 M HCl

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76

34 The procedure for antimony purification was adapted from
35 Resongles et al. (2015)¹³. An aliquot of the digest solutions
36 containing 120 ng of Sb, when possible, was evaporated at 75 °C
37 in PTFE vials. Residues were dissolved in 10 mL of 0.5 M HCl, an
38 aliquot of the solution was kept to check Sb concentration.

39 Water sample (*NIST 1643f*) did not undergo through the
40 digestion process, it was directly acidified to 0.5 M HCl. Sb(V)
41 was reduced into Sb(III) by adding 10% w/v of KI-ascorbic acid
42 (KI/AA) solution to obtain a final concentration of 0.5% w/v and
43 allowing a 3 h reduction time¹⁵. The elution scheme is
44 summarised in Table 3. The TSP cartridges (0.2 g or 0.7 mL TSP)
45 were set on a Gilson® peristaltic pump with 1.02 mm i.d. Tygon®
46 tubing allowing to run six samples simultaneously (Figure S1).
47 The pump speed was set at 8 rpm, corresponding to a flow rate
48 of 1.0 mL min⁻¹. First, the system was cleaned by delivering
49 successively 10 mL of ultrapure water, 5 mL of 6 M HCl and 10
50 mL of ultrapure water. TSP was then conditioned with 10 mL of
51 0.5 M HCl. Next, the samples were loaded in 0.5 M HCl, 0.5%
52 w/v KI/AA. One hundred ng of Sb were loaded except for
53 *Seronorm™ Whole Blood level II* (80 ng), and *NCS-DC-73349* (37
54 ng). Antimony was adsorbed on the TSP while major elements
55 and metals passed through with no interaction or weaker
56 interaction. Next, TSP was washed successively with 5 mL of 0.5
57 M HCl and 6 mL of 2.5 M HCl to desorb all the elements which
58 are weakly retained. Finally, Sb was eluted with 6 mL of 6 M HCl.
59 Purified solution was collected and stored at 4 °C until Sb
60 concentration determination, isotopic analyses and interferent
61 concentration measurements.

62 Five procedural blanks were performed to ensure that no Sb
63 contamination occurred at each step: three blanks underwent
64 the purification step only; two other blanks underwent both the
65 digestion and the purification steps. The peristaltic pump tubing
66 used for the purification procedure was changed every five sets
67 of six purified samples to prevent any Sb contamination which
68 could occur due to tubing degradation.

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2.5. Analysis

All the analyses (ICP-MS, HG-ICP-MS and HG-MC-ICP-MS) were performed on the AETE-ISO Platform (OSU OREME, Université de Montpellier).

Antimony and trace element concentration measurement by ICP-MS:

ICP-MS iCAP TQ (ThermoScientific®) was used to measure the concentration of antimony and other elements (As, Cd, Co, Cr, Cu, Fe, Ni, Pb, Se, Sn, Zn) in the digest solutions of CRM. Concentrations of residual elements in Sb purified samples were also determined after evaporating an aliquot (one mL at 75 °C) and residue dissolution in 5 mL of 1.5 M HNO₃. Instrument settings are presented in Supplementary Information (Table S1). A collision cell, using He as collision gas, and the KED Mode (Kinetic Energy Discrimination) were used to eliminate polyatomic interferences created in the plasma. Isobaric interferences between two different elements were corrected using mathematical equations based on natural abundance ratios of the interfering elements (routine corrections preset in the instrument software). Element concentrations were determined using an external calibration curve analysed every 20-30 samples. A solution, containing Be, Sc, Ge, Rh and Ir was added on-line to the samples to correct changes in sensitivity (internal standard correction) due to matrix effect and instrument drift. Samples were diluted in 0.15 M HNO₃ and SLRS-6 certified material was systematically analysed to check the accuracy of the measurement. Typically, the SLRS-6 was measured at $0.331 \pm 0.004 \mu\text{g L}^{-1}$ of Sb (n=6, RSD = 1.2%) within 2% of the certified Sb value (average accuracy better than 6% for the other elements).

Antimony concentration measurement by HG-ICP-MS: Hydride generation (MP2 hydride ICP, Elemental Scientific®) coupled with ICP-MS iCAP Q (ThermoScientific®) was used to determine the recovery rate of antimony after the purification step¹³. Antimony (¹²¹Sb) was measured in the unpurified samples and in purified samples after an adequate dilution in 3 M HCl with 0.5% w/v of KI/AA at least three hours before analysis. Complete instrument settings for HG-ICP-MS are summarised in Supplementary Information (Table S1). An external calibration curve was analysed and internal standard correction (¹²⁸Te) was applied to correct sensitivity drifts. Average detection limit for Sb was $0.008 \pm 0.001 \mu\text{g L}^{-1}$. Accuracy was assessed by analysing two certified reference freshwaters. Antimony concentration was on average within 1.5% of the certified value for NIST 1643f ($55.7 \pm 1.8 \mu\text{g L}^{-1}$, n=3) and within 5.8% of the certified value for SLRS-6 ($0.319 \pm 0.005 \mu\text{g L}^{-1}$, n=3).

Antimony recovery (in %) after the purification step was calculated according to equation 1.

$$Sb_{recovery} = \frac{(m_F)}{(m_I)} \cdot 100$$

with m_i the mass of Sb in unpurified sample loaded on the TSP cartridge and m_F the mass of Sb recovered in the purified sample (in ng). m_i and m_F were calculated using Sb

concentrations measured by HG-ICP-MS. We estimated the uncertainty associated with the calculation of the purification recovery rate at $\pm 7\%$ (relative standard deviation) using the uncertainty of HG-ICP-MS measurement and conventional error propagation equations²⁷. In addition, the external reproducibility of the purification step, evaluated on four different CRM (n=3), was better than 5%.

Antimony isotope ratio measurement by HG-MC-ICP-MS:

Antimony stable isotope measurements were performed with a MC-ICP-MS (Neptune Plus, ThermoScientific®) coupled with a hydride generation system (MP2 hydride ICP, Elemental Scientific®) introducing the sample at $475 \mu\text{L min}^{-1}$. All instrumental settings are summarised in Table 4. Hydrides are formed by reacting the sample ($1 \mu\text{g L}^{-1}$ of Sb in 3 M HCl and 0.5% w/v of KI/AA) with sodium borohydride (1% w/v NaBH₄, 0.05% w/v NaOH). A Stable System Introduction quartz cyclonic spray chamber (Elemental Scientific®) was used to stabilise the signal.

Every measurement was composed of one block of 80 cycles of 4.194 seconds. The $1 \mu\text{g L}^{-1}$ Sb concentration resulted in a signal of 1.8-2 V for the ¹²¹Sb isotope (with a background noise under 2%). ¹²⁶Te has been measured to correct ¹²³Te isobaric interferences on the ¹²³Sb. However, the average signal intensity on the ¹²⁶Te (0.01 to 0.1 mV) did not made necessary the correction on the ¹²³Sb intensity (difference of $7.10^{-5}\%$ on the final ¹²³Sb/¹²¹Sb ratio).

SnH and SbH₂ interferences for ¹²¹Sb (¹²⁰SnH) and ¹²³Sb (¹²²SnH, ¹²¹SbH₂) was not significant. Indeed, literature showed that the formation of ¹²⁰SnH is negligible (less than 0.1% of the ¹²¹Sb signal intensity)¹. The intensity for ¹²⁰Sn (isotope abundance of 32.6%) remained constant for all the samples and did not exceed 100 mV. In addition, no increase in ¹²²Sn intensity in SPEX solution with $1 \mu\text{g L}^{-1}$ Sb was observed compared to blank solutions showing that formation of ¹²¹SbH was not detectable. Thus, no corrections were made on ¹²¹Sb and ¹²³Sb from the ¹²⁰SnH, ¹²²SnH and ¹²¹SbH₂ interferences.

A conventional external correction with the sample-standard bracketing approach was used to correct the mass bias²⁸. An in-house isotopic Sb standard solution (SPEX) was analysed before and after every sample as no certified isotopic standard exists for antimony yet. The isotopic composition of Sb was expressed as $\delta^{123}\text{Sb}$ (Equation 2) which represents the deviation between the isotope ratio measured for the sample $\left(\frac{^{123}\text{Sb}}{^{121}\text{Sb}}\right)_{sample}$ and the mean isotope ratio of the in-house isotopic standard (SPEX) measured before and after the sample $\left(\frac{^{123}\text{Sb}}{^{121}\text{Sb}}\right)_{mean std}$. Each $\delta^{123}\text{Sb}$ result is the average value for three different isotopic measurements (n=3), if not specified otherwise.

Eq. 1

$$\delta^{123}\text{Sb}(\text{‰}) = \left(\frac{\left(\frac{^{123}\text{Sb}}{^{121}\text{Sb}}\right)_{sample} - \left(\frac{^{123}\text{Sb}}{^{121}\text{Sb}}\right)_{mean std}}{\left(\frac{^{123}\text{Sb}}{^{121}\text{Sb}}\right)_{mean std}} \right) \times 1000 \quad \text{Eq. 2.}$$

1 Table 4: Instrument parameter settings used for Sb isotope analysis by HG-

2 MC-ICP-MS.

Hydride Generation Parameters

System	MP2 HydrideICP - Elemental Scientific
Peristaltic Pump Speed	25 rpm
Reducing agent medium	NaBH ₄ 1% w/v in NaOH 0.05% w/v
Acid medium	HCl 3M
<u>Flow rate (mL min⁻¹); tubing colour code – Internal Diameter ID (mm)</u>	
Waste	1.28; Yellow/Blue - 1.52 ID
Sample	0.48; Black/Black - 0.76 ID
NaBH ₄ =	0.24; Orange/Yellow - 0.51 ID
HCl	0.12; Orange/Green - 0.38 ID
<u>Gas flow (Ar) (L min⁻¹)</u>	
Sample gas	0.31
Additional Gas	0.45
<u>Instrument Settings</u>	
Instrument	Neptune Plus - Thermo Scientific
Forward power	1275 W
Skimmer Cone	X version
Sample Cone	Jet version
Measured isotopes	¹²⁰ Sn, ¹²¹ Sb, ¹²² Sn, ¹²³ Sb (¹²³ Te), ¹²⁶ Te
Cups	L1, C, H1, H2, H3
Sensitivity ¹²¹ Sb (V/ppb)	1.8 - 2
Resolution	Low resolution (M/ΔM = 400)
<u>Acquisition Parameters</u>	
Uptake time (s)	140
Number of block	1
Number of cycles per block	80
Integration Time (s)	4.194

3
4**3. Results and discussion****3.1. Efficiency of the purification method**

Sb recovery after CRM digestion: For most certified materials, Sb extraction yield after digestion was within 100 ± 10% (Table 5). Only the low-density polyethylene (*ERM-EC680m*) showed a relatively low antimony extraction yield (83%) despite the complete dissolution of PET pellets. This might be due to Sb content heterogeneity between pellets (only two pellets digested). GSD-3 showed an extraction yield between 113 and 147% (n=3), based on different indicative data^{29–31}. Considering the uncertainty associated with these indicative concentrations and the age of this certified material, it was decided to pursue the purification step with GSD-3 despite this inconsistency.

Antimony recovery after the purification step: Blank samples that have undergone both digestion and TSP purification contained less than 1 ng of Sb (Sb was lower than detection limit in blanks) which accounted for a maximum of 0.3 to 2% of the amount of Sb in processed samples (37–100 ng of Sb). For most CRM, the recovery rate was within 100 ± 7% (Table 5). These recovery values are similar to the ones found in the recent literature (Table 1) that used a two-step procedure with anion- and cation-exchange resins combining either AG 1-X4 and AG 50W-X8 (recovery of Sb > 98% for Liu et al. 2020¹⁴) or Dowex AG50-X8 and Amberlite IRA 743 resin (recovery > 94% for Lobo et al. 2014⁸). For the CRM *NCS-DC-73349* and *GXR-4*, the recovery rates were 79%, and 84 ± 3%, respectively. These lower recovery rates could be related to the high ionic strength in the sample solution loaded on the TSP cartridge; indeed these two CRM exhibited the highest matrix:Sb concentration ratio considering the sum of all measured elements by ICP-MS. Investigation of the nature of interactions between matrix elements, antimony and thiol moieties would require further research. We recommend to systematically check Sb recovery rate and concentrations of potential interfering elements in the purified samples before performing Sb isotope measurement on a particular new type of material. Indeed, peculiar sample matrix may lead to unexpected incomplete recovery; in particular, Fe-rich sample (Fe:Sb > 50000) may still need a pre-treatment as observed by Rouxel et al. 2003¹. Nevertheless, the isotopic composition for these CRM is further presented as indicative values to be confirmed in future works.

Elimination of potential interfering elements: Two main groups of elements may interfere with antimony hydride formation. On one hand, transient metals such as Cd, Cr, Cu Fe, Ni can produce a matrix effect during hydride generation¹⁹. The matrix effect mainly originates from the precipitation of metal borides which affects the release efficiency of hydrides and decomposition of the reducing agent. Besides, iron can decrease the efficiency of Sb hydride formation by oxidizing Sb(III) into Sb(V), which prevents further hydride formation (since Sb(V) forms hydrides more slowly than Sb(III))³². On the other hand, hydride-forming elements including As, Pb, Se, Sn, Ge, Bi and Te may compete with Sb for its reduction¹⁹ with NaBH₄ but also may cause matrix effect during the analysis by MC-ICP-MS. Selenium may also induce Sb signal suppression prior to hydride formation by precipitating Sb in the form of Sb₃Se₃¹⁹. Finally, non-hydride forming elements can interfere with Sb isotopes measurement by MC-ICP-MS by being transported to the plasma as fine aerosols²¹ with the excess of H₂ gas³³.

Average removal rates for interfering elements in all CRM were ≥ 97% (Table 6). The concentrations of these elements in the purified samples analysed by HG-MC-ICP-MS were systematically lower than the Sb concentration (metal:Sb ratios < 1, Table 6), except for iron and copper. For iron, there is a body of evidence which suggests that no interference can occur from Fe in the purified CRM: 1) Sb signal suppression related to the oxidation of Sb(III) into Sb(V) by Fe(III) was only evidenced at

74
75

1 Table 5: Extraction yield and purification recovery for the certified reference materials.

CRM	Digestion				Purification	
	Measured concentration ($\mu\text{g g}^{-1}$)	Certified value ($\mu\text{g g}^{-1}$)	Sb extraction yield (%)	n	Sb purification recovery (%)	n
SDO-1	4.58	4.45 \pm 0.35	102.9	1	98	1
GXR-4	4.50 \pm 0.01	4.4 \pm 0.8	102.8 \pm 0.8	3	84 \pm 3	3
ERM-EC680m	8.0	9.6 \pm 0.7	83.3	1	103	1
BCR 176R	836	850 \pm 50	98.3	1	94	1
BCR 723	26.4 \pm 0.3	28.2 \pm 2.3 ^a	93.6 \pm 0.9	3	97 \pm 3	3
NIST 2711a	25.3	23.8 \pm 1.4	107.3	1	97 \pm 2	3
NCS-DC-70317	4.82	4.44 \pm 0.44	108.5	1	89	1
GSD-3	7.4	5.02 \pm 0.12 ^b , 5.4 ^c , 6.52 ^d	147.4 ^b , 137.0 ^c , 113.5 ^d	1	97	1
PACS-3	14.1	14.6 \pm 2.4	96.6	1	98	1
NCS-DC-73349	0.106	0.095 \pm 0.027	112.0	1	79	1
BCR 482	0.35 \pm 0.01	0.35 ^a	99 \pm 3	3	95 \pm 4	3
Whole blood trace elements II	0.026 [*]	0.026 \pm 0.005 [*]	99.0	1	99	1
Urines Control Clincheck [®] level II	0.051 [*]	0.0475 \pm 0.0095 [*]	107.1	1	99	1

^{a,b}Indicative values : ^aInstitute for Reference Materials and Measurements ; ^bHall and Pelchat (1997)³⁰, ^cGovindaraju (1994)²⁹, ^dFadda et al. (1995)³¹ ; ^{*} $\mu\text{g mL}^{-1}$.

2 Fe(III):Sb mass ratio greater than 22³² whereas the highest Fe:Sb ³¹ that there was no influence of Fe or Cu for metal:Sb mass ratios
3 value in our purified CRM was 13.4 (Table 6), 2) precipitation of ³² of 50 on Sb isotope measurement ($\delta^{123}\text{Sb}_{\text{Fe}} = 0.02 \pm 0.07$, 2 sd,
4 iron borides was evidenced only for high Fe:Sb ratios, in the ³³ $\delta^{123}\text{Sb}_{\text{Cu}} = -0.02 \pm 0.02$, 2 sd) compared with a pure SPEX
5 range 1000 to 10,000 (50 to 100 mg L⁻¹ of Fe)^{30,34,35} and 3) the ³⁴ solution. ¹²³Sb intensities were also not influenced by the
6 amount of Fe transported to the plasma during the hydride ³⁵ presence of these elements. This demonstrates that Fe
7 generation process was estimated to be less than 0.001%³³, and ³⁶ Table 6: Average removal rates obtained from all CRM for the potential
8 thus would be negligible considering the measured residual Fe ³⁷ interfering elements and the highest element:Sb ratios measured for
9 concentrations in purified samples. ³⁸ each element in purified samples. The uncertainties were calculated as

10 Cu:Sb ratio was lower than 1 in all the samples, except for ³⁹ the standard deviation obtained from all CRM for each element.
11 GXR-4 (Cu:Sb = 4.7, Table 6), and Seronorm[™] Whole blood level ⁴⁰ Residual element:Sb ratios for individual CRM are given in
12 II in a lesser extent (Cu:Sb = 2.3, Table S2). GXR-4 has a high ⁴¹ Supplementary Information, Table S2.

13 copper concentration (6500 $\mu\text{g g}^{-1}$) and despite a good
14 abatement rate (> 99.7%), the residual concentration of Cu in
15 the purified sample analysed by HG-MC-ICP-MS was 4.7 $\mu\text{g L}^{-1}$.
16 However, potential interference from Cu might be masked by
17 precipitation of CuI when using potassium iodide as reductant
18 for hydride generation³⁶. Furthermore, Cu transportation in the
19 gas phase to the plasma with hydride generation in 3 M HCl was
20 reported to be 0.38% of Cu present in solution²¹. Thus,
21 interference from Cu in GXR-4 and Seronorm[™] Whole Blood
22 Level II might be negligible.

23 However, no investigation of Fe and Cu effects at these
24 concentrations and configurations for Sb hydride generation
25 was reported in the literature, so further tests have been
26 carried out to ensure that these residual concentrations of Fe
27 and Cu did not have an impact on the formation of Sb hydrides
28 and isotopic measurement. Antimony standard solution at 1 μg
29 L⁻¹ (in-house isotope standard SPEX) was spiked with 50 $\mu\text{g L}^{-1}$
30 of Fe, or Cu and measured by HG-MC-ICP-MS. Results showed

	Element	Percentage removed (%)	Highest Element:Sb ratio in purified samples
Transition metals	Cd	99.7 \pm 0.5	0.00
	Co	98 \pm 3	0.1
	Cr	97 \pm 3	0.9
	Cu	99 \pm 1	4.7
	Fe	99.9 \pm 0.2	13.4
	Ni	97 \pm 4	0.3
Hydride-forming elements	As	99.8 \pm 0.3	0.03
	Pb	100.0 \pm 0.1	0.2
	Se	> 89	< 0.1
	Sn	97 \pm 3	0.05

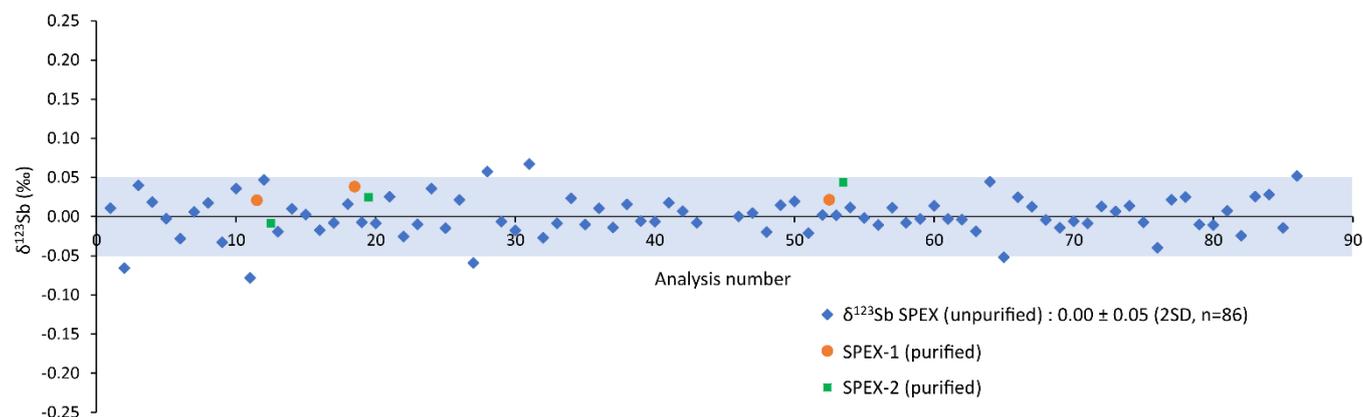


Figure 1: $\delta^{123}\text{Sb}$ values for purified and unprocessed in-house SPEX isotopic standard analysed over a 3-day analytical session.

1 and Cu do not interfere at any step of the HG-MC-ICP-MS ²⁴ simultaneous drop in the $^{123}\text{Sb}/^{121}\text{Sb}$ ratio (up to 0.1%) and
 2 analysis of Sb (i.e. reduction, hydride formation, ionisation, ²⁵ affected the internal standard error on $^{123}\text{Sb}/^{121}\text{Sb}$ ratio (10 to
 3 extraction and focusing steps) for metal:Sb mass ratio lower ²⁶ 25 ppm). Such instabilities were also observed in other
 4 than 50. ²⁷ studies³⁷, and are probably due to an over pressure in the
 28 hydride generation system. Two methods for excluding outliers

3.2. Precision and statistical data treatment of Sb isotope measurement

7 Sb signal intensity (^{121}Sb and ^{123}Sb) measured in blanks (3 M
 8 HCl, 0.5% v/v KI/AA) did not exceed 2% of the Sb signal intensity
 9 in standards and samples, resulting in an average difference of
 10 0.01‰ for $\delta^{123}\text{Sb}$. No correction was therefore made to account
 11 for the blank contribution.

12 The long-term external precision obtained for the repeated
 13 measurement of purified and unprocessed Sb SPEX solution
 14 corrected with the sample-standard bracketing method is
 15 presented in Figure 1. The precision was 0.05‰ (2 sd) for the
 16 unprocessed in-house isotopic standard SPEX measured over 3
 17 days. The drift over time of the $^{123}\text{Sb}/^{121}\text{Sb}$ ratio (data not
 18 shown) did not have an impact on the $\delta^{123}\text{Sb}$ of the in-house
 19 isotopic standard SPEX (Figure 1).

20 Despite the relatively stable ^{121}Sb signal (standard deviation
 21 < 0.1 V (RSD < 5%)), short-term instabilities randomly occurred
 22 (up to an increase of 20% of ^{121}Sb and ^{123}Sb signal over less than
 23 30 seconds). These short-term instabilities caused a

24 simultaneous drop in the $^{123}\text{Sb}/^{121}\text{Sb}$ ratio (up to 0.1%) and
 25 affected the internal standard error on $^{123}\text{Sb}/^{121}\text{Sb}$ ratio (10 to
 26 25 ppm). Such instabilities were also observed in other
 27 studies³⁷, and are probably due to an over pressure in the
 28 hydride generation system. Two methods for excluding outliers
 29 values from the eighty cycle values of $^{123}\text{Sb}/^{121}\text{Sb}$ ratio were
 30 compared to limit the impact of the short-term instabilities and
 31 determine how heavily it impacts the final $\delta^{123}\text{Sb}$ value (Figure
 32 S2). The first treatment (method A) is routinely used (preset in
 33 the instrument software) and consists in excluding values of
 34 $^{123}\text{Sb}/^{121}\text{Sb}$ ratio overpassing two standard deviations from the
 35 calculation of $^{123}\text{Sb}/^{121}\text{Sb}$ ratio average (i.e. excluding ratios
 36 outside the confidence interval of 95%). The second method
 37 (method B) consists in excluding the values of $^{123}\text{Sb}/^{121}\text{Sb}$ ratios
 38 measured during the short-term instability period based on the
 39 variation in ^{121}Sb intensity (i.e. cycles with ^{121}Sb intensity
 40 exceeding 5% of the average signal intensity are excluded, with
 41 two cycles before and after the disruption) (Figure S2). The
 42 method A did not efficiently remove outlier values of $^{123}\text{Sb}/^{121}\text{Sb}$
 43 ratio; only four impacted cycles over the ten visually identified
 44 were removed (Figure S2). On the other hand, method B
 45 removed efficiently all the impacted cycles. $\delta^{123}\text{Sb}$ values for the
 46 in-house isotopic standard SPEX were more gathered around 0
 47 using method B (85% of the $\delta^{123}\text{Sb}$ values exceeded 0.03‰)
 48 than method A (85% of the $\delta^{123}\text{Sb}$ values are below or equal to

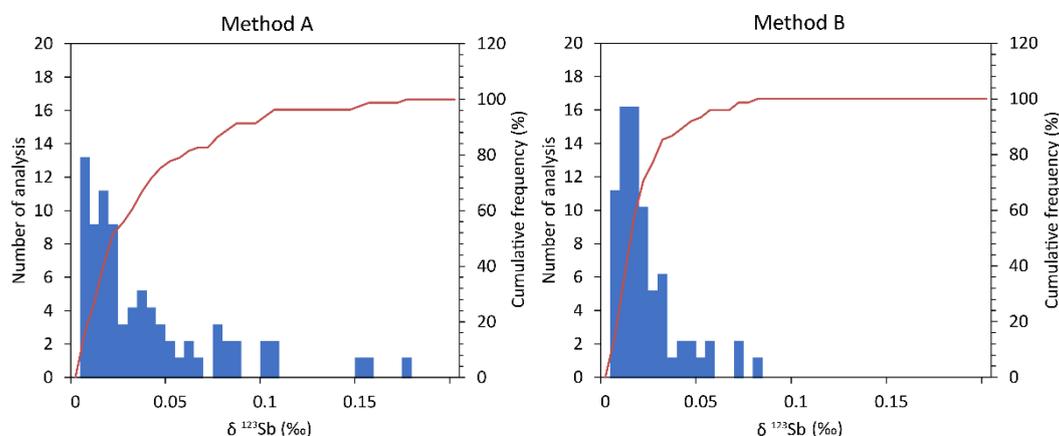


Figure 2: Comparison of the $\delta^{123}\text{Sb}$ values (‰) for the in-house isotopic standard SPEX after $^{123}\text{Sb}/^{121}\text{Sb}$ outliers exclusion using methods A and B.

1 0.07‰) (Figure 2). Average values of $\delta^{123}\text{Sb}$ calculated for CRM 54
2 with both methods were not significantly different but the 55
3 precision is improved with method B (Table S3). Therefore, 56
4 method B was selected to further process isotope data. 57

5 Two aliquots of the in-house isotopic standard SPEX (named 58
6 SPEX-1 and SPEX-2) were processed using the purification 59
7 procedure and analysed by HG-MC-ICP-MS to ensure that the 60
8 protocol did not cause isotope fractionation. For SPEX-2, the 61
9 first millilitre of the Sb elution step was collected independently 62
10 to check whether Sb isotopes were fractionated due to 63
11 incomplete Sb elution from TSP. $\delta^{123}\text{Sb}$ measured for the two 64
12 aliquots of the purified in-house isotopic standard SPEX (SPEX-1 65
13 and SPEX-2, Figure 1) did not show a significant difference with 66
14 the unpurified SPEX. Results of the purified SPEX-1 (purification 67
15 recovery of 94%) showed that no fractionation occurred during 68
16 the purification ($\delta^{123}\text{Sb} = 0.03 \pm 0.02\%$, 2 sd, n=3). For SPEX-2, 69
17 92% of the total Sb was recovered, $\delta^{123}\text{Sb}$ was identical to 70
18 unpurified in-house isotopic standard SPEX ($\delta^{123}\text{Sb} = 0.02 \pm$ 71
19 0.05% , 2 sd, n=3). Thus, partial Sb elution did not induce 72
20 fractionation of Sb isotopes. A reduction of the volume of Sb 73
21 elution from 6 mL to 1 mL in the purification procedure could 74
22 be considered in future work. 75

3.3. Sb isotopic composition in pure Sb standard solutions

25 The isotopic composition of PlasmaCAL-1 and Fisher pure Sb
26 standard solutions were similar to the in-house isotopic
27 standard SPEX, with $\delta^{123}\text{Sb}$ values of $0.04 \pm 0.08\%$ (n=6) and
28 $0.01 \pm 0.04\%$ (n=3), respectively (Figure 3). Only PlasmaCAL-2
29 showed a contrasted isotopic composition ($\delta^{123}\text{Sb} = 0.62 \pm$
30 0.02% (n=4)). All these standards were prepared from
31 antimony(III) oxide. The similarities between in-house isotopic
32 standards SPEX, Fisher, and PlasmaCAL-1 could indicate a
33 common source of supply of antimony(III) oxide. Conversely, a
34 different source or a different standard preparation procedure
35 might explain different $\delta^{123}\text{Sb}$ signature observed for
36 PlasmaCAL-2. This point deserves further research.

3.4. Sb isotopes in certified reference materials (CRM)

38 Isotopic composition of Sb in studied CRM are presented in
39 Figure 3 and in Supplementary Information (Table S4). $\delta^{123}\text{Sb}$
40 values ranged between $-0.52 \pm 0.06\%$ and $0.40 \pm 0.03\%$ (Figure
41 3). However, most of the CRM had a $\delta^{123}\text{Sb}$ value within a
42 narrower range, between -0.20 and 0.20% . A few CRM had a
43 slightly negative $\delta^{123}\text{Sb}$ value including *BCR-176R* ($-0.03 \pm$
44 0.03% , 2 sd), *NCS-DC-70317* ($-0.11 \pm 0.03\%$, 2 sd) and *NIST*
45 *1643f* ($-0.08 \pm 0.09\%$, 2 sd). The slightly positive $\delta^{123}\text{Sb}$ values
46 were: *BCR-482* ($0.05 \pm 0.05\%$, 2 sd, n=3), *Clincheck® Urines level*
47 *II* ($0.17 \pm 0.04\%$, 2 sd), *Seronorm™ whole blood level II* ($0.09 \pm$
48 0.02% , 2 sd), *GSD-3* ($0.15 \pm 0.05\%$, 2 sd), *PACS-3* ($0.16 \pm$
49 0.02% , 2 sd), *NIST 2711a* ($0.06 \pm 0.02\%$, 2 sd) and *BCR-723*
50 ($0.03 \pm 0.05\%$, 2 sd). The greatest deviations from these
51 narrow range of $\delta^{123}\text{Sb}$ values were observed for *ERM-EC680m*
52 ($0.40 \pm 0.03\%$, 2 sd), *GXR-4* ($0.35 \pm 0.04\%$, 2 sd, n=3), *SDO-1*
53 ($0.22 \pm 0.03\%$, 2 sd) and *NCS-DC-73349* ($-0.52 \pm 0.04\%$, 2 sd).

Some of the CRM (*NIST 1643f*, *ERM-EC680m*, *Seronorm™*
Whole blood level II, *Clincheck® Urines level II*) were artificially
enriched with Sb while others (*SDO-1*, *GRX-4*, *BCR 176R*, *BCR*
723, *NIST 2711a*, *NCS-DC-70317*, *GSD-3*, *PACS-3*, *NCS-DC-73349*,
BCR-482) originally contained Sb. Among the first group, all
these standards exhibited different $\delta^{123}\text{Sb}$ values. This could be
explained by Sb enrichment from different sources. *Clincheck®*
urine control level II was enriched with Sb using Sb standard
prepared from SbCl_3 . Conversely, *ERM-EC680m* was artificially
enriched using the Sb pigment Sb_2O_3 , it exhibited a different
 $\delta^{123}\text{Sb}$ signature. *NIST 1643f* was enriched using antimony(III)
trinitrate and also exhibited a different $\delta^{123}\text{Sb}$ signature.

The other CRM had a natural Sb content; they are likely
more representative of the $\delta^{123}\text{Sb}$ isotopic range which could be
found in the environment. Among these CRM, Tibet sediments
(*NCS-DC-70317*) had a distinct $\delta^{123}\text{Sb}$ compared to the other
river and marine sediments (*GSD-3* and *PACS-3*). Such
difference might reflect different geographic provenance (Tibet
for *GSD-3*, marine sediments from Esquimalt harbour, British
Columbia for *PACS-3*). *NCS-DC-73349* and *BCR-482*, both vegetal
samples have a highly different $\delta^{123}\text{Sb}$ signature. *NCS-DC-73349*
was branches and leaves of bushes from China while *BCR-482*
was lichen collected from pines in Switzerland. Geographic
location and vegetal species have probably influenced $\delta^{123}\text{Sb}$
signature. However, many processes may have left their own

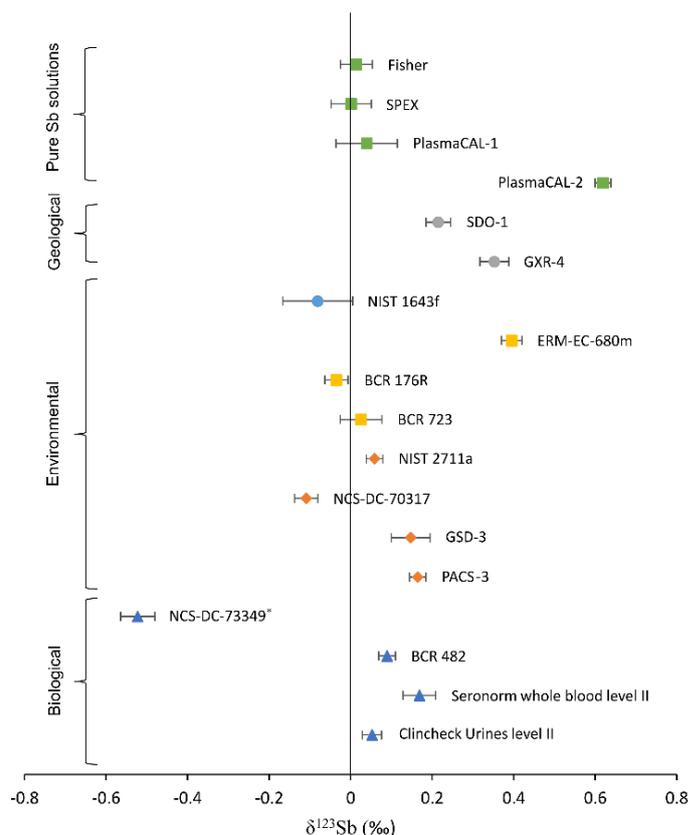


Figure 3: $\delta^{123}\text{Sb}$ in studied biological, environmental, and geological CRM (‰).
*Indicative value, to be confirmed in future works.

$\delta^{123}\text{Sb}$ imprint and the origin of different isotopic signatures deserves further research.

The external reproducibility of the whole procedure (i.e. including the digestion and purification steps) was assessed for two CRM (*GXR-4* and *BCR-482*). Three independent digested solutions were purified and analysed for Sb isotope ratio. The errors associated to $\delta^{123}\text{Sb}$ values were comparable to the other CRM ($\delta^{123}\text{Sb} = 0.05 \pm 0.05\%$ for *BCR-482*, and $\delta^{123}\text{Sb} = 0.35 \pm 0.04\%$ for *GXR-4*), which demonstrated the good external reproducibility of the method.

Four CRM (*GXR-4*, *GSD-3*, *BCR-176R* and *SDO-1*) had been previously analysed by Rouxel et al. (2003)¹. Compared to previous $\delta^{123}\text{Sb}$ data obtained by these authors, we found a $\delta^{123}\text{Sb}$ difference of -0.13% for *GXR-4*, -0.02% for *GSD-3*, -0.06% for *BCR-176R* and -0.01% for *SDO-1*. These differences were not significant for *GSD-3*, *SDO-1* and *BCR-176R*. This suggests that the in-house isotopic standard used by Rouxel et al. (2003)¹ had a similar isotopic composition than the Sb SPEX solution used in this study. However, a slight difference was observed for *GXR-4*, which could be explained by a significant heterogeneity between the bottles of *GXR-4*, as reported by Kane et al. (1992)³⁸ or incomplete Sb recovery (Table 5). Overall, the $\delta^{123}\text{Sb}$ variation range in geological and environmental CRM reported in Rouxel et al. (2003)¹ (from $-0.05 \pm 0.04\%$ to $0.48 \pm 0.03\%$, 2 sd) is similar to the ones measured in this paper for additional environmental and biological CRM.

4. Conclusions

A single-step purification method for antimony was developed to analyse isotopic composition by HG-MC-ICP-MS in samples with low Sb concentration and complex solid matrices. The purification method has been tested and validated over a wide range of CRM with various matrices (geological, environmental, and biological). The good recovery rates ($100 \pm 7\%$) for Sb and abatement rates for interfering elements (Fe > 99%, Ti > 99%, Cu > 99%, Cr > 97%, Ni > 97%, Cd > 99%, As > 99%, Sn > 96%) allowed the precise measurement of Sb isotope ratio. This validates the efficiency of the TSP protocol to isolate Sb from complex and diverse matrices, to be analysed by HG-MC-ICP-MS without a pre-treatment step to eliminate metals as previously reported^{1,14}, with a maximal Fe:Sb initial mass ratio of 50,000. Due to its high affinity with Sb and its high specific surface area with an important thiol density per nm^2 , TSP is efficient to purify antimony in samples containing from $0.026 \mu\text{g mL}^{-1}$ (*Seronorm™ whole blood II*) to $850 \mu\text{g g}^{-1}$ (*BCR-176R*) of Sb. Purification recovery rates were similar to the ones found in the literature for environmental samples^{13,14,17}.

Extreme isotopic values were found to be $-0.52 \pm 0.06\%$ (2 sd) for the branches and leaves of bush originally containing Sb (*NCS-DC-73349*) and $0.40 \pm 0.03\%$ (2 sd) for polyethylene artificially enriched with Sb (*ERM-EC680m*) while most of the CRM had an isotopic composition between -0.2 and $+0.2\%$.

These data give an overview of the $\delta^{123}\text{Sb}$ isotopic variation in CRM which may be analysed during future study using Sb isotopes as environmental tracer.

To date, there is no internationally shared isotopic standard for Sb isotopes. The community should make efforts to intercalibrate the different in-house isotopic standards and if possible to use the same standard solution in the future to be able to compare Sb isotope data.

Conflicts of interest

There are no conflicts of interest to declare.

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