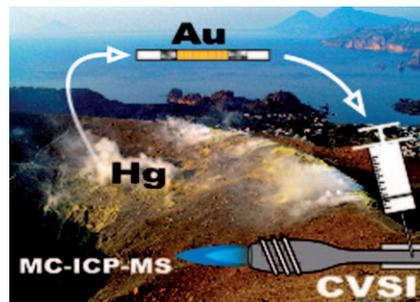


## Indirect gold trap–MC-ICP-MS coupling for Hg stable isotope analysis using a syringe injection interface

Jeroen E. Sonke, Thomas Zambardi and Jean-Paul Toutain

Cold vapor syringe injection (CVSI) was developed to indirectly couple gold amalgamation traps to MC-ICP-MS and provide high precision stable isotopic analysis of volcanic elemental mercury emissions.



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# Indirect gold trap–MC-ICP-MS coupling for Hg stable isotope analysis using a syringe injection interface

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Gold traps are part of standard instrumentation to quantitatively pre-concentrate gaseous elemental mercury,  $\text{Hg}^0_{(\text{g})}$ , and are a pre-requisite for atmospheric  $\text{Hg}^0_{(\text{g})}$  analysis. High precision mercury stable isotope ratio analysis by on-line coupling of gold traps to multi collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) has up to now been problematic due to the transient nature of the signal. We present a new off-line technique, where amalgamated elemental  $\text{Hg}^0$  is volatilized from the gold trap in an argon gas stream and temporarily stored in a large volume gas tight syringe.  $\text{Hg}^0_{(\text{g})}$  contained in the syringe is then injected on-line into the MC-ICP-MS interface using a syringe pump at a continuous flow rate and resulting in a steady state Hg signal. Different syringe injection schemes are discussed, as well as matrix effects. The 2SD external precision on an in-house  $\text{Hg}^0$  vapor standard was found to be 0.24‰ for  $\delta^{202}\text{Hg}$ . The method is illustrated for fumerole  $\text{Hg}^0_{(\text{g})}$  emissions at Vulcano (Italy) with  $\delta^{202}\text{Hg}$  of  $-1.74\text{‰}$  relative to NIST SRM 3133.

## 1. Introduction

Stable mercury (Hg) isotope abundance analysis has a remarkably long history that began almost one hundred years ago with the characterization of its isotopes by Aston.<sup>1</sup> Early thereafter,<sup>2</sup> Brønsted and von Hevesey reported on the fractionation of Hg isotopes by vacuum distillation and pycnometry detection (density measurements). Nier<sup>3</sup> made the first high precision gas source mass spectrometry measurements of Hg, and it took more than 60 years before Klaue *et al.*<sup>4</sup> introduced cold vapor-multi collector-inductively coupled plasma-mass spectrometry (CV-MC-ICP-MS) as a viable technique for exploring the natural variations in Hg isotope abundances. Thus far, work has been published on Hg isotopic variations in meteorites,<sup>5</sup> cinnabar,<sup>6,7</sup> sediments,<sup>8,9</sup> biological samples,<sup>10,11</sup> and upon processes such as volatilization,<sup>12,13</sup> bacterial reduction<sup>14</sup> and photoreduction.<sup>15</sup> The overall terrestrial variation in mercury isotopic compositions is substantial,  $\sim 7\text{‰}$  for  $\delta^{202}\text{Hg}$ . Guidelines for CV-MC-ICP-MS and reporting Hg isotope ratio analyses have been published recently.<sup>16</sup> Interest in the natural isotopic variations of Hg stems mainly from its quantification potential of sources and Hg transformation processes in our environment, and the substantial anthropogenic influence of human activities on global Hg cycling.<sup>17</sup>

Classical elemental analysis of mercury is often based on using a gold trap to pre-concentrate  $\text{Hg}^0_{(\text{g})}$  by gold–mercury amalgamation at ambient  $T$ , and subsequent heating of the trap to  $500\text{ °C}$  to rapidly produce a concentrated transient  $\text{Hg}^0_{(\text{g})}$  pulse that can be detected by atomic adsorption spectrometry (AAS) or atomic fluorescence spectrometry (AFS).<sup>18</sup> Gold traps typically consist of a constricted quartz tube that contains gold coated quartz beads, but other designs exist: tightly packed

gold wire, cylindrically rolled up gold film, and gold mesh traps. Although gold traps can be directly coupled to ICP-MS for Hg detection, ICP-MS is both technically and financially not competitive with respect to AAS and AFS. However, when the purpose of study is to quantify the natural stable isotopic abundances of Hg with high precision, MC-ICP-MS detection is necessary. Evans *et al.* were the first to explore the on-line gold trap–MC-ICP-MS coupling and observed that as the transient  $\text{Hg}^0_{(\text{g})}$  signal is released from the gold trap and detected by the mass spectrometer, the Hg isotope ratios were drifting dramatically (Fig. 1). During the rise of the transient signal  $^{200}\text{Hg}/^{202}\text{Hg}$  ratios increase gradually, indicating that heavy isotopes are released more rapidly from the gold trap than lighter isotopes. The drift in  $^{200}\text{Hg}/^{202}\text{Hg}$  ratio is approximately 10‰ per atomic mass unit, and is therefore of the same order of magnitude as steady state instrumental mass bias for a heavy element such as Hg. The observed transient mass bias drift is difficult to correct for, and Evans *et al.* opted to integrate the entire

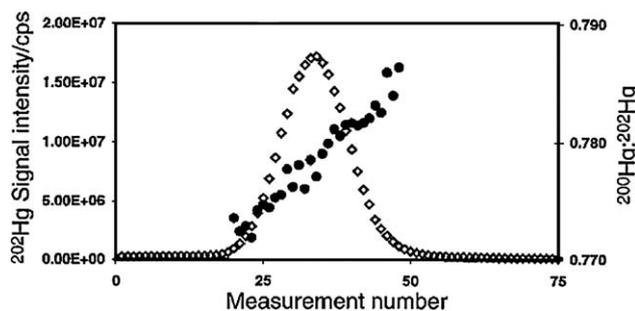


Fig. 1 Reprinted from Evans *et al.* Transient Hg isotope ratio analysis of  $\text{Hg}^0_{(\text{g})}$  that is desorbed from a gold trap and directly transferred into an MC-ICP-MS. During passage of transient  $^{202}\text{Hg}$  signal (volts, open diamonds),  $^{200}\text{Hg}/^{202}\text{Hg}$  ratios increase gradually, indicating that heavy isotopes are released more rapidly from the gold trap than lighter isotopes.

Observatoire Midi-pyrénées, Laboratoire des Mécanismes et Transferts en Géologie, CNRS/IRD/Université Paul Sabatier Toulouse 3, 14 avenue Edouard Belin, Toulouse, 31400, France

transient peak. Although this conserves an isotopic mass balance and thus yields an accurate result, it also makes the measurement substantially less precise (0.3 to 4.0‰, 2SD). As the Hg on the gold trap was pre-concentrated from a combusted coal sample, it was not clear whether the direction of the  $^{200}\text{Hg}/^{202}\text{Hg}$  ratio drift results from the combustion and pre-concentration step or from the release step.<sup>19</sup> An improved gold trap release protocol has been developed by extending the peak width, yet still suffers from the same mass bias drift during transient passage and associated large external reproducibility.<sup>10</sup>

Here we detail an alternative method that indirectly couples the gold trap with MC-ICP-MS by use of a cold vapor syringe injection (CVSI) interface. Rather than introducing a transient gold trap signal, we tested whether capturing the  $\text{Hg}^0_{(g)}$  released from the gold trap could be stored temporarily in a gas tight syringe, and subsequently injected at a fixed rate into the MC-ICP-MS in order to obtain a steady-state signal.

## 2. Materials and methods

Gold traps used in this study contain gold-coated quartz beads and were purchased from BrooksRand Inc. (Seattle, USA). Liquid Hg, 99.995% (NormaPur) and  $\text{SnCl}_2$  (NormaPur) were purchased from Alfa Aesar. NIST SRM 3133 mercury and NIST SRM 997 thallium solution were purchased from NIST. All isotopic measurements were made on a Thermo-Finnigan Neptune at the Laboratoire des Mécanismes et Transferts en Géologie (Toulouse, France). A Hg vapor standard was made constructed by putting 2 mL of Alfa Aesar liquid Hg into an acid-cleaned 500 mL borosilicate glass bottle, capped with a teflon-lined silicone septum. The bottle was immersed in a water bath at 22 °C.

### 2.1. CV-MC-ICP-MS

In order to develop the CVSI interface, repeated injections of Hg vapor needed to be made. Although Hg vapor is conveniently produced from a closed septum vessel containing a few mL of liquid  $\text{Hg}^0_{(l)}$  in equilibrium with its vapor,  $\text{Hg}^0_{(g)}$ , the vapor itself is isotopically fractionated relative to the liquid at room temperature.<sup>13</sup> Therefore, we first had to undertake a thorough characterization of the isotopic composition of the liquid Hg starting material and its equilibrated vapor at 22 °C relative to the currently accepted delta-0 standard NIST SRM 3133. A small drop of  $\text{Hg}^0_{(l)}$  was dissolved in concentrated  $\text{HNO}_3$  (15 mol  $\text{L}^{-1}$ ) and diluted to 25 ng  $\text{g}^{-1}$  in 2%  $\text{HNO}_3$  in an acid cleaned amber glass vial.  $\text{Hg}^0_{(g)}$  vapor in equilibrium with liquid  $\text{Hg}^0_{(l)}$  was withdrawn using BD plastic disposable syringes and injected into 3 mL of 2%  $\text{HNO}_3$  in an amber glass septum vial. After injection, the vial was vigorously shaken for 24 h. Oxidation and dissolution of  $\text{Hg}^0_{(g)}$  was shown to be complete. Hg isotopic compositions of  $\text{Hg}^0_{(l)}$  and  $\text{Hg}^0_{(g)}$  were determined by CV-MC-ICP-MS. A Perkin Elmer XX cold vapor generator, a CETAC ASX-100 auto sampler, and a CETAC 'Aridus II' desolvation system for SRM 997 thallium introduction were used (operating conditions are shown in Table 1).  $\text{Hg}^{2+}$  in samples and standards was reduced on-line in the cold vapor generator using 3 w/v%  $\text{SnCl}_2$  in 1 N HCl. Typical instrument sensitivity was 2 V on  $^{202}\text{Hg}$  for a 25 ng  $\text{g}^{-1}$  introduced at 0.3 mL  $\text{min}^{-1}$ . Isotopes

**Table 1** CV and CVSI and MC-ICP-MS operating conditions

MC-ICP-MS	
Cool gas/L $\text{min}^{-1}$	15
Auxiliary gas/L $\text{min}^{-1}$	0.63
Sample gas Aridus/L $\text{min}^{-1}$	1.20
Sweep Ar gas Aridus/L $\text{min}^{-1}$	6.0
$\text{N}_2$ gas Aridus/L $\text{min}^{-1}$	0.07
RF power/W	1100
Data acquisition; #blocks, #cycles, integration time/s	7, 8, 8
<b>Cold vapor</b>	
Sample and 3% w/v $\text{SnCl}_2$ flow/mL $\text{min}^{-1}$	0.3
Additional gas/L $\text{min}^{-1}$	0.1
<b>Cold vapor syringe injection</b>	
Syringe size/mL	3–50
Injection rates/mL $\text{min}^{-1}$	0.1–20

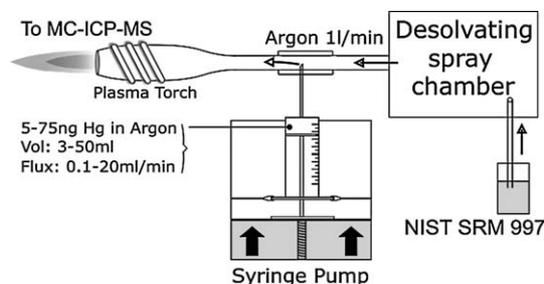
$^{198}\text{Hg}$ ,  $^{199}\text{Hg}$ ,  $^{200}\text{Hg}$ ,  $^{201}\text{Hg}$ ,  $^{202}\text{Hg}$ ,  $^{203}\text{Tl}$ ,  $^{205}\text{Tl}$  were detected on Faraday cups L3, L2, L1, C, H1, H, and H3, respectively, using 10 min total integration times. Wash-out times were 12 min to assure that the blank levels were <1% of the preceding sample or standard signal. Gain and baseline calibration was done on a daily basis. Thallium was used as internal standard for mass bias correction using the exponential law, and the standard-sample-standard bracketing mode, with SRM 3133 as standard, was used to calculate delta values for Hg based on international guidelines.<sup>16</sup>

$$\delta^{xxx}\text{Hg} = \left( \frac{\left( \frac{^{xxx}\text{Hg}}{^{198}\text{Hg}} \right)_{\text{sample}}}{\left( \frac{^{xxx}\text{Hg}}{^{198}\text{Hg}} \right)_{\text{SRM 3133}}} - 1 \right) \times 1000\text{‰} \quad (1)$$

Reduction efficiency of the CV generator was tested by analyzing the waste stream. No detectable  $\text{Hg}^{2+}$  was found, suggesting that reduction was >99% efficient.

### 2.2. CVSI-MC-ICP-MS

A Hamilton syringe pump was interfaced with the MC-ICP-MS according to Fig. 2. A 10 cm piece of thick-walled silicone tubing (3 mm) was inserted between the Aridus exit line and the ICP torch, and replaced on a daily basis. Diverse volume (5, 10, 50 and 100 mL) plastic disposable syringes (BD, polypropylene) were outfitted with a teflon valve and stainless steel needle for  $\text{Hg}^0_{(g)}$  injection. A typical injection was made as follows: a  $\text{Hg}^0_{(g)}$  containing syringe was inserted in the syringe pump,



**Fig. 2** Drawing of the cold vapor syringe injection (CVSI) interface for introduction of gaseous  $\text{Hg}^0$  into the MC-ICP-MS.

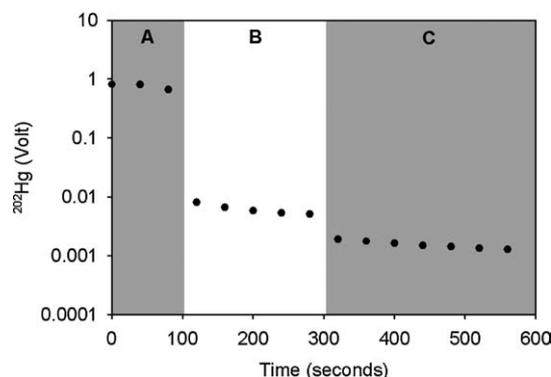
1 followed by manual piercing of the silicone tubing by the syringe  
 5 needle. Subsequently the teflon valve was opened and the syringe  
 pump flow rate adjusted to obtained the desired steady-state  
 signal of  $\sim 1\text{--}2$  V on  $^{202}\text{Hg}$ . The time span between syringe  
 loading with  $\text{Hg}^0_{(\text{g})}$  and injection into the MC-ICP-MS was  
 kept to a minimum of 1–5 min, in order to avoid  $\text{Hg}^0_{(\text{g})}$  losses  
 due to wall adsorption. Thallium was continuously introduced  
 by the Aridus for on-line mass bias correction using the exponen-  
 tial law.

### 3. Results and discussion

The isotopic composition of the Alfa Aesar (AA) liquid  $\text{Hg}^0_{(\text{l})}$   
 starting material and its equilibrated vapor  $\text{Hg}^0_{(\text{g})}$  are summa-  
 rized in Table 2. Relative to NIST SRM 3133, liquid AA- $\text{Hg}^0_{(\text{l})}$   
 was found to have a  $\delta^{202}\text{Hg}$  of  $-0.32\text{‰}$  and its equilibrated vapor  
 AA- $\text{Hg}^0_{(\text{g})}$  a  $\delta^{202}\text{Hg}$  of  $-1.25\text{‰}$ , the difference between the two,  
 $\Delta_{\text{vap-liq}}$  being  $-0.93\text{‰} \pm -0.17\text{‰}$  (2SD) These results confirm  
 a recent study by Estrade *et al.* that Hg vapor in equilibrium  
 with liquid Hg in the 2–22 °C range undergoes isotopic fractio-  
 nation by  $-0.86\text{‰} \pm -0.05\text{‰}$  (2SD), *i.e.* the vapor phase is  
 enriched in the lighter isotopes by  $-0.86\text{‰}$  relative to the liquid  
 Hg.<sup>13</sup>

#### 3.1. CVSI injections of $\text{Hg}^0_{(\text{g})}$

Instrumental sensitivity was compared among CV and CVSI  
 modes (see also Table 1). CV sensitivity was 1.1 V on  $^{202}\text{Hg}$  for  
 a steady-state introduction of 10 ng  $\text{g}^{-1}$  at a solution flow rate  
 of 0.3  $\text{g min}^{-1}$ . This corresponds to a Hg flux of 3.0  $\text{ng min}^{-1}$ .  
 For CVSI, 2 mL of  $\text{Hg}^0_{(\text{g})}$  vapor was withdrawn from the head-  
 space of the equilibrated Alfa Aesar liquid Hg–vapor standard  
 and contained 14  $\text{ng mL}^{-1}$  Hg at 20.7 °C. The 2 mL were injected  
 into the MC-ICP-MS at 0.2  $\text{mL min}^{-1}$ , giving a signal of 1.0 V on  
 $^{202}\text{Hg}$  for a corresponding Hg flux of  $14 \times 0.2 = 2.8$   $\text{ng min}^{-1}$  Hg.  
 CV and CVSI signal intensities of 1.1 and 1.0 V for respective Hg  
 fluxes of 3.0 and 2.8  $\text{ng min}^{-1}$  are therefore identical within error  
 and suggest that CVSI provides similar advantages as CV  
 compared to the less sensitive solution introduction of ionic  
 $\text{Hg}^{2+}$ . Memory effects from the CVSI interface are shown in  
 Fig. 3. Following a starting signal of 0.82 V, the syringe pump



**Fig. 3** Washout profile for gaseous  $\text{Hg}^0_{(\text{g})}$  in the CVSI interface. Following the measurement of a sample (period A), at 100 s the valve is closed on the syringe and results in blank level B, and at 300 s the syringe is removed from the introduction system, resulting in an immediate drop to mV blank levels.

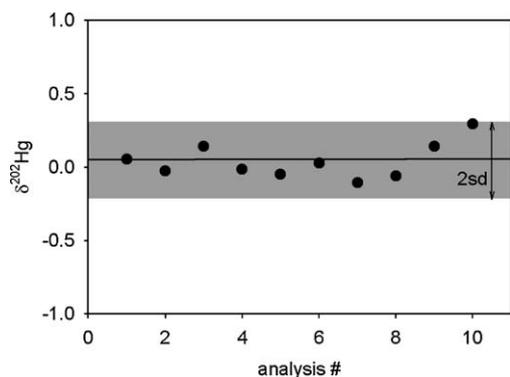
is turned off and the teflon valve closed at 100 s, resulting in  
 an instantaneous signal drop of a factor 100, followed by  
 removing the syringe, valve, and needle assembly altogether  
 form the silicone injection circuit, resulting in another signal  
 drop by a factor 10 and an approximate 1 mV background  
 $^{202}\text{Hg}$  signal.

Subsequently, the use of 50 mL syringes was tested for sample  
 purposes. Two mL of AA- $\text{Hg}^0_{(\text{g})}$  vapor were withdraw from the  
 standard headspace and injected into a larger 50 mL syringe  
 filled with air. The 50 mL syringe was injected into the  
 MC-ICP-MS at a Hg flux of 2.8  $\text{ng min}^{-1}$ . Corresponding  
 $^{202}\text{Hg}$  intensities were only 0.5 V, suggesting that even a minimal  
 amount of air induces a plasma perturbation and 100% drop in  
 sensitivity. This was confirmed by large deviations of  $\sim 3.4\text{‰}$  in  
 Hg and Tl isotope ratios, *e.g.*  $^{205}\text{Tl}/^{203}\text{Tl}$  ratio increase from  
 2.4222 to 2.4308 upon introduction of air. Although the moni-  
 tored Tl isotope ratios could reasonably well correct parallel  
 Hg isotope ratio shifts for this large air matrix induced mass  
 bias shift, the effect on the whole was considered undesirable.

Large volume syringe testing was continued after making two  
 important changes. Firstly, a closed system Hg extraction line  
 that consists of a high purity argon gas supply, dual amalga-  
 mation gold traps was used to avoid the presence of air.  
 Secondly, large volume syringes were used for both bracketing  
 standards and samples such that all sample preparation was  
 identical. Standards and samples were produced by the syringe  
 injection of 2 mL of saturated AA- $\text{Hg}^0_{(\text{g})}$  vapor into a 40 mL  
 $\text{min}^{-1}$  argon stream and pre-concentration on the analytical  
 gold trap. The trap was flash-heated to 500 °C and the released  
 $\text{Hg}^0_{(\text{g})}$  vapor directly purged into a 50 mL disposable syringe.  
 The argon provided pressure to slowly push the syringe plunger  
 to its maximum position in 75 s, while  $\text{Hg}^0_{(\text{g})}$  was slowly collected  
 in the syringe. The syringe filled with 31.1 ng of  $\text{Hg}^0_{(\text{g})}$  vapor in  
 50 mL argon gas was then injected into the MC-ICP-MS. The  
 Hg vapor pressure in the syringe of  $28/50 = 0.56$   $\text{ng cm}^{-3}$  was  
 a factor 28 lower than the saturation pressure of 15.55  $\text{ng cm}^{-3}$   
 at 22 °C, which avoids condensation of liquid  $\text{Hg}^0$ .  $\delta^{202}\text{Hg}$  values  
 for the repeated standard injections are shown in Fig. 4 and  
 average  $+0.04 \pm 0.24\text{‰}$  (2SD).

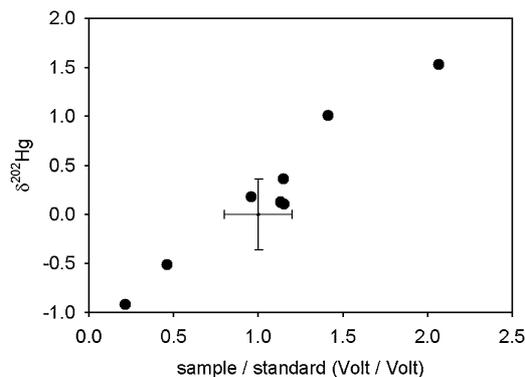
**Table 2** CV-MC-ICP-MS results for  $\text{Hg}^0_{(\text{l})}$  and  $\text{Hg}^0_{(\text{g})}$  starting materials. Isotopic composition (‰) given in delta notation relative to NIST SRM3133

		$\delta^{199}\text{Hg}$	$\delta^{200}\text{Hg}$	$\delta^{201}\text{Hg}$	$\delta^{202}\text{Hg}$
<b>Liquid <math>\text{Hg}^0_{(\text{l})}</math></b>	Replicate 1	-0.06	-0.21	-0.22	-0.29
	Replicate 2	-0.08	-0.10	-0.31	-0.32
	Replicate 3	-0.11	-0.13	-0.29	-0.34
	Average	<b>-0.08</b>	<b>-0.15</b>	<b>-0.27</b>	<b>-0.32</b>
	2SD	<b>0.04</b>	<b>0.11</b>	<b>0.09</b>	<b>0.06</b>
<b>Vapor <math>\text{Hg}^0_{(\text{g})}</math></b>	Replicate 1	-0.22	-0.61	-0.86	-1.29
	Replicate 2	-0.24	-0.48	-0.88	-1.32
	Replicate 3	-0.24	-0.54	-1.01	-1.24
	Replicate 4	-0.29	-0.62	-0.98	-1.26
	Replicate 5	-0.26	-0.62	-0.93	-1.23
	Replicate 6	-0.15	-0.56	-0.86	-1.16
	Average	<b>-0.24</b>	<b>-0.57</b>	<b>-0.92</b>	<b>-1.25</b>
2SD	<b>0.09</b>	<b>0.11</b>	<b>0.13</b>	<b>0.11</b>	



**Fig. 4** Repeated CVSI injections using identical volume syringes for both bracketing standards and samples. External reproducibility for  $\delta^{202}\text{Hg}$  is  $+0.04 \pm 0.24\%$ .

The effect of imperfect concentration matching between samples and standards was investigated by varying the syringe pump rate of sample injections, such that sample signals ranged from half to twice that of the bracketing standards at 1.6 V on  $^{202}\text{Hg}$ . The results are shown in Fig. 5 and clearly show that a higher sample signal results in a positive shift in  $\delta^{202}\text{Hg}$  and *vice versa*. This emphasizes the need to match within 10% the



**Fig. 5** Effect of matching standard and sample signals (V) on measured isotopic composition, after TI exponential mass bias correction. Matching within 25% is recommended to stay within the method's external reproducibility of  $0.24\%$  (2SD).

**Table 3** Analysis of a volcanic  $\text{Hg}^0_{(\text{g})}$  sample using CVSI-MC-ICP-MS. Raw and mass bias corrected isotope ratios, and isotopic compositions using the delta notation are given. Delta values were measured relative to bracketing standard AA-Hg, and re-expressed relative to NIST SRM 3133 for comparison with other studies

	$^{199/198}\text{Hg}$		$^{200/198}\text{Hg}$		$^{201/198}\text{Hg}$		$^{202/198}\text{Hg}$		$^{205/203}\text{Tl}$ Raw
	Corrected	Raw	Corrected	Raw	Corrected	Raw	Corrected	Raw	
<b>F0</b>	1.68738	1.70154	2.30377	2.34253	1.31169	1.34482	2.96048	3.06029	2.42627
<b>AA-Hg</b>	1.68768	1.70184	2.30463	2.34335	1.31221	1.34533	2.96195	3.06176	2.42622
		$\delta^{199}\text{Hg}$		$\delta^{200}\text{Hg}$		$\delta^{201}\text{Hg}$		$\delta^{202}\text{Hg}$	
<b>F0-AA</b>		-0.18		-0.38		-0.41		-0.49	
<b>F0-NIST</b>		-0.42		-0.95		-1.33		-1.74	
<b>ISD</b>		0.16		0.26		0.11		0.18	

sample and standard signals by optimization of the standard CVSI injection rate.

### 3.2. Application to atmospheric $\text{Hg}^0_{(\text{g})}$ sampling

In January 2005, we sampled elemental  $\text{Hg}^0_{(\text{g})}$  emissions from the passive degassing volcano 'Vulcano' in Italy. The sampled was collected by pumping fumarole F0 emissions at  $0.3 \text{ L min}^{-1}$  for 3 h through a sampling chain consisting of a GF/F filter (particulates), a soda lime trap (acid and  $\text{H}_2\text{O}$  absorption) and two gold bead traps that were kept at  $40^\circ\text{C}$  to prevent potential  $\text{H}_2\text{O}$  condensation. The second gold trap was used to monitor potential saturation of the first trap, yet no such behavior was observed. Following sampling, the trap was tightly sealed with teflon sleeves and end caps and transported to the lab, where it was analyzed using the protocol described above: the trap was heated to  $500^\circ\text{C}$ , the released  $\text{Hg}^0_{(\text{g})}$  vapor collected in a new 50 mL disposable syringe, and injected at  $10 \text{ mL min}^{-1}$  into the CVSI interface for MC-ICP-MS detection. The obtained signal was 0.62 V on  $^{202}\text{Hg}$ , the total acquisition time was 5 min, and the total amount of Hg analyzed was 5 ng. A bracketing AA- $\text{Hg}^0_{(\text{g})}$  standard was analyzed immediately afterwards, using the same injection preparation and with the injection flow rate adjusted to match the sample signal within 10% (see Table 3 for raw and processed isotope ratio data). The  $\delta^{202}\text{Hg}$  of fumarole sample F0 was thus found to be  $-0.49\% \pm 0.32\%$  relative to the AA- $\text{Hg}^0_{(\text{g})}$  bracketing standard. As we have shown above, the AA- $\text{Hg}^0_{(\text{g})}$  itself is  $-1.25\%$  lighter than the international delta-0 standard for Hg, NIST SRM 3133. Sample F0 can now be expressed on the SRM 3133 scale with  $\delta^{202}\text{Hg}$  of  $-0.49\% + (-1.25\%) = -1.74\% \pm 0.36\%$  (2SD internal precision). The isotopic composition of gaseous elemental Hg emitted from Vulcano is therefore enriched in the lighter isotopes relative to the majority of terrestrial Hg isotopic compositions of sediments,<sup>8</sup> cinnabars,<sup>6</sup> and fish tissues.<sup>15</sup> Similar behavior, *i.e.* an isotopically light gas phase, was found by our group for volcanic emissions of Zn.<sup>20</sup> Finally, the analysis of sample F0 revealed mass dependent fractionation within the measurement uncertainties.

## 4. Conclusions

A novel method is presented to indirectly couple gold traps for atmospheric Hg sampling with multi-collector ICP-MS for

high precision stable isotope analysis. The method is based on cold vapor syringe injection (CVSI) of  $\text{Hg}^0_{(g)}$  into the ICP-MS plasma. In essence,  $\text{Hg}^0_{(g)}$  collected in the environment on gold traps are transported to the lab, heated and the recovered  $\text{Hg}^0_{(g)}$  transferred into a large volume syringe. The syringe contents,  $\text{Hg}^0_{(g)}$  and argon, are subsequently injected at a constant rate into the ICP-MS argon stream, avoiding thereby the problems associated with transient signal detection. The memory effects of the CVSI interface are superior to those of classical cold vapor (CV) generation, and a similar external reproducibility of 0.24% (2SD) has been obtained for 50 ng Hg injections.

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