Méthodologie Analytique



<u>Table des matières</u>

Chapitre 2: Méthodologie Analytique	67
A. Article: "Measuring Hg isotopes in Bio-Geo-Environmental Referen material	69
A.1. Abstract	69
A.2. Introduction	70
A.3. Experimental	71
A.4. Results and Discussion	74
A.5. Conclusion	81
A.6. References	82



Measuring Hg Isotopes in Bio-Geo-Environmental Reference Materials

Nicolas Estrade (1, 2)*, Jean Carignan (1), Jeroen E. Sonke (3) and Olivier F.X. Donard (2)

 Centre de Recherche Pétrographique et Géochimique, Nancy Université, CNRS UPR 2300, BP 20, 54501 Vandoeuvre les Nancy, France

(2) Institut Pluridisciplinaire de Recherche sur l'Environennement et les Matériaux, Laboratoire de Chimie-Analytique Bio-Inorganique et Environnement, Université de Pau et des Pays de l'Adour, CNRS UMR 5254, HELIOPARC, 64053 Pau, France

(3) Observatoire Midi-Pyrénées, Laboratoire des Mécanismes et Transferts en Géologie, CNRS/IRD/Université de Toulouse 3, UMR 5563, 14 avenue Edouard Belin, 31400 Toulouse, France.

Corresponding author. e-mail: nestrade@crpg.cnrs-nancy.fr

With the emergence of new analytical techniques and the expansion of scientific fields explored by using mercury isotopes, the community needs reference materials (RM) to validate and assure the accuracy of the results. The present work investigates (1) the characterisation of secondary RM in order to validate analytical systems, (2) the effects of two complex matrices on isotopic determination using stannous chloride cold vapour generation coupled to MC-ICP-MS (CV-MC-ICP-MS), (3) the effects of multiple digestion techniques for total Hg extraction and (4) the characterisation of nine geo-bio-environmental RM. Two secondary monoelemental RMs analysed using two different analytical setups yielded isotopic compositions on $\delta^{202}\text{Hg}$ of -3.54 \pm 0.27‰ (CRPG-F65A, 2SD, n = 38) and +2.59 \pm 0.19‰ (CRPG-RL24H, 2SD, n = 30) relative to the CRM NIST SRM 3133. These two RMs cover the whole range of Hg isotopic fractionation in natural samples and are made available to the scientific community. Complex fly ash and hydroxysulfate green rust matrices were synthesised, spiked with NIST SRM 3133, then digested and finally analysed versus the monoelemental NIST SRM 3133 to show potential effect of these complex matrices during CV-MC-ICP-MS. Three digestions techniques, including traditional acid digestion, microwave digestion and high pressure-high temperature digestion, were applied to the lichen RM BCR-482 in order to compare advantages and drawbacks of these methods. Finally, the isotopic compositions of nine RMs including soils (NIST SRM 2711; GXR-2; GSS-4), sediment (GSD-10), jasperoid (GXR-1), ore deposit (GXR-3), fly ashes (BCR-176; BCR-176R) and lichen (BCR-482) are reported. These selected materials

Devant l'émergence des nouvelles techniques analytiques et l'expansion des champs scientifiques explorés par l'utilisation des isotopes du mercure, la communauté scientifique a besoin de matériaux de références pour valider et assurer la justesse des résultats de mesures. Ce travail investique (1) la caractérisation de matériaux de référence secondaires afin de valider les différents systèmes analytiques, (2) l'effet de deux matrices complexes sur la mesure des compositions isotopiques en utilisant la génération de vapeur froide (chlorure stanneux) couplé à l'ICP-MS multicollecteur (CV-MC-ICP-MS), (3) l'effet de plusieurs techniques de digestion pour l'extraction du Hg total, (4) la caractérisation de neuf matériaux de référence d'origine géologique, biologique ou environnementale. Les deux matériaux de référence secondaires mono élémentaires ont été analysés avec plusieurs systèmes analytiques et ont montré des compositions isotopiques sur $\delta^{202} Hg~de$ -3.54 \pm 0.27‰ (CRPG-F65A, 2SD, n = 38) et $+2.59 \pm 0.19\%$ (CRPG-RL24H, 2SD, n = 30) par rapport au matériau de référence certifié NIST SRM 3133. Ces deux matériaux de référence couvrent intégralement la gamme de fractionnement isotopique de Hg mesurée dans la nature et sont disponibles pour toute la communauté scientifique. Des matrices complexes comme des cendres volantes et des rouilles vertes sulfatées ont été synthétisées, le matériau de référence NIST SRM 3133 a ensuite été ajouté et elles ont été digérées pour être enfin analysées par rapport à ce même matériau de référence dans le but de montrer l'effet potentiel d'une matrice complexe lors de la CV-MC-ICP-MS. Trois techniques de digestions comprenant une digestion acide classique, une

 ${\ensuremath{\mathbb C}}$ 2009 The Authors. Journal compilation ${\ensuremath{\mathbb C}}$ 2009 International Association of Geoanalysts



have $\delta^{202}\text{Hg}$ values ranging from -1.75‰ to +0.11‰. Some RMs also presented mass-independent fractionation with $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ of up to -0.6‰.

Keywords: mercury, isotopic composition, reference material, digestion techniques, matrix effects.

digestion micro-ondes et une digestion haute température, haute pression ont été appliquées au lichen de référence BCR-482 afin de comparer les avantages et les inconvénients de ces méthodes pour l'analyse isotopique. Finalement, la composition isotopique de neuf matériaux de référence incluant des sols (NIST SRM 2711; GXR-2; GSS-4), un sédiment (GSD-10), un jasperoid (GXR-1), un minerai (GXR-3), des cendres volantes (BCR-176; BCR-176R) et un lichen (BCR-482) est reportée. Ces matériaux présentent une gamme de fractionnement isotopique sur le δ^{202} Hg de -1.75‰ à +0.11‰. Certains matériaux présentent aussi des fractionnements indépendants de la masse avec des Δ^{199} Hg et Δ^{201} Hg jusqu'à -0.6‰.

Received 23 Feb 09 — Accepted 20 Jul 09

Mots-clés : mercure, composition isotopique, matériaux de références, technique de digestion, effets de matrice.

Mercury comprises seven isotopes from mass 196 to 204. Its exact atomic weight, estimated from the relative abundance of its isotopes, was precisely evaluated by Alfred Nier almost 60 years ago (Nier 1950). In the last 10 years, other analysts have reported the relative isotope abundance of "terrestrial mercury" in various samples, such as cinnabar from the Almaden mines or Hg from NIST reference materials (SRM 1641d and SRM 3133) (Lauretta et al. 2001, Hintelmann and Lu 2003, Xie et al. 2005, Smith et al. 2005, 2008, Foucher and Hintelmann 2006, Blum and Bergquist 2007). Although MC-ICP-MS measurements of Hg isotopic composition may be precise to fractions of ‰, the determination of an absolute ratio is a difficult task. Indeed, whereas individual measurement of ²⁰²Hg/¹⁹⁸Hg ratios have low reported uncertainties, variations of a few ‰ on that ratio for a given sample may be calculated when comparing proposed values from one group to another (Hintelmann and Lu 2003, Xie et al. 2005, Foucher and Hintelmann 2006, Ridley and Stetson 2006, Blum and Bergquist 2007, Yang and Sturgeon 2009). This highlights the fact that the best way to express Hg isotopic compositions is to use delta values relative to a common RM, for example, NIST SRM 3133 as proposed by Blum and Bergquist (2007).

Up to now, most Hg isotope determinations were conducted using stannous chloride (SnCl₂) cold vapour generation coupled to MC-ICP-MS, allowing the characterisation of the total Hg isotopic composition. This method is based on the quantitative transformation of Hg(II) in solution into a mono-elemental Hg⁰ vapour directly introduced into the MC-ICP-MS after being mixed with a Tl isotopic reference solution for the purpose of mass bias correction (e.g., Blum and Bergquist 2007). As only Hg vapour is introduced into the MC-ICP-MS, the method allows measurements on a matrixfree sample and, therefore, prevents instrumental matrix element interferences and benefits from a high sensitivity compared with solution nebulisation. However, some authors (e.g., Malinovsky *et al.* 2008) have pointed out that the kinetics of Hg(II) reduction by SnCl₂ may vary significantly with complex sample matrices, leading to incomplete reduction in the introduction system and possible isotope fractionation (Zheng *et al.* 2007).

In parallel, new approaches for Hg isolation from the matrix are emerging in order to determine the isotopic composition of the various Hg phases or chemical forms of a given sample. Sonke et al. (2008) developed a Hg⁰ vapour preconcentration technique by amalgam onto a gold trap and desorption into a syringe that was then directly coupled to the MC-ICP-MS for isotope determination of atmospheric gaseous elemental Hg (Zambardi et al. 2009). Malinovsky et al. (2008) used anion exchange chromatography and a solution nebulisation introduction system for the separation of total Hg. Epov et al. (2008) developed an online gas chromatography (GC) separation coupled to a MC-ICP-MS to determine simultaneously the Hg(II) and MeHg isotopic composition. Finally, Dzurko et al. (2009) also developed a GC separation method



coupled to a MC-ICP-MS to investigate mercury methylation. A combustion method was developed to liberate Hg from large quantities of solid samples for subsequent CV-MC-ICP-MS analysis and applied to mineral, rock, coal and sediment matrices (Smith *et al.* 2005, 2008, Biswas *et al.* 2008, Sherman *et al.* 2009, Gehrke *et al.* 2009). The emergence of these new analytical techniques for measuring Hg isotopic compositions justifies the need for a multitude of reference materials of biological, geological, environmental and atmospheric origin, characterised for their Hg isotope composition.

After the validation of different digestion techniques and the quantitative reduction of Hg(II) with various matrices, this study presents the Hg isotopic composition of some new and existing bio-geo-environmental reference materials. Mono-elemental fractionated solutions were characterised for their Hg isotopic composition to ensure accuracy and reproducibility of isotopic measurements using different analytical setups. These solutions are available to the community. In addition, the Hg isotopic composition of existing soils, sediments, lichens and anthropogenic reference materials is provided.

Experimental

Reagents

For the present study, PROLABO[®] and NORMAPUR HNO₃ and H₂SO₄ solutions (69% (m/v) and 98.5% (m/v) respectively) were used for the trace determination of Cd, Hg and Pb. The HCl used was a double distilled solution. All dilutions were undertaken with MilliQ water (18 MQ). Prior to digestions, dilutions or analyses, glass and Teflon vials were cleaned twice in a 10% (w/v) nitric acid bath with ultrasonic agitation.

Mono-elemental Hg solutions

Two mono-elemental Hg solutions having distinct isotopic compositions were produced using liquid mercury evaporation as described in Estrade *et al.* (2009). The starting material was a commercial liquid metal mercury solution (Rhône-Alpes Technologies). One solution, named CRPG-RL24H, represents the residual liquid fraction evaporated at 22 °C for 24 hours. The second, named CRPG-F65A, represents the condensed fraction evaporated at 65 °C for 15 minutes. These two solutions were intended to be secondary reference solutions for Hg isotopic determination.

Synthesis of artificial matrices

To evaluate the quantitative reduction of Hg(II) into Hg(0) by tin chloride and related matrix effects, the NIST SRM 3133 Hg solution was added to two Hg-free samples having various elemental concentrations. The complex synthesised matrices were chosen to be representative of samples analysed at the CRPG/IPREM/LMTG laboratories. One of the samples was prepared to have a matrix composition similar to that of the fly ash BCR-176. The starting material was the RM IWG-GIT basalt BE-N heated at 1000 °C (hereafter named BE-N*) to remove entirely the original 40 ng g⁻¹ Hg. Analyses of BE-N* using a Milestone DMA-80 mercury analyser showed a Hg concentration of 1.04 \pm 0.06 ng g^{-1} (2SD; n = 10), which represented a maximum contribution of 2% to the total added Hg. This latter contribution cannot alter the isotopic composition of the NIST SRM 3133 spiked into the BE-N*, unless the original isotopic composition of the BE-N was 10% fractionated (δ^{202} Hg) relative to NIST SRM 3133, which is unlikely considering the fractionation range of Hg isotopes in terrestrial rocks. Compared to the fly ash BCR-176, the BE-N* matrix was depleted in several major elements (Al, Ca) and mostly in trace elements. For this reason, Al and Ca were added as Al(NO₃)₃·9H₂O_(s) (1.46 g) and CaCO $_{\rm 3(S)}$ (0.145 g) to 2 g of BE-N*. Two preparations of that mixture (1 g and 0.75 g) were digested using the procedure described in the following section. NIST SRM 3133 was added to the solution at the initial step of the digestion procedure to reach a concentration of 10 μ g l⁻¹ Hg(II) in 10 ml and a final step consisted of adding 100 μ l of a 1000 mg l⁻¹ multi-elemental solution (As, Cu, Zn, etc). One synthesis of this matrix was performed using the same conditions without adding Hg in order to assess blank issues.

A second complex Hg-free matrix, the sulfated green rust (GR₂SO₄) was synthesised (Géhin *et al.* 2002) to constrain any matrix effect during online Hg(II) reduction and analysis. This sample consisted of a mixture of Fe(II)/Fe(III) hydroxides that have layered structures. In our case, the interlayer hydrated anion was SO₄²⁻ with the form Fe^{II}₄Fe^{III}₂(OH)¹²SO₄·8H₂O. Matrix tests were performed using a 3.16 mmol I⁻¹ (GR₂SO₄) solution containing 12.6 mmol I⁻¹ iron in solution. A 1 ml sample was then filtered (0.45 μ m Teflon syringe filter) and added to 1 ml of concentrated HNO₃ in a Teflon beaker in order to keep the solution oxidised. NIST SRM 3133 Hg was then added to reach a concentration of 50 μ g I⁻¹ Hg(II) in 10 ml (water dilution).



Reference material descriptions

In this study, nine reference materials were chosen on the basis of (1) matrix (various geological, anthropogenic and biological matrices), (2) Hg concentration (280 ng g⁻¹ to 34.1 μ g g⁻¹) and (3) geographical origin (Europe, USA and China). The reference materials BCR CRM 176, CRM 176R and CRM 482 are distributed by the Community Bureau of Reference (BCR), Institute for Reference Materials and Measurements, Belgium. NIST SRM 2711 is distributed by the National Institute of Standards and Technology (NIST, USA). The samples GXR-1, GXR-2 and GXR-3 are distributed by United States Geological Survey (USGS, USA). GSS-4 and GSD-10 are distributed by the Institute of Geophysical and Geochemical Exploration (IGGE, China).

BCR CRM 176 is a fly ash from a municipal waste incineration plant (31.4 µg g⁻¹ Hg, Amsterdam, Netherlands). However, this RM is now exhausted and has been replaced by BCR CRM 176R, which is a fly ash from the same sampling site (1.6 μ g g⁻¹ Hg). BCR CRM 482 is an epiphytic lichen (Pseudevernia furfurcea) sampled in the European Alps (0.48 μ g g⁻¹ Hg, Axalp, Switzerland). NIST SRM 2711 is an agricultural soil (6.3 μ g g⁻¹ Hg, Montana, USA). GXR-1 is a jasperoid from the Drum mountains (4.4 $\mu g~g^{\text{-1}}$ Hg, Utah, USA), GXR-2 is a soil from a city park (3.6 $\mu g~g^{-1}$ Hg, Utah, USA) and GXR-3 is a Fe-Mn-W rich hot spring deposit from Humboldt County (0.42 µg g⁻¹ Hg, Nevada, USA). GSS-4 is a soil sampled in a subtropical climate (0.59 μ g g⁻¹ Hg, China) and GSD-10 is a stream sediment from a tributary draining carbonate rocks (0.28 $\mu g~g^{-1}$ Hg, China). Additional details of RM compositions and descriptions are available from the respective RM suppliers, from Govindaraju (1994) and on the geological and environmental reference materials (GeoReM) website (http://georem.mpchmainz.gwdg.de).

Sample preparation for analysis

Depending on the Hg concentration, between 0.1 and 1.5 g of material was introduced into a 10 ml glass tube along with 2 ml of concentrated HNO₃ and 2.5 ml of concentrated H₂SO₄ (HNO₃/H₂SO₄/H₂O mixture; 4:5:11; v/v) and then digested at 100 °C in a water bath. The NIST SRM 3133 Hg was added to the Hg-free prepared samples to reach a concentration of 50 μ g l⁻¹. Droplets of KMnO₄ solution (5% w/v) were added to all samples until there was a permanent purple colouration to keep the mixture oxidised.

Samples were cooled to room temperature and MilliQ water was then added to make solutions up to a volume of 10 ml. Mercury concentrations were measured using CV-AAS (2SD = \pm 10%).

The addition of the HNO_3/H_2SO_4 mixture at 100 °C to the biological matrix of the lichen reference sample BCR CRM 482 ($C_{org} = 42.1\%$ m/m) caused a vigorous reaction and led to the formation of a thick foam above the liquid due to the degassing of CO_2 and nitrous vapours. No more than 0.25 g of this biological matrix could be digested using the method described. To investigate the Hg isotopic composition of lichens at low Hg concentrations (< 100 ng g⁻¹), two methods were tested: one using an Anton Paar High Pressure Asher[®] (HPA) and the other using an Anton Paar microwave oven[®]. In each case, up to 1 g of lichen sample was digested in a small amount of acid.

Between 0.5 and 1 g of BCR CRM 482 and acid mixtures (6 ml concentrated HCl/HNO3, 1:5; v/v, and 6 ml HNO₃ 100%, and 3 ml HNO₃ 100%) were introduced into specifically designed 50 ml quartz tubes that fit the HPA oven rack (five samples per run). Prior to HPA introduction, a pre-digestion procedure was performed to remove $CO_{2^{\prime}}$ avoiding foam generation and so reducing the risk of overpressure in the HPA. The pre-digestion consisted of dipping the sample tubes into a 70 °C ultrasonic bath. This step involved the development of foam, which could be restrained using cold water. The tubes were then shaken on a shaking plate to reactivate the reaction. This was repeated until no foam was produced during ultrasonic treatment. Final digestion in the HPA was done at 260 °C and 130 bars (nitrogen) for 3 hours (5 hours total: heating-digestion-cooling). Samples were then transferred into clean amber vials and the quartz tubes were rinsed twice with 2 ml MilliQ water, and also transferred into the vial samples. The quartz tube cleaning procedure consisted of rinsing with MilliQ water and then filling with HNO3 (50% v/v, 10 ml) before being placed for 3 hours in the HPA at 260 °C and 130 bars. An alternative cleaning procedure was tested and consisted of filling the quartz tube with HNO₃ (50% v/v) and heating at 110 °C overnight. A few droplets of concentrated HF were then added and the tubes were ultrasonically treated for 5 minutes to remove any organic matter (carbon) stuck to the tube walls. The two methods showed an excellent quality of the Hg blank level, equal to blanks measured with reagent acid use for isotopic determination (< 1% signal intensity of the reference material samples).



The microwave digestion involved introducing 0.5 to 1 g of lichen BCR CRM 482 into an hermetically sealed tube along with 8 ml of *aqua regia* (HNO₃:HCl, 1:3). The digestion procedure was set at 220 °C for 1 hour. The pressure in the tube reached up to 20 bars. The tubes were cleaned by placing them twice in a 10% HNO₃ bath with ultrasonic agitation.

To check the total recovery of Hg after the digestion of these RMs, Hg concentrations were determined. The CV-AAS technique was used for all RMs digested using the HNO₃/H₂SO₄ mixture. Recovery digestion yields performed on the lichen BCR CRM 482 using HPA and microwave methods were directly measured from the MC-ICP-MS signal intensities compared to reference solutions having a similar acidic matrices measured prior to isotopic determination (2SD assumed was \pm 10%).

Isotopic determination

The isotopic composition of Hg solutions, matrix samples and the various RMs was determined by CV-MC-ICP-MS, as proposed by Blum and Bergquist (2007). Two mass spectrometers (Thermo Finnigan Neptune, at the Laboratoire des Mécanismes et Transferts en Geologie (LMTG) in Toulouse and a Nu Plasma HR at the Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux (IPREM) in Pau) and two introduction settings were used and results were compared. A Perkin Elmer FIAS-400 coupled to the Neptune and an in-house fabricated cold vapour (CV) generator coupled to the Nu plasma HR were used, the latter having a longer reaction loop and a liquid-gas separation chamber much larger than the commercial CV generator. In all cases, liquid samples and references were diluted in a similar

acidic matrix to appropriate Hg concentrations (5 to 20 μ g |-1) and Hg(II) was reduced on-line with 3% w/v SnCl₂ (Alfa Aesar NormaPur) in 1 mol l-1 doubledistilled HCl. The drift in the instrumental mass bias was monitored by using the standard solution-samplestandard solution bracketing method with NIST SRM 997 thallium as the internal standard. Any detected drift was corrected with the exponential mass fractionation law. The NIST SRM 997 thallium solution was continuously introduced using a desolvation unit (CETAC Aridus II or DSN). Mixing with Hg⁰ was done just after the Hg gas production (T-piece connection after the cold vapour generator). Additional descriptions are provided in Estrade *et al.* (2009) and information on settings are shown in Table 1.

Variations in Hg isotopic composition are expressed relative to the certified reference material NIST SRM 3133, using the delta notation and following recent recommendations for Hg isotope measurement (Blum and Bergquist 2007):

$$\delta^{X/198}(\%)_{\text{sample/NIST SRM 3133}} = \left(\frac{\chi/198}{\chi/198} \text{Hg}_{\text{sample}} - 1\right) \times 1000 \quad (1)$$

where X represents Hg isotopes other than 198. Mass -independent fractionation (MIF) is expressed as described in Blum and Bergquist (2007):

- $\Delta^{199}\text{Hg} = \delta^{199}\text{Hg}_{\text{measured}} 0.252 \times \delta^{202}\text{Hg}_{\text{measured}}$ (2)
- $\Delta^{200}\text{Hg} = \delta^{200}\text{Hg}_{\text{measured}} 0.502 \times \delta^{202}\text{Hg}_{\text{measured}}$ (3)
- $\Delta^{201}\text{Hg} = \delta^{201}\text{Hg}_{\text{measured}} 0.752 \times \delta^{202}\text{Hg}_{\text{measured}}$ (4)
- $\Delta^{204}Hg = \delta^{204}Hg_{measured} 1.493 \times \delta^{202}Hg_{measured}$ (5)

Table 1.

Operating conditions	for CV-MC-ICP-MS and	llyses using two differ	ent instruments and settings
----------------------	----------------------	-------------------------	------------------------------

Instrumentation Monitored isotopes Cup configuration	Thermo Finnigan Neptune MC-ICP-MS (LMTG, Toulouse) 198, 199, 200, 201, 202, 203, 205 13, 12, 11, C, H1, H2, H3	Nu Plasma HR MC-ICP-MS (IPREM, Pau) 198, 199, 200, 201, 202, 203, 204, 205, 206 12, 11, Ax, H1, H2, H3, H4, H5, H6,
RF power	1200 W	1300 W
Cones	Ni	Ni typeB dry plasma
Accelerating voltage	10000 V	6000 V
CV generator system	Perkin Elmer FIAS-400	In-house quartz liquid/gas separator
Liq/gas separation volume	≈ 5 ml	≈ 50 ml
Tl introduction	Cetac Aridus II desolvation unit	DSN desolvation unit
Tl-Hg gas coupling	T-piece connection after CV	T-piece connection after CV
Sample gas introduction	Direct	Direct
Sample uptake (ml min-1)	0.600	0.550
Hg intensity (V/μg ml-1)	670	900
²⁰² Hg SE (%)	0.1	0.1
^{202/198} Hg SE (‰)	0.03	0.01

© 2009 The Authors. Journal compilation © 2009 International Association of Geoanalysts

73

GEO GEOANALYTICAL RESEARCH

The long-term external reproducibility of the method was determined by repeated analyses of the well-characterised UM-Almaden RM for which our results were compared to published values (-0.54 \pm 0.08, 2SD, Blum and Bergquist 2007). The external reproducibility of unknown samples was calculated as 2 standard errors (2SE) of the mean value (from different brackets of the sample), except when this value was lower than the external reproducibility of the method, as proposed by Goldstein et al. (2003).

The isotopic composition of two mono-elemental Ha solutions CRPG-RL24H and CRPG-F65A was determined using the Neptune MC-ICP-MS at the LMTG and the Nu Plasma at the IPREM. Measurements were made with sample concentrations of between 5 and $25~\mu g$ l-1 in various matrices according to sample preparation (see Results and discussion).

Results and discussion

Analytical performance of the methods and secondary reference material isotopic compositions

The isotopic composition of the two Hg solutions was investigated over a period of 12 months in multiple diluted acidic matrices (HNO3, HNO3/HCl and HNO3/H2SO4, KMnO4/H2SO4, K2CrO7/NH2OH) at various concentrations (5 to 25 μ g l⁻¹) using the Neptune setting configuration. During this period, we started isotopic measurements on the UM-Almaden reference material in a simple 5% v/v HNO_3 matrix to determine the long-term reproducibility of the method. Our results yielded a mean δ^{202} Hg of -0.51 ± 0.15‰ (2SD, n = 10), in agreement with published data of Blum and Bergquist (2007). The 2SD determined for the reference material UM-Almaden will be reported unless the 2SE of a sample is larger than this value. Results are presented in Table 2 and Figure 1.

The CRPG-RL24H Hg displayed a δ^{202} Hg of 2.59 ± 0.17‰ (2SD, n = 20) whereas CRPG-F65A Hg had a δ^{202} Hg of -3.55 ± 0.27‰ (2SD, n = 30). These values cover almost the entire compositional range of natural terrestrial isotopic variations. These two Hg samples also displayed very small, but significant, Δ^{199} Hg and Δ^{201} Hg values, suggesting some massindependent fractionation of odd Hg isotopes (Estrade et al. 2009).

These two CRPG samples were then used to validate isotopic measurements conducted on the Nu Plasma HR MC-ICP-MS at the IPREM, with a different CV introduction system. The in-house CV generator designed with a higher liquid-gas separation volume coupled to the Nu plasma HR resulted in a higher sensitivity and a better stability of the ion beam. Internal

Table 2.					
Isotopic compositions of Hg solutions	CRPG F	RL24H,	CRPG F65A	and UM	Almaden

Sample	Instrumentation	n ^{a)}	δ ¹⁹⁹ Hg	2SD	δ 200Hg	2SD	$\delta^{201}Hg$	2SD	δ 202Hg	2SD	δ 204Hg	2SD
CRPG RL24H	Neptune	20	0.59	0.15	1.33	0.16	1.94	0.19	2.59	0.17	-	-
	Nu Plasma HR	10	0.60	0.08	1.29	0.12	1.89	0.17	2.58	0.24	3.85	0.39
		30 ^{b)}	0.60	0.14	1.32	0.16	1.92	0.19	2.59	0.19	3.85	0.39
CRPG F65A	Neptune	30	-0.81	0.10	-1.77	0.16	-2.66	0.24	-3.57	0.27	-	-
	Nu Plasma HR	8	-0.78	0.12	-1.73	0.15	-2.56	0.16	-3.46	0.20	-5.20	0.33
		38 ^{b)}	-0.81	0.10	-1.76	0.16	-2.64	0.23	-3.54	0.27	-5.19	0.31
UM Almaden	Neptune	10	-0.14	0.09	-0.26	0.10	-0.41	0.11	-0.51	0.15	-	-
Sample	Instrumentation	n ^{a)}	∆ ¹⁹⁹ Hg	2SD	∆ ²⁰⁰ Hg	2SD	Δ^{201} Hg	2SD	∆ ²⁰⁴ Hg	2SD		
CRPG RL24H	Neptune	20	-0.05	0.05	0.01	0.06	-0.06	0.06	-	-		
	Nu Plasma HR	10	-0.05	0.05	-0.01	0.05	-0.06	0.06	-0.01	0.12		
		30 ^{b)}	-0.05	0.05	0.00	0.06	-0.06	0.06	-0.01	0.12		
CRPG F65A	Neptune	30	0.09	0.05	0.03	0.07	0.04	0.06	-	-		
	Nu Plasma HR	8	0.09	0.08	0.01	0.06	0.04	0.04	-0.03	0.13		
		38 ^{b)}	0.09	0.08	0.03	0.07	0.04	0.06	-0.03	0.13		
	NI 1	10	0.01	0.07	0.01	0.06	0.02	0.04				

 δ^{204} Hg and Δ^{204} Hg were calculated only using measurement acquired on the Nu Plasma HR. Number of measurements. b)

© 2009 The Authors. Journal compilation © 2009 International Association of Geoanalysts

GEO



GEOANALYTICAL RESEARCH Figure 1. Isotopic compositions

ANDARDS and

(δ^{202} Hg) of Hg solutions CRPG-F65A, CRPG-RL24H and UM-Almaden measured by different cold vapour generators coupled to a Thermo Finnigan Neptune and a Nu Plasma HR.

Table 3.
Isotopic composition of NIST SRM 3133 into spiked BE-N* matrix and GR2(SO ₄)
matrix relative to NIST SRM 3133 prepared into the corresponding acidic matrix

Sample	Matrix	Hg (μg I-1)	n ^{a)}	δ ¹⁹⁹ Hg	2SD	δ 200Hg	2SD	δ ²⁰¹ Hg	2SD	δ 202Hg	2SD
Е1ь)	Spiked BE-N* (1g)	25	3	-0.01	0.04	-0.03	0.13	-0.06	0.08	-0.10	0.12
E2 ^{b)}	Spiked BE-N* (0.75 g)	25] d)	-0.01	0.09	-0.03	0.10	-0.07	0.11	-0.09	0.15
E3 ^{c)}	GR2(SO₄)	25] d)	-0.03	0.09	-0.01	0.10	-0.11	0.11	-0.06	0.15
	(3.16 mmol -1)										
Sample	Matrix	Hg (μg I-1)	nª)	∆ ¹⁹⁹ Hg	2SD	∆ ²⁰⁰ Hg	2SD	$\Delta^{201}Hg$	2SD		
Е1ь)	Spiked BE-N* (1g)	25	3	0.02	0.04	0.00	0.01	0.02	0.05		
E2 ^{b)}	Spiked BE-N* (0.75 g)	25] d)	0.02	0.07	0.01	0.06	-0.01	0.04		
E3 ^{c)}	GR2(SO ₄₎ (3.16 mmol -1)	25] d)	-0.01	0.07	0.02	0.06	-0.07	0.04		

a) b) E1 and E2 were bracketed using 12.5% H₂SO₄, 10% HNO₃ acidic matrix. Number of measurements. c) d) E3 was bracketed using 10% HNO₃ acidic matrix. 2SD of CRPG-RL24H was used.

reproducibility on isotopic ratio measurements was thus improved two-fold relative to the Neptune configuration (Table 1). Isotopic measurements conducted on CRPG RL24H and CRPG F65A led to similar isotopic delta values and external reproducibility than the one acquired using the Neptune set-up configuration (CRPG RL24H: δ^{202} Hg = 2.58 ± 0.24‰ (2SD, n = 10) and CRPG F65A: δ^{202} Hg = -3.46 ± 0.20‰ (2SD, n = 8), see Table 2 and Figure 1).

CRPG RL24H and CRPG F65A are proposed as secondary reference materials for Hg isotopic determination. Average isotopic compositions and associated external reproducibility determined using two MC-ICP-MS settings in several matrices are given in Table 2. These two secondary mono-elemental reference materials are available from the authors in amber glass bottles of 20 ml in 5% v/v HNO3 at a concentration of 1 mg |-1 Hg.

igestion method	Analysis	Test	Digested	Digestion	lsotopic	δ ¹⁹⁹ Ηg (‰)	δ ²⁰⁰ Hg (‰)	δ ²⁰¹ Hg (‰)	δ ²⁰² Hg (‰)	∆ ¹⁹⁹ Hg (‰)	∆ ²⁰⁰ Hg (‰)	∆ ²⁰¹ Hg (‰)
	number (#)	portion	mass (g)	yield (%)	concentration (µg l-1)							
NO ₃ /H ₂ SO ₄ /H ₂ O	- 0	A	0.297	100	4	-0.95	-0.72	-1.80	-1.60	-0.55	0.08	-0.60
iixture 1:5:11; v/v)	N M	Ш	0.294	100	4	-1.13 -1.13	-0.95 -0.90	-2.13 -1.62	-2.00 -1.79	-0.57 -0.68	0.05 0.00	-0.63 -0.27
0 ml	4				Averade (#2:#3) b)	-0.98 -0.97	-0.74	-1.83 -182	-1.64 -1.62	-0.56 -0.56	0.08	-0.59
					2SD (#2;#3) b)	0.04	0.03	0.04	0.06	0.01	0.00	0.01
PA CI (HNC	5	υ	0.413	94	5	-1.03	-0.75	-1.82	-1.59	-0.62	0.06	-0.62
1:5; v/v)	0 - 0	D	0.716	16	5	-1.13	-0.71 -0.71	-1.90	-1.61	-0.01	0.11	-0.67
III	∞ 0	ш	1.036	16	Ω	-0.97 -1.04	-0.69 -0.66	-1.73 -1.87	-1.53 -1.56	-0.59 -0.65	0.08 0.12	-0.58 -0.69
	0 II	ш	1.036	100	20	-1.06 -1.05	-0.73 -0.93	-1.81 -1.93	-1.62 -1.78	-0.65 -0.60	0.09 -0.04	-0.59 -0.59
	12				Average 2SD	-1.09 -1.05 0.10	-0.73 -0.74 0.16	-1.90 -1.85 0.13	-1.63 -1.62 0.15	-0.68 -0.64 0.09	0.09 0.07 0.10	-0.68 -0.63 0.09
PA NO_ (100% v)	13	U	0.401	06	Ω	-0.92	-0.62	-1.75	- 1.47 -1 50	-0.55	0.12	-0.64
ml or 3 ml a)	15	т	0.712	88	5	-1.16 2011-	0.80	-1.72 -1.86	-1.68	-0.74	0.05	-0.59
	01					-1.03 -0.95	-0./1 -0.62	-1./8 -1.67	-1.38	-0.64	0.08	-0.63
	91 19	-	1.089	98	Υ	-1.09 -0.96	-0.77 -0.67	-1.79 -1.74	-1.53 -1.50	-0.71 -0.58	0.00 0.09	-0.64 -0.61
	20	7	1.089	98	20	-0.94 -1.07	-0.70 -0.86	-1.63 -1.89	-1.43 -1.68	-0.58 -0.64	0.02	-0.56 -0.63
	22 23	¥	0.500	95	5	-1.09 -0.86	-0.73 -0.58	-1.90 -1.57	-1.63 -1.33	-0.68 -0.52	0.09 0.09	-0.68 -0.57
	24 25	_	0.495	95	ŝ	-0.92 -0.93	-0.58 -0.66	-1.55 -1.57	-1.33 -1.36	-0.59 -0.59	0.09 0.03	-0.55 -0.55
	26 27					-0.96 -0.92	-0.64 -0.66	-1.59 -1.63	-1.35 -1.43	-0.62 -0.56	0.04 0.06	-0.57 -0.55
					Average 2SD	-0.99 0.17	-0.68 0.16	-1.71 0.24	-1.48 0.24	-0.62 0.12	0.06 0.08	-0.60 0.08
Aicrowave	28	٤ï	0.423	85	ı O'I	-0.95	-0.63	-1.69	-1.46	-0.58	0.11	-0.60
ICI/HNO ₃ 8:1; v/v)	30 30	zo	0.783 0.986	90 87	o رo	-1.07 -1.04	-0./2 -0.73	-1.81 -1.85	-1.58 -1.56	-0.68 -0.65	0.0	-0.62 -0.68
Ē	31	۵.	1.175	78	20	-1.10	-0.92	-1.96	-1.83	-0.64	00.00	-0.59
	32					-1.14	-0.85	-2.07	-1.86	-0.67	0.08	-0.68
					Average (#31-#32) b)	- 1.02	-0.69	-1.78	-1.53	-0.64	0.08	-0.63
					2SD (#31-#32) b)	0.12	0.11	0.17	0.13	0.10	0.05	0.08
				Ave	erage (#2-#3; #31-#32)	10.1 - (d)	-0.70	-1.77	-1.53	-0.62	0.07	-0.61
				c				000				

86

© 2009 The Authors. Journal compilation © 2009 International Association of Geoanalysts

76



Hg matrix samples

Two artificial and complex matrix samples were synthesised to assess potential isotopic bias during reduction with stannous chloride cold vapour generation. Two samples of the basalt BE-N* matrix spiked with NIST SRM 3133 were digested using the H₂SO₄/HNO₃ method and analysed against the mono-elemental NIST SRM 3133 Hg (Table 3). Three replicate analyses of the most concentrated matrix (1 g BE-N*) and one analysis of the other digest (0.75 g BE-N*) did not show any isotopic variation from NIST SRM 3133 with δ^{202} Hg = -0.10 ± 0.15‰ (2SD, n = 3) and δ^{202} Hg = -0.09‰ (n = 1) respectively. The same observation was made for the other matrix sample (Ferich) with a δ^{202} Hg = -0.06‰ (n = 1; Table 3). Results for these limited samples show that potential matrix effects during SnCl₂ - Hg⁰ CV generation fell within the analytical uncertainties of the method. We therefore suggest that ${\rm SnCl}_2$ - ${\rm Hg^0}~{\rm CV}$ generation from an acid digestion of complex mineral matrices does not lead to significant isotopic fractionation of Hg isotopes.

In addition to this conclusion, compared to monoelemental RMs, raw results (measurement made during isotopic determination) for complex matrix samples (lichen, soil, etc) showed clearly an effect on isotopic ratios (isotope drift, isotope ratio SD increasing), which may be attributable to the matrix. In our specific case, these perturbations did not significantly influence isotopic determination but need to be carefully investigated for the isotopic determination of new sample matrices.

Lichen BCR CRM 482 digestion procedure

The H_2SO_4/HNO_3 digestion applied to two test portions (0.3 g) of lichen displayed digestion yields of 100% relative to the certified value (Table 4). The HCI/HNO₃ mixture and concentrated HNO₃ were the only digestion methods using the HPA that showed digestion yields of 94 ± 8% (2SD, n = 4: G, H, I, K) for digested masses of 0.4 to 1 g respectively (in 6 ml total acid). The addition of HCl to the mixture did not affect the digestion performance. Furthermore, to reduce acid volume and increase concentrations for Hg isotope determinations, two test portions (J and L) were digested using only 3 ml HNO3. The digestion yields (98 and 95% respectively) were in agreement with those measured with larger volumes of acids (Table 4). The microwave oven digestion method displayed digestion yields below 90% for test portions M, N and O, most probably due to small aggregates remaining



Figure 2. Average isotopic composition (δ^{202} Hg and Δ^{199} Hg) of lichen BCR CRM 482 obtained using three different acid digestion methods (sixteen test portions digested for thirty-two measurements). Replicate analyses numbered 2, 3, 31 and 32 were removed from calculations (see Table 4 and text).

 ${\ensuremath{\mathbb C}}$ 2009 The Authors. Journal compilation ${\ensuremath{\mathbb C}}$ 2009 International Association of Geoanalysts



in the solution after the digestion procedure. Coarse aggregates of organic matter were found after digestion of test portion P, for which a low digestion yield of 78% was measured.

Overall, Hg isotope determinations conducted on the various preparations of BCR CRM 482 yielded very similar results (Table 4). In total, BCR CRM 482 was analysed thirty-two times on sixteen test portion preparations from four different digestion methods. Only four measurements were removed from the following results due to either analytical issues (analysis #3: $\delta^{202}\text{Hg}$ out of the range of the average value at 2SD; analysis #4: Δ^{201} Hg was out of the range of the average value, see Table 4) or digestion procedure issues (test portion P was removed due to its low digestion yield; see Table 4). The average δ^{202} Hg was -1.53 ± 0.24‰ (2SD, n = 28). The sample also displayed a negative MIF on odd $^{199-201}$ Hg isotopes with an average Δ^{199} Hg of -0.62 ± 0.11% and Δ^{201} Hg of -0.61 ± 0.08%. (2SD, n = 28) (see Table 4 and Figure 2). Except for test portion P, having the lowest chemical yield (78%), the measured isotopic composition was neither related to the calculated yield (85 to 100%) nor to the Hg concentration (4, 5, 20 μ g |-1) of the analysed solution (Figure 2).

Hg isotopic composition of reference materials

The isotopic composition of eight reference materials digested using the H₂SO₄/HNO₃ method and analysed with CV-MC-ICP-MS is presented in Table 5. The measured Hg concentrations (Table 5) for most RMs were in agreement with certified, recommended or inhouse CRPG laboratory values. GSS-4 and GXR-3 displayed slightly different Hg concentrations from the proposed values, when the uncertainties of the measured values are taken into account. Unfortunately, uncertainties in the proposed reference values are not always available from the compilation of Govindaraju (1994). In such cases, the homogeneity of the Hg concentration of a given RM cannot be assessed. Although our measurements yielded generally higher Hg contents than proposed in the literature, our procedure blank did not reveal any contamination problems and was always negligible in comparison to sample Hg.

Isotopic compositions of the nine RM analysed in this study present a range of $\delta^{202}\text{Hg}$ values from -1.75 to +0.11% referenced to the NIST SRM 3133 scale (Table 5 and Figure 3). Some RM data also demonstrated mass-independent fractionation on odd

 $^{199\cdot201}\text{Hg}$ isotopes with significant negative $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ values from -0.62 to +0.03‰. (Table 5 and Figure 4).

Multiple digestion replicates of eight out of nine RMs digested with the H₂SO₄/HNO₃ method yielded homogeneous δ^{202} Hg and $\Delta^{199-201}$ Hg values (Table 4 and Table 5). Only two test portions of the soil GSS-4 RM yielded isotopic compositions that exceeded the external reproducibility of the method, suggesting a lack of homogeneity of the material. Three digestion replicates of the soil NIST SRM 2711 gave an average isotopic composition of δ^{202} Hg = -0.24 ± 0.15‰, Δ^{199} Hg = -0.20 ± 0.05‰ and Δ^{201} Hg = -0.16 ± 0.06‰. These values are in agreement with those reported by Wiederhold *et al.* (2008) and Biswas *et al.* (2008).

The low-Hg soil GSS-4 (0.6 µg g⁻¹ Hg) had a δ^{202} Hg of -1.75 ± 0.21‰. In contrast, the Hg-rich soils NIST SRM 2711 (6.3 µg g⁻¹ Hg) and GXR-2 (3.6 µg g⁻¹ Hg) displayed δ^{202} Hg values of -0.24 ± 0.15‰ and +0.11 \pm 0.15% respectively, very close to the value of the primary delta RM NIST SRM 3133. The Hg-rich jasperoid GXR-1 (4.4 $\mu g~g^{\text{-1}}$ Hg) and the deposit GXR-3 (0.4 µg g⁻¹ Hg) displayed intermediate isotopic compositions with $\delta^{202}\text{Hg}$ values of -0.26 \pm 0.15‰ and -0.70 ± 0.15‰ respectively. Furthermore, the isotopic composition of the deposit GXR-3 was in agreement with the average isotopic composition reported by Smith et al. (2008) for several mercury ore deposits (hot spring: average δ^{202} Hg of -0.66‰; silica-carbonate: average δ^{202} Hg of -0.63‰) having a large range of fractionation (-2 to +1%). The sediment GSD-10 (0.3 $\mu g~g^{-1}$ Hg) had a $\delta^{202} \text{Hg}$ value of -0.93 ± 0.35% , which is within the isotopic composition range reported for sapropel and background sediments of the Mediterranean sea by Gehrke et al. (2009) or in various sediments measured by Foucher and Hintelmann (2006). Fly ash samples BCR CRM 176 (31.4 μ g g⁻¹ Hg) and 176R (1.6 μ g g⁻¹ Hg) originating from the same urban waste combustor presented a large contrast in Hg concentration but isotopic compositions that were identical within error, with δ^{202} Hg values of -0.96 ± 0.15‰ and -1.03 ± 0.15‰ respectively. The lichen BCR CRM 482 sampled in the Swiss Alps, which accumulated atmospheric mercury deposition, demonstrated a strong enrichment in light isotopes with a mean δ^{202} Hg value of -1.53 ± 0.24‰ compared to crustal mercury. This isotopic composition also falls within the fractionation range reported by Carignan et al. (2009) for lichens from Canada and France. Most RMs analysed in this study presented a

 ${\ensuremath{\mathbb C}}$ 2009 The Authors. Journal compilation ${\ensuremath{\mathbb C}}$ 2009 International Association of Geoanalysts

89

Table 5. Isotopic	composition	of eight re	sference material	s relati	ive to NI	ST SRA	A 3133											
Sample	Digested mass (g)	Hg measured (ng g ^{-1)a)}	Hg recommended (ng g- ¹)	(4 H	۵ ۱۹۹۹	2SE	δ ²⁰⁰ Hg	2SE	δ ²⁰¹ Hg	2SE	δ ²⁰² Hg	2SE	0199Hg	2SE	∆ ²⁰⁰ Hg	2SE	∆ ²⁰¹ Hg	2SE
Soils NIST SRM 2	0.1 1172 0.1 0.1	6540 6740 6680	6250 ± 200 b)	0004	-0.26 -0.28 -0.23	0.09 0.09 0.09	-0.12 -0.17 -0.05	01.0 01.0 01.0	-0.34 -0.38 -0.30	11.0 11.0 11.0	-0.24 -0.30 -0.17	0.15 0.15 0.15	-0.20 -0.21 -0.19	0.07 0.07 0.07	0.00 -0.02 0.04	0.0 0.0 0.0 0.0 0.0	-0.16 -0.15 -0.17	0.04 0.04
GXR-2 GSS-4	0.1 0.1 0.1	3960 690 745	3610 ± 170 c) 590 d)	00004	-0.20 0.00 -0.74 -0.90 -0.82	0.09 0.09 0.09 0.09	-0.10 -0.82 -0.96 -0.89	0.10 0.10 0.10 0.00	-0.09 -1.45 -1.80 -1.63	0.11 0.11 0.11 0.21	-0.24 -1.58 -1.92 -1.75	0.15 0.15 0.15 0.15 0.21	-0.20 0.03 -0.34 -0.38	0.07 0.07 0.07 0.05	0.04 0.03 0.00 0.00	0.06 0.06 0.06 0.02	-0.10 0.01 -0.36 -0.31	0.04 0.04 0.04 0.06
Sediment GSD-10	1.0	310	280 d)	5	-0.51	0.01	-0.48	0.08	-0.91	0.16	-0.93	0.35	-0.28	0.07	-0.01	0.05	-0.21	0.06
Jasperoid GXR-1	0.1	5080	4380 ± 260 ^{e)}	т	-0.16	0.09	-0.12	0.10	-0.26	0.11	-0.26	0.15	-0.10	0.07	0.01	0.06	-0.07	0.04
Deposit GXR-3	0.1	341	415 d)	5	-0.19	0.14	-0.32	0.16	-0.52	0.15	-0.70	0.15	-0.01	0.05	0.03	0.06	0.00	0.06
Fly as h BCR CRM 1	176 0.1 0.1	33580 34460	31400 ± 1100 ^{f)}	004	-0.28 -0.29 -0.28	0.09 0.09 0.09	-0.49 -0.50 -0.50	0.10 0.10 0.10	-0.75 -0.77 -0.76	0.11 0.11 0.11	-0.95 -0.97 -0.96	0.15 0.15 0.15	-0.04 -0.04 -0.04	0.07 0.07 0.07	-0.02 -0.01	0.06 0.06 0.01	-0.03 -0.04 -0.04	0.04 0.04 0.04
BCR CRM	176R 0.1 0.25 0.5 1.0	1333 1387 1528 1405	1600 ± 230 9)	8 9 9 9 9	-0.30 -0.34 -0.32 -0.33	0.09 0.09 0.09 0.09	-0.46 -0.51 -0.53 -0.55 -0.51	0.10 0.10 0.10 0.10 0.10	-0.80 -0.84 -0.83 -0.87 -0.83	0.11 0.11 11.0 11.0 11.0	-1.03 -1.01 -1.00 -1.07 -1.03	0.15 0.15 0.15 0.15 0.15	-0.04 -0.08 -0.07 -0.06 -0.06	0.07 0.07 0.07 0.07 0.07	0.06 0.03 -0.03 0.00	0.06 0.06 0.06 0.06 0.06	-0.03 -0.08 -0.07 -0.07 -0.07	0.04 0.04 0.04 0.04
a) 2SD f) Reco	of the method = mmended IRMM	10%. b) value. §) Certified value. 9) Indicative IRMM v	c) value.	CRPG-SAR h)	M value. Number	for n = 36. of measurer	ments.	d) Com	piled val	lues in Gov	indaraju	(1994).	(ə	CRPG-SA	.RM value	e for n = 23	

Chapitre 2, "Measuring Hg Isotopes in Bio-Geo-Environmental Reference Materials"

> GEO DARDS and GEOANALYTICAL RESEARCH



Figure 3. Mercury isotopic compositions (8202Hg, ‰) referenced to the NIST SRM 3133 scale for the nine RMs measured in this study, with selected RMs from the literature and isotopic variations measured in natural samples. (1) Smith et al. (2005), (2) Foucher et Hintelmann (2006) (IAEA-356: -0.32 ± 0.08%; NIST SRM 1944: -0.53 ± 0.08‰; BCR-580: -0.46 ± 0.08; MESS-3: -2.5 ± 0.5‰), (3) Bergquist and Blum (2007) (DOLT-2: -0.65 ± 0.10%; DORM-2: 0.11 ± 0.16‰), (4) Malinovsky et al. (2008) (DOLT-3: -0.65 ± 0.16%; DORM-2: 0.18 ± 0.08‰), (5) Blum and Bergquist (2007), (6) Lauretta et al. (2001), (7) Smith et al. (2008), (8) Gehrke et al. (2009), (9) Biswas et al. (2008).

Figure 4. Mercury isotope anomalies (Δ^{201} Hg, ‰) for the nine RMs measured in this study, selected RMs from the literature and isotopic variations measured in natural samples. (1) Bergquist and Blum (2007) (DORM-2: 0.88 ± 0.05%; DOLT-2: $0.59 \pm 0.05\%$), (2) Malinovsky et al. (2008) (DORM-2: 0.93%; DOLT-3: 0.65‰), (3) Ghosh et al. (2008) (NIST SRM 2710: 0.13 \pm 0.02; ES-1646: 0.12 ± 0.03), (4) Biswas et al. (2008), (5) Blum and Bergquist (2007).

90

© 2009 The Authors. Journal compilation © 2009 International Association of Geoanalysts





Figure 5. The relationship between isotopic Δ^{201} Hg and Δ^{199} Hg measured in the various reference materials. All the data fit a 1:1 relationship within uncertainties (1.05 ± 0.17, 2SD). Soils (NIST SRM 2711; GXR-2; GSS-4), sediment (GSD-10), Jasperoid (GXR-1), ore deposit (GXR-3), fly ashes (BCR CRM 176; 176R) and lichen (BCR CRM 482).

 δ^{202} Hg value $\leq 0\%$ relative to NIST SRM 3133. Moreover, all were within the fractionation range reported in the literature for other natural samples (Figure 3). The range in isotopic composition covered by the CRPG Hg solutions characterised in this study spanned that of reported values for terrestrial samples (Figure 3).

Considering mass-independent fractionation, lichen BCR CRM 482, soil GSS-4, sediment GSD 10 and soil NIST SRM 2711 gave Δ^{201} Hg values of -0.61 ± 0.08‰, -0.31 ± 0.06‰, -0.21 ± 0.06‰, -and -0.16 ± 0.06% respectively. The relationship between Δ^{201} Hg and Δ^{199} Hg presented in Figure 5 shows a slope $(\Delta^{199}Hg/\Delta^{201}Hg = 1.05 \pm 0.17, 2SD)$ similar to the 1:1 line that involves magnetic isotope effects as a dominant MIF process for natural samples, as reported by Ghosh et al. (2008) and Biswas et al. (2008). Bergquist and Blum (2007) show that photo-reduction reactions produce such isotopic anomalies. This strongly suggests that part of the Hg content in sediments, soils and lichens may have undergone photo-reduction reactions before being stored in these environments. Mercury in the ore deposit GXR-3 did not show MIF, in agreement with the isotopic composition of natural cinnabar ore deposit values from Smith et al. (2005, 2008). The jasperoid GXR-1 (Δ^{201} Hg = -0.07 ±

0.06‰) did not reveal significant MIF, which suggests a Hg contribution from geological environments only. Fly ashes BCR CRM 176 and 176R also showed no significant MIF. Although MIF was reported in coal (Biswas *et al.* 2008), this suggests that industrial processes such as evaporation/condensation do not cause MIF and that anthropogenic Hg directly emitted into the environment may be characterised by mass dependent fractionation. This is in agreement with results on other fly ashes from a municipal waste combustor reported by Estrade *et al.* (2007).

Figure 4 reports a compilation of Hg isotopic anomalies (significant $\Delta^{199-201}$ Hg) in natural terrestrial samples as reported in the literature. Aquatic Hg (mainly in fish tissues) presents systematically positive $\Delta^{199-201}$ Hg values whereas atmospheric Hg (mosses and lichens) displays various deficits in odd Hg isotopes. In addition to mass dependent fractionation of Hg isotopes, mercury isotopic anomalies may potentially be used to characterise Hg fluxes between natural reservoirs.

Conclusions

This work reports the Hg isotopic composition of various bio-geo-environmental reference materials



using cold vapour (CV) MC-ICP-MS. Our results have demonstrated that acid digestion of complex matrices associated with the conventional CV generation system (SnCl₂) did not result in isotopic bias during Hg isotope determination. Also, various acid digestion methods conducted on samples that are rich in organic matter (lichen BCR CRM 482) showed that the high pressure asher method was capable of digesting 1 g of lichen sample into only 3 ml of concentrated HNO₃. Again, this did not involve isotopic bias during isotopic measurements.

In addition to the available RMs, two Hg solutions were prepared and analysed for their isotopic compositions. These samples, CRPG F65A and CRPG RL24H, displayed δ^{202} Hg values of -3.54 ± 0.27‰ (2SD, n = 38) and +2.59 ± 0.19‰ (2SD, n = 30) respectively, which cover the whole range of natural isotopic variations reported in the literature. However, these two solutions did not revealed strong mass-independent fractionation on odd ¹⁹⁹Hg and ²⁰¹Hg isotopes. These solutions are proposed as secondary reference materials for the determination of Hg isotopic composition, and are available from the authors at the CRPG.

Isotopic compositions of nine RMs including soils, ores, sediments, lichens and anthropogenic materials, are also reported. Measured δ^{202} Hg values ranged from -1.75 to +0.11‰. Some RMs such as lichen, sediments and soils, possess significant deficits of odd ¹⁹⁹Hg and ²⁰¹Hg isotopes relative to mass dependent fractionation. Mass-independent fractionation ($\Delta^{199-201}$ Hg) values from -0.62‰ (lichen) to +0.03‰ (soils) were measured with a Δ^{201} Hg/ Δ^{199} Hg ratio of ~ 1 in all the samples for which isotopic anomalies were identified. This suggests that Hg in these samples was affected by magnetic isotope effects probably as a result of photo-reduction reactions in the environment.

Acknowledgements

We would like to thank Laurie Reisberg and Catherine Zimmermann (CRPG) for HPA assistance, Luc Marin and Jitka Lhomme (CRPG-SARM) for their technical support, Damien Plaa (UT2A) for microwave digestion assistance and Remy Freydier and Sylvain Berail for analytical assistance on the LMTG Neptune and the IPREM Nu Plasma respectively. Two anonymous reviewers are also thanked for their constructive comments.

References

Bergquist B.A. and Blum J.D. (2007)

Mass-dependent and -independent fractionation of Hg isotopes by photo reduction in aquatic systems. Science, 318, 417-420.

Biswas A., Blum J.D., Bergquist B.A., Keeler G.J. and Xie Z.Q. (2008)

Natural mercury isotope variation in coal deposits and organic soils. Environmental Science and Technology, 42, 8303-8309.

Blum J.D. and Bergquist B.A. (2007)

Reporting of variations in the natural isotopic composition of mercury. Analytical and Bioanalytical Chemistry, 388, 353-359.

Carignan J., Estrade N., Sonke J.E. and Donard O.F.X. (2009)

Odd isotope deficits in atmospheric Hg measured in lichens. Environmental Science and Technology, 43, 5660-5664.

Dzurko M., Foucher D. and Hintelmann H. (2009) Determination of compound-specific Hg isotope ratios from transient signals using gas chromatography coupled to multicollector inductively coupled plasma-mass spectrometry (MC-ICP/MS). Analytical and Bioanalytical Chemistry, 393, 345-355.

Epov V.N., Rodriguez-Gonzalez P., Sonke J.E., Tessier E., Amouroux D., Bourgoin L.M. and Donard O.F.X. (2008)

Simultaneous determination of species-specific isotopic composition of Hg by gas chromatography coupled to multicollector ICP-MS. Analytical Chemistry, 80, 3530-3538.

Estrade N., Carignan J., Sonke J. and Donard O.F.X. (2007)

Mass independent fractionation of Hg isotopes during evaporation and condensation processes (Goldschmidt conference, abstract). Geochimica et Cosmochimica Acta, 71, Supplement 1, A262.

Estrade N., Carignan J., Sonke J. and Donard O.F.X. (2009)

Mercury isotope fractionation during liquid-vapor evaporation experiments. Geochimica et Cosmochimica Acta, 73, 2693-2711.

Foucher D. and Hintelmann H. (2006)

High-precision measurement of mercury isotope ratios in sediments using cold-vapor generation multi-collector inductively coupled plasma-mass spectrometry. Analytical and Bioanalytical Chemistry, 384, 1470-1478.

Géhin A., Ruby C., Abdelmoula M., Benali O., Ghanbaja J. and Génin J.-M.R. (2002) Synthesis of Fe(II-III) hydroxysulphate green rust by co-precipitation. Solid State Sciences, 4, 61-66.

Gehrke G., Blum J.D. and Meyers P.A. (2009)

The geochemical behavior and isotopic composition of Hg in a mid-Pleistocene western Mediterranean sapropel. Geochimica et Cosmochimica Acta, 73, 1651-1665.

© 2009 The Authors. Journal compilation © 2009 International Association of Geoanalysts



references

Ghosh S., Xu Y.F., Humayun M. and Odom L. (2008)

Mass-independent fractionation of mercury isotopes in the environment. Geochemistry Geophysics Geosystems, 9, Q03004, doi: 10.1029/2007GC001827.

Goldstein S.L., Deines P., Oelkers E.H., Rudnick R.L. and Walter L.M. (2003)

Standards for publication of isotope ratio and chemical data in Chemical Geology. **Chemical Geology**, **202**, 1-4.

Govindaraju K. (1994)

Compilation of working values and sample description for 383 geostandards. Geostandards Newsletter, 18 (Special Issue), 158pp.

Hintelmann H. and Lu S.Y. (2003)

High precision isotope ratio measurements of mercury isotopes in cinnabar ores using multi-collector inductively coupled plasma-mass spectrometry. **The Analyst, 128**, 635-639.

Lauretta D.S., Klaue B., Blum J.D. and Buseck P.R. (2001)

Mercury abundances and isotopic compositions in the Murchison (CM) and Allende (CV) carbonaceous chondrites. Geochimica et Cosmochimica Acta, 65, 2807-2818.

Malinovsky D., Sturgeon R.E. and Yang L. (2008)

Anion-exchange chromatographic separation of Hg for isotope ratio measurements by multicollector ICP-MS. Analytical Chemistry, 80, 2548-2555.

Nier A.O. (1950)

A redetermination of the relative abundances of the isotopes of neon, krypton, rubidium, xenon and mercury. **Physical Review, 79**, 450-454.

Ridley W.I. and Stetson S.J. (2006)

A review of isotopic composition as an indicator of the natural and anthropogenic behavior of mercury. Applied Geochemistry, 21, 1889-1899.

Sherman L.S., Blum J.D., Nordstrom D.K., McCleskey R.B., Barkay T. and Vetriani C. (2009) Mercury isotopic composition of hydrothermal systems in the Yellowstone Plateau volcanic field and Guaymas Basin sea-floor rift. Earth and Planetary Science Letters, 279, 86-96.

Smith C.N., Kesler S.E., Blum J.D. and Rytuba J.J. (2008)

Isotope geochemistry of mercury in source rocks, mineral deposits and spring deposits of the California Coast Ranges, USA Earth and Planetary Science Letters, 269, 398-406.

Smith C.N., Kesler S.E., Klaue B. and

Blum J.D. (2005) Mercury isotope fractionation in fossil hydrothermal systems. Geology, 33, 825-828.

Sonke J.E. Zambardi T. and Toutain J.P. (2008)

Indirect gold trap-MC-ICP-MS coupling for Hg stable isotope analysis using a syringe injection interface. Journal of Analytical Atomic Spectrometry, 23, 569-573.

Wiederhold J.G., Bourdon B. and

Kretzschmar R. (2008) Hg isotopes in contaminated soils. Geochimica et Cosmochimica Acta, 72, A1019-A1019.

Xie Q.L., Lu S.Y., Evans D., Dillon P. and

Hintelmann H. (2005) High precision Hg isotope analysis of environmental samples using gold trap-MC-ICP-MS. Journal of Analytical Atomic Spectrometry, 20, 515-522.

Yang L. and Sturgeon R. (2009)

Isotopic fractionation of mercury induced by reduction and ethylation. Analytical and Bioanalytical Chemistry, 393, 377-385.

Zambardi T., Sonke J.E., Toutain J.-P., Sortino F. and Shinohara H. (2009)

Mercury emissions and stable isotopic compositions at Vulcano Island (Italy). Earth and Planetary Science Letters, 277, 236-243.

Zheng W., Foucher D. and Hintelmann H. (2007)

Mercury isotope fractionation during volatilization of Hg(0) from solution into the gas phase. Journal of Analytical Atomic Spectrometry, 22, 1097-1104.