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RESEARCH PAPER

High Precision Determination of Mercury Isotope Ratios Using Online Mercury Vapor Generation System Coupled with Multicollector Inductively Coupled Plasma-Mass Spectrometer

YIN Run-Sheng[1,2], FENG Xin-Bin[1,*], Delphine Foucher[3], SHI Wen-Fang[1,2], ZHAO Zhi-Qi[1], WANG Jing[1]

[1] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China
[2] Graduate University of the Chinese Academy of Sciences, Beijing 100039, China
[3] Department of Chemistry, Trent University, 1600 West Bank Drive, Peterborough, Ontario, K9J 7B8, Canada

Abstract: In this study, a method for high-precision measurement of Hg isotope ratios by multiple collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) with on-line Hg reduction technique was developed. The procedure was evaluated to obtain high-precision measurements that were good enough to significantly detect the anticipated small differences in Hg isotope compositions in natural samples. Typically, internal precision was better than 0.02‰ (1 RSE) on all Hg ratios investigated. The external reproducibility for standard NIST SRM3133 and UM-Almadén secondary solution, nature samples were 0.06‰ (2SD) and 0.10‰ (2SD) over a period of 7 months, respectively. The extent of fractionation has been investigated in a series of natural samples from different locations in China. The ratio $^{202}Hg/^{198}Hg$ expressed as δ values (per mil deviations relative to NIST SRM 3133 Hg standard solution) displayed differences from −3.48‰ to 0.633‰. These results indicated a wide perspective application of tracing Hg in the environment.

Key Words: Mercury; Stable isotopes; Multicollector; Inductively coupled plasma-mass spectrometer

1 Introduction

Mercury is of global concern due to its toxicity [1,2]. A global crackdown on this poisonous pollutant was agreed by environment ministers at the end of the UN Environment Programme's (UNEP) Governing Council held in Nairobi on 20th February 2009. The landmark decision, taken by over 140 countries, sets the stage for the lifting of a major health threat from the lives of hundreds of millions of people. Governments unanimously decided to launch negotiations on an international mercury treaty to deal with world-wide emissions and discharges of a pollutant that threatens the health of millions, from fetuses and babies to small-scale gold miners and their families.

Isotope geochemistry has become one of the most important fields of earth sciences. Recent detections of variable isotopic compositions for nontradition elements (such as Li, Mg, Ca, Fe, Cu, Zn, Se, Mo, Tl) have spurred interest in unraveling likely isotopic fractionation mechanisms affecting these elements in natural systems. Both the nuclear field shift effect and the magnetic isotope effect[1,3] predict differences in isotope fractionation of heavy metals. Mercury has active redox chemistry, a volatile form (Hg0), and a tendency to form covalent bonds, thus kinetic effects may also play an important role in mercury isotopic fractionation. Hg has seven natural stable isotopes, ^{196}Hg (0.15%), ^{198}Hg (9.97%), ^{199}Hg

(16.87%), ^{200}Hg (23.10%), ^{201}Hg (13.18%), ^{202}Hg (29.86%), and ^{204}Hg (6.87%)[4]. Hg, chemically similar to sulfur, occurs +2, +1 or 0 valences in various inorganic and organic (such as Me-Hg) compounds. The mobility, bioavailability, and toxicity of Hg are different with valence state and organic speciation. Reactions affecting Hg speciation, whether biotic or abiotic, can affect isotope ratios of reactants and products[5]. Therefore, isotope geochemistry of Hg could be used as tracers of pollution sources, biogeochemical reactions, and processes. Recent works have confirmed that biotic and abiotic reactions are the main mechanisms of Hg isotope fractionation[6–12].

The analysis of Hg stable isotope abundance has a remarkably long history that began almost one hundred years ago. Hg isotopic compositions were measured in a series of terrestrial and extraterrestrial materials with variable success by several techniques, including density measurements[13], neutron activation analysis[14], gas-source mass spectrometry[15], Q-ICP-MS[16], single-collector ICP/MS[16], and ICP-time-of-flight-MS (ICP-TOF-MS)[16]. However, these findings are considered questionable because the low-level Hg in natural matrices represents an additional analytical challenge to resolve meaningful variations in the natural abundances of Hg isotopes[17]. Lauretta *et al* (2001) first used the multiple collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) to achieve the high-precision measurements of Hg isotope ratios in environmental matrices[18]. Significant Hg isotope variations in natural samples, such as meteorites[18], hydrothermal ores[6], coals[10], soil and sediment cores[12,19], aquatic food webs[9] and microbes[8], have recently been observed by MC-ICP-MS. Unfortunately, most of these published data suffer from a description of the analytical details including optimization procedure and figure of merits. Thus, the precision of individual laboratories for Hg isotope analysis varies. On the basis of the previous work, a method with details was developed for high-precision measurement of Hg isotope ratios by MC-ICP-MS using an on-line Hg reduction technique in this study. The above-mentioned procedure was evaluated to get high-precision measurements that were good enough to significantly detect the anticipated small differences in Hg isotope compositions in natural samples. The external reproducibility of this method for UM-Almadén secondary solution was 0.06‰ (2SD). The extent of fractionation has been investigated in a series of natural samples, the δ^{202}Hg values of which displayed differences from –3.48‰ to 0.633‰. These results indicated a wide perspective application of Hg isotopes in tracing mercury in the environment.

2　Experimental

2.1　Instruments and nebulization system

Isotopic measurements were performed on a Nu-Plasma multicollector inductively coupled plasma-mass spectrometer (Nu-Plasma MC-ICP/MS, Nu Instruments, Great Britain) in State Key Lab of Environmental Geochemistry, Chinese Academy of Sciences, China.

An on-line cold-vapor generation system, rather than thermal releasing Hg approach, was well developed for Hg isotope analysis[20]. The detail of the CV generation apparatus is illustrated schematically in Fig.1. The reaction chamber of the CV generation system was flushed with the "mix" gas of the instrument. The Tl delivery for the Apex nebulizer (CETAC Technologies, Omaha, USA) was set in the free flow-mode using the "nebulizer" gas of the ICP-MS, the Hg isotope ratios were corrected for instrumental mass discrimination by simultaneously monitoring the ^{205}Tl/^{203}Tl ratio of a standard solution. A Minipuls 3 peristaltic pump (Gilson Corp., USA) was used to control the intake rates of tin chloride and mercury sample solutions.

2.2　Procedure of MC-ICP-MS measurement

The Nu-Plasma MC-ICP-MS has a double focusing system, 12 Faraday cups, and 3 iron counters. For Hg and Tl isotope ratio measurements, seven of the 12 independently adjustable Faraday cups of the MC-ICP/MS were used as detectors. The order of various collectors is shown in Table 1. Because the isotope abundance of ^{196}Hg and ^{204}Hg are very low, both the isotopes were not measured. High-purity argon gas without mercury was used for sample uptake. The operating conditions and parameters are listed in Table 2.
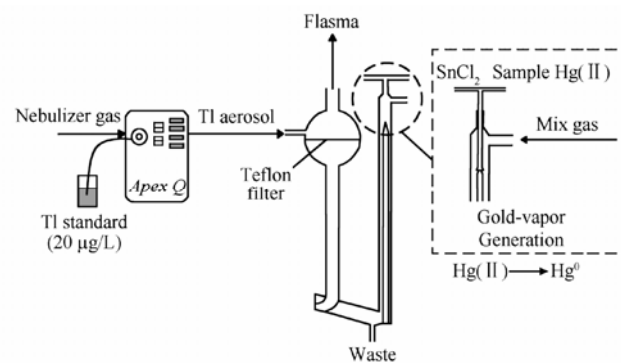

Fig.1　Schematic of on-line introduction systems (Foucher and Hintelman, 2006)

Table 1　Adjustment of Faraday collectors for Hg isotope ratio measurements

Faraday cups	Hg & Tl
H5	^{205}Tl
H4	^{203}Tl
H3	^{202}Hg
H2	^{201}Hg
H1	^{200}Hg
Ax	^{199}Hg
L1	^{198}Hg

Table 2   Operating parameters of Nu-Plasma MC-ICP-MS and sample introduction systems

Plasma parameters	
Nebulizer gas	27.0–34.0 mL min^{-1}
Mix gas	0.06–0.15 mL min^{-1}
RF power	1300 W
Apex-Q Nebulizer	
Heater temperature	100 °C
Chiller temperature	2 °C
Sensitivity for ^{205}Tl	0.16–0.18 V L μg^{-1}
HGX-200 Hydride generation system	
Solution uptake rate	0.75 mL min^{-1}
Sensitivity for ^{202}Hg	0.20–0.24 V L μg^{-1}

2.3   Reagents and solutions

HNO$_3$, HCl and SnCl$_2$ were of analytical grade. Mill-Q water (18.2 MΩ·cm) and high-purity argon were used. A 0.16 M (3%, w/V) solution of tin chloride was prepared with 1.20 M HCl. The reductant solution was purged before use with Hg-free nitrogen for a few hours to release mercury traces. The mercury (NIST SRM 3133) and thallium (NIST SRM 997) working standard solutions were prepared daily. A secondary standard solution (UM-Almadén, 1.0 μg g^{-1} Hg in 4% nitric acid) was obtained from University of Michigan[19]. All teflon materials and glassware were immersed in HNO$_3$ (10%, V/V) and HCl (10%, V/V) for 48 h and triple rinsed with Milli-Q water.

2.4   Sample preparation

A series of natural samples, including rice leaves, paddy soils, Hg-ores, Hg mine-waste calcines, and zinc ores, were digested with a fresh mixture of HNO$_3$-H$_2$SO$_4$ (4:1, V/V) in a water bath (95 °C) for total mercury (T-Hg) analysis[21]. T-Hg concentrations in these samples were determined by BrCl oxidation, SnCl$_2$ reduction, purge, gold trap, and cold vapor atomic fluorescence spectrometry (CVAFS, Tekran 2500, < 0.1 pg Hg). The concentrations between samples and standard solutions were matched within 10%. The efficiency of Hg extraction should be ≥ 95%, and the acid concentration within each sample should be below 20%. All digests were diluted to a concentration of approximately 5 ng mL^{-1} for Hg isotope analysis.

3   Result and discussion

3.1   Mass bias correction

In recent years, it has been recognized that different elements can be isotopically fractionated slightly different by MC-ICP-MS. Thus, it is necessary to correct samples for any additional instrument mass bias. Thallium as internal correction was combined with external sample-standard bracketing for high precise and accurate measurements. Similar elements can be used to determine mass bias corrections in systems with only two isotopes (e.g., Tl for Pb). The mass bias response of the two elements is not identical and should be accounted for[22]. First, instrumental mass bias was corrected by simultaneous measurement of the certified thallium isotope standard (NIST SRM 997; ^{205}Tl/^{203}Tl ratio of 2.38714). Because the most high-precision measurements of Hg isotope were carried out by introduction of a cold Hg vapor into the MC-ICP-MS plasma source, meanwhile dry Tl aerosol was generated using a desolvating nebulizer, and then the dry Tl aerosol mixed with the Hg vapor in a gas–liquid separator, both Tl and Hg were introduced into the plasma with carrier gas. An exponential fractionation law was used to determine the instrumental mass bias factor β_0 for Tl, and then, the β_0 could be applied to an exponential mass bias correction of all of the Hg isotope abundances.

To obtain the highest precision and accuracy, a standard bracketing approach was also used to compare relative per mil (‰) deviation (using the δ notation) of all our measurements to a common in-house standard solution (NIST SRM 3133 Hg standard), according to:

$$\delta^{xxx}\mathrm{Hg}\ (^0/_{00}) = \left\{ \left[\frac{^{xxx}\mathrm{Hg}/^{198}Hg_{sample}}{^{xxx}Hg/^{198}\mathrm{Hg}_{standard}} \right] - 1 \right\} \times 1000$$

where, ^{XXX}Hg/^{198}Hg$_{sample}$ is the measured corrected value of the sample, and ^{XXX}Hg/^{198}Hg$_{standard}$ is the reference standard solution (NIST SRM 3133).

The background signal was measured for 3 min by on-peak zero mode and immediately followed by the measurements of Hg. To avoid memory effects from the previous sample, the system was rinsed between tow measurements with a blank solution of 2 M HNO$_3$ until the normal background was reached (blank signal of ^{202}Hg was approximately 10 mV).

3.2   Optimization of parameters

3.2.1   Data acquisition time

Acquisition parameters were first optimized to achieve the best internal precision on all Hg ratios investigated. The influence of total data acquisition time on the precision was investigated. By varying the number of integration cycles (from 50 to 300) and/or the integration time per cycle (from 2 to 12 s), the final acquisition time per measurement was progressively increased from 2 to 20 min. The test used a solution of 5 ng mL^{-1} of mercury standard (NIST SRM 3133). The internal uncertainties (1 RSE %) for all ratios are as a function of acquisition time (Fig.2). It is evident that the isotope ratio precision improved with longer total acquisition time, i.e., with increasing number of cycles or integration
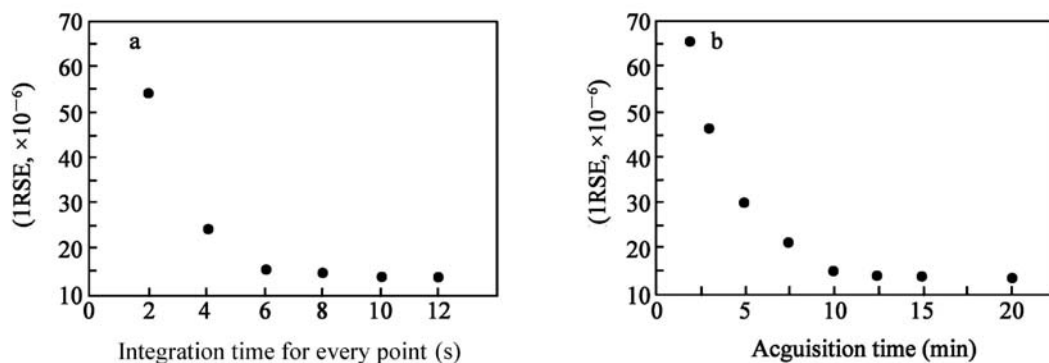
Fig.2   Effect of integration time (a) and acquisition time (b) on isotope ratio precision of ^{202}Hg/^{198}Hg

time. When using mercury concentration (5 ng mL^{-1}), the internal precision was better than 0.0015% (1 RSE) for all Hg ratios when the acquisition time was extended to 10 min (100 cycles, 6-s integration time).

The results by Foucher et al[19] demonstrated that the number of blocks had no effect on accuracy and internal precision as long as the total number of cycles was maintained a constant. Therefore, all our measurements were deliberately acquired using only a single block in 10 min (100 integration cycles with 6 s integration time per cycle). The data acquisition parameters were finally optimized to achieve a final internal isotope ratio precision of better than 0.002% (1 RSE).

3.2.2   Mercury concentration

The precision of isotope ratio measurement was also optimized as a function of the mercury concentration in the introduced solution. As shown in Fig.3, the internal uncertainty (1 RSE) versus the intensity of the ^{202}Hg was obtained in the range of 0.5–20 μg L^{-1} of mercury. The uncertainty of the measurement decreased from 0.006% to less than 0.0015% with increasing concentration. Setting a 10-min acquisition time, the method required a minimum signal of approximately 460 mV (obtained with a solution of

2 μg L^{-1} Hg) for ^{202}Hg to improve the internal precision (< 0.002%, 1 RSE). Higher concentrations lead to better precision (< 0.0015% for all ratios). However, no significant improvement on the standard error of the measurement was observed for signal strength beyond 1550 mV (with 5 μg L^{-1} Hg). Thus, an optimum concentration range was defined between 2 and 5 ng mL^{-1} of mercury as the best compromise between analyte consumption and obtainable precision. At lower concentrations (< 1 μg L^{-1}), the internal uncertainty increased rapidly to > 0.0035%. On the other hand, higher concentrations would increase the rinsing time and the risk of carry over between samples, but it did not improve the internal precision.

3.3   Reproducibility of Hg isotope ratio

The external precision is commonly considered as the long-term reproducibility of the overall method. Figure 4 shows the long-term reproducibility achieved using repeated NIST SRM 3133 Hg standard measurements (n = 45) during nine individual measuring sessions in a period of 7 months (from April 2009 to October 2009). Plotted is the entire set of the δ^{202}Hg$_{NIST3133}$ obtained after mass bias correction.

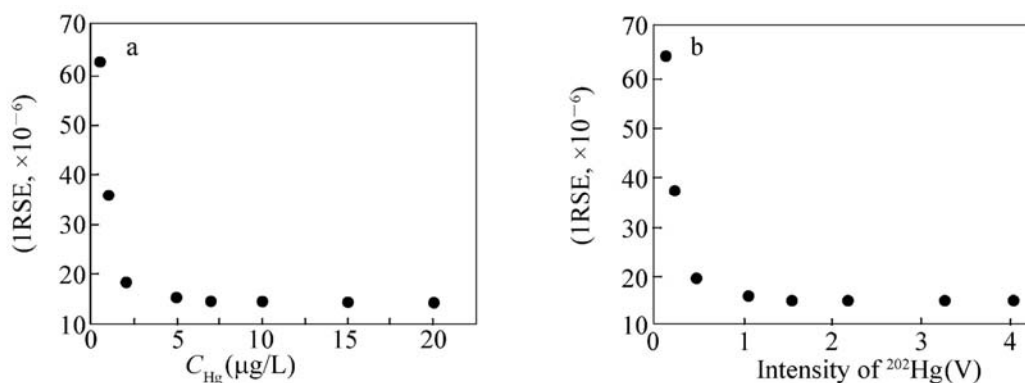The long-term precision of several measurement sessions was better than < 0.06‰ (2SD, n = 45). The corrected

Fig.3   Effect of Hg concentration (a) and signal sensitivity (b) on isotope ratio precision (1 RSE, × 10^{-6}) of ^{202}Hg/^{198}Hg

δ^{202}Hg$_{\text{NIST3133}}$ values were in the range of ±0.05‰ with an average value of 0.00 ± 0.06‰ (2SD, n = 45). We also repeated the measurements of the UM-Almadén Hg secondary standard parallel to the NIST SRM 3133 Hg (from September 2009 to October 2009). Fresh mercury standard solutions (both NIST SRM 3133 and UM-Almadén) were prepared before each working day. The δ^{202}Hg values (related to NIST SRM 3133) for UM-Almadén secondary solution were –0.53 ± 0.05‰ (2SD, n = 15), which were well compared with the University of Michigan.

3.4 Hg isotopic composition of several natural samples

The δ value of environmental samples (including rice leaves, paddy soils, Hg-ores, Hg mine-waste calcines, and zinc ores) are listed in Table 3. Replicate measurements were nearly consistent and yielded a precision of ±0.10‰ for δ^{202}Hg. Figure 5 shows that the δ^{202}Hg and δ^{200}Hg are within the error range along the theoretical mass fractionation line (theoretical line, y = 0.502x), which indicates that the Hg isotopic composition can be determined without interference and the results are reliable. In these samples, δ^{202}Hg ranged from –3.48‰ to 0.63‰, which is about two magnitude orders higher than the external uncertainties. This suggests a potentially wide application of Hg isotopes in the environmental study.
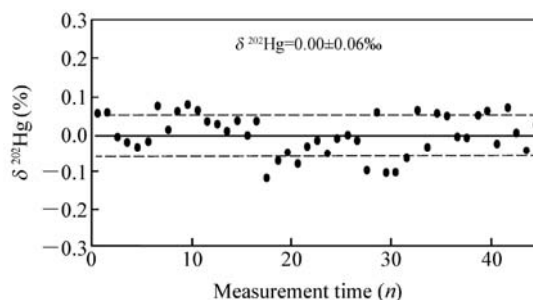

Fig.4   Long-term reproducibility for δ^{202}Hg$_{\text{NIST3133}}$ determined from repeated measurements of NIST SRM 3133 Hg standard at 5 µg L^{-1} over a time period of 7 months

The data were acquired in one block, 100 cycles, and with a 6 s integration time per cycle with a 10-min acquisition time
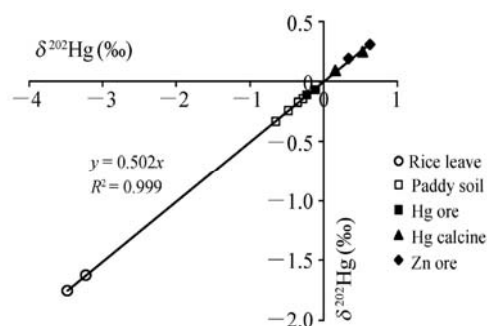

Fig.5   Comparison between theoretical relationship of δ^{200}Hg and δ^{202}Hg and their correlation for natural samples

Table 3   Hg isotope compositions in several nature samples measured by MC-ICP-MS

Sample ID	Sample type	T-Hg (µg g^{-1})	δ^{202}Hg (‰)	2SD	δ^{200}Hg (‰)	2SD
R(5#-2)	Rice leave	0.86	–3.23	0.03	–1.62	0.02
R(GX-1)	Rice leave	3.56	–3.48	0.05	–1.75	0.04
S(GX-1)	Paddy soil	151.14	–0.48	0.10	–0.24	0.05
S(GX-2)	Paddy soil	145.17	–0.65	0.08	–0.33	0.05
S(WK-1)	Paddy soil	127.83	–0.28	0.02	–0.14	0.01
S(WK-2)	Paddy soil	102.45	–0.35	0.02	–0.17	0.02
C(WC-2)	Hg ore	820.39	–0.11	0.03	–0.07	0.02
C(WC-4)	Hg ore	1015.91	–0.23	0.05	–0.11	0.03
T(WC-1)	Hg calcine	57.52	0.16	0.03	0.09	0.01
T(WC-2)	Hg calcine	28.14	0.53	0.04	0.25	0.02
T(WC-3)	Hg calcine	61.87	0.16	0.01	0.09	0.02
Z(HN-1)	Zinc ore	20.61	0.34	0.02	0.19	0.00
Z(HN-2)	Zinc ore	14.40	0.63	0.06	0.31	0.04

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