

Isotope ratios on transient signals with GC–MC–ICP–MS

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Received 10 November 2004; accepted 30 November 2004

Available online 8 January 2005

Abstract

ICP–MS instruments with multiple ion collectors (MC–ICP–MS) provide highly precise and accurate isotope ratio measurements. These instruments are easily coupled to chromatography, laser ablation or flow injection devices because of the ICP source, and thus attract general analytical interest for measurement of highly precise element isotope ratios on transient signals. Some few papers have been published today where MC–ICP–MS was employed for isotope ratios on transient signals, and in general, results are encouraging. Isotope ratio precision obtained is usually at least 10-fold superior compared to measurements with ICP–QMS. Nevertheless, most authors describe a drift of isotope ratios during the transient peak. This behaviour was either interpreted as a problem in the sample introduction system, or was related to instrumental mass bias drift, but has to date not been completely evaluated or explained. In this paper, we systematically investigate the drift observed on lead and mercury isotopes during short transient signals obtained from GC coupled to different MC–ICP–MS systems. We can clearly show that neither changes in instrumental mass bias, nor chromatographic fractionation effects are the source of the observed isotope ratio drift. An influence of analyte concentration on the observed drift was as well excluded as a source for this drift, because the slope on isotope ratios show the same values for different concentrations evaluated. In contrast, the peak width was found to influence the extent to which the isotope ratio drifts during peak elution. Thus, the relative intensity change per time seems to be an important factor for the measurements of transient signals with MC–ICP–MS.

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Keywords: MC–ICP–MS; Gas chromatography; Transient signals; Isotope ratios

1. Introduction

Isotope ratio determination on short transient signals using ICP–QMS has gained rising significance in the recent years, for example in species-specific IDMS using chromatography coupled to ICP–MS.

The precision that can be obtained on isotope ratios for short transient signals using ICP–QMS is limited due to the sequential scanning mode, and is the limiting factor with regards to quantitative results obtained when using species-specific IDMS: the uncertainty on isotope ratio precision may represent 50% or more of the overall uncertainty budget as obtained from error propagation calculations [1]. Here, the introduction of high resolution ICP–MS with multiple ion collectors (MC–ICP–MS) has been an important step. With

these instruments, highly precise isotope ratio determination is possible, while the ICP source enables all kinds of front-end-toys to be coupled. So far, only a handful of papers have been published describing MC–ICP–MS used for the determination of isotope ratios on short transient signals, mainly obtained using GC or HPLC coupling [1–7].

Regarding the precision obtained in isotope ratio analysis for continuous sample introduction, it is distinguished between “internal” and “external” precision. The “internal” precision herein is related to the reproducibility of isotope ratio data obtained during several single measurements of one main run, while the “external” precision is the reproducibility between repeated runs. Data obtained from a single run are thus the average of a certain number of single measurements, which are then again subject to averaging repeated runs. When this concept is translated to transient signals, then the “internal” precision on a transient will be the reproducibility of isotope ratio values for each point dur-

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ing peak elution of a single injection, while the “external” precision will be the reproducibility between repeated injections of the same sample. Obviously, the internal precision of a transient is much more difficult to determine than for continuous signals, because the signal intensities change during peak elution. Therefore, according to counting statistics, isotope ratios obtained for the peak start and peak end must be less precise than in the peak centre, where isotope signals are high. That means, the “internal” precision on a transient signal changes throughout peak elution.

The classical approach for determination of isotope ratios on transient signals is whole peak integration with subsequent division of the integrated peak areas obtained for the respective isotopes. Data precision is then calculated from the standard deviation of repeated measurements of the same sample [8].

This approach has been adopted for GC–MC–ICP–MS of PbEt_4 , resulting in precision on isotope ratio determination for different lead isotope ratios below 0.06% RSD, being at least 10-fold improved when compared to precision obtained for the same experiment using ICP–QMS [2,3]. In general, all approaches using MC–ICP–MS for isotope ratio determination on transient signals report a significant improvement in precision compared to ICP–QMS.

However, regarding the internal precision, most authors describe a drift of the isotope ratios when observing the single data points within the transient signal, thus translating to the fact that internal precision is poor.

Different explanations have been given by some authors for the occurrence of this drift. For the measurement of SF_6 with GC–MC–ICP–MS, isotope drift was assigned to insufficient background correction, and results on isotope ratio precision were greatly enhanced by defining a limited peak integration zone, in which this drift was less pronounced [4].

Wehmeier et al. [5] reported drifting antimony isotope ratios for trimethylantimony measured with cryo-GC coupled to the Isoprobe MC–ICP–MS, and interpreted these finding with chromatographic fractionation on the GC column, stating that the heavier isotope species elutes first from the column. Evans et al. [6] observed drifting isotope ratios during transient signals obtained by thermodesorption of elemental mercury from gold traps. The same trend was seen with three different MC–ICP–MS instruments, and the authors assumed differences in the desorption behaviour between the mercury isotopes. Heavier isotopes seem to be volatilised first, ascribed to stronger interaction of lighter isotopes with the gold amalgam. Nevertheless, this finding is contradictory to reaction kinetics, after which bonds between lighter isotopes are less strong than bonds between heavier isotopes.

Günther-Leopold et al. [7] found isotope ratio drift for the determination of neodymium and uranium with HPLC coupled to the Neptune MC–ICP–MS. They concluded that the effect could not be explained by fractionation on the chromatographic column, because the same isotope ratio drift was found when HPLC was replaced by FIA injections.

In summary, the findings reported to date in the cited references are contradictory, and no common concept was found to be the origin for isotope ratio drift during the acquisition of transient signals with MC–ICP–MS. Moreover, in the most cases a single isotope pair is investigated and used for data interpretation.

Due to the observed drift, several questions arise related to the data evaluation procedure: is it necessary to take the whole peak width into account, as proposed by Evans et al. [6], or is it better to use a certain range of data inside the transient only, as proposed by Krupp et al. [4] and Clough et al. [1], and what implications does the drift have on isotope ratio accuracy?

However, the drift observed on the transient signals obtained with MC–ICP–MS must have a reason, which to date is yet not identified. It is thus of special interest to systematically investigate this phenomenon, and to identify and subsequently eliminate this effect.

In this work, the authors will attempt to identify the source of the observed isotope ratio drift, using transient signals obtained on lead and mercury species with different GC–MC–ICP–MS systems. Of main interest are mass bias and chromatographic effects, as these parameters have most frequently been supposed to be the origin of the observed drift. Thus, theoretical considerations are compared with experimental results in order to confirm or exclude certain assumptions. For this purpose, all possible isotope ratio pairs are examined in the attempt to draw a common conclusion.

2. Experimental

2.1. Instrumental

Capillary GC was coupled to different MC–ICP–MS instruments via a home-made transfer line for the measurement of a volatile lead species (PbEt_4) and two volatile mercury species, HgEt_2 and HgMeEt . For lead measurements, two different MC–ICP–MS systems were employed, the Axiom MC–ICP–MS (Thermo, Winsford) and the Isoprobe MC–ICP–MS (GV Instruments, Manchester). Details on the setup of the coupling for lead species work, as well as details on sample preparation can be found in Ref. [2] for measurements with the Axiom MC instrument, and in Ref. [3] for work carried out with the Isoprobe MC.

For the measurement of mercury species, again an Axiom MC–ICP–MS was used, but these measurements were carried out on a different instrument. The same overall instrumental setup was used as previously described [2,3]. GC parameters were identical for all experiments, and are listed in Table 1. MC–ICP–MS acquisition parameters for the three different experiments are provided in Table 2.

An important detail in this coupling is that during all GC runs a standard solution (thallium) was continuously added to the plasma by using a T-piece as connection of GC and spray chamber to the plasma torch. With this

Table 1
GC parameters

GC Instrument	HP 6850
Column	Restek MXT-1, 30 m, 0.53 mm i.d., d_f 1 μ m
Injection mode	Splitless
Injection port temperature	250 °C
Injection volume	1 μ L
Carrier gas flow	He 25 mL/min
Make up gas flow	Ar 250 mL/min
Transfer line temperature	250 °C isothermal
Oven program	
Initial temperature	60 °C
Initial time	1 min
Ramp rate	50 °C/min
Final temperature	260 °C
Final time	1 min

setup, the MC–ICP–MS was optimised for sensitivity in standard liquid introduction conditions, which were respected throughout all experiments. The thallium solution serves in several ways. First of all, MC–ICP–MS conditions like torch position or nebulizer gas flow can be optimised using a continuous signal. Then, during GC runs, the plasma conditions can be continuously monitored in order to assure optimal acquisition conditions during analyte elution. This is illustrated in Fig. 1, where the plasma perturbation by the solvent elution (assigned “solvent dip”) and subsequent stabilisation can be clearly seen. Moreover, the isotope ratio of $^{205}\text{Tl}/^{203}\text{Tl}$ can be used for simultaneous mass bias correction on the lead or mercury signal, respectively [2,3,8].

2.2. Sample preparation

For lead measurements, analysed as PbEt_4 , an isotopic certified standard solution of NIST 981 lead material was prepared, and the inorganic lead solution was derivatized with NaBEt_4 to form PbEt_4 . Simultaneously with the derivatization, the organolead compound was extracted into isoctane

Table 2
MC–ICP–MS parameters

Instrument	Axiom MC	Isoprobe MC	Axiom MC
Analyte	PbEt_4	PbEt_4	MeHgEt , HgEt_2
Continuous internal standard (10 $\mu\text{g/L}$)	Tl	Tl	Tl
Nebulizer	GE concentric, 0.4 mL/min self-aspirating	Meinhard concentric, self-aspirating	GE concentric, 0.4 mL/min self-aspirating
Spray chamber	Cyclonic	Cyclonic	Cyclonic, impact bead
Power (W)	1250	1350	1250
Argon gas flows (L/min)			
Plasma	15	13.5	16
Auxiliary	1	0.6	1
Nebulizer	0.5	0.67	0.5
Hexapole		1.79	
Isotopes monitored (Faraday cups)	^{202}Hg , ^{203}Tl , ^{204}Pb , ^{205}Tl , ^{206}Pb , ^{207}Pb , ^{208}Pb	^{203}Tl , ^{204}Pb , ^{205}Tl , ^{206}Pb , ^{207}Pb , ^{208}Pb	^{198}Hg , ^{199}Hg , ^{200}Hg , ^{201}Hg , ^{202}Hg , ^{203}Tl , ^{204}Pb , ^{205}Tl , ^{206}Pb
Integration time (ms)	50	160	150

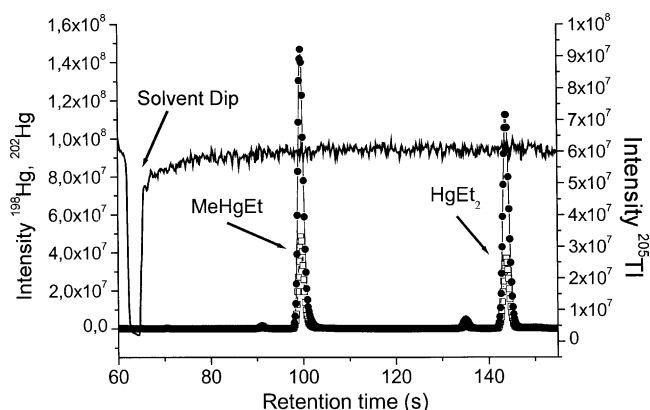


Fig. 1. Chromatogram of a methylmercury and inorganic mercury standard obtained with GC coupled to Axiom MC–ICP–MS. Open squares: ^{198}Hg trace, filled circles: ^{202}Hg trace, black line: ^{205}Tl trace continuously introduced as liquid solution.

(2,2,5-trimethylpentane), and each 1 μL of the organic solution repeatedly injected into the GC–MC–ICP–MS.

Two different mercury species were investigated, inorganic mercury (Hg^{2+}) and methylmercury (HgMe^+). Inorganic mercury was derivatized to HgEt_2 from a commercial inorganic mercury standard solution (SPEX, Metuchen, NJ). Methylmercury was obtained as MeHgCl (Strem, Bismarck, 99%). Dilute solutions of MeHgCl were prepared in 1% HCl and derivatized with NaBEt_4 (Strem, Bismarck) to form MeHgEt , and organic mercury species were extracted into hexane. Details concerning sample preparation and derivatization have been published by Rodriguez et al. [8].

3. Results and discussion

The injection of ethylated lead or mercury species results in chromatograms, as illustrated for mercury species measurements in Fig. 1. The first mercury peak to elute at a retention time of about 100 s is the derivatized methylmercury, assigned as HgMeEt . The second mercury species, HgEt_2

corresponding to inorganic mercury, elutes at about 145 s. The elution order follows the chromatographic separation by boiling point of the species, i.e., the lower boiling species elute first. Observation of the simultaneously aspirated thallium solution reveals the elution of the solvent, here assigned “solvent front”. At a retention time of about 60 s, hexane elutes from the column, leading to severe plasma perturbation: the thallium signal breaks away. About 15 s after solvent elution, the thallium signal regains its initial value, indicating that the plasma has stabilised. So we assume that the plasma has completely recovered from the injection of organic solvent, before the first analyte species is introduced.

In the following, a description of the isotope ratio development during peak elution is given. For lead isotope measurements, the signals of ^{206}Pb , ^{207}Pb and ^{208}Pb were evaluated. Intensity for ^{204}Pb (isotope abundance 1.4%) was too low to get meaningful isotope ratio values.

Mercury has seven stable isotopes, of which the five most abundant (^{198}Hg , ^{199}Hg , ^{200}Hg , ^{201}Hg and ^{202}Hg) were evaluated. During all measurements, ^{203}Tl and ^{205}Tl were mon-

itored simultaneously. All signal intensities were automatically corrected for instrumental background on each Faraday cup.

Isotope ratios were calculated by using the higher mass isotope as enumerator and the lower mass isotope as denominator. Thus, values >1 are obtained where the abundance of the higher mass ion is higher than the abundance of the lower mass ion, and values <1 are obtained for the opposite case.

In Fig. 2a–d, the analyte peak of the highest abundant isotope (^{208}Pb for lead, ^{202}Hg for mercury measurements) together with isotope ratios obtained during peak elution are illustrated. Fig. 2a shows $^{208}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ as well as $^{205}\text{Tl}/^{203}\text{Tl}$ obtained for measurements with GC coupled to the Axiom MC-ICP-MS and Fig. 2b shows the same isotope ratios for measurements obtained with the Isoprobe MC-ICP-MS. Fig. 2c illustrates mercury isotope ratios $^{201}\text{Hg}/^{198}\text{Hg}$, $^{200}\text{Hg}/^{199}\text{Hg}$ and $^{200}\text{Hg}/^{198}\text{Hg}$, for the peak obtained for methylmercury (Hg-MeEt), in Fig. 2d the peak obtained for inorganic mercury (as HgEt_2) is enlarged.

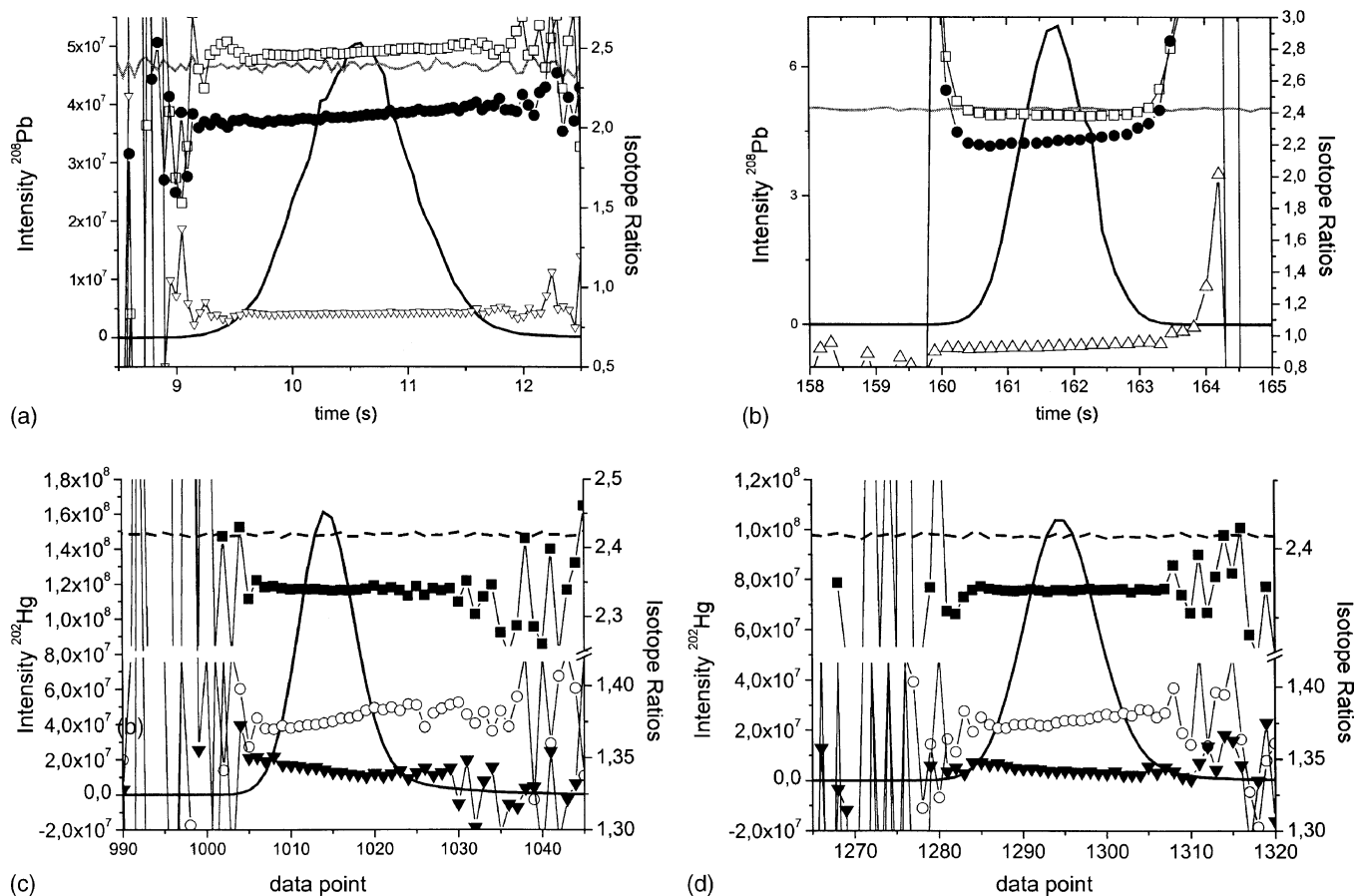


Fig. 2. (a) Lead peak (PbEt_4) and lead isotope ratios for GC coupled to Axiom MC-ICP-MS: straight line: ^{208}Pb trace, grey line: $^{205}\text{Tl}/^{203}\text{Tl}$, empty squares: $^{208}\text{Pb}/^{207}\text{Pb}$, full circles: $^{208}\text{Pb}/^{206}\text{Pb}$, empty triangles: $^{207}\text{Pb}/^{206}\text{Pb}$; (b) lead peak (PbEt_4) and lead isotope ratios for GC coupled to Isoprobe MC-ICP-MS: straight line: ^{208}Pb trace, grey line: $^{205}\text{Tl}/^{203}\text{Tl}$, empty squares: $^{208}\text{Pb}/^{207}\text{Pb}$, full circles: $^{208}\text{Pb}/^{206}\text{Pb}$, empty triangles: $^{207}\text{Pb}/^{206}\text{Pb}$; (c) methylmercury peak (MeHgEt) and mercury isotope ratios for GC coupled to Axiom MC-ICP-MS: straight line: ^{202}Hg trace, dashed line: $^{205}\text{Tl}/^{203}\text{Tl}$, filled squares: $^{200}\text{Hg}/^{198}\text{Hg}$, open circles: $^{200}\text{Hg}/^{199}\text{Hg}$, filled triangles: $^{201}\text{Hg}/^{198}\text{Hg}$; (d) inorganic mercury peak (HgEt_2) and mercury isotope ratios for GC coupled to Axiom MC-ICP-MS: straight line: ^{202}Hg trace, dashed line: $^{205}\text{Tl}/^{203}\text{Tl}$, filled squares: $^{200}\text{Hg}/^{198}\text{Hg}$, open circles: $^{200}\text{Hg}/^{199}\text{Hg}$, filled triangles: $^{201}\text{Hg}/^{198}\text{Hg}$.

When regarding the development of the isotope ratios illustrated in Fig. 2a (GC–Axiom MC–ICP–MS), a shift towards higher ratios throughout the elution of PbEt₄ is visible for all observed lead isotope ratios, while ²⁰⁵Tl/²⁰³Tl seems to be stable during peak elution. In Fig. 2b the same species was measured using GC coupled to the Isoprobe MC–ICP–MS, and here, ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb drift towards higher values over the duration of peak elution, while the ratios ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁵Tl/²⁰³Tl seem to be stable over the whole range.

In Fig. 2c and d, only three of the possible 10 isotope ratio pairs of the five mercury isotopes considered are illustrated. The three mercury isotope ratios show either a positive slope versus higher ratios during peak elution (²⁰⁰Hg/¹⁹⁹Hg), or negative slope, i.e., lower isotope ratios during peak elution (²⁰¹Hg/¹⁹⁸Hg), or no obvious drift at all (²⁰⁰Hg/¹⁹⁸Hg). As observed for the lead measurements, the isotope ratio of the internal standard (²⁰⁵Tl/²⁰³Tl) does not show a drift throughout peak elution. The effect obtained here is similar for both mercury peaks obtained, as can be seen when comparing Fig. 2c and d.

Theoretically, different effects can be considered as the source of this behaviour, that may either be related to the MC–ICP–MS acquisition, or the chromatographic separation and sample input from the GC side, namely:

- (i) a general drift in the overall instrumental mass bias or a drift in mass bias concerning the analyte only due to the change in concentration and/or matrix during peak elution;
- (ii) a chromatographic separation between analyte molecules incorporating lower and higher mass metal isotopes;
- (iii) a drift in the background signal, which is not compensated by the automatic instrumental background correction;
- (iv) the influence of analyte concentration and peak width.

In order to make the observed effects comparable, the isotope ratio drift was described mathematically by forming a linear equation from single data points. Therefore, a defined range of values was considered. Five points before and five points after the peak maximum as observed on the highest abundant isotope were used for lead measurements with the Isoprobe MC–ICP–MS, and for the mercury measurements with the Axiom MC–ICP–MS, resulting in 11 data points used for the calculation of slope and regression coefficient. For lead measurements with the Axiom MC–ICP–MS, each 15 points before and after peak maximum were used, thus in all 31 points. This difference is due to the integration times used for one data point. While for the two first measurements integration times of 150 and 160 ms, respectively, were applied, the latter measurement was performed using 50 ms integration time (compare Table 2). By observing more data points for shorter integration time, about the same net peak width was taken into account for all measurements performed.

The slope and linear regression coefficients are used to describe the magnitude of the observed drift effect. This parameter should follow certain rules, as for example a change in mass bias should show a linear behaviour versus mass difference of the isotope pairs concerned, and should always change into the same direction, i.e., to either higher or lower mass bias for all isotope ratios observed.

The same should be true if a chromatographic effect is behind the observed effect; if the analyte species is separated due to slight differences in molecular weight caused by the different isotopic mass of the central atom incorporated, then the observed effect should be stronger for isotope pairs with higher mass difference, and the relation between retention time and molecular weight may be considered linear. In order to enable a direct comparison of the observed magnitude in drift, the calculated slopes were normalized by division through the mean value of the single points used.

Note: the isotopes of carbon and hydrogen, also present in the organometallic species, should as well cause chromatographic separation by molecular weight. Nevertheless, due to their low natural abundance (0.02% for ²H and 1.11% for ¹³C) their contribution to the overall effect was considered negligible.

In Table 3a and b, the obtained results for the calculation of values and regression parameters for lead measurements are listed, while Table 3c and d shows the calculated parameters for the peaks of methylmercury and inorganic mercury, respectively. Here, the mean values for three repeated injections are shown.

The repeatability of the results concerning the calculated slopes on isotope ratios during peak elution was determined for three repeated injections of a 500 pg MeHgEt and HgEt₂ standard. In general, the relative standard deviation (RSD) for the mean values on the absolute isotope ratios calculated is better than 0.1%, while the RSDs for three different measurements for the slope on isotope ratios greatly depend on the linearity of the isotope ratio observed. For slopes on isotope ratios with high linear correlation coefficients ($R^2 > 0.9$), the RSDs for the three different values obtained for the slopes on three measurements are between 5 and 20%. Isotope ratios showing poor correlation for the observed drift ($R^2 < 0.5$) show significantly higher RSDs on repeated measurements.

In the following, the experimentally obtained results will be investigated in order to confirm or disqualify the above-mentioned possible sources. Of special interest are the mercury measurements, as 10 different isotope ratio pairs can be evaluated, compared to three possibilities only for the lead isotope ratio pairs.

3.1. Instrumental mass bias

The instrumental mass bias observed in MC–ICP–MS is today mainly believed to be produced in the field-free region between the sampler and the skimmer cones. Mass-dependent diffusion leads to the preferred sampling of heavier mass isotopes, which is reflected in the fact that measured heavy to

light isotope ratios are higher than the true ratios. The mass bias observed is also depending on the relative mass difference, decreasing with increasing atomic mass. Instrumental mass bias for heavy elements is usually observed to be around 1% per mass unit, and linear or exponential equations can be used to mathematically correct for it. For a certain element, the mass bias is expressed per mass unit, regardless which isotope pair is observed. Changes in mass bias due to sample matrix, deposits on the cones, torch position, gas flow rate or other plasma parameters have recently been evaluated by Andr  n et al. [9]. Obviously, plasma parameters influence the optimal sampling zone of individual element isotopes, thus changing the observed mass bias. Nevertheless, higher or lower mass bias should always affect all isotopes of the same element in the same direction: either towards higher or towards lower mass bias per mass

unit. Otherwise, overall slow drift of mass bias leading to changes in observed isotope ratio during long measurements is usually observed, and one of the reasons why bracketing with isotopic certified standard material is a common method when precise isotope ratio measurements are performed.

In the following, the experimental results will be evaluated with respect to theoretical considerations of mass bias effects that can influence isotope ratio values.

In Fig. 2a–d, we can observe that the thallium isotope ratio is not drifting during the elution of the analyte peak, and this is observed for all experiments conducted. This fact is stressed by the mathematical parameters calculated and listed in Table 3. In all cases, the linear regression factors for $^{205}\text{Tl}/^{203}\text{Tl}$ are extremely poor, with other words, there is no linear relation, values fluctuate randomly. A general, overall

Table 3

Mean values and linear regression parameters for drift observed during peak elution on lead, mercury and thallium isotope ratios for GC–MC–ICP–MS measurements

Isotope ratio	Mean value ($n = 31$)	RSD%	Slope	R^2	Normalized slope	ΔM
(a) PbEt ₄ by GC–Axiom MC–ICP–MS						
208/207	2.478	0.683	0.0017823	0.9163	0.0007194	1
208/206	2.078	1.151	0.0025438	0.9352	0.0012242	2
207/206	0.839	0.521	0.0004232	0.7743	0.0005046	1
205/203	2.391	0.942	0.0001355	0.0030	0.0000567	2
Isotope ratio	Mean value ($n = 11$)	RSD%	Slope	R^2	Normalized slope	ΔM
(b) PbEt ₄ measurements with GC–Axiom MC–ICP–MS						
208/207	2.383	0.171	–0.0009049	0.5442	–0.0003797	1
208/206	0.933	0.927	0.0025825	0.9797	0.0027679	2
207/206	2.224	0.811	0.0053121	0.9552	0.0023888	1
205/203	2.424	0.228	–0.0001729	0.0107	–0.0000713	2
Isotope ratio Hg	Mean value ($n = 11$)	RSD%	Slope	R^2	Normalized slope	ΔM
(c) MeHgEt by GC–Axiom MC–ICP–MS (mean of three injections)						
202/201	2.273	0.307	–0.0020658	0.9625	–0.0009090	1
202/200	1.303	0.470	–0.0018403	0.9904	–0.0014118	2
202/199	1.793	0.254	–0.0012920	0.8822	–0.0007208	3
202/198	3.048	0.491	–0.0044948	0.9904	–0.0014745	4
201/200	0.574	0.175	–0.0002884	0.9131	–0.0005029	1
201/199	0.789	0.077	0.0001486	0.6450	0.0001884	2
201/198	1.341	0.192	–0.0007583	0.9557	–0.0005654	3
200/199	1.375	0.240	0.0009512	0.9127	0.0006916	1
200/198	2.339	0.050	–0.0001460	0.4101	–0.0000624	2
199/198	1.701	0.257	–0.0012814	0.9449	–0.0007535	1
205/203	2.418	0.085	0.0000277	0.0259	0.0000115	2
Isotope ratio	Mean value ($n = 11$)	RSD%	Slope	R^2	Normalized slope	ΔM
(d) HgEt ₂ by GC–Axiom MC–ICP–MS (mean of three injections)						
202/201	2.272	0.189	–0.0012747	0.9199	–0.0005610	1
202/200	1.303	0.320	–0.0012782	0.9768	–0.0009808	2
202/199	1.793	0.149	–0.0007671	0.8592	–0.0004279	3
202/198	3.048	0.315	–0.0029455	0.9729	–0.0009664	4
201/200	0.573	0.143	–0.0002409	0.8842	–0.0004200	1
201/199	0.789	0.076	0.0001051	0.3383	0.0001332	2
201/198	1.341	0.142	–0.0005440	0.8421	–0.0004056	3
200/199	1.376	0.187	0.0007612	0.9006	0.0005533	1
200/198	2.339	0.056	0.0000336	0.0712	0.0000144	2
199/198	1.700	0.185	–0.0009158	0.8677	–0.0005387	1
205/203	2.418	0.107	0.0000777	0.1332	0.0000321	2

change in mass bias can thus be excluded as the source for the observed isotope ratio drift.

Otherwise, a drift in mass bias can be related to the analyte only, due to the fact that the matrix in the plasma changes with amount of analyte introduced. If the analyte concentration is the determining factor, then isotope ratios will drift into one direction during the rise in analyte concentration, and then drift into the opposite direction soon as the peak maximum is passed, as illustrated in Fig. 3a and b. This behaviour cannot be observed in the experiments. As shown in Fig. 2a and b, the isotope ratios drift into the same direction during the entire peak elution. Nevertheless, a retarded mass bias effect may be assumed, relating to the fact that the plasma conditions can stabilise slow, or due to slow removal of carbon deposits on the cones from the introduction of organic matter.

Therefore, the regression coefficients and normalized values for the slopes obtained on lead and mercury isotope ratios, respectively, are examined: provided the mass bias on the analyte isotopes is subject to change during peak elution, a similar effect must be observed on all analyte isotope ratios, being more pronounced with higher mass difference. In Table 3a and b, values obtained for lead measurements are listed either with the Axiom MC–ICP–MS or with the Isoprobe MC–ICP–MS. For PbEt₄ measurements with the Axiom MC, all lead isotope ratios observed show a positive drift, i.e., the higher mass isotope sensitivity rises during peak elution. This indicates a change towards higher mass bias, in other words the preferred sampling of the higher mass ion. Theoretically, this mass bias change must affect the isotope pair ²⁰⁸Pb/²⁰⁶Pb with 2 amu mass difference double as much as the isotope pairs ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁷Pb/²⁰⁶Pb with 1 amu mass difference. Thus, the normalized slopes must show the same value for ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁷Pb/²⁰⁶Pb, while the observed slope must be twice as high for ²⁰⁸Pb/²⁰⁶Pb. As can be seen in Table 3a, the normalized slopes are roughly reflecting this behaviour, slope values being around 0.0007 and 0.0005 for ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁷Pb/²⁰⁶Pb, respectively, while ²⁰⁸Pb/²⁰⁶Pb shows a slope of around 0.0012. Thus, for this

set of measurements a mass bias drift is a possible source for the observed effect.

Regarding the values obtained with the Isoprobe MC–ICP–MS (Table 3b), the behaviour is completely different. While ²⁰⁸Pb/²⁰⁷Pb shows poor linear relation with very small and negative values for the slope, ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb reveal a positive linear drift with $R^2 > 0.995$, with very similar values for the normalized slope. These results do not reflect the theoretical assumption that the mass bias should have a similar influence on all isotopes of the same element. Therefore, here a mass bias effect can be excluded as a source for the observed isotope ratio drift. This is different from what was seen in Table 3a for lead measurements with the Axiom MC–ICP–MS.

Regarding the mercury isotope ratios obtained for MeHgEt and HgEt₂ (Table 3c and d), no common behaviour is found when all isotope pairs are evaluated. While most isotope pairs show a negative slope indicating a decrease in mass bias, ²⁰⁰Hg/¹⁹⁹Hg shows a positive slope, and no significant drift is seen for ²⁰⁰Hg/¹⁹⁸Hg and ²⁰¹Hg/¹⁹⁹Hg with correlation coefficients <0.65. These findings show that there is no common rule in the behaviour of the mercury isotopes, and a systematic drift in mass bias with a similar effect on all mercury isotopes can definitely be ruled out.

3.2. Chromatographic fractionation in the GC column

The chromatographic separation technique is the same in all experiments performed. The capillary GC column employed separates species by boiling point, the separation is accelerated using a linear GC temperature program.

For the same species, i.e., molecule, the boiling point is related to the molecular weight. Thus, molecules, where isotopes with different masses are incorporated may be separated on the GC column. Such a separation would obey physical laws, and result in an elution order where the light mass molecules elute first, and the heavier mass molecules elute one after the other with rising molecular weight. In the small retention time window to be expected, the relation be-

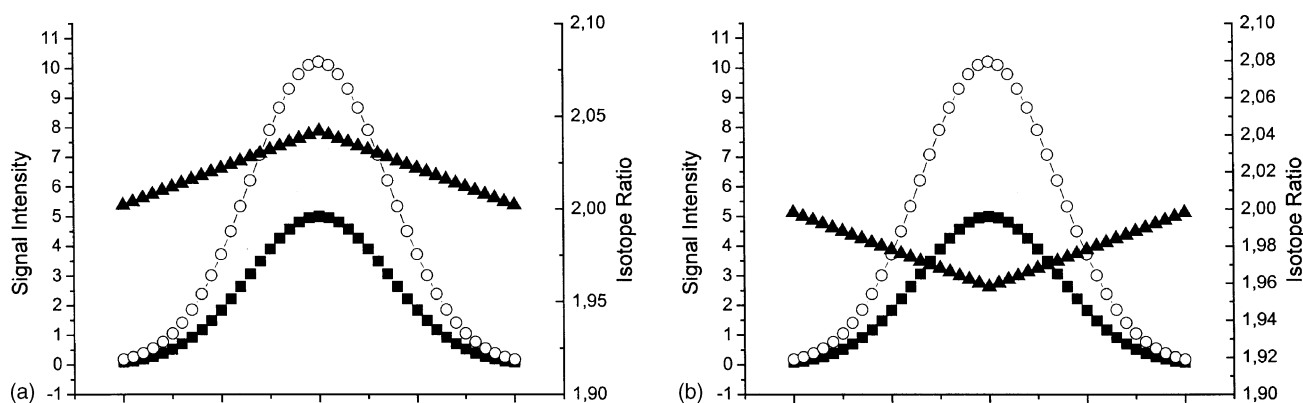


Fig. 3. (a) Theoretical isotope ratio drift for *rising* mass bias caused by rise in analyte concentration: filled square: isotope 1, empty circle: isotope 2, filled triangle: isotope ratio of isotope 2 divided by isotope 1; (b) theoretical isotope ratio drift for *descending* mass bias caused by rise in analyte concentration: filled square: isotope 1, empty circle: isotope 2, filled triangle: isotope ratio of isotope 2 divided by isotope 1.

tween molecular weight and retention time is assumed to be linear.

Theoretically, when the molecules elute successively with the lightest isotope first and the heaviest last, a drift in isotope ratio during the peak elution will be observed. Provided all isotope ratios are formed by using the heavier isotope as enumerator and the lighter isotope as denominator, all slopes must be positive, and the normalized slopes will be a proportional multiple of the mass difference. Normalized slopes for isotope ratios with the same mass difference must be equal.

When comparing the theoretical considerations with the experimental results as illustrated in Fig. 2a–d and detailed in Table 3a–d, a chromatographic fractionation effect can only be assumed for the measurements of PbEt₄ using the Axiom MC–ICP–MS. Here, all isotope ratio pairs show a positive drift, and approximate double intensity for the isotope pair ²⁰⁸Pb/²⁰⁶Pb is obtained with 2 amu mass difference compared to the slopes obtained for ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁷Pb/²⁰⁶Pb with 1 amu mass difference. On the contrary, the measurements of PbEt₄ with the Isoprobe MC–ICP–MS reveal no drift for ²⁰⁸Pb/²⁰⁷Pb, and as such do not correspond to the theoretical expectations.

The majority of mercury isotope ratios show negative slopes in contrast to the expected positive slopes, besides two isotope ratios that do not show any drift ($R^2 < 0.7$), and ²⁰⁰Hg/¹⁹⁹Hg with positive slope. The same trend in the results are observed for MeHgEt and HgEt₂.

These findings clearly exclude the hypothesis that the observed isotope ratio drift is due to chromatographic fractionation on the GC column. Regarding the lead measurements, the same effects should be found for both instrumental setups, as the chromatography and the species measured are identical in both cases. In the case of mercury, the chromatographic fractionation might be observed to a lesser or higher extent compared to lead measurements, but the general trend should be identical.

3.3. Background correction

In a tailing peak, as observed for the mercury measurements, the background is enhanced towards the end of the peak. It is thus possible that this shift in background causes the overall isotope ratio shift. Therefore, two different ways of chromatographic background correction as illustrated in Fig. 4 were investigated in order to find out whether the rise in background provoked by a peak tailing may be the origin of the observed drift in isotope ratios during the peak elution. Either a straight or a sloped subtraction of the background signal was applied, and the results compared with the values obtained when no chromatographic background correction was performed. The results listed in Table 4 are very similar for non-chromatographic background correction as well as the two chromatographic background correction strategies, as can be seen from the relative standard deviations calculated for the three kinds of correction methods described above, which are below 1% for the major part of the values. Higher

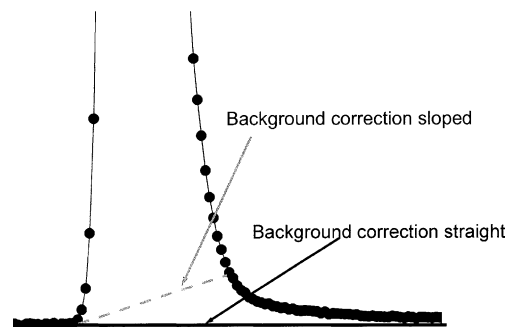


Fig. 4. Illustration of the two methods of chromatographic background correction applied to mercury measurements. Black line: straight correction, grey dashed line: sloped correction.

RSDs (1–3%) are observed for the isotope ratios only where no significant drift can be stated.

These results show that a problem related to background correction issues may be excluded as source for the observed drift in isotope ratio during peak elution.

3.4. Analyte concentration and peak shape

Another point to investigate is whether the drift in isotope ratio depends on the peak shape and/or analyte concentration. Therefore, the results for the two different mercury species were closer investigated. As shown in Table 3c and d, the general tendency for all isotope ratios is the same for MeHgEt and HgEt₂, but all values obtained for the MeHgEt peak are slightly higher. For better comparison, slopes for MeHgEt were plotted against the slopes obtained for HgEt₂, as illustrated in Fig. 5a. If slopes were similar for both species, a bisecting line with a slope of 1 should be obtained. Instead, the slope has a value of about 0.7, indicating that the isotope ratio slope values obtained for the two mercury species differ systematically. Regarding the mercury peaks as illustrated in Fig. 3c and d, it can be seen that the peak for HgEt₂ is larger than the one for MeHgEt. In order to investigate if there is a relation to the peak shape, slopes were normalized by the peak width obtained for the respective peaks. With these nor-

Table 4

Comparison of slopes obtained for drift on mercury isotope ratios during peak elution of MeHgEt without chromatographic background correction and with two different kinds of background correction

Isotope ratio	No correction	Straight correction	Sloped correction	RSD%
202/201	–0.0009090	–0.0009103	–0.0009069	0.19
202/200	–0.0014118	–0.0014121	–0.0014168	0.20
202/199	–0.0007208	–0.0007208	–0.0007136	0.58
202/198	–0.0014745	–0.0014758	–0.0014765	0.07
201/200	–0.0005029	–0.0005019	–0.0005094	0.81
201/199	0.0001884	0.0001898	0.0001933	1.33
201/198	–0.0005654	–0.0005655	–0.0005693	0.39
200/199	0.0006916	0.0006917	0.0007035	0.98
200/198	–0.0000624	–0.0000635	–0.0000597	3.19
199/198	–0.0007535	–0.0007548	–0.0007627	0.66

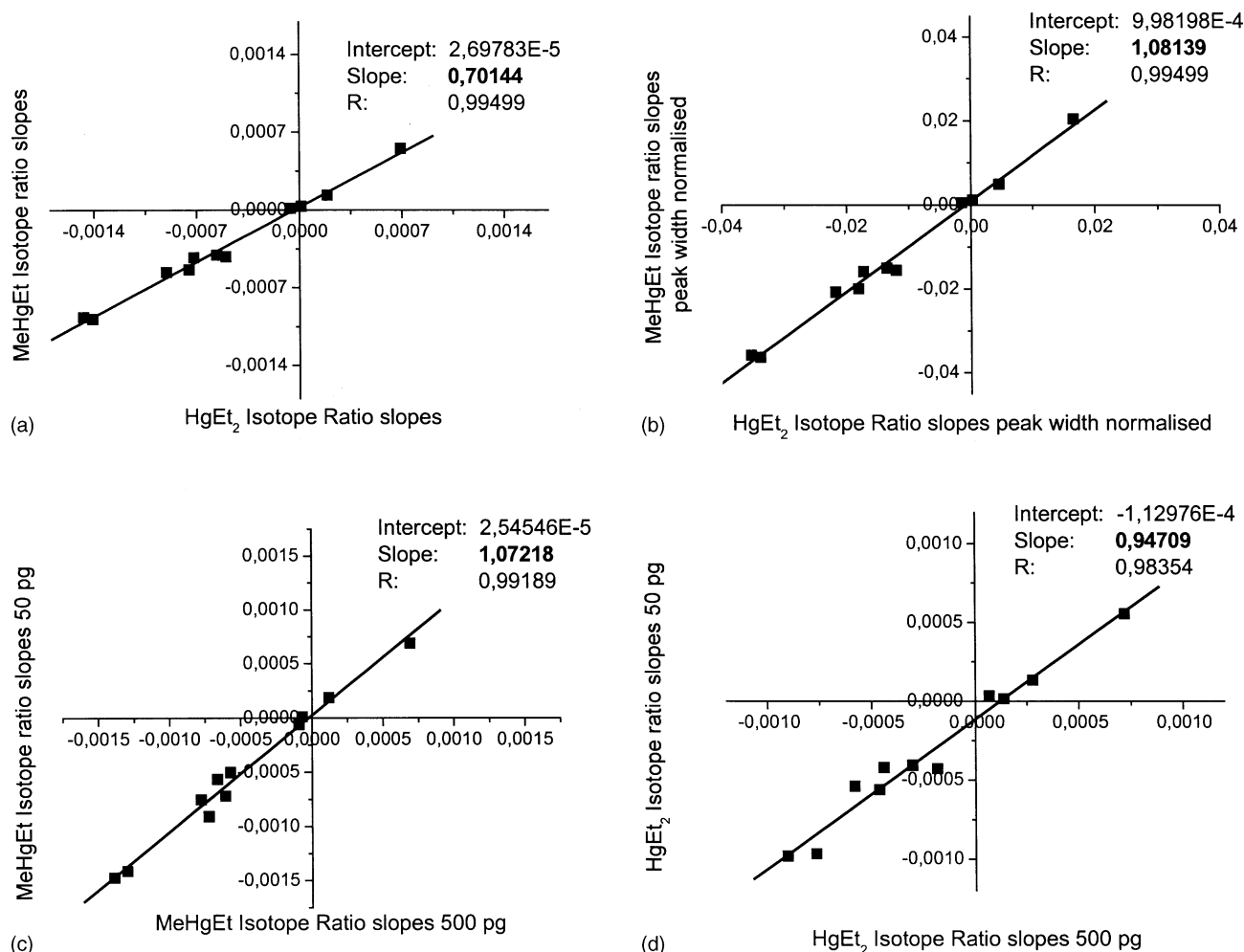


Fig. 5. (a) Mercury isotope slopes obtained for MeHgEt and HgEt₂ plotted vs. one another; (b) mercury isotope slopes obtained after normalization for peak width for MeHgEt and HgEt₂ plotted versus one another; (c) mercury isotope slopes obtained for the injection of 50 and 500 pg MeHgEt plotted versus one another; (d) mercury isotope slopes obtained for the injection of 50 and 500 pg HgEt₂ plotted vs. one another.

malized values, a slope of about 1 is obtained, as illustrated in Fig. 5b. Thus, the extent of the isotope ratio drift observed is likely to be dependent on the relative change in analyte concentration per time, being more pronounced the narrower the transient signal is.

This finding may also be related to the analyte concentration, i.e., the total peak height. Therefore, the isotope ratio slopes obtained for 50 and 500 pg injections of MeHgEt and HgEt₂, respectively, were plotted versus each other, as illustrated in Fig. 5c for MeHgEt and Fig. 5d for HgEt peaks. In both cases, bisecting lines with slopes around 1 are obtained, clearly showing that the extent of the drift observed is not related to the analyte concentration.

4. Conclusion

The repeatedly observed drift on isotope ratios on short transient signals obtained for measurements with MC-ICP-MS poses a major problem for the data evaluation of those

experiments. To date, neither satisfactory explanation, nor solution for this problem has been found. In this work, we could clearly show that neither chromatographic fractionation, nor changes in instrumental mass bias can be responsible for the observed drift. Likewise, an instrumental background shift could be excluded, as well as the influence of overall analyte concentration. The one parameter that seems to have influence on the extent of this drift is the overall width of the transient, pointing to the possibility that the relative change in intensity per time is the major problem.

However, a satisfactory solution to the described problem cannot be given, but may put the focus on other parameters, which may be ascribed to the concept of MC-ICP-MS in general. One important result described here and confirmed in literature is that a drift of analyte isotope ratios on transient signals occurs, no matter which MC-ICP-MS is used: similar effects are observed for the Axiom, the Isoprobe and the Neptune [7] instruments, thus giving rise to the assumption that the reason lies in the overall instrument concept. In fact, the data acquisition system behind the Faraday cups is con-

cepted for continuous signals, not for fast changing signals (L. Rottmann, Thermo Bremen, Germany, personal communication). This concept may lead to problems in the correct acquisition with integration times as short as 150 ms or less and additionally changing analyte concentration. Hirata et al. [10] described a similar effect for laser ablation work done with MC–ICP–MS, and attributed it to a slow response of the Faraday amplifier. In a recent work of Günther-Leopold et al. [11], a difference in response was found when one isotope was measured on a different Faraday cup, thus again pointing to an instrumental problem related to the ion detection system.

Here, additional experiments must be conducted, for example by using ion counters instead of faraday cups, or to carry out the same experiment while measuring on different faraday cups or changing the amplification system behind the faraday cups, as is possible with the Neptune MC–ICP–MS.

Nevertheless, the analytical possibilities and challenges that are achieved in terms of superior isotope ratio precision gained by using MC–ICP–MS are worthwhile to be translated to short transient signals. Here, superior results not only for speciation, but also for laser ablation of, e.g., fluid inclusions are of major interest for the analytical society, and instrument manufacturers are invited to tackle the presented problem in cooperation with analytical chemists.

Acknowledgements

The authors wish to thank Thermo Electron (Winsford, UK) for the possibility to work on the Axiom MC–ICP–MS, and GV Instruments (former Micromass, Manchester, UK)

for the possibility to work with the Isoprobe MC–ICP–MS. Special thanks go to Christophe Pecheyran for lots of experimental help and good humour. For fruitful discussions during the 5th International Conference on High Resolution ICP–MS in Omaha, Nebraska (August 2004), the authors would like to thank Lothar Rottmann, Bjorn Klaue and Bert Mueller. Thanks do also go to Jeroen Sonke, and finally to Bill Fitzgerald, who initiated the mercury measurements – thanks for all the fish!!

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