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**Metrological triangle for measurements of isotope amount ratios of
silver, indium and antimony using MC-ICPMS: the 21st century
Harvard method**

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ABSTRACT

The calibration of measurements of isotope amount ratio using a log-linear regression method with multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) is the latest development in isotope amount ratio metrology. This calibration method, however, is often met with criticism. In this work, we evaluate the robustness of this calibration strategy wherein measurements of antimony and indium isotope amount ratios are calibrated against isotope amount ratio of silver, despite the significant difference in their atomic mass. In addition, a metrological triangle comprising Ag-Sb-In measurement results is constructed from three pairs of inter-elemental isotope amount ratio calibrations: $N(^{123}\text{Sb})/N(^{121}\text{Sb})$ from the $N(^{109}\text{Ag})/N(^{107}\text{Ag})$ of NIST SRM 978a measurement standard, $N(^{115}\text{In})/N(^{113}\text{In})$ from the $N(^{123}\text{Sb})/N(^{121}\text{Sb})$, and then calibration of $N(^{109}\text{Ag})/N(^{107}\text{Ag})$ from the obtained $N(^{115}\text{In})/N(^{113}\text{In})$ measured ratio values to verify consistency with the known $N(^{109}\text{Ag})/N(^{107}\text{Ag})$. This calibration method revives one of the salient features of the classical ‘Harvard method’—a network of relationships amongst the isotopic compositions of various elements. The atomic weights of antimony and indium, reported here for the first time using MC-ICPMS, $121.7590(22)_{k=2}$ and $114.818\,27(35)_{k=2}$, are in good agreement with their current Standard Atomic Weights. In addition, this study provides the first calibrated mass spectrometric isotope amount ratio measurements for indium.

KEYWORDS Metrologically traceable isotope ratios, atomic weight, mass bias correction, MC-ICPMS, indium, antimony, silver, metrology, commutability.

1. INTRODUCTION

Building on the accomplishments of Berzelius, Cannizzaro and Stas, high-accuracy determinations of atomic weights culminated in the early 20th century in the work of Theodore W. Richards.¹ For this, he was awarded the 1914 Nobel Prize in Chemistry. The Harvard method, as it was known, essentially established a firm relationship between the atomic weights of metallic elements by precipitation of their halides with silver salts. The atomic weight of antimony, for example, was established by titration of pure SbBr_3 with AgNO_3 . Thus, the isotopic composition of antimony was calibrated against the isotopic composition of silver (and bromine).²⁻³ Although now entirely absent from the scientific arsenal, such an approach had the advantage of cross-validating isotopic composition amongst the elements—a feature that is lacking with modern mass spectrometry methods, wherein isotopic composition for each element is determined in isolation using blends of near-pure isotopes of the same element for calibration.⁴⁻⁷ In modern metrological parlance, this corresponds to establishing commutability of isotope amount ratio measurement results.

Traditionally, thermal ionization mass spectrometry (TIMS) has been the authoritative technique for delivering the smallest possible measurement uncertainty of isotope amount ratios⁸. Recent developments in multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) have enabled this technique to become a powerful research tool with over four-hundred papers published annually in the past several years⁹. In addition to its simple and robust sample introduction system, the ICP source is capable of ionizing nearly all elements, providing relative repeatability of the isotope amount ratio measurements as low as $1 \cdot 10^{-5}$, similar to that achieved with TIMS⁸. The simultaneous multi-element measurement capability enables correction of isotope amount ratio values against readily available certified isotopic reference materials of other elements. For example, measurements of isotope amount ratios for mercury can be calibrated using thallium admixed to the Hg sample¹⁰. Although this principle of ‘external normalization’ in mass spectrometry dates back to 1987¹¹, its full potential remains untapped due to several difficulties with its implementation.

First, there is a common belief that an effective isotope amount ratio correction can only be achieved when working in close vicinity to the atomic mass of the measurand due to higher likelihood that both it and the calibrant will have identical mass-bias, or nearly so. In other words, silver would typically be dismissed as a calibrant for the establishing the value of $N(^{123}\text{Sb})/N(^{121}\text{Sb})$ owing to their large difference in atomic masses. Rather, that selection is more rationally undertaken using the adjacent element tin¹². It is clear that such a mode of operation restricts the number of potential applications of external normalization even within the limitations of current MC-ICPMS instruments, which allow for an ~20% spread in atomic mass to be measured simultaneously.

Second, the mathematical formalism of the mainstream isotope amount ratio measurement protocol—the exponential correction model—is based on the assumption of identical mass-bias between the isotopes in the calibrant and those of the measurand.⁸ In recent years, however, it has been recognized that the extent of isotope fractionation differs from element to element. Consequently, the isotope amount ratios derived in this manner can be erroneous⁸. For example, errors of up to half a per cent have been noted when the $^{202}\text{Hg}/^{200}\text{Hg}$ ratio is calibrated *via* $^{205}\text{Tl}/^{203}\text{Tl}$ using the exponential correction model¹⁰. Moreover, the isotope amount ratios corrected using the exponential model can show dependence on the concentration of the measurand, which clearly invalidates the use of such a correction approach¹⁰. The modern log-linear regression model of isotope amount ratio calibration abandons both of these restrictions while delivering metrologically traceable isotope amount ratios with unprecedented small measurement uncertainties.^{10, 13-15}

To date, there is a limited set of published MC-ICPMS Sb isotope amount ratio measurements, all of which report variations against a common working calibrator (delta scale) to circumvent the challenge of mass-bias correction for measurements of metrologically traceable data and to achieve much smaller uncertainty for relative measurements, not necessarily metrologically traceable isotope amount ratios.^{12, 16-17} There are none for indium by MC-ICPMS. To the best of our knowledge, this is first report of measurements of metrologically traceable isotope amount ratios of antimony and indium using MC-ICPMS.

As noted earlier, mass bias is traditionally corrected for using the principle of least difference between the atomic masses of the measurand and calibrant. In this study, we test the robustness of the regression calibration both in the domain of time and mass difference between the measurand and the calibrant. A metrological triangle comprising Ag-In-Sb measurement results is constructed from the three pairs of inter-elemental isotope amount ratio calibrations: $N(^{123}\text{Sb})/N(^{121}\text{Sb})$ from the $N(^{109}\text{Ag})/N(^{107}\text{Ag})$ provided by a NIST SRM 978a calibrant, $N(^{115}\text{In})/N(^{113}\text{In})$ from the $N(^{123}\text{Sb})/N(^{121}\text{Sb})$, and then calibration of $N(^{109}\text{Ag})/N(^{107}\text{Ag})$ from the obtained $N(^{115}\text{In})/N(^{113}\text{In})$ to verify consistency with the known value of $N(^{109}\text{Ag})/N(^{107}\text{Ag})$. Such a two-step mass bias transfer provides a robustness test of the regression model.

2. EXPERIMENTAL SECTION

2.1. Instrumentation. A Neptune MC-ICPMS (Thermo Fisher Scientific, Bremen, Germany) equipped with nine Faraday cups and a combination of cyclonic and Scott-type spray chambers with a self-aspirating perfluoroalkoxy polymer nebulizer MCN50 (Elemental Scientific, Omaha NE, USA) was used for all measurements. The plug-in quartz torch with sapphire injector was fitted with a platinum guard electrode. Low resolution mode was employed. Optimization of the Neptune was performed as recommended by the manufacturer¹⁸ and typical operating conditions are summarized in Table 1. The gain on each Faraday cup was monitored daily to ensure normalization of its efficiency.

2.2. Reagents and solutions. Reagent grade nitric and hydrochloric acids (Fischer Scientific Canada, Ottawa ON, Canada) were purified in-house prior to use by sub-boiling distillation of reagent grade feedstock in a quartz still. High-purity (18 M Ω -cm) deionized water was obtained from a NanoPure mixed bed ion exchange system fed with reverse osmosis domestic feed water (Barnstead/Thermolyne Corp, Iowa, USA). Isotopic standard reference material for silver, SRM 978a (AgNO_3), was obtained from the National Institute of Standards and Technology (Gaithersburg MD, USA). A 1000 $\mu\text{g g}^{-1}$ stock solution of silver was prepared by quantitative dissolution of SRM 978a in HNO_3 and diluted with water to a 2% volume fraction of HNO_3 . A 1000 $\mu\text{g g}^{-1}$ stock solution of antimony was prepared by quantitative dissolution of high purity antimony metal

(99.9999%, Johnson Matthey, London, UK) in a mixture of HNO₃ and HCl, which was then diluted with deionized water. A 1000 µg g⁻¹ stock solution of indium was prepared by quantitative dissolution of high purity indium metal (99.9999%, Johnson Matthey, London, UK) in HNO₃ and then diluted with deionized water. SCP Science (Quebec, Canada) was used to source 1000 µg g⁻¹ stock solutions of In and Sb.

2.3. Sample preparation and analysis. Sample preparation was conducted in a class-100 clean room. Replicate solutions of 0.25 to 2 µg Sb g⁻¹ or 0.25 to 1 µg In g⁻¹ were prepared by diluting the antimony stock solution in a mixture of 1% HNO₃ and 3% HCl followed by an addition of the NIST 978a Ag stock solution. The mass fraction of silver in the test solutions varied from 250 to 500 ng g⁻¹. Samples were introduced into the plasma in a self-aspiration mode at a flow rate of 50 µL min⁻¹. Ion currents of Sb or In and Ag isotopes obtained from a blank solution containing 1% HNO₃ and 3% HCl were subtracted from those of all samples. A static run was employed to collect isotope ions of each pair of elements, as shown in Table 2. Ten to fifteen measurements were made on each sample solution, the duration of each session of measurements being of the order of 10–15 h. Data reported here were collected between March and June of 2010.

3. RESULTS AND DISCUSSION

3.1. Instrument settings. To obtain optimum results, a static measurement procedure is desired whereby the ion currents from all isotopes of interest are simultaneously collected. As the Neptune allows for a maximum 17% difference in atomic mass between the outermost detectors¹⁸, their configurations for each pair or for all three elements, presented in Table 2, permitted monitoring of Ag, In and Sb isotope ions currents simultaneously, or separately in pairs of Ag→Sb and Ag→In.

3.2. Mass bias correction. With metrologically traceable values of isotope amount ratios being of interest, the log-linear regression mass bias correction model was used to measure isotope amount ratios of Sb and In in this study, in a manner similar to that used in previous studies of Zn¹⁴, Cu¹⁴, Hg¹⁶ and Ge¹³ isotopes. This model is based on monitoring the temporal drift in the simultaneous isotopic ratio measurements where the intercept and slope of the constructed log-linear regressions between the observed (uncorrected) isotope amount ratios of the measurand $N(^{123}\text{Sb})/N(^{121}\text{Sb})$ (r_{Sb}) or

$N(^{115}\text{In})/N(^{113}\text{In})$ (r_{In}) and the calibrant $N(^{109}\text{Ag})/N(^{107}\text{Ag})$ (r_{Ag}) forms the basis for calibration of Sb and In isotope amount ratio measurements.^{8, 10, 13} The present approach for measurements of Sb and In isotope amount ratios uses silver isotopic measurement standard (NIST SRM 978a); thus, it resembles the classical Harvard method wherein the atomic weight of antimony was essentially calibrated using the atomic weight value of silver. The major advantage of the regression model over the traditional exponential correction model is that the regression approach is free of the assumed need for identical fractionation behaviour between the element pairs.^{10, 13} Additionally, the regression model is not hampered by the untestable assumption regarding the very nature of the fractionation (linear, exponential, etc.). Equation (2) forms the basis for the Sb (or In) isotope amount ratio calibration with silver as the calibrant:^{10, 13}

$$\ln r_{\text{Sb}} = \ln R_{\text{Sb}} - \underbrace{\frac{\ln K_{\text{Sb}}}{\ln K_{\text{Ag}}} \cdot \ln R_{\text{Ag}}}_{\text{intercept, } a} + \underbrace{\frac{\ln K_{\text{Sb}}}{\ln K_{\text{Ag}}} \cdot \ln r_{\text{Ag}}}_{\text{slope, } b} \quad (2)$$

It is worth emphasizing that this expression is a logarithmic rearrangement of the expressions $R_{\text{Sb}} = K_{\text{Sb}} r_{\text{Sb}}$ and $R_{\text{Ag}} = K_{\text{Ag}} r_{\text{Ag}}$, where K is the isotope amount ratio correction factor (constant) that links measured isotope amount ratio value (r) with the mass bias corrected isotope amount ratio (R). As evident from Figure 1, the drift in the $N(^{123}\text{Sb})/N(^{121}\text{Sb})$ and $N(^{109}\text{Ag})/N(^{107}\text{Ag})$ measured isotope ratios defines a log-linear relationship over a measurement session of 10–15 h in accordance with equation (2). The corresponding intercept (a) and slope (b) of the log-linear regression are calculated using a least squares approach and the estimates are then used to obtain the mass bias corrected isotope ratios of antimony using an expression that follows directly from equation (2).¹⁹

$$R_{\text{Sb}} = R_{\text{Ag}}^b \cdot e^a \quad (3)$$

In this work, the NIST certified value of $N(^{109}\text{Ag})/N(^{107}\text{Ag}) = R_{\text{Ag}} = 1.076\,39(22)_{k=2}$ is used. Although equation (3) resembles the traditional exponential mass-bias correction in its appearance, the underlying logic of the two models is significantly different¹³.

3.3. Spectral interferences. Potential spectral interferences from $^{91}\text{Zr}^{16}\text{O}^+$, $^{90}\text{Zr}^{16}\text{OH}^+$, $^{93}\text{Nb}^{16}\text{O}^+$, $^{92}\text{Zr}^{16}\text{OH}^+$, $^{92}\text{Mo}^{16}\text{OH}^+$, $^{97}\text{Mo}^{16}\text{O}^+$, $^{96}\text{Mo}^{16}\text{OH}^+$, $^{40}\text{Ar}^{73}\text{Ge}^+$, $^{40}\text{Ar}^{75}\text{As}^+$, $^{99}\text{Ru}^{16}\text{O}^+$, $^{123}\text{Te}^+$, $^{105}\text{Pd}^{16}\text{O}^+$, $^{104}\text{Ru}^{16}\text{OH}^+$, $^{107}\text{Ag}^{16}\text{O}^+$ and $^{106}\text{Pd}^{16}\text{OH}^+$ on Sb, In and Ag isotopes may arise in samples containing these elements and thus could enlarge the measurement

uncertainty of the determined Sb or In isotope amount ratios. They require elimination or correction. Semi-quantitative analysis of the Sb and In sample solutions revealed that the mass fractions of potential interference-forming elements, Zr, Nb, Mo, Te, Pd and Ru, were less than 5 pg g⁻¹. Such amounts would give rise to insignificant isobaric interferences since the mass fraction of Ag, In and Sb in the samples was some six orders of magnitude larger, i.e., 0.2 and 2 µg g⁻¹, respectively. Although silver was added to the Sb or In sample solutions at mass fractions of up to 0.5 µg g⁻¹, the ion current measured at m/z 123 (¹⁰⁷Ag¹⁶O⁺) was 1.1·10⁻¹⁴ A from a 0.5 µg g⁻¹ standard solution of silver and is similar to that obtained from a blank solution (1% HNO₃ and 3% HCl). This clearly indicates that any interference from ¹⁰⁷Ag¹⁶O⁺ on ¹²³Sb⁺ is insignificant.

3.4. Measurements. For the measurements of Sb, In and Ag isotope amount ratios, replicate sample solutions of 0.25 to 2 µg Sb g⁻¹, 0.25 to 1 µg In g⁻¹ and 0.2 to 0.5 µg Ag g⁻¹ were prepared and each was measured under the optimized experimental conditions during a 10–15 h measurement session. Over the four-month period encompassing March to June, 2010, many sets of the N(¹²³Sb)/N(¹²¹Sb) or N(¹¹⁵In)/N(¹¹³In) vs. N(¹⁰⁹Ag)/N(¹⁰⁷Ag) or N(¹¹⁵In)/N(¹¹³In) vs. N(¹²³Sb)/N(¹²¹Sb) log-linear regressions were acquired, each yielding the respective intercepts and slopes. Of these, 54 high-quality Ag→Sb sets, 30 high-quality Ag→In sets and 18 high-quality Sb→In sets exhibiting coefficient of determination larger than 0.99 were selected. The size of each result set was simply idiosyncratic and determined by the effort and investment of labour. One such measurement series is shown in Figure 1. The mass bias corrected Sb or In isotope amount ratios were then obtained using equation (3) with subsequent calculation of the corresponding isotope abundances and atomic weight.²⁰

3.5. Uncertainty evaluation. Uncertainty estimations for the mass bias corrected Sb and In isotope amount ratios as well as isotopic abundances and atomic weight were done in accordance with the JCGM 100:28 “Guide to the Expression of Uncertainty in Measurement”.²² The actual calculation procedure is described in detail elsewhere.^{10, 23} To wit, measurement uncertainty propagation of equation (3) leads to the following for antimony (Ag→Sb):

$$u_r^2(R_{\text{Sb}}) = b^2 \cdot u_r^2(R_{\text{Ag}}) + (u_a + \rho_{a,b} \cdot u_b \ln R_{\text{Ag}})^2 \quad (4)$$

The estimates of the Ag→Sb and Sb→In regression intercepts and slopes are perfectly anticorrelated ($\rho_{a,b} = -1$), whereas in the In→Ag measurement system—positively correlated. Note that the uncertainty of the isotope amount ratio of silver is incorporated into the combined uncertainties of the Sb and In isotope ratios. Although trivial, this aspect is not widely appreciated.⁹ The uncertainty in the measurements of isotope abundance is obtained from equation (5) as isotope abundance is calculated from isotope amount ratios, i.e., $x_{121} = 1/(1 + R_{\text{Sb}})$ and $x_{123} = 1 - x_{121}$, hence:

$$u(x_{121}) = u(x_{123}) = \frac{u(R_{\text{Sb}})}{(1 + R_{\text{Sb}})^2} \quad (5)$$

Lastly, the uncertainty in the measurements of atomic weight was calculated as follows:^{20, 24}

$$A_r(\text{Sb}) = x_{121}m_{121} + x_{123}m_{123} \quad (6)$$

$$u_{A_r(\text{Sb})}^2 = (m_{123} - m_{121})^2 \cdot u^2(x_{121}) + x_{121}^2 u^2(m_{121}) + x_{123}^2 u^2(m_{123}) \quad (7)$$

Using this approach, each regression plot yields a set of Sb isotope ratios, isotope abundances and atomic weight with their corresponding uncertainties for each estimate. The grand average of experimental results is then obtained which serves as the property value for all measurands. Similar equations were derived for Sb→In, In→Ag and Ag→In regressions.

The combined uncertainty of the grand mean, u_c , was obtained by combining the uncertainties of the individual estimates and the variations between these means as per recent guidelines from NIST—the Type B model of the bias method.²⁵ The following equation was used:

$$u_c = \sqrt{s_m^2 + \frac{1}{p} \sum u_i^2}, \quad (8)$$

where s_m is the standard deviation of the p means and u_i is the uncertainty of the individual measurand estimates, $i = [1 \dots p]$.

3.6. Measurement results

Metrological triangle. As a result of the availability of isotopic silver measurement standard (NIST SRM 978a), Sb and In were selected for study as they cover the largest possible atomic mass interval (17%) compatible with simultaneous MC-ICPMS

measurements. This was done to evaluate the robustness of the regression calibration in the domain of atomic mass difference between the measurand and the calibrant. The crux of the estimation of accuracy of the regression mass bias correction model itself lies in a “triangle” of three isotope amount ratio calibrations constructed from nine high-quality sets of simultaneously measured Sb, In and Ag amount ratios in the samples prepared from same stock solutions. First, the NIST SRM 978a value of $N(^{109}\text{Ag})/N(^{107}\text{Ag}) = R_{\text{Ag}} = 1.07639(22)_{k=2}$ is used to calibrate $N(^{123}\text{Sb})/N(^{121}\text{Sb})$ (R_{Sb}). Subsequently, the value obtained for R_{Sb} is used to calibrate $N(^{115}\text{In})/N(^{113}\text{In})$ (R_{In}). Lastly, the R_{In} is used to calculate R_{Ag} in NIST SRM 978a. Results are shown in Figure 2a. Despite the 17% difference in atomic mass between the measurand and calibrant (Ag and Sb), an output result of $R_{\text{Ag}} = 1.0763(60)_{k=2}$ is obtained, confirming the accuracy of this mass bias correction model.

Furthermore, the robustness of the regression model was tested by performing the pair-wise isotope amount ratio calibrations sequentially over an extended period of time (see Table 2 for the Faraday cup configurations). This was done with samples prepared from different stock solutions. Again, the NIST SRM 978a value of $R_{\text{Ag}} = 1.07639(22)_{k=2}$ was used to calibrate $N(^{123}\text{Sb})/N(^{121}\text{Sb})$ (R_{Sb} , March-April 2010) which was used to calibrate $N(^{115}\text{In})/N(^{113}\text{In})$ (May-June 2010). Finally, the R_{In} was used to determine R_{Ag} in NIST SRM 978a (June 2010). Note also that each measurement step in the ‘triangle’ was performed using different Faraday cups. Results are shown in Figure 2b. Two conclusions can be made. First, the regression model delivers mass bias transfer stable to $1 \cdot 10^{-4}$ over extended periods of time despite the 17% difference in atomic mass between the measurand and calibrant (Ag→Sb→In). Second, the uncertainty estimates of the calibrated isotope amount ratios are not underestimated. In other words, the output result (R_{Ag}) is consistent with the input value of the NIST SRM 978a. The uncertainty in the antimony and indium isotope amount ratio measurement results is largely driven by the repeatability and reproducibility of the measurements and not the uncertainty in the silver isotope amount ratio specified for the NIST calibrant.

Isotopic composition. The final results for the metrologically traceable isotope amount ratios of Sb and In were calculated by combining all high-quality data sets obtained from March to June 2010 by MC-ICPMS with use of the regression mass bias correction

model based on the NIST SRM 978a Ag isotopic measurement standard. Results are summarized in Table 3. The corresponding atomic weights of $A_r(\text{Sb}) = 121.7590(22)_{k=2}$ and $A_r(\text{In}) = 114.818\,27(35)_{k=2}$ are in good agreement with the current Standard Atomic Weights—121.760(1) and 114.818(3), respectively.²⁰

CONCLUSIONS

The robustness of the log-linear regression method for mass bias correction has been evaluated for measurement of isotope amount ratios characterized by small measurement uncertainty. The approach is straightforward and offers significant advantages over other popular mass bias correction models currently in use. Most notably, the concept of commutability has been demonstrated, whereby the perceived constraint of selecting a calibrant having atomic mass close to that of the measurand has been obviated. Any calibrant isotope pair lying within the static run mass range of the spectrometer can be used for this purpose. Currently, this means that any reference pair within the approximately 17% range of the multicollector field would be suitable. Ideally, a mass spectrometer capable of simultaneous full mass range detection (“all the signal, all the time”), such as that developed by Hieftje and co-workers²⁶ (and currently available from Spectro), would require only a single isotopic measurement standard to enable mass bias correction for any measurand.

REFERENCES

1. Hartley, H. J. *Chem. Soc.*, **1930**, 1937-1969.
2. Willard, H. H.; McAlpine, R. K. *J. Am. Chem Soc*, **1921**, 43, 797–818.
3. Weatherill, P. F. *J. Am. Chem. Soc.* **1924**, 46, 2437–2445.
4. De Laeter, J. R.; Hosie, D. J. *Int. J. Mass Spectrom. Ion Processes*, **1988**, 83, 311–318.
5. Wachsmann, M.; Heumann, K. G. *Int. J. Mass Spectrom. Ion Processes*, **1991**, 108, 75–86.
6. Chang, T. L.; Qian, Q. Y.; Zhao, M. T.; Wang, J. *Int. J. Mass Spectrom. Ion Processes*, **1993**, 123, 77–82.
7. De Laeter, J. R.; Böhlke, J. K.; De Bièvre, P.; Hidaka, H.; Peiser, H. S.; Rosman, K. J. R.; Taylor, P. D. P. *Pure Appl. Chem.* **2003**, 75, 768-769.
8. Yang, L. *Mass Spectrom. Rev.* **2009**, 28, 990-1011.
9. Douthitt, C. B. *J. Anal. At. Spectrom.* **2008**, 23, 685-689.
10. Meija, J.; Yang, L.; Sturgeon, R. E.; Mester, Z. *J. Anal. At. Spectrom.* **2010**, 25, 384-389.
11. Longerich, H. P.; Fryer, B. J.; Strong, D. F. *Spectrochim. Acta* **1987**, 42B, 39-48.
12. Clayton, R.; andersson, P.; Gale, N. H.; Gillis, C.; Whitehouse, M. J. *J Anal. At. Spectrom.*, **2002**, 17, 1248-1256.
13. Yang, L.; Meija, J. *Anal. Chem.*, **2010**, 82, 4188-4193.
14. Marechal, C. N.; Telouk, P.; Albarede, F. *Chem. Geol.* **1999**, 156, 251-273.
15. Yang, L.; Sturgeon, R. E. *Anal. Bioanal. Chem.* **2009**, 393, 377-385.
16. Rouxel, O.; Ludden, J.; Fouquet, Y. *Chem. Geol.*, **2003**, 200, 25-40.
17. Wehmeier, S.; Ellam, R.; Feldmann, J. *J Anal. At. Spectrom.*, **2003**, 18, 1001-1007.
18. http://www.thermo.com/eThermo/CMA/PDFs/Various/File_26979.pdf, Neptune Produce Brochure, BR30028_F12/08C.
19. Meija, J.; Yang, L.; Sturgeon, R. E.; Mester, Z. *Anal. Chem.* **2009**, 81, 6774-6778.
20. De Laeter, J. R.; Böhlke, J. K.; De Bièvre, P.; Hidaka, H.; Peiser, H. S.; Rosman, K. J. R.; Taylor, P. D. P. *Pure Appl. Chem.* **2003**, 75, 683-800.
21. *International Vocabulary of Metrology – Basic and General Concepts and*

- Associated Terms*; VIM, 3rd edition, JCGM 200:2008,
<http://www.bipm.org/en/publications/guides/vim.html>
22. (21)*Evaluation of Measurement Data-Guide to the Expression of Uncertainty in Measurement*; JCGM 100:28: <http://www.bipm.org/en/publications/guides/gum.html>
  23. Meija, J.; Mester, Z. *Metrologia* **2008**, 45, 53-62.
  24. Audi, G.; Wapstra, A. H.; Thibault, C. *Nuclear Phys. A*, **2003**, 729, 337-676.
  25. Levenson, M. S.; Banks, D. L.; Eberhardt, K. R.; Gill, L. M.; Guthrie, W. F.; Liu, H. K.; Vangel, M. G.; Yen, J. H.; Zhang, N. F. *Journal of the Research of the national Institute of Standards and Technology*, **2000**, 105, 571-579.
  26. Schilling, G. D.; Ray, S. J.; Sperline, R.P.; Denton, M.B.; Barrinaga, C. J.; Koppenaal, D.W.; Hieftje, G.M. *J. Anal. At. Spectrom.*, **2010**, 25, 322 – 327.

Table 1. MC-ICPMS operating conditions

Instrument settings	
Reflected forward power	1250 W
Plasma gas flow rate	15.0 L Ar min ⁻¹
Auxiliary gas flow rate	1.00 L Ar min ⁻¹
Carrier gas flow rate	1.020 L Ar min ⁻¹
Orifice of the nickel sampler cone	1.1 mm
Orifice of the high-performance nickel skimmer cone	0.8 mm
Lens settings	Optimized for maximum analyte ion current
Data acquisition parameters	
Mass resolution, $m/\Delta m$	~300
Signal integration time	33.5 s
Number of integrations, cycles, blocks	1, 10, 4

Table 2. MC-ICPMS Neptune detector configurations and typical isotope ion intensities obtained for sample¹ and blank solutions

Faraday cups ²	L4	L2	L1	C	H2	H3
(1) Ag→Sb	¹⁰⁷ Ag	¹⁰⁹ Ag		¹¹⁵ In	¹²¹ Sb	¹²³ Sb
Cup position, mm	94.170	62.150		0.000	61.092	85.785
Signal intensity, ·10 ⁻¹¹ A	2.11	2.04		15.52	2.00	1.55
Blank signal, ·10 ⁻¹⁴ A	0.08	0.07		16	1.5	1.1
(2) Sb→In			¹¹³ In	¹¹⁵ In	¹²¹ Sb	¹²³ Sb
Cup position, mm			19.266	0.000	61.092	85.785
Signal intensity, 10 ⁻¹¹ A			0.666	15.52	17.255	13.315
Blank signal, 10 ⁻¹⁴ A			0.7	16	1.5	1.1
(3) In→Ag		¹⁰⁷ Ag	¹⁰⁹ Ag	¹¹³ In	¹¹⁵ In	
Cup position, mm		68.951	43.046	0.000	24.238	
Signal intensity, 10 ⁻¹¹ A		2.11	2.04	0.666	15.52	
Blank signal, 10 ⁻¹⁴ A		0.08	0.07	0.7	16	
(4) Ag→Sb→In	¹⁰⁷ Ag	¹⁰⁹ Ag	¹¹³ In	¹¹⁵ In	¹²¹ Sb	¹²³ Sb
Cup position, mm	94.170	62.150	19.268	0.000	61.092	85.785
Signal intensity, 10 ⁻¹¹ A	2.11	2.04	0.666	15.52	2.00	1.55
Blank signal, 10 ⁻¹⁴ A	0.08	0.07	0.7	16	1.5	1.1

¹ Mass fraction of Sb, In and Ag is 0.3, 0.5 and 0.15 µg g⁻¹, respectively.

² Faraday cups L3, H1 and H4 were not used in this study to collect isotope ions.

Table 3. Isotope amount ratios, abundances and atomic weights of Sb and In^a

	Atomic mass number,	Isotope amount ratio,	Isotope abundance,
	A	$N(^A\text{Sb}/^{121}\text{Sb})$ or $N(^A\text{In}/^{113}\text{In})$	x_A
Sb	121	1 (exact)	0.5725(11)
	123	0.7468 (33)	0.4275(11)
	Atomic weight, $A_r(\text{Sb}) = 121.7590(22)$		
In	113	1 (exact)	0.042 81(19)
	115	22.36 (10)	0.957 19(19)
	Atomic weight, $A_r(\text{In}) = 114.818\,27(35)$		

^a Values are presented in a concise notation whereby the expanded uncertainty is given in parenthesis next to the least significant digits to which it applies; for example, $x_{121} = 0.5725(11)$ is the concise form of the expression $x_{121} = 0.5725 \pm 0.0011$. It is intended that the expanded uncertainty encompasses every aspect that reasonably contributes to the uncertainty in measurements of quantity value. A coverage factor of two (2) was applied. Atomic masses used for calculation are from the 2003 Atomic mass evaluation²³.

Figures and Captions

Figure 1. Temporal drift of the determined $N(^{123}\text{Sb})/N(^{121}\text{Sb})$ (r_{sb}) and $N(^{109}\text{Ag})/N(^{107}\text{Ag})$ (r_{Ag}) isotope amount ratios in a typical 14 h measurement session.

Figure 2. Metrological triangles for silver→antimony→indium→silver isotope amount ratio calibrations using MC-ICPMS (a) constructed from sets of simultaneously measured isotope amount ratios of Sb, In and Ag and (b) constructed from data sets obtained sequentially during March to June 2010 in pairs of Ag→Sb, Sb→In and In→Ag.

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