

Anal Bioanal Chem (2013) 405:2973–2986  
DOI 10.1007/s00216-012-6542-1

ORIGINAL PAPER

# Copper and tin isotopic analysis of ancient bronzes for archaeological investigation: development and validation of a suitable analytical methodology

Eleonora Balliana · Maite Aramendía · Martín Resano · Carlo Barbante · Frank Vanhaecke

Received: 29 August 2012 / Revised: 30 October 2012 / Accepted: 31 October 2012 / Published online: 22 November 2012  
© Springer-Verlag Berlin Heidelberg 2012

**Abstract** Although in many cases Pb isotopic analysis can be relied on for provenance determination of ancient bronzes, sometimes the use of “non-traditional” isotopic systems, such as those of Cu and Sn, is required. The work reported on in this paper aimed at revising the methodology for Cu and Sn isotope ratio measurements in archaeological bronzes via optimization of the analytical procedures in terms of sample pre-treatment, measurement protocol, precision, and analytical uncertainty. For Cu isotopic analysis, both Zn and Ni were investigated for their merit as internal standard (IS) relied on for mass bias correction. The use of Ni as IS seems to be the most robust approach as Ni is less prone to contamination, has a lower abundance in bronzes and an ionization potential similar to that of Cu, and provides slightly better reproducibility values when applied to

NIST SRM 976 Cu isotopic reference material. The possibility of carrying out direct isotopic analysis without prior Cu isolation (with AG-MP-1 anion exchange resin) was investigated by analysis of CRM IARM 91D bronze reference material, synthetic solutions, and archaeological bronzes. Both procedures (Cu isolation/no Cu isolation) provide similar  $\delta^{65}\text{Cu}$  results with similar uncertainty budgets in all cases ( $\pm 0.02$ – $0.04$  per mil in delta units,  $k=2$ ,  $n=4$ ). Direct isotopic analysis of Cu therefore seems feasible, without evidence of spectral interference or matrix-induced effect on the extent of mass bias. For Sn, a separation protocol relying on TRU-Spec anion exchange resin was optimized, providing a recovery close to 100 % without on-column fractionation. Cu was recovered quantitatively together with the bronze matrix with this isolation protocol. Isotopic analysis of this Cu fraction provides  $\delta^{65}\text{Cu}$  results similar to those obtained upon isolation using AG-MP-1 resin. This means that Cu and Sn isotopic analysis of bronze alloys can therefore be carried out after a single chromatographic separation using TRU-Spec resin. Tin isotopic analysis was performed relying on Sb as an internal standard used for mass bias correction. The reproducibility over a period of 1 month ( $n=42$ ) for the mass bias-corrected Sn isotope ratios is in the range of 0.06–0.16 per mil (2 s), for all the ratios monitored.

Published in the topical collection *Isotope Ratio Measurements: New Developments and Applications* with guest editors Klaus G. Heumann and Torsten C. Schmidt.

**Electronic supplementary material** The online version of this article (doi:10.1007/s00216-012-6542-1) contains supplementary material, which is available to authorized users.

E. Balliana · F. Vanhaecke (✉)  
Department of Analytical Chemistry, Ghent University,  
Krijgslaan 281-S12,  
9000 Ghent, Belgium  
e-mail: frank.vanhaecke@UGent.be

M. Aramendía  
Centro Universitario de la Defensa, Carretera de Huesca s/n,  
50090 Zaragoza, Spain

M. Aramendía · M. Resano  
Department of Analytical Chemistry, University of Zaragoza,  
Calle Pedro Cerbuna 12,  
50009 Zaragoza, Spain

E. Balliana · C. Barbante  
Department of Environmental Sciences, Informatics and Statistics,  
Ca' Foscari University of Venice, Calle Larga S. Marta 2137,  
30123 Venice, Italy

**Keywords** Copper isotopic analysis · Tin isotopic analysis · Multi-collector ICP–mass spectrometry · Archaeological bronze · Archaeometry

## Introduction

Nowadays, archaeology and analytical chemistry form an essential tandem for investigating the past. Isotopic analysis, in particular, is a very powerful tool for discrimination purposes and for provenance studies and is therefore

presently replacing and/or complementing the more traditional multi-element analysis in the context of archaeometry [1–3]. Owing to the introduction of multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) instruments, the interest for isotopic analysis has grown considerably, not only for elements with radiogenic nuclides (such as Pb, Sr, or Nd) [3], for which larger isotopic variations are observed in nature, but also for “non-traditional” stable isotopic systems (such as those of Cu or Sn), showing smaller variation, mainly due to mass-dependent isotope fractionation [4–8]. At this point, systematic studies are still needed to fully assess the possibilities of these non-traditional isotopic systems in the field of archaeometry, starting from optimization of the analytical methodology, at a later stage deployed for trying to relate the isotopic information to, e.g., geographical origin of raw materials, mining activities, manufacturing technology, and/or trade routes [9, 10].

To fully understand the steps that need to be taken to be able to use isotopic information in the context of archaeometry, one can refer to Pb as an illustrative example. In fact, Pb is the element most commonly used for this purpose and has been successfully applied to many ancient artifacts for obtaining meaningful archeological conclusions [11–14]. Historically, Pb was among the first ore-extracted metals, and, because of this, ore-derived Pb is found abundantly in the composition of many ancient artifacts at many archaeological sites. Pb has four stable isotopes, three of which are radiogenic, which results in a wide range of natural variation in the isotopic composition of this element. Moreover, the isotopic composition of Pb does not seem to be measurably affected by isotope fractionation during ore processing and manufacturing of the objects. This fact renders Pb isotopic analysis a powerful tool for provenance studies, founded on the assumption that ore deposits can often be distinguished from one another based on their Pb isotopic signature [3, 14–18]. Ideally, the cluster of isotope ratios for a given deposit is visualized on a bivariate plot (e.g.,  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$ ) and provides a unique fingerprint for that deposit. Archaeologists can then match the isotope ratios of individual archaeological artifacts to the fingerprints of their parent ore source, such that archaeological conclusions can be drawn [18–20]. In some other instances, provenancing to the original ores is not aimed at, and lead isotopic analysis is used to fingerprint artifacts from a given workshop, period, or any other possible classification and to distinguish or discriminate them from one other [13, 17, 21–24].

Unfortunately, in some cases, serious limitations affect Pb isotopic analysis. For ore provenancing, e.g., overlapping fingerprints of two or more ores often occur, and the possibility that ores and/or recycled materials from different sources have been used for the production of a given object

always exists. In such situations, the combined study of different isotopic systems could be helpful for resolving the ambiguity [3]. In this context, the use of the Cu isotope ratio complementing Pb isotopic information for provenancing of Cu ores used in ancient metallic artifacts has already been proposed as a potential tool in this direction, although further studies are needed to ascertain the viability of this option [3, 25–28].

In some other cases, Pb cannot be used as a valid tracer, either because the amount of Pb in the final artifact is not high enough to carry out isotopic analysis of sufficient quality or because the Pb in the artifact is not linked to a particular ore, thus precluding its use for provenancing [7, 29]. These circumstances, for instance, occur in the study of ancient bronze samples with very low levels of Pb. Exploring the possibility of using Cu and Sn isotopic information for the study of such artifacts would obviously be interesting, and this is one of the goals of our investigation.

Considering the lack of information on this aspect, further studies have to be conducted for confirming the fact that the Cu and Sn isotopic signature of a given bronze artifact can be traced to the original ore or, at least, that a clear fingerprint can be obtained, allowing to distinguish between, e.g., different manufacturing workshops or periods. At a later stage, and if the first hypothesis is confirmed, extensive isotopic databases need to be built for provenancing studies. Before starting such an ambitious project, however, the development of an analytical methodology for determining Cu and Sn isotope ratios in archaeological bronze samples with the lowest uncertainty values possible needs to be carefully considered. Currently, the few papers available dealing with Cu and Sn isotopic analysis in the context of archaeometry are mainly focused on the interpretation of results [7, 25, 27, 28, 30], while little attention is paid to the analytical methodology itself, which, in fact, could be the clue to obtaining meaningful results. These papers suggest that isotopic analysis of Cu and Sn could be used for provenancing purposes but report a rather narrow range of isotopic variation (a few per mil delta units in the best case) for these two elements in different ores [4–6, 8, 16, 25, 26, 30, 31]. Data are still too scarce as to be conclusive, but it seems clear that optimization of the analytical methodology may be much more crucial in the case of Cu and Sn than in the case of Pb, for which isotopic variations up to 5 % can be observed. The aim of the present work is to revise the methodology for Cu and Sn isotope ratio measurements in ancient bronzes with the purpose of: (1) optimizing the analytical methodology for both Cu and Sn in terms of sample pre-treatment (digestion and, especially, target element isolation) and measurement protocol by means of MC-ICP-MS, with special attention to mass bias correction; (2) assessing the results obtained in terms of internal precision and reproducibility; and (3) applying the

protocol developed to some pre-Roman bronze utensils originating from northern Spain.

## Experimental section

### Standards and reagents

All sample pre-treatment procedures (digestion, target element isolation, and sample dilution) were performed in a class-10 clean lab. Teflon Savillex® beakers were used throughout the study for sample handling and storage. These beakers were previously cleaned with HNO<sub>3</sub> and HCl of pro-analysis purity level (Chem-Lab, Belgium) and further rinsed with ultrapure water (resistivity  $\geq 18.2$  M $\Omega$ cm) obtained from a Milli-Q Element water purification system (Millipore, France).

For sample preparation, pro-analysis-grade acids (Chem-Lab, Belgium) were further purified by sub-boiling distillation in either quartz (12 M HCl) or PTFE (14 M HNO<sub>3</sub>) stills. Ultrapure 9.8 M H<sub>2</sub>O<sub>2</sub> was purchased from Sigma-Aldrich (Belgium). Multi-element and single-element standard solutions used for quantitative analysis were prepared from commercially available 1-gL<sup>-1</sup> stock solutions (Inorganic Ventures, The Netherlands) after proper dilution with 0.4 M HNO<sub>3</sub>.

All isotope ratios determined are expressed as delta values, i.e., as a relative difference (in per mil) versus a material the isotopic composition of which is used as a reference. For Cu analysis, an in-house isotopic standard was prepared from a commercially available 1-gL<sup>-1</sup> stock solution (Inorganic Ventures, The Netherlands, lot C2-Cu02116). This in-house standard was used on a daily basis to reduce the consumption of the valuable NIST SRM 976 isotopic reference material, which is no longer available from NIST. The isotopic composition of the in-house standard was determined relative to the NIST SRM, and it was found to have a  $\delta^{65}\text{Cu}$  value of  $0.23 \pm 0.03$ ‰ ( $n=68$ ). All Cu delta values included in this paper are expressed relative to the internationally accepted NIST SRM 976 isotopic reference material, so that inter-comparability with other works is directly possible. For Sn analysis, as there is no isotopic reference material available, an in-house isotopic standard was prepared from a commercially available 1-gL<sup>-1</sup> stock solution (Fluka, Switzerland, lot 1342599), and all Sn delta values are expressed relative to this solution. Unfortunately, unless a certified isotopic standard becomes available for Sn, inter-comparability of tin isotope data is not yet possible. Commercially available 1-gL<sup>-1</sup> stock solutions were also used for the internal standards used for mass bias correction: Zn (Inorganic Ventures, The Netherlands, lot D2-Zn02061), Ni (SCP Science, Canada, lot SC 3258038), and Sb (SCP Science, Canada, lot SC 7053507).

A bronze-certified reference material (IARM 91D, Analytical Reference Material International, Colorado, USA) was used throughout the study for optimization and validation purposes. This material has a certified major element composition of 82.0 wt% Cu, 7.8 wt% Pb, 6.5 wt% Sn, 3.20 wt% Zn, and 0.4 wt% Ni.

Polypropylene columns used for Cu and Sn isolation were purchased from Bio-Rad (Belgium). These columns have an internal diameter of 8 mm and are 10 cm long. Anion exchange resin AG-MP-1 (100–200 mesh) was also purchased from Bio-Rad (Belgium) and used for Cu isolation. For the selective separation of Sn, the anion-exchange TRU-Spec resin from EICHROM (France) was used and loaded into Bio-Rad polypropylene columns. Ethanol, used for sample cleaning after mechanical cleaning, was purchased from Sigma Aldrich (Belgium).

### Samples

Thirty-two archaeological bronzes originating from the main pre-Roman and Roman archaeological sites in Teruel and Huesca, both located in Aragón (northern Spain), were used to explore the potential of Cu and Sn isotopic analysis for archaeological purposes. Samples from Teruel originated from five different sites: Alto Chacón, La Romana, El Palomar, La Loma del Regadio, and La Caridad, while samples from Huesca originated from six different sites: El Campaz, Sancho Abarca, Plaza Lizana, La Codera, Círculo Católico, and Escolapios. All samples are small fragments of household and agricultural objects that have been examined and dated by archaeologists and cover the period from VII BC to VAD. After digestion (see section “[Sample preparation for isotopic analysis](#)” for details), the samples were analyzed by means of quadrupole-based inductively coupled plasma-mass spectrometry (ICP-MS) to determine the major elemental components (see section “[Instrumentation and measurements](#)” for details), which were found to be Cu ( $57 \pm 12$  %; average  $\pm$  s) and Sn ( $6.9 \pm 2.5$  %). These results, together with the fact that oxygen was detected in the samples via scanning electron microscopy combined with energy dispersive X-ray analysis (using a JEOL JSM-6360LV instrument, Japan), indicate alteration of its composition during burial (i.e., oxidation) as otherwise higher values would be obtained. Very low amounts of other common elements found in ancient Cu alloys, such as Pb or Zn, were also found in most of the samples.

### Sample preparation for isotopic analysis

Before digestion, the samples were polished with a diamond Dremel® tool. Afterward, any corrosion layer or organic residues were removed with diluted HNO<sub>3</sub>. After this first mechanical and chemical cleaning, the samples were placed in deionized water in an ultrasonic bath for 10 min; subsequently

they were manually dried with a tissue and further cleaned with ethanol and dried in an oven at 45 °C. Then, 100-mg aliquots of each sample were obtained with a diamond drill and accurately weighed. The material thus obtained was dissolved in 5 mL of a 1:3 mixture of 14 M HNO<sub>3</sub> and 12 M HCl (aqua regia) in closed screw-top Savillex® Teflon beakers, which were heated on a hot plate at 90–100 °C for 2 h. For some of the samples, a white precipitate, probably Sn oxides, appeared upon digestion. This precipitate was effectively decomposed by drying down the samples, adding 5 mL of 12 M HCl, and heating in a closed beaker at 100 °C for 5 h. The digests obtained were diluted with Milli-Q water to a final volume of 30 mL and were kept in closed vials until further analysis. For validation of the protocol, the reference material IARM 91D was subjected to the same digestion protocol, and the contents of the major and minor elements were determined with a quadrupole-based ICP-MS instrument (see section “Instrumentation and measurements” for details). Results obtained upon analysis were in good agreement with the certified values in all cases (see Table 1).

Sn isotopic analysis of the digested bronzes was performed on purified fractions obtained after column exchange chromatography. For this purpose, Bio-Rad polypropylene columns were cleaned with 2 M HCl and filled with 0.3 mL of TRU-Spec resin [7, 32]. Before use, the resin was rinsed abundantly with Milli-Q water and was allowed to settle. The supernatant was thrown away to eliminate the finest resin particles. Prior to each elution, the resin was pre-cleaned three times by alternately passing fractions of 5 mL of 0.4 M HNO<sub>3</sub> and 5 mL of Milli-Q water. Afterward, the column was conditioned with 5 mL of 1 M HCl. For sample loading, 2 mL of the bronze digests were vaporized to dryness at 70 °C and retaken in solution with 2 mL of 1 M HCl. The matrix was quantitatively eluted with 10 mL of 1 M HCl, while a purified Sn fraction was obtained with 20 mL of 1 M HNO<sub>3</sub>. Immediately after column separation, 10 µL of concentrated HF were added to the Sn fraction in order to prevent precipitation. Before isotopic analysis, these fractions were diluted to a final concentration of 1 mgL<sup>-1</sup> of Sn with an appropriate volume of 0.4 M HNO<sub>3</sub> and were doped with 1 mgL<sup>-1</sup> of Sb for mass

bias correction (see section “Optimization of the MC-ICP-MS measurement protocol: mass bias correction” for details).

Cu isotopic analysis, on the other hand, was directly performed on the matrix fraction obtained from the Sn separation protocol described above. Adequate amounts of these matrix fractions were dried at 70 °C, retaken in solution using 1 M HNO<sub>3</sub>, diluted to a concentration of 500 µg L<sup>-1</sup> Cu with 0.4 M HNO<sub>3</sub>, and doped with 500 µg L<sup>-1</sup> Ni for mass bias correction.

The possibility of performing Cu isotopic analysis on purified Cu solutions was also investigated, and an adaptation of the methodology proposed by Maréchal et al. [33] was used for Cu isolation. Bio-Rad polypropylene columns (i.d. 8 mm) were cleaned with 2 M HCl and filled with 2 mL of AG-MP-1 (100–200 mesh) strong anion exchange resin. A piece of cotton was used as a stopper on top of the resin bed for reducing possible tailing effects in the Cu elution [34]. Before use, the AG-MP-1 resin was allowed to settle three to four times in water, and the supernatant was thrown away in order to eliminate the finest resin particles. Prior to each elution, the resin was gently washed with approximately 10 mL of Milli-Q water and then pre-cleaned three times with 5 mL of 2 M HNO<sub>3</sub> and 4 mL of Milli-Q water. The resin was subsequently conditioned with 5 mL of (7 M HCl+0.002 % H<sub>2</sub>O<sub>2</sub>). After sample loading (1 mL of sample, corresponding to 20–50 µg of Cu), the sample matrix was eluted with 10 mL of (7 M HCl+0.002 % H<sub>2</sub>O<sub>2</sub>), and subsequently, Cu was eluted with 25 mL of the same solution. Finally, the samples were dried at 70 °C and retaken into solution with 2 mL of 1 M HNO<sub>3</sub>. Prior to isotopic analysis, the samples were diluted to 500 µg L<sup>-1</sup> of Cu in an appropriate volume of 0.4 M HNO<sub>3</sub>, and the solution was doped with the proper amount of internal standard for mass bias correction (see section “Optimization of the MC-ICP-MS measurement protocol: mass bias correction” for details).

#### Instrumentation and measurements

Target element (Cu and Sn) concentrations in the sample and IARM 91D digests, and the concentrations of the elements tested as internal standards (Ni, Zn and Sb), some typical major and minor elements constituting Cu alloys, and potential interfering elements (Na, Mg, Cd, Tl, In, Fe) were determined using a quadrupole-based ICP-MS instrument (Thermo X-Series II, Bremen, Germany), equipped with a 1 mL min<sup>-1</sup> quartz concentric nebulizer mounted onto a Peltier-cooled, low-volume conical spray chamber. External calibration versus aqueous standard solutions was relied on, while 100 µg L<sup>-1</sup> of Ga and Y acted as internal standards, correcting for potential matrix effects and instrument instability. Instrumental settings and data acquisition parameters for this analysis are summarized in Table 2.

For the isotope ratio measurements, a Neptune MC-ICP-MS instrument (Thermo Scientific, Bremen, Germany) was used.

**Table 1** Elemental concentrations for the bronze reference material IARM 91D as determined using quadrupole-based ICP-MS after sample digestion

	Cu	Zn	Sn	Pb	Ni
PN-ICP-MS (w/w %)	82.6	3.3	6.7	8.0	0.4
IARM 91 D certificate (w/w %)	82.0±0.4	3.20±0.04	6.5±0.1	7.8±0.1	0.43±0.01

The relative uncertainty on the results reported amounts to typically 3–4 %



**Table 2** Instrument settings and data acquisition parameters for the Thermo Scientific X Series II quadrupole-based ICP-MS instrument and for the Thermo Scientific Neptune multi-collector ICP-MS instrument

Instrument settings		Data acquisition parameters							
Thermo Scientific X Series II									
RF Power	1400 W	Detector mode	Dual						
Nebulizer gas flow rate	0.84–0.90 Lmin <sup>-1</sup>	Scanning mode	Peak jump						
Plasma gas flow rate	13 Lmin <sup>-1</sup>	Dwell time	30 ms						
Auxiliary gas flow rate	0.70 Lmin <sup>-1</sup>	Sweeps/reading	106						
Sample uptake rate	1 mLmin <sup>-1</sup>	Replicate time	55 s						
Sampler cone	Ni	Number of replicates	5						
Skimmer cone	Xt type, Ni	Nuclides monitored	<sup>54</sup> Fe, <sup>57</sup> Fe, <sup>58</sup> Ni, <sup>62</sup> Ni, <sup>63</sup> Cu, <sup>65</sup> Cu, <sup>64</sup> Zn, <sup>66</sup> Zn, <sup>67</sup> Zn, <sup>118</sup> Sn, <sup>120</sup> Sn, <sup>123</sup> Sb, <sup>124</sup> Sb, <sup>206</sup> Pb, <sup>207</sup> Pb						
Thermo Scientific Neptune MC-ICP-MS									
RF power <sup>a</sup>	1150 – 1250 W	Integration time	4.2 s for Cu and Sn						
Plasma gas flow rate	15 Lmin <sup>-1</sup>	Number of cycles	10 per block						
Auxiliary gas flow rate	0.7 Lmin <sup>-1</sup>	Number of blocks	5 for Cu, 6 for Sn						
Nebulizer gas flow rate <sup>a</sup>	0.950–1.005 Lmin <sup>-1</sup>	Measurement time per sample	~5–6 min						
Sampler/skimmer cones	Ni	Rinsing time	3 min						
Sample uptake rate	100 μLmin <sup>-1</sup>	Mass resolution	Low mass resolving power						
Lens settings	Optimized for maximum analyte signal intensity	Baseline correction	30 cycles (1.05 s each) at the start of every measurement						
Collector configuration									
Position	L4	L3	L2	L1	C	H1	H2	H3	H4
Mass for Cu	–	<sup>60</sup> Ni	–	<sup>61</sup> Ni	<sup>62</sup> Ni	<sup>63</sup> Cu	–	<sup>65</sup> Cu	–
Mass for Sn	–	<sup>63</sup> Cu	<sup>64</sup> Zn	<sup>66</sup> Zn	<sup>67</sup> Zn	<sup>68</sup> Zn	–	–	–
		<sup>116</sup> Sn	–	<sup>118</sup> Sn	<sup>120</sup> Sn	<sup>121</sup> Sb	<sup>122</sup> Sn	<sup>123</sup> Sb	<sup>124</sup> Sn

<sup>a</sup> Optimized daily for maximum <sup>63</sup>Cu<sup>+</sup> or <sup>120</sup>Sn<sup>+</sup> signal intensity

The sample introduction system used consists of a 100 μL min<sup>-1</sup> PFA nebulizer mounted onto a high-stability spray chamber [35], a combination of a Scott-type and a cyclonic spray chamber. The instrument settings and data acquisition parameters for Cu and Sn isotopic analysis are also included in Table 2.

For Cu analysis, the only two stable isotopes of this element were monitored, and two different cup configurations were used, depending on whether Ni or Zn was used as internal standard for mass bias correction. In the case of Sn, only the even isotopes were measured (<sup>116</sup>Sn, <sup>118</sup>Sn, <sup>119</sup>Sn, <sup>120</sup>Sn, <sup>122</sup>Sn, <sup>124</sup>Sn) to avoid the influence of mass-independent fractionation [36], which has been shown to potentially affect the odd-numbered isotopes of Sn [37]. All measurements were conducted at low mass resolving power. In the case of Cu, the possible occurrence of spectral interferences was checked for the sample solutions via mass scan at medium mass resolving power, and no interfering species were detected, for the purified or for the non-purified samples.

Measurements of blanks for both standards (acid blanks) and samples (procedural blanks) were performed at the beginning of every working session so that signal intensities for standards and samples were corrected for the respective blank contributions. Samples and isotopic standards for

delta calculation were diluted to a concentration of 1 mg L<sup>-1</sup> of Sn and Sb and 500 μg L<sup>-1</sup> of Cu and Ni or Zn to avoid variations in concentration from affecting the extent of mass bias. The measurements were carried out in a standard-sample-sample-standard bracketing sequence. The sample introduction system was rinsed with 0.4 M HNO<sub>3</sub> after every sample or standard measurement. The signals at *m/z* of 63 and 65 returned to the original blank level after about 1 min while, at the *m/z* corresponding to the Sn isotopes, it took about 3 min to return to the original blank level. To be on the safe side, a rinsing time of 4 min was used in all cases, ensuring the absence of significant memory effects in all measurements.

The data obtained were treated off-line for mass bias correction and delta calculation after automatic removal of the outliers based on a 2 s-test. To correct for instrumental mass bias, the so-called “revised Russell’s law,” described by Baxter et al. [38], was used in all cases. This method is based on the application of Eq. 1:

$$R_{\text{corrX,sample}} = R_{\text{expX,sample}} \cdot \frac{R_{\text{theoX}}}{e^a \cdot (R_{\text{expIS,sample}})^b} \quad (1)$$

Where  $R_{\text{corr},X,\text{sample}}$  represents the corrected isotope ratio for the target analyte (Cu or Sn) in the sample ( $X=M_2/M_1$ , where  $M_1$  and  $M_2$  are the masses of the lighter and heavier isotope, respectively).  $R_{\text{exp},X,\text{sample}}$  represents the measured isotope ratio for the target analyte in the sample;  $R_{\text{exp},\text{IS},\text{sample}}$  represents the measured isotope ratio for the internal standard admixed to the sample (i.e., Ni for Cu and Sb for Sn), and  $R_{\text{theo},X}$  corresponds to the theoretical isotope ratio for the target element calculated based on the isotopic abundances given by the IUPAC [39]. On the other hand, a and b correspond to the intercept and the slope of the linear fit obtained when plotting the natural logarithm of the isotope ratio of the IS versus the natural logarithm of the isotope ratio of the target element, measured simultaneously in standard solutions. These standard solutions, in our particular case, were the in-house standards described in section “Standards and reagents” (either for Cu or for Sn), measured in a standard–standard–sample–standard–standard bracketing approach.

Variations in the isotopic composition of Cu or Sn were expressed in  $\delta\%$  units calculated following Eq. 2:

$$\delta = \frac{R_{X,\text{sample}} - R_{X,\text{standard}}}{R_{X,\text{standard}}} \times 1000 \quad (2)$$

Where  $R_{X,\text{sample}}$  is the corrected isotope ratio for the target element obtained for a particular sample by using Eq. 1, and  $R_{X,\text{standard}}$  is the average of the corrected ratios for the target element obtained for the in-house isotopic standards measured immediately before and after the sample considered ( $n=4$ ). All Cu delta values thus obtained were finally recalculated relative to the internationally accepted NIST SRM 976 isotopic reference material (previously characterized), so that inter-comparability with other works is directly possible.

## Results and discussion

Optimization of the MC-ICP-MS measurement protocol: mass bias correction

To achieve accurate isotope ratio data when working with MC-ICP-MS, it is essential to correct for instrumental mass bias or, in other words, to calibrate the measurement of isotope ratios in the mass spectrometer. The method used for its correction is a critical parameter that needs to be carefully optimized as, in fact, it typically remains the single largest source of uncertainty in the measurement [38]. In the last years, different methods have been applied for this purpose. A summary of the most commonly used, with their pros and cons, and a critical evaluation of these methods can be found in a review by Yang [40] and a book chapter by Meija et al.[41], respectively. In summary, these methods can be formally classified according to two parameters: whether data from the measurand and calibrant

are acquired simultaneously and whether the measurand and calibrant are isotope ratios of the same element. Best results can be expected if measurand and calibrant are measured simultaneously (as matrix matching and stability of the instrument are less determining) and, at least in theory, if a different isotope ratio for the same element is used for calibrating the target isotope ratio (as exactly the same behavior in the instrument can be expected for calibrant and measurand). According to this, a very powerful approach for correcting mass bias is based on admixing known amounts of the analyte of interest that are enriched in two isotopes different from the target isotopes, with an isotopic composition perfectly known in advance [42]. The relative amounts of the target and calibrant isotopes are measured simultaneously in the samples, and by applying an appropriate mass bias model for MC-ICP-MS (e.g., exponential law), accurate isotope ratios can be obtained.

One of the main problems of applying this so-called “Double-Spike calibration,” besides the need for a high-purity enriched double spike for which the isotopic composition is known, is that at least four isotopes of an element have to be measured, which precludes its use for elements such as Cu. Besides, uncertainty budgets for this method strongly depend on the composition and the amount of the admixed isotopic spikes, and finding the optimal isotopic composition is sometimes a challenge, although mathematical models exist for simplifying the problem [42]. An alternative to this method also frequently used consists of the substitution of the double spike with another element (an internal standard) for which an isotope ratio is known and is used to obtain mass bias corrected ratios for the measurand after applying an appropriate mass bias model. The problem with this easier-to-implement calibration method is that matrix-induced mass bias cannot be fully compensated for and that a perfect matrix separation and close matching of analyte and calibrant concentrations are required for obtaining accurate isotope ratios. In any case, the main challenge for assuring the utility of this method is still the necessity to ensure the accuracy of the mass bias transfer between measurand and calibrant (which is not always the case), as traditional mass bias models rely on the equality between discrimination functions for measurand and calibrant.

This limitation can be obviated by using a regression model for mass bias correction, which takes advantage of the significant temporal drift of the mass bias when using MC-ICP-MS. In our case, the regression method proposed by Baxter et al. [38] was used for obtaining accurate isotopic information, expressed as delta values (see section “Instrumentation and measurements” for a detailed explanation on the application of this method). Although requiring long measurement sessions for controlling the uncertainty associated to the correction process, this method is acknowledged as one of the best choices, as both the matrix-induced mass bias and the temporal mass bias drift can be corrected for [40], and the necessity

for equal discrimination functions for measurand and calibrant is avoided.

For application of the Baxter correction method, an element with a mass close to that of the target element is selected as internal standard for correcting for mass bias. For Cu isotopic analysis, two elements are commonly used for this purpose, Zn [5, 43–48] and Ni [49–54]. According to the literature, both elements seem to be well-suited for mass bias correction affecting the Cu isotope ratio, although marginal precision improvements have been recorded when Ni is used [49–54]. As a consequence, a comparative study of Ni and Zn performance was carried out in our investigation. For this purpose, all the samples analyzed for their Cu isotopic composition along the study were separated in two aliquots, each of which was doped with Zn and Ni, respectively. In the subsequent MC-ICP-MS measurement sessions, either the  $^{66}\text{Zn}/^{64}\text{Zn}$  or the  $^{62}\text{Ni}/^{60}\text{Ni}$  ratio was relied upon for correcting the measured  $^{65}\text{Cu}/^{63}\text{Cu}$  ratios.

Both Zn and Ni provided well-defined linear relationships ( $R^2 > 0.99$ ) in the ln–ln space over a single measurement session (10–12 h) as shown in Fig. 1a, b. The precision obtained when using both internal standards was compared using the NIST 976 isotopic reference material as a quality control sample, which was monitored at the beginning, at the end, and after every four to five samples in every analytical session. In this way, the internal precision for each analytical session and the long-term reproducibility over a year were obtained. Reproducibility values (calculated as 2 s) for the  $\delta^{65}\text{Cu}$  values obtained for the NIST 976 standard along the period of an entire year ( $n = 113$ ) were  $\pm 0.027\text{‰}$  and  $\pm 0.039\text{‰}$  for Ni and Zn, respectively, showing that, as concluded in other recent Cu isotope ratio studies [49–54], the use of Ni as internal standard provides superior precision ( $F$ -test;  $F_{\text{value}} = 2.155$ ;  $F_{\text{critical, (}P=0.05)} = 1.366$ ). In any case, both elements are well-suited for mass bias correction of Cu ratios. For the analysis of ancient bronzes, however, we consider the use of Ni as more robust than that of Zn, considering that (1) Ni is less prone to contamination and (2) Ni is less often present in archaeological bronzes than Zn. Moreover, and although the condition that the mass bias discrimination affecting both the analyte and the internal standard is identical is not necessary when a regression model such as that of Baxter is used for mass bias correction as discussed before [38], the fact that the first ionization potential of Ni (7.46 eV) is closer to that of Cu (7.73 eV) than that of Zn (9.39 eV) is [52] should result in a more similar mass bias effect observed for Cu and Ni than for Cu and Zn. This could in turn explain the slightly better performance observed for the former element. In the following, all  $\delta^{65}\text{Cu}$  values reported are based on Ni mass bias correction, unless otherwise stated.

For Sn isotopic analysis, on the other hand, the choice of internal standard is limited to Sb, as other elements with

masses close to those of Sn isotopes give rise to isobaric interferences with some of the Sn isotopes (e.g.,  $^{112,114,116}\text{Cd}$ ,  $^{115}\text{In}$ ,  $^{120,122,124}\text{Te}$ ) [55]. Also in this case and for all of the ratios monitored during a measurement session lasting 10–12 h, the correlation recorded in ln–ln space was excellent (see Fig. 1c);  $R^2 > 0.99$ . Reproducibility along a period of 1 month ( $n = 42$ ) for the corrected Sn isotope ratios monitored (i.e.,  $^{118}\text{Sn}/^{116}\text{Sn}$ ,  $^{120}\text{Sn}/^{116}\text{Sn}$ ,  $^{122}\text{Sn}/^{116}\text{Sn}$ ,  $^{124}\text{Sn}/^{116}\text{Sn}$ ,  $^{120}\text{Sn}/^{118}\text{Sn}$ ,  $^{122}\text{Sn}/^{118}\text{Sn}$ ,  $^{124}\text{Sn}/^{118}\text{Sn}$ ,  $^{122}\text{Sn}/^{120}\text{Sn}$ ,  $^{124}\text{Sn}/^{120}\text{Sn}$ ,  $^{124}\text{Sn}/^{122}\text{Sn}$ ) in the in-house standard was in the range of 0.003–0.008 % RSD, corresponding to a reproducibility in the delta scale of 0.06‰ to 0.16‰ 2 s for all the ratios monitored.

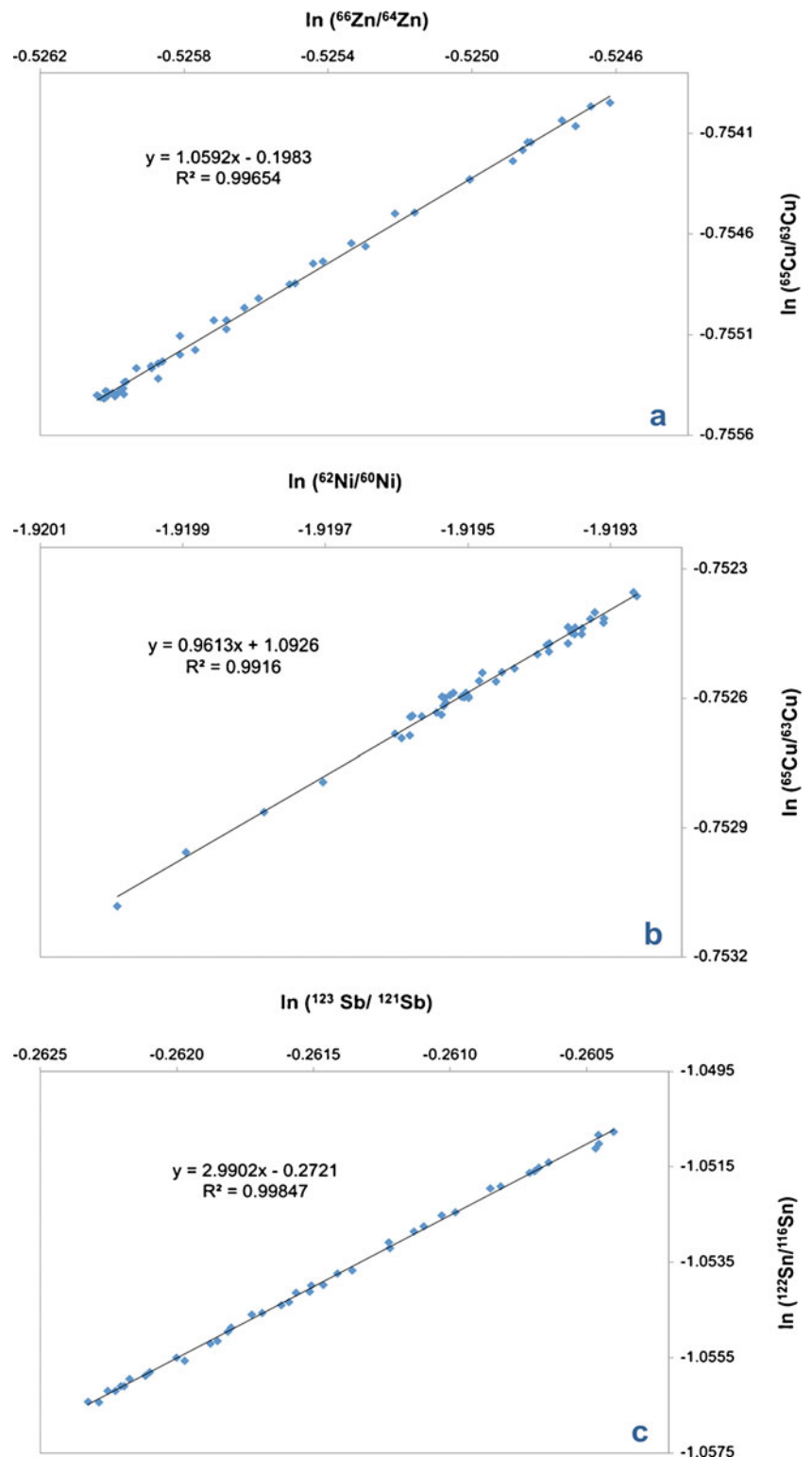
### Isolation of the target elements

When measuring isotope ratios with MC-ICP-MS, it is generally accepted that the target element needs to be isolated in order to minimize spectral and non-spectral effects originating from the sample matrix [56]. Chemical isolation is usually carried out via ion exchange chromatography. Although many different commercial resins exist, achieving efficient separation with quantitative recovery is not always straightforward, and additional problems, such as on-column isotopic fractionation, can arise if the separation protocol is not carefully optimized.

In the case of Cu isotopic analysis, the possibility of observing on-column isotopic fractionation has been widely acknowledged [33, 52, 57], and, therefore, optimization of the isolation protocol in terms of quantitative Cu recovery is crucial. At present, the protocols most commonly used for Cu purification [46–48, 51, 58, 59] are based on the methodology firstly developed by Maréchal et al., which relies on the use of a strong anion exchange resin (AG-MP-1) [33] for isolation of Cu as Cu(II). This chromatographic separation, however, is not perfect and still shows problems related to the poor specificity of the resin for this element: (1) difficulty to obtain quantitative recovery and therefore, the necessity to check for possible on-column fractionation; (2) non-efficient removal of potentially interfering elements (e.g., Na, giving rise to formation of  $^{40}\text{Ar}^{23}\text{Na}^+$ , the signal of which overlaps with that of  $^{63}\text{Cu}^+$ ); (3) strong dependence of the elution protocol on the sample characteristics. For these reasons, some authors have avoided the use of Cu column isolation and have proposed alternative approaches such as hand-picking of Cu-containing fractions in Cu minerals [28, 59], or even direct Cu isotopic analysis without target element isolation, which could provide acceptable results in some instances [54, 56].

Direct Cu isotopic analysis of bronze artifacts without prior Cu isolation could indeed be an interesting option. In fact, Cu is the major element in bronze samples (60–90 %), and the contribution of other minor and trace elements could

**Fig. 1** Plot of  $\ln(\text{isotope ratio, internal standard})$  versus  $\ln(\text{isotope ratio, target element})$  obtained for a standard solution of  $500 \mu\text{gL}^{-1}$  Cu doped with **a**  $500 \mu\text{gL}^{-1}$  Zn ( $n=45$ ) and **b**  $500 \mu\text{gL}^{-1}$  Ni ( $n=45$ ); **c**  $\ln$ - $\ln$  plot for a  $1 \text{ mgL}^{-1}$  solution Sn doped with  $1 \text{ mgL}^{-1}$  Sb ( $n=41$ )



be negligible in terms of potential matrix-related spectral interferences and/or mass bias, especially considering the high dilution factors preceding MC-ICP-MS measurement. To test the validity of this hypothesis and ascertain whether direct Cu isotopic analysis of ancient bronze samples could be safely performed, several experiments were carried out.

First, the IARM 91D reference material was analyzed for its Cu isotopic composition: (1) without Cu isolation and (2) after Cu isolation with an optimized separation protocol based on the work of Maréchal et al. [33], using AG-MP-1 resin. Although cumbersome and time-consuming, the optimized isolation approach (see section “Sample preparation



for isotopic analysis” for details) provided good Cu recovery values for the reference sample ( $98 \pm 2$  %; confidence interval given as analytical uncertainty calculated following the Nordtest calculation approach [60]  $k=2$ ,  $n=5$ ) so that potential on-column isotope fractionation would not have a significant effect on the final result. To further prove this assumption, solutions of NIST SRM 976 Cu were measured before and after column chemistry without detecting any effect of on-column isotope fractionation. Table 3 reports the  $\delta^{65}\text{Cu}$  values obtained for analysis of the IARM 91D sample in both cases. As seen from these data, there is no statistically significant difference between the  $\delta^{65}\text{Cu}$  values obtained in all instances, suggesting that Cu isolation is not necessary for bronze samples, at least for those with Cu contents close to 80 wt%, as in IARM 91D. Moreover, the presence of the elements used as internal standards for mass bias correction in this reference material (3 wt% Zn and 0.4 wt% Ni) did not seem to have a significant influence on the results obtained.

For further assessment of the influence of matrix elements on Cu isotopic analysis in bronze samples, a pure Cu solution (the in-house Cu isotopic standard) doped with different amounts of other elements commonly present in bronzes was relied upon, such that the worst-case scenario, i.e., the lowest ratio of Cu/matrix elements, could be reproduced. This matrix-matched Cu solution was prepared taking into account the minimum Cu content and the maximum concentration levels for other elements present in bronzes according to literature [4, 9, 16, 27] and showed a final composition of  $500 \text{ mgL}^{-1}$  Cu,  $120 \text{ mgL}^{-1}$  Sn,  $82 \text{ mgL}^{-1}$  Pb,  $37 \text{ mgL}^{-1}$  Zn, and  $15 \text{ mgL}^{-1}$  Fe. Additionally,  $500 \text{ mgL}^{-1}$  Ni was added as internal standard for mass bias correction.  $\delta^{65}\text{Cu}$  values for this solution were also measured without Cu isolation and after Cu isolation with the AG-MP-1 resin. Results are also included in Table 3. As seen from these data, no statistically significant difference was found between the  $\delta^{65}\text{Cu}$  value obtained for the matrix-matched and the pure Cu solution, respectively. From these

data, it can be concluded that the presence of the most common matrix elements accompanying Cu in bronze samples do not influence the Cu isotope ratio results, even when the Cu/matrix elements ratio is low and the elements to be used as internal reference for mass bias correction are present to some extent. Therefore, direct Cu isotopic analysis of digested ancient bronze samples without target element isolation seems feasible in most occasions. For the samples under investigation, analysis with and without Cu isolation was carried out to further test this hypothesis, and similar results were obtained in all cases. As a consequence, measurement of Cu isotope ratios in bronze samples without target element isolation is recommended, as it provides much higher sample throughput and avoids the risks of possible on-column fractionation and contamination.

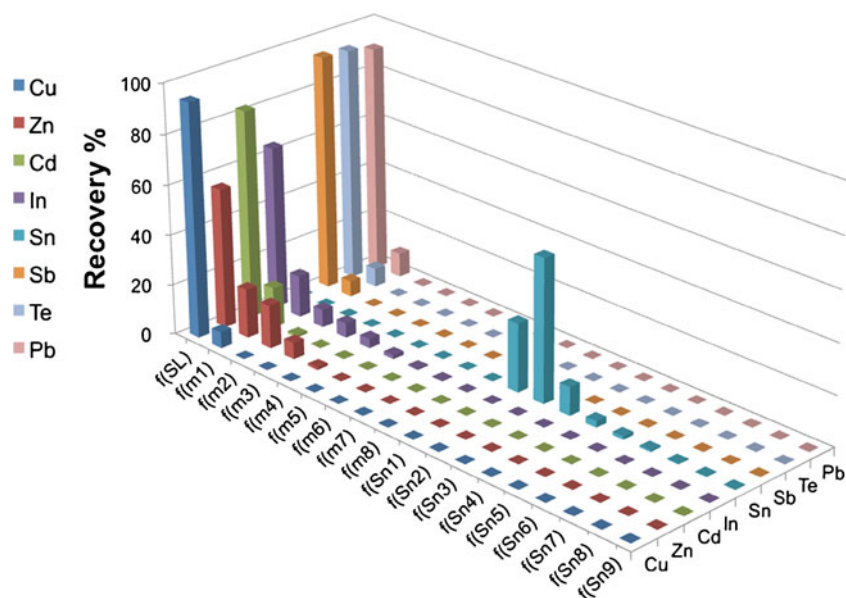
For Sn isotopic analysis, the situation is not so favorable, as this element only represents up to 15 % (in the best case) of the final bronze formulation, and thus, there is a higher risk of matrix effects if the analyte is not isolated. Moreover and unlike Cu, several of the Sn isotopes targeted suffer from potential isobaric interference ( $^{112}\text{Cd}$ ,  $^{114}\text{Cd}$ ,  $^{116}\text{Cd}$ ,  $^{115}\text{In}$ ,  $^{120}\text{Te}$ ,  $^{122}\text{Te}$ ,  $^{124}\text{Te}$ ), and hence, chemical isolation of Sn seems mandatory. For many years, it was assumed that natural isotopic variation for Sn was inexistent or only very small [61–64], and therefore, isolation of this element with the purpose of isotopic analysis has received little attention. The first attempt to separate Sn with ion exchange chromatography was done on meteorite material in the 1960s [61, 62]. Both anion and cation exchange resins were tested, and the high affinity of Sn for hydrochloric acid was exploited in both instances. Later on, some other chromatographic [65–67], extraction [68], and precipitation [69] protocols were presented for Sn isolation, although most of these protocols were characterized by long procedures, low Sn recoveries, and/or insufficient separation from potentially interfering elements. In this work, a faster and simpler procedure first suggested by Yi et al. [66] for Sn isolation from basalts and recently used by Hausteiner et al. for the isotopic analysis of Sn ores and one bronze object [7] was adopted. This protocol relies on the use of a TRU-Spec resin, which selectively and strongly retains Sn, U, Mo, and some actinide elements from a diluted HCl medium, while most of the other metals are not retained on the column [32]. In a second step, Sn is recovered with diluted  $\text{HNO}_3$  (see section “Sample preparation for isotopic analysis” for experimental details). For the purpose of fine-tuning the separation protocol for the bronze samples, a synthetic solution containing the common elements accompanying Sn in bronze formulations, as well as Cd, In, and Te as elements giving rise to isobaric interferences was prepared from mono-element standard solutions ( $200 \text{ mgL}^{-1}$  of Cu,  $5 \text{ mgL}^{-1}$  of Sn,  $20 \text{ mgL}^{-1}$  of Pb and of Zn, and  $10 \text{ mgL}^{-1}$  of Cd, In, and Sb). Figure 2 shows the elution profile for the elements present in

**Table 3** Comparison of  $\delta^{65}\text{Cu}$  values obtained for the IARM 91D bronze reference material and a synthetic solution (containing some of the major and minor elements accompanying Cu in bronze samples), without Cu isolation with Cu isolation using AG-MP1 and after Sn isolation using TRU-Spec

	No separation $\delta^{65}\text{Cu}$	Cu isolation AG-MP-1 $\delta^{65}\text{Cu}$	Cu isolation TRU-Spec $\delta^{65}\text{Cu}$
IARM 91D	$0.143 \pm 0.022$	$0.144 \pm 0.039$	$0.144 \pm 0.029$
Synthetic solution	$-0.316 \pm 0.048$	$-0.313 \pm 0.034$	$-0.312 \pm 0.045$

All delta values are expressed relative to NIST SRM 976 Cu isotopic reference material. Results are expressed as the average delta value  $\pm 2$  s in per mil units ( $n=4$ )

**Fig. 2** Elution profile for a synthetic solution containing Sn, Cu, Zn, Cd, In, Sb, Te, and Pb from a BioRad polypropylene column packed with 0.3 mg of dry TRU-Spec resin.  $f(\text{SL})=2$  mL of 1 M HCl for sample loading,  $f(\text{mx})=2$  mL of 1 M HCl for matrix elution fraction  $x$ ,  $f(\text{Sn}x)=2$  mL of 1 M  $\text{HNO}_3$  for Sn elution fraction  $x$



this synthetic solution following the optimized separation protocol with the TRU-Spec resin described in section “[Sample preparation for isotopic analysis](#).” As seen from this figure, the matrix elements are easily separated off in a first phase with 12 mL of 1 M HCl, while Sn is strongly retained on the column and is only eluted when the column is flushed with 1 M  $\text{HNO}_3$ . This isolation protocol provided good Sn recoveries for the IARM 91D reference material ( $98 \pm 2$  %, confidence interval given as analytical uncertainty calculated by using the Nordtest calculation approach [60]  $k=2$ ,  $n=5$ ) and did not induce isotope fractionation when tested on the in-house Sn isotopic standard (measurements before and after column separation).

On the other hand, Cu is quantitatively recovered in the matrix fraction, which, in principle and considering our previous conclusions about Cu separation, would allow direct Cu isotopic analysis in this fraction. In order to test this possibility, the Cu-containing fraction obtained from the TRU-Spec column separation protocol performed on the IARM 91D reference material was analyzed for its Cu isotope ratio, and the results obtained were compared with those obtained without any column separation and after AG-MP-1 separation. Results of this analysis are also gathered in Table 3. As can be seen from these data, there is no statistically significant difference among the results, further proving that Sn and Cu isotopic analysis in bronze samples can be performed with the use of a single separation protocol using TRU-Spec resin. Consequently, this working methodology was applied to the set of archaeological samples under investigation.

Copper and tin isotope ratios of the archaeological bronzes

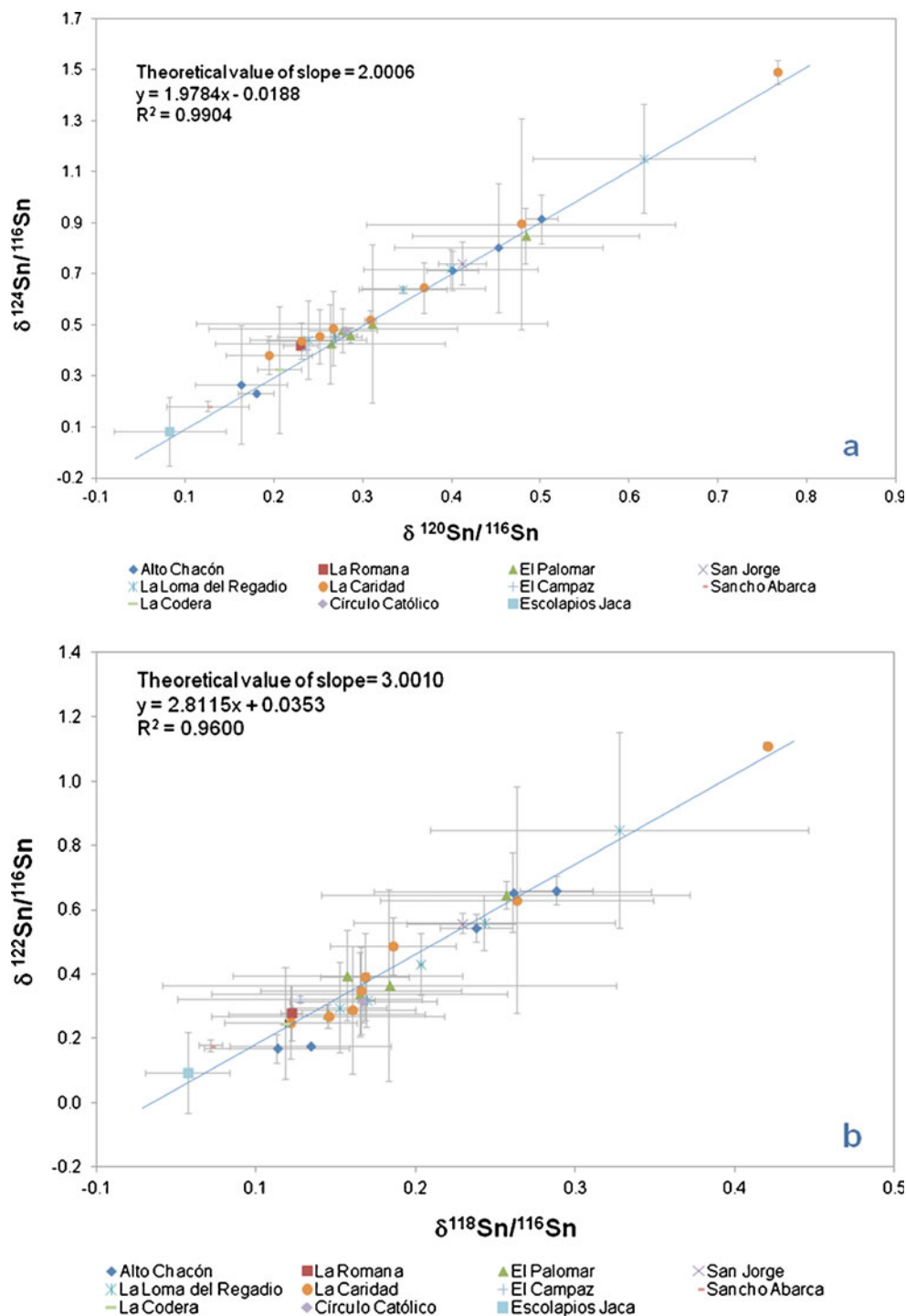
Finally, the protocol optimized for Cu and Sn isotopic analysis of bronze samples was applied to the set of

archaeological bronzes under investigation. For the purpose of measurement validation, results for Sn isotope ratios were plotted in a three-isotope space [1]. Data for the five Sn isotopes measured ( $^{116}\text{Sn}$ ,  $^{118}\text{Sn}$ ,  $^{120}\text{Sn}$ ,  $^{122}\text{Sn}$ , and  $^{124}\text{Sn}$ ) are plotted in Fig. 3a, b, wherein the information is given in the delta scale, with respect to the Sn in-house isotopic standard. The lighter isotope measured,  $^{116}\text{Sn}$ , is used as common reference for delta calculation in both graphs. Results included in these figures serve as a means of quality control for the measurement protocol for Sn, as all Sn isotope data fall on a straight line in agreement with the theoretical fractionation curve, and there is no evidence of spectral interferences on any of the Sn isotopes measured for the bronze samples (the line passes close to zero). As Cu only has two isotopes, this validation protocol could not be carried out for this element.

Figure 4 summarizes the most significant isotope ratio results for Sn and Cu analysis of the bronze samples, combining the average  $\delta^{65}\text{Cu}$  (calculated against the NIST 976 Cu isotopic standard) and the average  $\delta^{122}\text{Sn}/^{116}\text{Sn}$  (calculated against the in-house Sn isotopic standard) obtained for four different determinations. An extensive table containing the isotopic data obtained for the set of samples analyzed in this work is included in the Electronic supplementary material (Table S1 and Table S2).

As seen in Fig. 4, all the bronze objects fit in a large cluster without any evident group classification. Dispersion of the isotopic composition of the different samples is, on the other hand, rather limited, with most of the samples showing a  $\delta^{65}\text{Cu}$  between  $-0.8$ ‰ and  $+0.3$ ‰, and  $\delta^{122}\text{Sn}/^{116}\text{Sn}$  varying from  $0.09$ ‰ to  $0.65$ ‰. Incorporation of the Cu/Sn relative contents and/or the rest of the Sn isotope ratios did not improve the situation in terms of sample grouping.

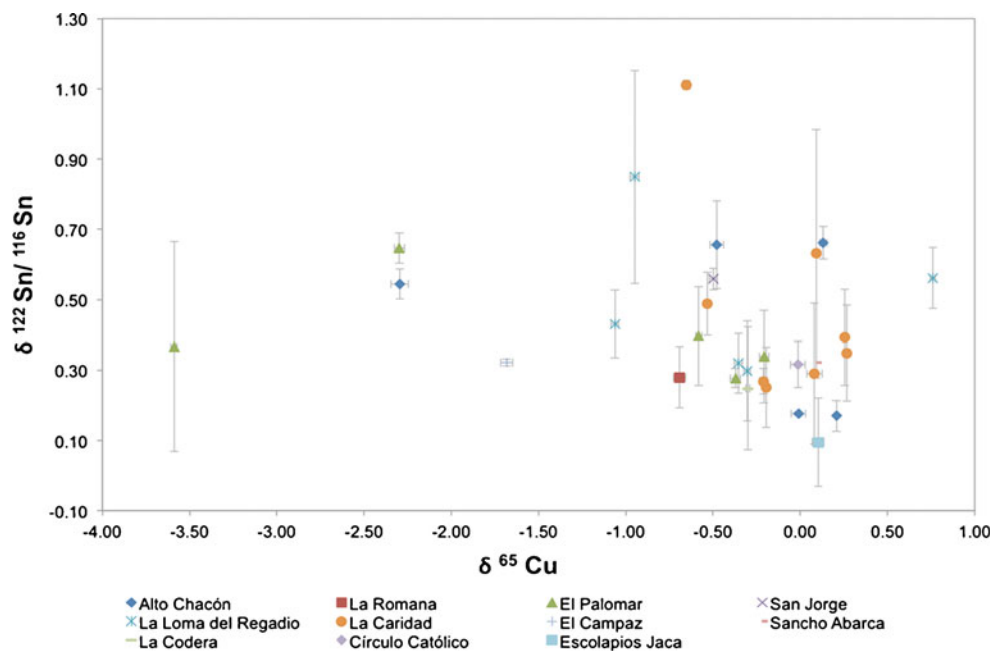
**Fig. 3** Three-isotope plots involving the five Sn isotopes measured ( $^{116}\text{Sn}$ ,  $^{118}\text{Sn}$ ,  $^{120}\text{Sn}$ ,  $^{122}\text{Sn}$ , and  $^{124}\text{Sn}$ ) plotted in the delta scale, with respect to the in-house isotopic standard used for the investigation: **a**  $\delta^{124}\text{Sn}/^{116}\text{Sn}$  versus  $\delta^{120}\text{Sn}/^{116}\text{Sn}$  and **b**  $\delta^{122}\text{Sn}/^{116}\text{Sn}$  versus  $\delta^{118}\text{Sn}/^{116}\text{Sn}$ . Measurements correspond to four replicates (separate sample preparation) performed during four different sessions. Error bars represent analytical uncertainty ( $k=2$ ) calculated following the Nordt-test calculation approach [60]; non-visible error bars are the size of the data markers on the plot or smaller. The lighter isotope measured,  $^{116}\text{Sn}$ , is used as common reference for isotope ratio calculation



Different tentative interpretations of the results for the samples under investigation are possible. Recycling and remelting of the bronze objects through the years could explain the relatively low isotopic variability among the samples. This hypothesis would be sustained by the fact that all samples come from common household and working objects, for which not the best raw materials would have been used. On the other hand, the fact that the same source of raw materials was used for all the bronze samples

investigated cannot be excluded, considering the narrow geographical area covered by the different sites where the samples were found. To ascertain the possible origin for this (hypothetically) single ore source, comparison of isotopic data obtained for Cu with results published by other scientists is possible as all measurements are traceable to the NIST 976 isotopic reference material. In this regard, the data obtained compare well with the results obtained in the study of Klein [25, 27] on Roman coins and copper metal

**Fig. 4** Isotope ratio results for Sn and Cu analysis of the bronze samples combining  $\delta^{122}\text{Sn}/^{116}\text{Sn}$  (calculated against the in-house Sn isotopic standard) versus  $\delta^{65}\text{Cu}$  (calculated against NIST SRM 976 Cu isotopic standard). Error bars represent analytical uncertainty ( $k=2$ ) calculated following the Nordtest calculation approach [60] for four different replicates performed during four different sessions; non-visible error bars are the size of the data markers on the plot or smaller



objects from the south of Spain, although this conclusion has to be further tested and validated with analysis of alternative samples.

In the case of Sn, the hypothesis of a single ore source is much more likely, as Sn mine sources were scarce in Europe compared with those of other metals [7]. In fact, the dispersion of the Sn delta values found for these samples is in the same range or even lower than that observed in previous studies for a single Sn ore site [7]. From this point, and in order to further test the feasibility for Sn ore provenancing by using isotopic information, additional analysis on alternative sets of samples and/or ores from known or expected different origin should be carried out. In the authors' opinion, it is sufficiently proven that the analytical protocol developed provides reliable results, so that this investigation can be carried out.

## Conclusions

The present study represents the first phase of a project investigating the potential of Cu and Sn isotopic analysis for the fingerprinting and/or provenancing of archaeological bronzes and deals with optimization of the analytical methodology. In this regard, we have demonstrated that:

1. For Cu isotopic analysis, mass bias discrimination can be successfully corrected using either Zn or Ni as internal standard. Both elements provide reproducibility values (1 year period) in the range of  $\pm 0.03\%$  (2 s) for a quality control standard. Ni, however, provides superior precision values, and its use seems more robust due a lower risk of contamination, a similar ionization potential to that of Cu and lower Ni contents in Cu alloys.
2. For archaeological bronzes, the Cu isotope ratio can be directly measured without prior column isolation with a precision equal to that for the corresponding purified solution using AG-MP-1 anion exchange resin (reproducibility in the range of  $\pm 0.02\%$  in the delta scale as 2 s,  $n=5$ ). Minor elements typically present in bronze Cu alloys (i.e., Sn, Zn, Pb, Ni), including those used for mass bias correction, do not affect the results for Cu isotopic analysis at their usual concentration levels. In this regard, there is no evidence of spectral interference or a matrix-induced effect on the extent of mass bias discrimination with the measurement methodology used.
3. Sn isolation needed for Sn isotopic analysis can be carried out using the anion-exchange TRU-Spec resin, which provides Sn recovery values close to 100 % and does not introduce on-column isotope fractionation. Cu, on the other hand, can be quantitatively recovered together with the bronze matrix with this isolation protocol. Isotopic analysis of this Cu-containing fraction provides  $\delta^{65}\text{Cu}$  results similar to those obtained after AG-MP-1 Cu isolation. Cu and Sn isotopic analysis of bronze Cu alloys can therefore be carried out after a single chromatographic separation using the TRU-Spec resin.
4. Tin isotope ratios can be directly measured in the Sn isolate as obtained from the TRU-Spec column. The use of Sb as an internal standard for mass bias correction provides good reproducibility for all isotope ratios monitored (in the range of 0.06–0.16% 2 s) and excellent validation results using three-isotope plots.

As for the isotopic data interpretation, further work with the optimized methodology needs to be carried out to



ascertain the usefulness of Cu and Sn isotopic analysis for provenancing/discriminating purposes. In this regard, it has been sufficiently proven that the method developed in this work provides reliable results so that further investigation concerning this issue can be carried out. In the case of Sn, however, progress in this direction is hampered by the fact that no reference material or standard is available for this element at present, so that isotopic data from different labs cannot be directly compared.

**Acknowledgments** R. Alloza and M. P. Marzo are kindly acknowledged for providing access to the samples investigated in this work. M.A. acknowledges the Flemish Research Foundation (FWO) for her postdoctoral grant. F.V. acknowledges the FWO for financial support under the form of a research project (G002111N). M.R. acknowledges the Spanish Ministry of Science and Innovation (Project CTQ2009-08606). F.V. and M.R. acknowledge the Special Research Foundation (BOF) of Ghent University for financial support of their bilateral cooperation.

## References

1. Vanhaecke F, Degryse P (2012) Isotopic analysis. Fundamentals and applications using ICP-MS. Wiley-VCH, Weinheim
2. Vanhaecke F, Balcaen L, Malinovsky D (2009) Use of single-collector and multi-collector ICP-mass spectrometry for isotopic analysis. *J Anal At Spectrom* 24:863–886
3. Balcaen L, Moens L, Vanhaecke F (2010) Determination of isotope ratios of metals (and metalloids) by means of inductively coupled plasma-mass spectrometry for provenancing purposes—a review. *Spectrochim Acta B* 65:769–786
4. Gale NH, Stos-Gale ZA (1982) Bronze Age copper sources in the Mediterranean—a new approach. *Science* 216:11–19
5. Zhu XK, O’Nions RK, Guo Y, Belshaw NS, Rickard D (2000) Determination of natural Cu-isotope variation by plasma source mass spectrometry: implications for use as geochemical tracers. *Chem Geol* 163:139–149
6. Albarède F, Beard B (2004) Analytical method for non-traditional isotopes. In: Johnson CM, Beard BL, Albarède F (eds) *Rewies in mineralogy and geochemistry*, vol. 55, geochemistry of non-traditional stable isotopes. Mineralogical Society of America, Washington
7. Haustein M, Gillis C, Pernicka E (2010) Tin isotopic analysis—a new method for solving old questions. *Archaeometry* 52:816–832
8. Gale NH, Woodhead AP, Stos-Gale ZA, Walder A, Bowen A (1999) Natural variations detected in the isotopic composition of copper: possible applications to archaeology and geochemistry. *Int J Mass Spectrom* 184:1–9
9. Rehener T, Pernicka E (2008) Coins, artefacts and isotopes—archaeometallurgy and archaeometry. *Archaeometry* 50:232–248
10. Radivojevic M, Rehren T, Pernicka E, Silvar D, Brauns M, Boric D (2010) On the origin of extractive metallurgy: new evidence from Europe. *J Archaeol Sci* 37:2775–2787
11. Resano M, Marzo MP, Alloza R, Saénz C, Vanhaecke, Yang L, Willie S, Sturgeon RE (2010) Laser ablation single-collector inductively coupled plasma mass spectrometry for lead isotopic analysis to investigate evolution of the Bilbilis mint. *Anal Chim Acta* 677:55–63
12. Cattin F, Guénette-Beck B, Besse M, Serneels V (2009) Lead isotopes and archaeometallurgy. *Archaeol Anthropol Sci* 1: 137–148
13. Resano M, Marzo P, Pérez-Arategui J, Aramendía M, Cloquet C, Vanhaecke F (2008) Laser ablation-inductively coupled plasma-dynamic reaction cell-mass spectrometry for the determination of lead isotope ratios in ancient glazed ceramics for discriminating purposes. *J Anal At Spectrom* 23:1182–1191
14. Thibodeau AM, Chesley JT, Ruiz J (2012) Lead isotope analysis as a new method for identifying material culture belonging to the Vázquez de Coronado expedition. *J Archaeol Sci* 39:58–66
15. Attanasio D, Bultrini G, Ingo GM (2001) The possibility of provenancing a series of bronze Punic coins found at Tharros (Western Sardinia) using the literature lead isotope database. *Archaeometry* 43:529–547
16. Durali-Müller S (2005) Roman lead and copper mining in Germany—their origin and development through time, deduced from lead and copper isotope provenance studies. <http://www.mineralogie.uni-frankfurt.de/petrologie-geochemie/forschung/dissertationen/diss0106/index.html>
17. Marzo P, Laborda F, Pérez-Arategui J (2007) A simple method for the determination of lead isotope ratios in ancient glazed ceramics using inductively coupled plasma: quadrupole mass spectrometry. *At Spectrosc* 28:195–201
18. Stos-Gale ZA (1995) Isotope archaeology—a review. In: Beavis J, Barker K (eds) *Science and site: evaluation and conservation*. Bournemouth University School of Conservation Sciences, Dorset
19. Gale N (2001) Archaeology, science-based archaeology and the Mediterranean Bronze Age metals trade: a contribution to the debate. *Eur J Archaeol* 4:113–130
20. Wilson L, Pollard AM (2001) The provenance hypothesis. In: Brothwell DR, Pollard AM (eds) *Handbook of archaeological sciences*. Wiley & Sons, Chichester
21. De Wannemacker G, Vanhaecke F, Moens L, Van Mele A, Thoen H (2000) Lead isotopic and elemental analysis of copper alloy statuettes by double focusing sector field ICP mass spectrometry. *A Anal At Spectrom* 15:323–327
22. Begemann F, Schmitt-Strecker, Pernicka E, Lo Schiavo F (2001) Chemical composition and lead isotopy of copper and bronze from Neuragic Sardinia. *Eur J Archaeol* 4:43–85
23. Desaulty AM, Telouk P, Albalat E, Albarède F (2011) Isotopic Ag-Cu-Pb record of silver circulation through 16th–18th century Spain. *PNAS* 108:9002–9900
24. Fortunato G, Ritter A, Fabian D (2005) Old masters’ lead white pigments: investigation of paintings from the 16<sup>th</sup> to the 17<sup>th</sup> century using high precision lead isotope abundance ratios. *Analyst* 130:898–906
25. Klein S, Brey GP, Durali-Müller S, Lahaye Y (2010) Characterization of raw metal sources used for the production of copper and copper-based objects with copper isotopes. *Archaeol Anthropol Sci* 2:45–56
26. Hull S, Fayek M, Mathien FJ, Shelley P, Durand KR (2008) A new approach to determining the geological provenance of turquoise artifacts using hydrogen and copper stable isotopes. *J Archaeol Sci* 35:1355–1369
27. Klein S, Lahaye Y, Brey GP (2004) The Early Roman Imperial AES coinage II: tracing the copper sources by analysis of lead and copper isotopes—copper coins of Augustus and Tiberius. *Archaeometry* 46:469–480
28. Mathur R, Titley S, Hart G, Wilson M, Davignon M, Zlatos C (2009) The history of the United States cent revealed through copper isotope fractionation. *J Archaeol Sci* 36:430–433
29. Begemann F, Kallas K, Schmitt-Strecker S, Pernicka E (1999) In: Hauptmann A, Pernicka E, Rehren T, Yalcin Ü (eds) *The beginnings of metallurgy*. Der Anschnitt, Beiheft, Deutsches Bergbau-Museum, Bochum
30. Klein S, Doumergue C, Lahaye Y, Brey GP, Von Kaenel HM (2009) The lead and copper isotopic composition of copper ores from the Sierra Morena (Spain)—Análisis de los isotopos de



- plomo y de cobre de los minerales de cobre de la Sierra Morena (Spain) por MC-ICP-MS. *J Iberian Geol* 35:59–68
31. Gale NH (1997) The isotopic composition of tin in some ancient metals and the recycling problem in metal provenancing. *Archaeometry* 39:71–82
  32. Huff EA, Huff DR (1993) TRU-Spec and RE-Spec chromatography: basic studies and applications. in 34th ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tennessee
  33. Maréchal CN, Télouk P, Albarède F (1999) Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chem Geol* 156:251–273
  34. Van Heghe L, Engström E, Rodushkin I, Cloquet C, Vanhaecke F (2012) Isotopic analysis of the metabolically relevant transition metals Cu, Fe and Zn in human blood from vegetarians and omnivores using multi-collector ICP-mass spectrometry. *J Anal At Spectrom* 27:1327–1334
  35. Krachler M, Rausch N, Feuerbacher H, Kelmens P (2005) A new HF-resistant tandem spray chamber for improved determination of trace elements and Pb isotopes using inductively coupled plasma-mass spectrometry. *Spectrochim Acta B* 60:865–869
  36. Epov VN, Malinovsky D, Vanhaecke F, Bégué D, Donard OFX (2011) Modern mass spectrometry for studying mass-independent fractionation of heavy stable isotopes in environmental and biological sciences. *J Anal At Spectrom* 26:1142–1152
  37. Malinovsky D, Moens L, Vanhaecke F (2009) Isotopic fractionation of Sn during methylation and demethylation reactions in aqueous solution. *Environ Sci Technol* 43:4399–4404
  38. Baxter DC, Rodushkin I, Engström E, Malinovsky D (2006) Revised exponential model for mass bias correction using an internal standard for isotope ratio measurements by multicollector inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 21:427–430
  39. De Laeter JR, Bohlke JK, De Bièvre P, Hidaka H, Peiser HS, Rosman KJR, Taylor PDP (2003) Atomic weights of the elements: Review 2000. *Pure Appl Chem* 75:683–800
  40. Yang L (2009) Accurate and precise determination of isotopic ratio by MC-ICP-MS: a review. *Mass Spectrom Rev* 28:990–1011
  41. Meija J, Yang L, Mester Z, Sturgeon R (2012) Correction of instrumental mass discrimination for isotope ratio determination with multi-collector inductively coupled plasma mass spectrometry in isotopic analysis. *Fundamentals and applications using ICP-MS*. Wiley-VCH, Weinheim
  42. Moeller K, Schoenberg R, Pedersen RB, Weiss D, Dong S (2012) Calibration of the new certified reference materials ERM-AE633 and ERM-AE647 for copper and IRMM-3702 for zinc isotope amount ratio determinations. *Geost Geoanal Res* 35:177–199
  43. Mason TFD, Weiss DJ, Horstwood M, Parrish RR, Russell SS, Mullane E, Coles BJ (2004) High-precision Cu and Zn isotope analysis by plasma source mass spectrometry part 1. Spectral interferences and their correction. *J Anal At Spectrom* 19:209–217
  44. Mason TFD, Weiss DJ, Horstwood M, Parrish RR, Russell SS, Mullane E, Coles BJ (2004) High-precision Cu and Zn isotope analysis by plasma source mass spectrometry part 2. Correcting for mass discrimination effects. *J Anal At Spectrom* 19:218–226
  45. Archer C, Vance D (2004) Mass discrimination correction in multiple-collector plasma source mass spectrometry: an example using Cu and Zn isotopes. *J Anal At Spectrom* 19:656–665
  46. Marthur R, Titley S, Barra F, Brantley S, Wilson M, Phillips A, Munizaga V, Makshev V, Vervoort J, Hart G (2009) Exploration potential of Cu isotope fractionation in porphyry copper deposits. *J Geochem Explor* 102:1–6
  47. Borok DM, Warty RB, Ridley WI, Wolf R, Lamothe RJ, Adams M (2007) Separation of copper, iron, and zinc from complex aqueous solutions for isotopic measurement. *Chem Geol* 242:400–414
  48. Chapman B, Mason TFD, Weiss DJ, Coles BJ, Wilkinson JJ (2005) Chemical separation and isotopic variations of Cu and Zn from five geological reference materials. *Geost Geoanal Res* 30:5–16
  49. Markl G, Lahaye Y, Schwinn G (2006) Copper isotopes as monitors of redox processes in hydrothermal mineralization. *Geochim Cosmochim Acta* 70:4215–4225
  50. Li W, Jackson SE, Pearson NJ, Alard O, Chappell BW (2009) The Cu isotopic signature of granites from the Lachlan Fold Belt, SE Australia. *Chem Geol* 258:38–49
  51. Asael D, Matthews A, Bar-Matthews M, Halicz L (2009) Copper isotope fractionation in sedimentary copper mineralization (Timna Valley, Israel). *Chem Geol* 262:147–158
  52. Larner F, Rehkämper M, Coles BJ, Kreissig K, Weiss DJ, Sampson B, Unsworth C, Strelkopytov S (2011) A new separation procedure for Cu prior to stable isotope analysis by MC-ICP-MS. *J Anal At Spectrom* 26:1627–1632
  53. Ehrlich S, Butler I, Halicz L, Rickard D, Oldroyd A, Matthews A (2004) Experimental study of the copper isotope fractionation between aqueous Cu (II) and covellite CuS. *Chem Geol* 209:259–269
  54. Ehrlich S, Ben-Dor L, Halicz L (2004) Precise isotope ratio measurement by multi collector-ICP-MS without matrix separation. *Can J Anal Sci Spectrosc* 49:136–147
  55. Clayton RE, Andersson P, Gale NH, Gillis C, Whitehouse M (2002) Precise determination of the isotopic composition of tin using MC-ICP-MS. *J Anal At Spectrom* 17:1248–1256
  56. Ikerata K, Notsu K, Hirata T (2008) In situ determination of Cu isotope ratios in copper-rich materials by NIR femtosecond LA-MC-ICP-MS. *J Anal At Spectrom* 23:1003–1008
  57. Maréchal CN, Albarède F (2002) Ion-exchange fractionation of copper and zinc isotopes. *Geochim Cosmochim Acta* 66:1499–1509
  58. Haest M, Muchez P, Petit JCI, Vanhaecke F (2009) Cu isotope ratio variations in the Dikulushi Cu-Ag deposit, DRC: of primary origin or induced by supergene reworking? *Econ Geol* 104:1055–1064
  59. Larson PB, Maher K, Ramos FC, Chang Z, Gaspar M, Meinert LD (2003) Copper isotope ratios in magmatic and hydrothermal ore-forming environments. *Chem Geol* 201:337–350
  60. Magnusson B, Naykki T, Hovind H, Krysell M (2003) Handbook for calculation of measurement uncertainty, 2nd edn. Nordtest, Espoo
  61. De Laeter JR, Jeffery PM (1965) The isotopic composition of terrestrial and meteoritic tin. *J Geophys Res* 12:2895–2903
  62. De Laeter JR, Jeffery PM (1967) Tin: its isotopic and elemental abundance. *Geochim Cosmochim Acta* 31:969–985
  63. De Laeter JR, McCulloch MT, Rosman KJR (1974) Mass spectrometric isotope dilution analyses of tin in stony meteorites and standard rocks. *Earth Planet Sci Lett* 22:226–232
  64. Rosman KJR, Loss RD, De Laeter JR (1984) The isotopic composition of tin. *Int J Mass Spectrom* 56:281–291
  65. McNaughton NJ, Rosman KJR (1991) Tin isotopic fractionation in terrestrial cassiterites. *Geochem Cosmochim Acta* 55:499–504
  66. Yi W, Halliday AN, Lee DC, Christensen JN (1995) Indium and tin in basalts, sulfides, and the mantle. *Geochim Cosmochim Acta* 59:5081–5090
  67. Hernández C, Fernández M, Quejido AJ, Sánchez DM, Morante R, Martín R (2006) Isotope dilution-thermal ionization mass spectrometry for tin in a fly ash material. *Anal Chim Acta* 571:279–287
  68. Patton TL, Penrose WR (1989) Fission product tin in sediments. *J Environ Radioact* 10:201–211
  69. Gale NH (1997) The isotopic composition of tin in some ancient metals and the recycling problem in metal provenancing. *Archaeometry* 39:31–38