

A simple method for Cu, Zn and Mo purification and mass bias correction for precise and accurate isotopic ratio determination in geological samples by MC-ICPMS

Suzana de Souza Guedes^{1*}
Valéria Regina Bellotto¹
Roberto Ventura Santos²
Elton Luiz Dantas²

¹Institute of Chemistry
University of Brasília,
Brasília-DF, Brazil
CEP 70910-900

²Institute of Geoscience
University of Brasília
Brasília-DF, Brazil
CEP 70910-900

*Corresponding author
suzanaguedesunb@gmail.com

RESUMO

Foi desenvolvido um método simples e rápido para separação e purificação simultânea de Cu, Zn e Mo e a medição exata e precisa das suas composições isotópicas em amostras geológicas utilizando espectrometria de massa com plasma indutivamente acoplado e sistema multicoletor (MC-ICPMS). O método envolve o uso de uma única coluna cromatográfica, preenchida com a resina de troca aniônica AG-MP-1 para separação e purificação desses três elementos a partir da sua matriz complexa. O método *Sample-Standard-Bracketing* (SSB) combinado à adição de padrão interno foi usado para a correção exata e precisa do viés de massa instrumental nas medições das razões isotópicas de Cu, Zn e Mo. O método foi aplicado a diferentes materiais geológicos, como granodiorito (GSP 2- USGS), calcário (JLS-1, Japão), sedimentos do Rio Buffalo (NIST SRM - 8704) e sedimentos da Bacia Amazônica. A precisão média para essas amostras foram: 0,08 ‰ para $\delta^{65/63}\text{Cu}$; 0,05 ‰ para $\delta^{66/67}\text{Zn}$ e 0,04 ‰ para $\delta^{98/95}\text{Mo}$. A principal vantagem é que o método proposto é simples e rápido, realiza a recuperação quantitativa dos elementos de diferentes massas atômicas e em concentrações muito baixas, principalmente para Mo. Em conjunto, a correção do viés de massa instrumental a partir de um método mais simples, produziu resultados consistentes aos outros métodos atualmente publicados. A comparação entre as composições isotópicas de Cu e Mo obtidas para granodiorito com os dados relatados na literatura, demonstra que o método mais simples e multielementar, desenvolvido neste estudo, estão dentro dos limites de precisão requeridas e pode ser utilizado adequadamente como ferramenta multi-proxy em geoquímica de isótopos.

Palavras-chaves: isótopos de Zn, Cu e Mo, MC-ICPMS, cromatografia de troca iônica, material geológico

ABSTRACT

A simple and quick method for simultaneous purification of Cu, Zn and Mo and accurate and precise measurement of their isotopic composition in geological samples using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has been developed. The method involves the use of a single chromatographic column filled with the anion exchange resin AG-MP-1 for complex matrix removal and further purification of these three elements. The external standard-sample-standard bracketing (SSB) procedure combined to internal standard addition was used for accurate mass bias correction and precise Cu, Zn and Mo isotopic ratio measurements. The method was applied to different geological materials, as granodiorite (GSP 2-USGS), limestone (JLS-1, Japan), Buffalo River Sediments (NIST SRM - 8704) and sediments from Amazon River Basin. The mean precision for these samples was: 0.08 ‰ for $\delta^{65/63}\text{Cu}$; 0.05 ‰ for $\delta^{66/67}\text{Zn}$ and 0.04 ‰ for $\delta^{98/95}\text{Mo}$. The main advantage is that the proposed method is simple and rapid, and carries out the quantitative recovery of elements of different atomic

masses and at very low concentration ranges, mainly for Mo. In addition, optimizations made the calibration and correction of instrumental mass bias easier, leading to consistent results with other methods that are currently published. The comparison of isotopic compositions of Cu and Mo obtained for granodiorite with respect to data reported in the literature demonstrate that the simpler and multi-element method developed in this study can be properly used within the required limits of accuracy as a multi-proxy tool in isotope geochemistry.

Keywords: Zn, Cu and Mo isotopes; MC-ICPMS; anion-exchange chromatography, geological materials

1. INTRODUCTION

Studies have shown that the isotopic compositions of transition metals in biological or geological natural samples, mainly Cu, Zn and Mo, can be used as biogeochemical tracers related to climate change, reconstruction of paleo-environments and biological evolution, among others (Maréchal *et al.* 1999; Zhu *et al.* 2000; Barling *et al.* 2001; Duan *et al.* 2010; Bigalke *et al.* 2010). These elements are essential micronutrients, participate in different biogeochemical cycles and their availability is affected by changes in the environmental oxygenation rates, mainly in aquatic systems. In this way, the fractionation of these isotopes may offer unique isotopic signatures preserved in the geological records, allowing the distinction between the oxic, suboxic or anoxic environments (Anbar & Rouxel 2007).

Under reducing conditions Mo is easily removed from ocean water, causing the enrichment of this metal (positive δ value) in sediments (Anbar & Rouxel 2007). Under these same conditions copper presents negative δ values, mainly due to the reduction of Cu (II) into Cu (I) by the anaerobic bacteria. As an example, the $\delta^{65}\text{Cu}$ of Cu (I) in marine sediments is 3 to 5‰ lighter than the Cu (II) species presented in interstitial waters (Anbar & Rouxel 2007; Albarède 2004). Zinc, in spite of its permanent divalent state has a well-marked behavior due to the preferential absorption of the lighter isotopes in biological processes, so that the enrichment of the zinc isotopes suggests environments under oxic conditions (Maréchal *et al.* 1999; Maréchal & Albarède 2002).

Thus, these three metals together are a complementary pair because they are geochemical opposites, that is, in the same environmental conditions they present different behaviors and complementary fractionation responses.

Although complex biogeochemical processes leading to isotopic fractionation in

natural environment are best understood by applying multi-proxy strategies, most studies employ the isotopic ratio of only one or two transition metals. The chemical separation of these elements in complex matrices and in samples with large concentration variation among them is a difficult task. In general, Fe is present in concentration up to a few percentages, while Cu and Zn are on the order of tens of $\mu\text{g g}^{-1}$ and Mo at much lower concentrations, sometimes less than one $\mu\text{g g}^{-1}$.

The most common method of chemical separation of metals is ion exchange chromatography. For Cu and Zn, the separation protocol proposed by (Maréchal *et al.* 1999) has been widely used and modified. Especially with natural samples of complex matrix, published studies show that a single step of ion exchange column is not sufficient to achieve the required purity for isotopic analysis. In most instances, it is also necessary a second ion exchange column and/or a pre or post column precipitation step (Borrok *et al.* 2007).

The separation of Mo is usually hampered by its low concentration in natural samples. In most studies (Siebert *et al.* 2001; Wieser & De Laeter 2003; Malinovsky *et al.* 2005; Pietruszka & Reznik 2008; Migeon *et al.* 2015) several separation steps are employed, including the use of at least two different resins: an anionic resin (AG1-X8) to eliminate concomitant elements; and a cationic resin (Chelex-100 and AG-50W) to retain mainly Fe and Zr, two important interfering elements in MC-ICPMS measurements. These complex procedures may lead to isotopic fractionation.

Due to the methodological difficulties described above, it is usual to employ the isotopic ratio only of one or two transition metals. However, a better understanding of the complex biogeochemical processes leading to isotopic fractionation in natural environment can be achieved by applying a multi-proxy strategy. This strategy implies the use of a

larger number of transition metals, which isotopic ratios show different behaviors under the same environmental conditions, thus providing a more accurate and consistent assessment of a paleo-environmental evolution.

This study presents accurate and precise determinations of isotopic ratios of Cu, Zn, and Mo by MC-ICPMS after developing and optimizing a procedure for simultaneous separation of these metals using a single separation chromatographic column. Quantita-

tive recoveries of more than 90% was achieved for all three metals, thus minimizing the likelihood of contamination and isotopic fractionation during the separation process (Borrok *et al.* 2007). In addition, the study demonstrates that mass bias correction by Sample-Standard-Bracketing (SSB) has the same level of accuracy as the isotopic ratios obtained by double-spike technique that is usually applied for the isotopic determinations of Zn or Mo in geological samples (Mason *et al.* 2004; Peel *et al.* 2008).

2. MATERIALS AND METHODS

All procedures were carried out in a clean room using ultra-purified water by the Nanopure system (18 M Ω cm) and high purity reagents: sub-distilled hydrochloric acid (HCl PA), hydrofluoric acid (HF PA), nitric acid (HNO₃ PA) and ultrapure hydrogen peroxide (Suprapur®, Merck). Teflon vessels (Savillex®) were used to collect the eluate; BioRad® polyethylene chromatography columns which were 5.0 cm long and had an

internal diameter of 1.0 cm, were filled with AG-MP-1 (100-200 mesh) BioRad® or AG1-X8 (200-400 mesh) Eichron® resins. The standard solution from Johnson Matthey Company (JMC) (Alfa Aesar Specpure®) and the Isotopic Reference Materials IRMM 653 and ERM-AE 633 were selected as the delta zero standard in the determinations of the isotopic ratios for Mo, Zn and Cu, respectively.

2.1. SAMPLE PREPARATION

For development of the purification method, a synthetic sample was produced by the combination of Cu, Zn, Fe and Mo from NIST traceable monoelementary (Tritisol®, Merck) solutions (Cu-lot HC 109865, Zn-lot HC 112017 and Fe-lot HC 114789) and a Mo standard solution from the JMC (Alpha Aesar Specpure®) (Lot 61200523). The concentrations of these elements in the synthetic sample simulated those found in rocks and sediments, which mean values are: 95 $\mu\text{g g}^{-1}$ for Zn, 33 $\mu\text{g g}^{-1}$ for Cu and 2.0 $\mu\text{g g}^{-1}$ for Mo (Salomons & Förstner 1984). Even not being an element of interest in the present study, Fe was added to the synthetic sample because it is usually a major constituent in geological matrices (~ 4.1%). It is also one of the main isobaric and polyatomic interferent with the metals of interest for the present study.

The following geological reference materials (certified for total metal content) were used as real samples: limestone (JLS-1; Cu- 0.36 $\mu\text{g g}^{-1}$; Zn- 3.19 $\mu\text{g g}^{-1}$ and Mo- 0.07 $\mu\text{g g}^{-1}$), granodiorite (GSP-2-US Geological Survey; Cu- 43 $\mu\text{g g}^{-1}$; Zn- 120 $\mu\text{g g}^{-1}$ and Mo- 2.1 $\mu\text{g g}^{-1}$) and Buffalo River sediment (NIST RM 8704; Cu- 83.4 $\mu\text{g g}^{-1}$; Zn- 408 $\mu\text{g g}^{-1}$ and

Mo- 1.97 $\mu\text{g g}^{-1}$). Two samples of fluvial sediments from different localities in the Amazon Basin (Brazil) were also investigated: one from Xingu River identified as CA2 (Cu- $18.60 \pm 0.14 \mu\text{g g}^{-1}$; Zn $53.40 \pm 0.30 \mu\text{g g}^{-1}$ and Mo $0.18 \pm 0.01 \mu\text{g g}^{-1}$) (1°58'42S - 53°54'00W); and another from the Amazon River, identified as CA7 (Cu $-59.82 \pm 0.38 \mu\text{g g}^{-1}$; Zn $184.24 \pm 2.91 \mu\text{g g}^{-1}$ and Mo $0.34 \pm 0.01 \mu\text{g g}^{-1}$) (0°07'11S - 51°08'56 W).

Aliquots of 500 mg for granodiorite and 300 mg for the others geological materials were weighed in Teflon vessels (Savillex®) followed by digestion with the addition of 5 ml HCl, 10 ml HNO₃ and 5 ml of HF with a hot plate, until complete dissolution of the material was achieved. After this step, the samples were evaporated to dryness and the resulting solids were dissolved in HCl 7 mol L⁻¹ and 0.001% H₂O₂ for subsequent passage through the ion exchange chromatography column. These procedures took place on a laminar flow bench.

Aliquots of the original solutions were reserved for use as a reference in the quantitative analysis of the recovery elements and to evaluate the isotopic fractionation in the chromatographic column.

2.2. ION-EXCHANGE PURIFICATION OF Cu, Zn AND Mo

The method was developed from the combination and optimization of the methods proposed by Maréchal *et al.* (1999) for Cu and Zn and by Wieser *et al.* (2007) for Mo. This new method allowed the separation of Cu, Zn and Mo, eliminating the matrix and removing Fe, with the use of a single ion exchange column.

Initially, two ion-exchange resins (AG-MP-1 and AG1-X8) were tested among the most employed in previous studies for the separation and purification of Cu, Zn or Mo (Wieser & De Laeter 2003; Malinovsky *et al.* 2005; Chapman *et al.* 2006; Borrok *et al.* 2007; Petit 2009). The resin with the best-combined recovery of the three analytes was then used for development of the method. Two factorial designs were carried out to optimize the parameters and steps of the separation and ion

exchange purification procedure. In the first one, three independent variables were selected: the column size (2.0 and 3.0 mL resin), the HCl concentration (5 and 6 mol L⁻¹) and the iron-eluting agent (HCl 1 mol L⁻¹ and the mixture HCl 0.5 mol L⁻¹ and HF 1 mol L⁻¹). In the second factorial experiment, the column size was tested at levels of 2.0 and 2.5 mL, and HCl was tested at the concentrations 6 and 7 mol L⁻¹.

Calculations involving the two factorial designs and optimization using the Response Surface Method (RSM) were performed on spreadsheets developed by the Theoretical and Applied Chemometric Laboratory at the Chemistry Institute of the State University of Campinas (Unicamp) using Microsoft Excel® software (Teófilo & Ferreira 2006).

2.3. INSTRUMENTATION

The quantifications of Cu, Zn and Fe to evaluate the recoveries after solid phase extraction were performed using Microwave Plasma Atomic Emission Spectrometer (MP-AES 4200 Agilent®) using nitrogen (N₂) as the plasma gas. The following wavelengths were selected: 327.395 nm (Cu), 481.053 nm (Zn) and 259.940 nm (Fe). An external calibration was used and all measurements were performed in triplicate.

For molybdenum, which is present in low concentrations in the samples, the determination was performed using Inductively Coupled Plasma Mass Spectrometry technique (ICP-MS, Thermo Scientific® X series2 model). An external calibration was used and the isotopes ⁹⁸Mo and ⁹⁵Mo were quantitatively determined. All analyses were performed in triplicate.

Zinc, copper and, molybdenum isotope ratio of samples and reference materials were determined at the University of Brasilia Geochronology Laboratory using a Thermo Fisher Scientific Neptune Plus multi-collector inductive coupling plasma mass spectrometer.

For Cu and Zn measurements the masses ⁶²Ni, ⁶³Cu, ⁶⁴Zn/⁶⁴Ni, ⁶⁵Cu, ⁶⁶Zn, ⁶⁷Zn and ⁶⁸Zn were simultaneously detected using Faraday cups. The analytical sequences were performed automatically by using a Cetac ASX-100

automatic extractor and low-mass (~ 300) collector slits, combining concentrations of Cu and Zn at 300 µg L⁻¹. The input system includes a stable introduction system (SIS) consisting of a tandem quartz glass (double standard cyclone plus Scott) spray chamber coupled with a low flow PFA nebulizer (50 µL min⁻¹). Each sample measure consisted of a block of thirty-seven integration cycles of 8 s.

For Mo Isotopic measurements were conducted in identical fashion to those developed for the Cu-Zn system. The isotopes ⁹²Mo, ⁹⁴Mo, ⁹⁵Mo, ⁹⁶Mo, ⁹⁷Mo, ⁹⁸Mo and ¹⁰⁰Mo were measured simultaneously along with ⁹¹Zr and ⁹⁹Ru. Analyzes were performed along a cycle of twenty measurements with integration time of 4s. An ultrasonic nebulizer CETAC Aridus (CETAC Technologies, Omaha, USA) was used for the introduction of the samples for Mo analysis. This device produced a drier spray, and thus reduced the oxygen and nitrogen content in the plasma. This strategy was used to minimize polyatomic interferences of these elements with Zn, since this metal was present in the Mo fraction after co-elution in the chromatographic separation process.

The instrument settings and the arrangements of isotopes in Faraday collectors are shown in Table 1.

Table 1- Isotope positions in Faraday collectors for measurements of the Cu, Zn and Mo isotope ratios and the operational conditions of the MC-ICPMS NEPTUNE instrument.

conditions of the MC-ICP-MS NEPTUNE instrument.

Cup	L4	L2	L1	C	H1	H2	H3		
Configuration	⁶² Ni	⁶³ Cu	⁶⁴ Zn	⁶⁵ Cu	⁶⁶ Zn	⁶⁷ Zn	⁶⁸ Zn		
Neptune instrumental parameters for the Cu and Zn analyses									
Acceleration potential (W)				1050					
Air Flow Rates (L min ⁻¹)				Cooling gas	15				
				Auxiliary Gas	0.70				
				Sample gas	0.85				
Cooling Gas				15					
Integration time				8 seconds					
Mass resolution				Low resolution ~ 300					
Number of Measurements				1 cycle of 37 measurements					
Neptune instrumental parameters for the Mo analyses									
Cup	L4	L3	L2	L1	C	H1	H2	H3	H4
Configuration	⁹¹ Zr	⁹² Mo	⁹⁴ Mo	⁹⁵ Mo	⁹⁶ Mo	⁹⁷ Mo	⁹⁸ Mo	⁹⁹ Ru	¹⁰⁰ Mo
Neptune instrumental parameters for the Cu and Zn analyses									
Acceleration potential (W)					1050				
Air Flow (L min ⁻¹)					Cooling Gas	15			
					Auxiliary Gas	0.72			
					Sample Gas	0.935			
Sample flow					50 µL min ⁻¹				
Integration time					4 seconds				
Mass resolution					Low resolution ~ 300				
Number of measurements					1 cycle de 20 measurements				
Ultrasonic nebulizer Aridus II Operating Conditions (CETAC)									
Temperature of the spray chamber					110°C				
Desolvator temperature					160 °C				
Sweep gas flow rate					1.75[L min ⁻¹]				
Nitrogen gas					0.03[L min ⁻¹]				

2.4. ANALYSES, INTERFERENCE CORRECTIONS AND CALIBRATION BY SSB

The isobaric interferences were monitored in the instrument (MC-ICPMS). For the Cu-Zn method, the data were corrected with the values of the blank measurements and the ⁶²Ni isotope (used to make corrections of isobaric interferences of ⁶⁴Ni with respect to ⁶⁴Zn). For Mo analysis, all seven isotopes were measured simultaneously along with ⁹¹Zr and ⁹⁹Ru, which were used to monitor and correct the signals of the other isotopes of these two elements which are isobaric interferences for Mo in atomic masses 92, 94, 96 and 100.

The calibration was performed according to the SSB method, in which the standard should

be analyzed several times during the analytical session to monitor the stability of the equipment over time and to correct the instrumental mass bias. In this sense, it was determined that measurements of the standard solution should occur every three consecutive samples. To avoid cross-contamination between samples and standards, washing of the aspiration probe was performed with a blank (HNO₃ 3%) for fifteen minutes. For the final five minutes, the intensities of the background signals were recorded to be subtracted from the signals of the samples or the subsequent standards.

2.5. INSTRUMENTAL MASS BIAS CORRECTION

The method of correction employed in this study is the simplest one and involves monitoring the temporal variation of mass bias using standards run between samples (here called SSB) and has been successfully used for isotopic analysis of Zn (Ponzenvera *et al.* 2006), Cu (Zhu *et al.* 2000; Mason *et al.* 2004) and Mo (Wen *et al.* 2010). A requirement of the standard-bracketing approach is that mass bias is relatively stable with time and that mass bias behavior of standards and samples is the same. Under these conditions, the SSB method

assumes a linear variation of the measurements over time. The mean isotopic ratios of the standard measured before and after the sample are used to correct instrumental mass bias. According to Albarède *et al.* (2004) the isotopic ratio of the corrected sample is obtained by

$$(Ri)_A = (Ri)_P \frac{(ri)_A}{\sqrt{(ri)_P^1 \times (ri)_P^2}}$$

Where $(Ri)_A$ is the theoretical isotope ratio of the standard, $(ri)_A$ is the mean of the isotopic ratios of the sample and $(ri)_P^1$ and $(ri)_P^2$ are the experimental means of the standards analyzed before and after the sample.

As in stable isotope studies the relative differences in isotopic ratios between samples are more important than their absolute values the result of the isotopic composition is defined relative to a common standard, and the isotopic data are reported by a delta value (δ), expressed in ‰ and determined by

$$\delta = \left(\left(\frac{[\text{isotope sample ratio}]}{[\text{standard isotope ratio}]} \right) - 1 \right) \times 10^3$$

In this work, the δ -values of Cu, Zn and Mo isotopic composition are relative to the Isotopic Reference Materials ERM-AE 633, IRMM 653 and Johnson Matthey Company (Alfa Aesar Specpure ®) standard solution, respectively.

3. RESULTS AND DISCUSSION

3.1 ION-EXCHANGE PURIFICATION OF Cu, Zn AND Mo

Several preliminary experiments were conducted with the two most commonly used resins from the previous works being selected (AG-MP-1 and AG1-X8). All experimental results show better mean recoveries of the three metals with the AG-MP-1 ($47.7 \pm 6.9\%$) compared to AG1-X8 ($34.5 \pm 12.9\%$), especially for Cu, with an average recovery of $42.1 \pm 6.0\%$ for AG-MP-1 and $25.5 \pm 9.1\%$ for AG1-X8. The AG-MP-1 was then selected for the development of the proposed method.

Optimized experimental conditions for the chemical purification of metals were evaluated by factorial design experiments. The results of the analysis of variance (ANOVA) indicated that the adjusted models are statistically significant and predictive at a 95% confidence level. The calculated F values were 13.77 for the Cu, 18.78 for the Zn and 9.19 for the Mo,

all with values of $p < 0.05$. The lack of fit in the models was not significant, with the same level of confidence. The coefficients of determination (R^2) were 0.9465, 0.9494 and 0.9220 for Cu, Zn and Mo, respectively, demonstrating that the model is adequate.

Analysis of the results showed that the three factors studied in this experimental design had effects on the response. Only the eluent for the removal of Fe was not significant for Cu. The effects of two of the several possible pairs of variables are shown in Figures 1, 2 and 3 for Cu, Zn and Mo, respectively.

The percentage of Cu recovered from the synthetic sample ranged from 5.49 to 60.58%. It was concluded from Fig 1 that the column and concentration of HCl at the highest levels (7 mol L^{-1} and the column containing 2.5 ml resin) contributed to increasing the recovery of Cu.

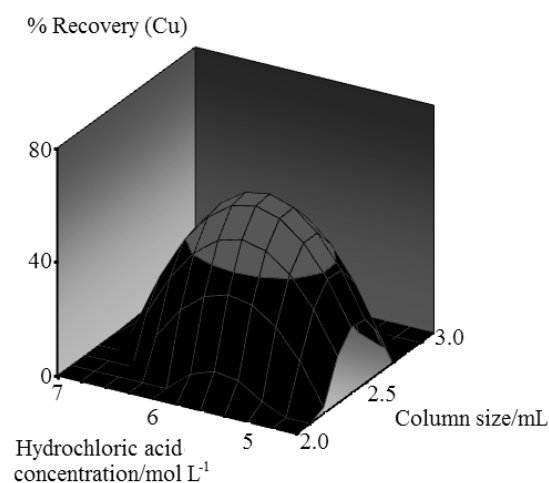


Figure 1
Response surface obtained from the factorial design for Cu recovery yield: hydrochloric acid concentration and column size.

For zinc in the synthetic sample, recoveries ranging from 0.20 to 97% were obtained. The highest yields occurred with the use of smaller columns and concentrated acids and HCl/HF mixtures for iron extraction (Fig 2a and 2b).

However, the maximum value of recovery the Cu was below 90%. Previous studies have

reported that Cu and Zn tends to be eluted faster from the column in the absence of matrix elements (Chapman *et al.* 2006; Petir 2009), justifying the result for the synthetic sample, which does not contain a similar matrix to geological materials, such as sediments and rocks.

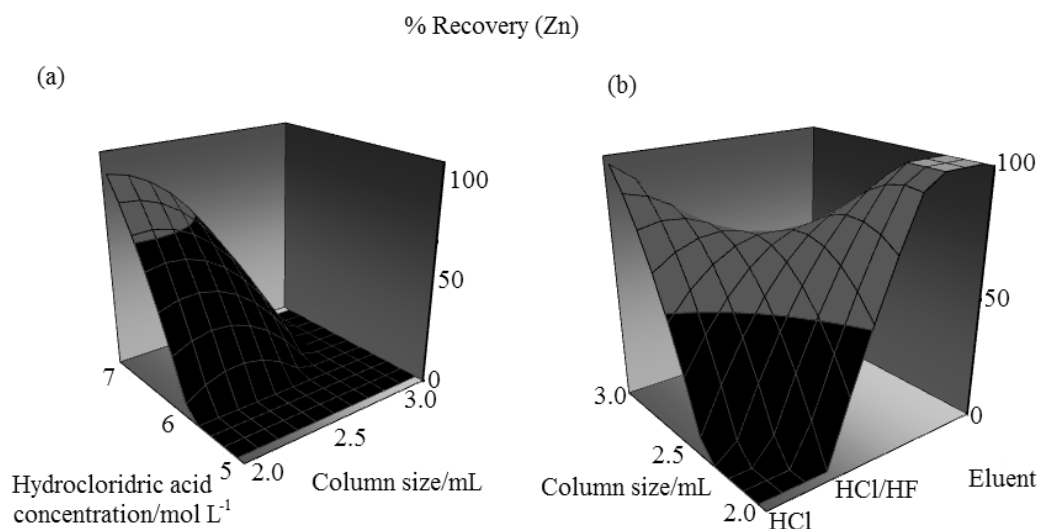


Figure 2
Response surfaces obtained from the factorial design for Zn recovery yield on (a) hydrochloric acid concentration and column size and (b) column size and eluent for Fe.

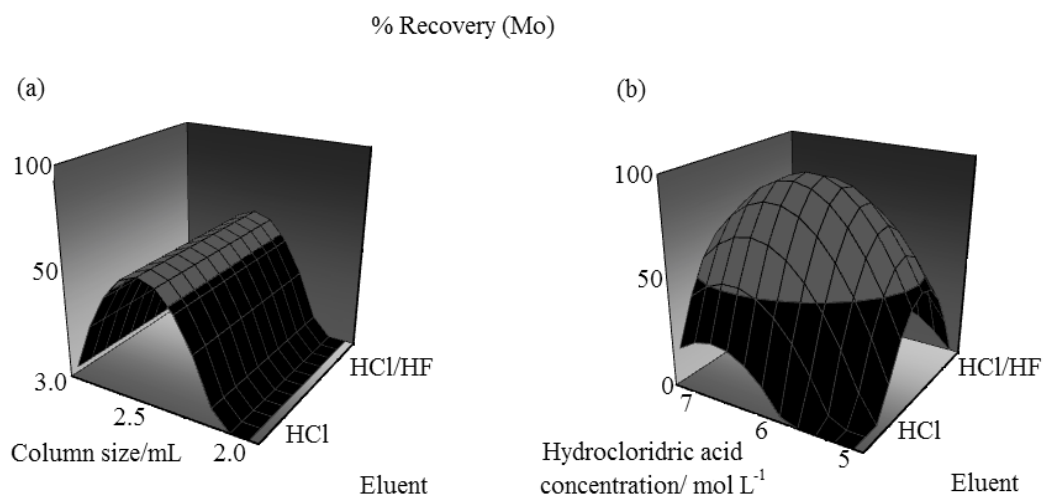


Figure 3
Response surfaces obtained from the factorial design for Mo recovery yield on (a) hydrochloric acid concentration and column size and (b) column size and eluent for Fe.

It was observed that Mo was co-eluted with Zn. In this fraction, yield percentages for Mo were found that ranged from 0.38 to 100%. According to Figs 3a and 3b, Mo recovery is maximized with the use of the mixture HCl/HF and associated with larger columns and more concentrated acid (HCl).

Therefore, considering the influences of the variables for each element and the commitment to obtaining the highest recoveries for Cu, Zn and Mo, the most favorable experimental conditions were: the use of a column (dimensions: 5.0 cm high and 1.0 cm in internal diameter) containing 2.5 mL of

AG-MP-1 (100-200 mesh), HCl at 7 mol L⁻¹ and the HCl/HF mixture as eluent to remove iron.

The metal recoveries are performed in three consecutive elutions: the Cu fraction (with HCl

7 mol L⁻¹), the elimination of Fe (with the HCl 0.5 mol L⁻¹ and HF 1 mol L⁻¹ mixture) and the co-elution of Zn and Mo (with HNO₃ 0.5 mol L⁻¹). The purification scheme is detailed in Table 2.

Table 2 - Protocol for Cu, Fe, Zn and Mo purification by ion-exchange.

Step	Reagent
Column washing	6 mL HNO ₃ 0.5 mol L ⁻¹ + 3 mL H ₂ O
Column conditioning	10 mL HCl 7 mol L ⁻¹ + 0.001% H ₂ O ₂
Sample load	2 mL HCl 7 mol L ⁻¹ + 0.001% H ₂ O ₂
Matrix removal	6 mL HCl 7 mol L ⁻¹ + 0.001% H ₂ O ₂
Cu elution	24 mL HCl 7 mol L ⁻¹ + 0.001% H ₂ O ₂
Fe elution	10 mL HCl:HF (0.5:1 mol L ⁻¹)
Mo and Zn elution	12 mL HNO ₃ 0.5 mol L ⁻¹

The HCl solutions used in the column conditioning steps for the removal of the matrix and Cu elution had the addition of 0.001% hydrogen peroxide. This is a strong oxidizing agent that keeps the elements in solution in a single oxidation state, thus avoiding isotopic fractionation Maréchal & Albarède (2002). Although co-elution occurred, the Zn and Mo-containing fraction can be used in the determinations of isotopic ratios of the two metals because there is no isobaric interference between them. Considering that the probability of occurrence of polyatomic ions is small and that there are strategies in the method that allow the minimization and/or correction of this type of interference, it would be disadvantageous to add more steps in the method to separate Zn from Mo. This is because there would be increased time and reagent expenses, the greater possibility of errors and contamination, and isotopic fractionation for both metals.

In order to decrease nitrogen- and oxygen-bearing interference species during the Mo

ICPMS measurements, we have used an ultrasonic nebulizer. The effective and efficient use of the ultrasonic nebulizer to reduce or even eliminate the formation of polyatomic interferences was evaluated by monitoring of ⁹⁷Mo. This isotope is free of interferences and can be used to assess possible changes in the ⁹⁵Mo isotope signal that undergoes the influence of the mentioned polyatomic species. The ^{97/95}Mo ratios of the pure standard (0.62655 ± 0.00004) and of the purified fraction of the synthetic sample (0.62656 ± 0.00004) were the same within the analytical error, thus revealing that there is no evidence of Zn interference in the Mo isotopic ratios.

The HCl/HF mixture was efficient in separating iron from the molybdenum without the need to introduce a second chromatographic column. In addition, the degree of separation achieved between these elements was equivalent to that indicated by Pietruszka & Reznik (2008), in which the main interferers (X) had an X/Mo < 1 ratio.

3.2. APPLICATION OF THE PURIFICATION METHOD FOR DIFFERENT GEOLOGICAL MATERIALS

Cu, Zn and Mo elution were performed in different geological materials (granodiorite, limestone and river sediments) using the purification scheme described above. To evaluate the degree of recovery, the concentration of the metals in the fraction eluted from the columns was compared with the concentrations of these metals in the aliquots that were not purified.

Recoveries of metals in real samples were better than the synthetic sample, reaching the following average percentages: 93.7 % for Cu, 94. % for Zn and 96.5% for Mo (table 3). This

effect can be explained by a premature elution mainly of Cu, but also of Zn, in the absence of matrix, as demonstrated by Chapman *et al.* (2006). These authors showed that this effect varies with matrix type and is most pronounced for samples rich in Fe, like the samples considered in the present work.

Furthermore, purification of Mo became simpler and faster compared to other methods currently described in the literature, which usually need several purification steps and use at least two different resins (Migeon *et al.* 2015).

Table 3 - Recovery of Cu, Zn and Mo after chromatographic column elution (n=3)

Sample	Element		
	Copper		
	Expected value (mg L ⁻¹)	Obtained value (mg L ⁻¹)	Recovery (%)
Granodiorite (GSP-2)	4.23 ± 0.21	3.93 ± 0.20	93.0 ± 1.32
Limestone (JLS-1)	1.40 ± 0.05	1.36 ± 0.02	91.0 ± 0.05
Buffalo river sediment (SRM 8704)	0.36 ± 0.04	0.34 ± 0.04	95.0 ± 0.11
Xingu river sediment (CA2)	2.80 ± 0.05	2.59 ± 0.11	93.0 ± 0.04
Amazon river sediment (CA7)	8.98 ± 0.56	8.66 ± 0.75	96.46 ± 0.06
	Zinc		
	Expected value (mg L ⁻¹)	Obtained value (mg L ⁻¹)	Recovery (%)
Granodiorite (GSP-2)	12.20 ± 0.19	11.18 ± 2.94	91.7 ± 1.81
Limestone (JLS-1)	3.20 ± 0.05	3.04 ± 0.01	95.0 ± 0.03
Buffalo river sediment (SRM 8704)	8.90 ± 0.03	8.50 ± 0.07	91.8 ± 0.01
Xingu river sediment (CA2)	8.03 ± 0.05	7.98 ± 0.05	99.37 ± 0.05
Amazon river sediment (CA7)	27.67 ± 0.43	25.77 ± 0.05	93.13 ± 0.05
	Molybdenum		
	Expected value (μg L ⁻¹)	Obtained value (μg L ⁻¹)	Recovery (%)
Granodiorite (GSP-2)	21.0 ± 0.02	20.0 ± 0.01	94.7 ± 2.01
Limestone (JLS-1)	15.2 ± 0.41	14.79 ± 0.44	97.0 ± 0.03
Buffalo river sediment (SRM 8704)	23.1 ± 0.24	22.84 ± 1.20	98.0 ± 0.05
Xingu river sediment (CA2)	27.5 ± 0.12	25.87 ± 0.67	94.0 ± 0.02
Amazon river sediment (CA7)	50.7 ± 0.21	50.29 ± 1.30	99.0 ± 0.03

3.3. Cu, Zn AND Mo ISOTOPIC MEASUREMENTS

To certify that the separation method does not cause isotopic fractionation, isotopic ratios of metals were measured in the pure monoelementary solutions used to produce the synthetic sample, with isotopic ratio values taken as a reference.

In the pure Cu solution (lot HC 109865), the value found for $\delta^{65/63}\text{Cu}$ reported in relation to ERM AE 633 was $-1.65 \pm 0.05 \text{ ‰}$ (2s), while in the synthetic sample after elution from the column it was $-1.57 \pm 0.05 \text{ ‰}$ (2s). For Zn solution (lot HC 112017) the values of $\delta^{66/67}\text{Zn}$ and $\delta^{68/67}\text{Zn}$, both reported in relation to IRMM 653 were $-0.62 \pm 0.04 \text{ ‰}$ for $\delta^{66/67}\text{Zn}$ and $-1.07 \pm 0.04 \text{ ‰}$ for $\delta^{68/67}\text{Zn}$, before purification and, in the same order, after purification were $-0.64 \pm 0.03 \text{ ‰}$ (2s) and $-1.10 \pm 0.03 \text{ ‰}$ (2s).

For Mo, the delta values of the JMC (Alfa Aesar Specpure®) (lot 61200523) standard solution were reported in relation to itself; therefore the calculation of $\delta^{98/95}\text{Mo}$ was performed after the passage of this solution through the column, and the value found was $0.00 \pm 0.02 \text{ ‰}$ (2s). As the delta values of the purified aliquots and the solutions without purification can be considered comparable, it

can be concluded that the proposed separation method does not cause isotopic fractionation in the metals investigated.

The results of geological samples obtained for Cu and Zn are given in Table 4 and those obtained for Mo are reported in Table 5. The uncertainties are presented as twice the standard deviation (2s) and also as expanded uncertainty U, calculated using the coverage factor $k = 2$, which gives a confidence level of approximately 95%.

Although most studies in this area do not consider the correlation of the different isotopes and merely express the uncertainty as twice the standard deviation (2s), in this study, the measurement results were corrected using the uncertainty propagation calculation based on "Guide to the Expression of Uncertainty in Measurement" (ISO GUM 95 2002) and the Eurachem/CITAC Guide (2005).

According to the ISO GUM 95 (2002) the indication of the combined standard uncertainties is very important to produce exact values. This, when associated with methodology, increases the traceability and reliability of the data.

Table 4 - δ values and precision of Cu and Zn for the selected samples.

Sample	$\delta^{65/63}\text{Cu}$ (‰)	U	2s	$\delta^{66/67}\text{Zn}$	U	2s	$\delta^{68/67}\text{Zn}$	U	2s
		(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)
Granodiorite (GPS 2)	+0.47	0.10	0.08	-1.75	0.10	0.04	-0.90	0.10	0.05
Limestone (JLS-1)	-0.30	0.41	0.10	-0.12	0.07	0.05	-0.23	0.07	0.05
Buffalo River sediment (SRM-8704)	+0.45	0.80	0.05	+2.97	0.09	0.06	+6.44	0.09	0.06
Xingu river sediment (CA2)	+1.51	0.10	0.07	+0.32	0.07	0.03	+0.55	0.07	0.03
Amazon river sediment (CA7)	+0.95	0.25	0.09	+0.70	0.09	0.08	+1.26	0.09	0.08

$\delta^{65/63}\text{Cu}$ - reported related to ERM-AE633. $\delta^{66/67}\text{Zn}$ and $\delta^{68/67}\text{Zn}$ - reported related to IRMM 653.

Table 5 - δ values and precision of Mo for the selected samples

Samples	$\delta^{98/95}\text{Mo}$ in relation to JMC Alfa Aesar (‰)	U	2s	$\delta^{98/95}\text{Mo}$ normalized para o NIST 3134
		(‰)	(‰)	
Granodiorite (GPS2)	+0.22	0.08	0.07	-0.11 $\pm$ 0.07
Limestone (JLS-1)	-0.90	0.10	0.06	-1.24 $\pm$ 0.06
Buffalo River sediment (SRM-8704)	+1.06	0.18	0.02	+0.72 $\pm$ 0.02
Xingu river sediment (CA2)	+0.64	0.02	0.02	+0.31 $\pm$ 0.02
Amazon river sediment (CA7)	+0.11	0.06	0.03	-0.23 $\pm$ 0.03

It is important to report that for Zn and Mo, the comparability of the delta values with the literature data is very restricted because they do not have an internationally accepted isotopic reference material.

Some studies (Ponzevera *et al.* 2006; Moeller *et al.* 2012) have been used IRMM-3732 as a zero delta for Zn. The advantage of this material is that it can be traced to JMC Lyon (reference material in the first Zn isotopic studies). However, further analysis by independent laboratories is needed to accurately calibrate IRMM-3702 in relation to JMC Lyon. In this study, the values of the investigated samples were reported in relation to IRMM 653 but it was not possible to compare them to other work, due to the lack of references in the literature.

Regarding Mo, it is quite common to use standards calibrated in the laboratory, mainly using standard solutions produced by Johnson Matthey Company (JMC). As described by Goldberg *et al.* (2013), ten Mo solutions had their $\delta^{98/95}\text{Mo}$ values normalized to NIST SRM 3134. Six of these were analyzed by four laboratories, and although the data showed a difference of up to 37 ‰ from one standard to the other, the results between laboratories were quite consistent, allowing them to be used as references for normalization. For example, Nakagawa *et al.* (2008) investigated the JMC identified standards Kyoto-Mo and Big Mo and found, for $\delta^{98/95}\text{Mo}$, a difference between them of $+0.12 \pm 0.01$ ‰ (2s). The same result was found by Goldberg *et al.* (2009) ($+0.11 \pm 0.06$ ‰ (2s)). Migeon *et al.* (2015) reported a value of $\delta^{98/95}\text{Mo}$ of -0.25 ± 0.02 ‰ for the JMC-Lyon standard, the same as Greber *et al.* (2012) and Goldberg *et al.* (2013) had found

for the Bern-Mo JMC standard (-0.29 ± 0.08 ‰ and -0.27 ± 0.06 ‰, respectively). On the other hand, Wen *et al.* (2010), referring to this pattern as "JMC Sie", reported the value of $+0.04 \pm 0.13$ ‰.

In the present study, as already mentioned, the standard solution JMC Mo Alfa Aesar Specpure® (Lot 61200523) was used as the delta zero. The delta values of the two sediments of the Amazon River Basin and that of the three certified reference materials were normalized to NIST SRM 3134. For data conversion, a value of $\delta^{98/95}\text{Mo}$ equal to -0.34 ± 0.05 ‰ was adopted for the standard JMC Alfa Aesar in relation to NIST SRM 3134 (value taken from Goldberg *et al.* 2013).

For granodiorite the value found for $\delta^{98/95}\text{Mo}$ in this study is consistent to that reported by Yang *et al.* (2015) (-0.17 ± 0.06 (2s)), within the uncertainty range. For the other samples, references that allow comparisons were not available in the literature. For copper, samples from this study were reported in relation to SRM ERM AE 633. This material is internationally recognized as the delta zero reference standard and was calibrated against the late NIST SRM 976. Moeller *et al.* (2012) presented the first isotopic data reported for ERM - AE 633 and investigated two standards, identified as Romil Cu and Bergen Cu; the $\delta^{65/63}\text{Cu}$ values found for them were $+0.17 \pm 0.06$ ‰ and -0.07 ± 0.04 ‰, respectively. These patterns, when reported to NIST SRM 976, showed similar values ($+0.18 \pm 0.06$ ‰ and -0.06 ± 0.06 ‰), and demonstrate the proximity between these two SRM. Thus, it can be considered that $\delta^{65/63}\text{Cu}$ values for granodiorite obtained with the proposed method are comparable, within

the uncertainty, to the values reported by Li *et al.* (2009) ($+0.30 \pm 0.04 \text{ ‰}$) and Bigalke *et al.* (2010) ($+0.35 \pm 0.04 \text{ ‰}$), even though the first two reported to NIST SRM 976.

This study presents the isotopic composition of Cu, Zn and Mo of samples from the Amazon Basin that present quite distinct environmental conditions. While sample from the Amazon River was collected in more oxidized conditions and partially affected by the Atlantic Ocean, sample from the Xingu River was collected in more reduced environment. These two rivers also display distinct hydrological features since the Amazon is dominated by suspended sediments derived mostly from the Andes, while the Xingu has much less suspended materials and drain old cratonic terrains of the Brazilian

Amazon shield. Except for the $\delta^{65/63}\text{Cu}$ values observed in the Xingu sediments, our results are within the range of previous data from the Amazon Basin. The higher value for the Amazon sediments probably reflects an influence of the ocean that is known to have positive $\delta^{66/64}\text{Zn}$ values (Little *et al.* 2014). Regarding Mo, the values reported in this study are the first for the Amazon basin and corroborate with the results found for Cu and Zn. The positive delta values for the Xingu river sediment reflects the reducing conditions and still show that this type of sediment contain Mo that is heavier than the sediment ocean input (Amazon river - $\delta^{98/95}\text{Mo} = -0.23 \text{ ‰}$) as also observed by Siebert *et al.* (2003).

3.4 ACCURACY AND PRECISION OF THE METHOD

To assess the accuracy of the method, the isotopic ratios for Cu and Zn of Isotopic Reference Materials ERM-AE 633 and IRMM 653, respectively, were measured several times over three analytical sessions. It was not possible to perform analysis for Mo due to the absence of isotopic reference material for this element.

The mean values of the $^{65/63}\text{Cu}$ and $^{66/67}\text{Zn}$ ratios, after the correction of data by the SSB method, were 0.44564 ± 0.0005 and 0.0245525 ± 0.0000053 , respectively. Considering the errors, there were no differences between the means obtained experimentally and the values reported for the Certified Reference Materials considered (0.44563 ± 0.00042 for $^{65/63}\text{Cu}$, 0.0245516 ± 0.0000070 for $^{66/67}\text{Zn}$).

During the same analytical session the variations in the measurements of the Cu and Zn isotopic ratios of the Isotopic Certified

Reference Materials and the Mo of the JMC reference solution were evaluated. Considering the three sessions carried out the precision in terms of repeatability ranged 0.06 to 0.11 ‰ (2s) for Cu; 0.04 to 0.06 ‰ (2s) for Zn and 0.02 ‰ to 0.03 ‰ (2s) for Mo.

Reproducibility, shown in Figs 4, 5 and 6, of the isotope ratio values was estimated from repeat measurements of Cu, Zn isotopic standards and Mo solution standards. For Cu, the reproducibility of $\delta^{65/63}\text{Cu}$ measurements is based on ten repeat analyses of the ERM-AE 633. These yielded a precision of $\pm 0.07 \text{ ‰}$ (2s). For Zn, thirty-eight repeat analyses of the IRMM 653 gave $\pm 0.09 \text{ ‰}$ (2s) for $\delta^{66/67}\text{Zn}$, and for Mo sixteen repeat analyses of the JMC (Alpha Aesar Specpure®) solution gave $\pm 0.02 \text{ ‰}$ (2s) for $\delta^{98/95}\text{Mo}$. Both data sets were obtained over a period of three years.

3.5. PRECISION IN THE ANALYSIS OF GEOLOGICAL MATERIALS

As listed in Table 6, the precision achieved in the determinations of the isotopic ratios of the geological materials employed in this study is compatible with or even better than other

studies that have also developed purification methods for Cu, Zn or Mo and performed determinations of their isotopic ratios by MC-ICPMS in real sample.

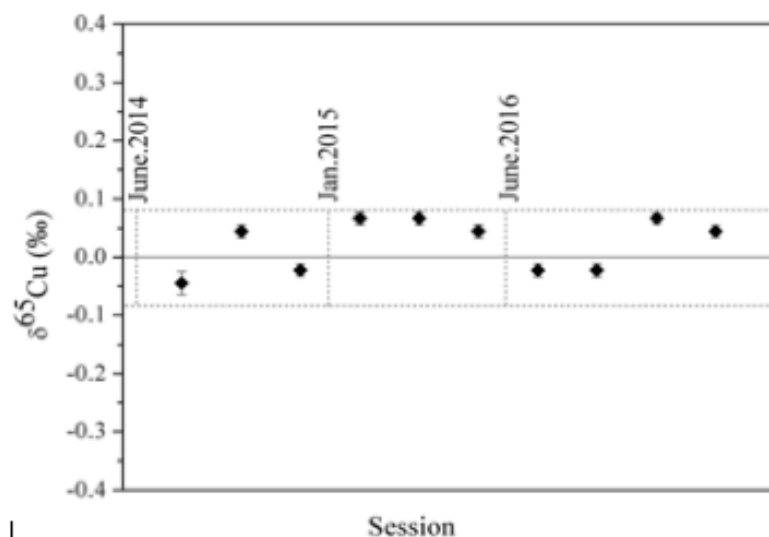


Figure 4
Reproducibility of $\delta^{65/63}\text{Cu}$ measurements (ERM-AE-633) for three analytical sessions. The mean long-term reproducibility is 0.07 ‰ (2s, n=10).

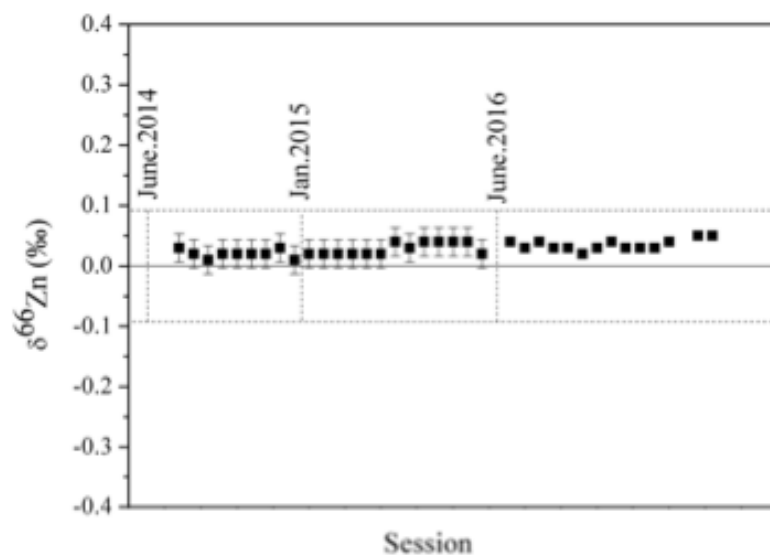


Figure 5
Reproducibility of $\delta^{66/67}\text{Zn}$ measurements (IRMM-653) for three analytical sessions. The mean long-term reproducibility is 0.09 ‰ (2s, n=38).

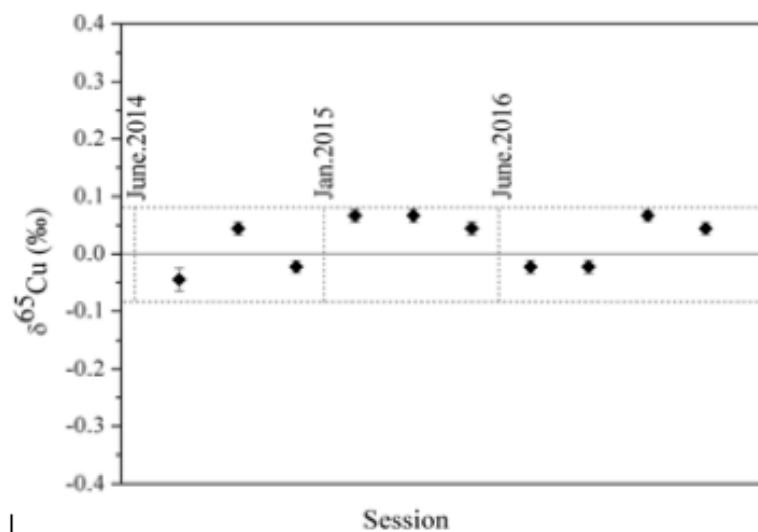


Figure 6.
Reproducibility of $\delta^{98/95}\text{Mo}$ (Alfa Aesar JMC) measurements for three analytical sessions. The mean long-term reproducibility is 0.02 ‰ (2s, n=16).

Table 6 - Precisions achieved by different methods and work groups (n=3)

Reference	Instrument (MC-ICPMS)	Correction of mass bias	External reproducibility (2s) ‰	
			$\delta^{65/63}\text{Cu}$	$\delta^{66/64}\text{Zn}$
This study	Thermo Finnigan Neptune	SSB (direct)	0.05 - 0.10 (n=3)	0.03 - 0.08 (n=3)
Maréchal <i>et al.</i> (1999)	Plasma 54	SSB (EEN)	0.04* (n=6)	0.04* (n=6)
Chapman <i>et al.</i> (2006)	GVi Isoprobe	SSB	0.08 - 0.15 (n=6 or 8)	0.07 - 0.17 (n=10)
Petit (2009)	Nu Plasma	SSB	0.01 - 0.03 (not reported)	0.01 - 0.07 (not reported)
Arnold <i>et al.</i> (2010)	Nu Plasma	Double-spike	-----	0.04 - 0.15 (n=3)
Skierszkan <i>et al.</i> (2016)	Nu Plasma	Double-spike	-----	0.001 - 0.11 (n=3)
Peel <i>et al.</i> (2008)	GVi Isoprobe	SSB	0.00- 1.00 (not reported)	0.02 - 1.43 (not reported)
$\delta^{97/95}\text{Mo}$ or $\delta^{98/95}\text{Mo}$				
Reference	Instrument (MC-ICPMS)	Correction of mass bias	External reproducibility 2s (‰)	
This study	Thermo Finnigan Neptune	SSB (direct)	0.02 - 0.07 (n=3)	
Malinovsky <i>et al.</i> (2005)	Thermo Finnigan Neptune	External normalization	0.08 - 0.10 (n=6)	
Skierszkan <i>et al.</i> (2016)	Nu Plasma	Double-spike	0.01 - 0.10 (n=3)	
Pearce <i>et al.</i> (2010)	Nu instruments	Double-spike	0.02 - 0.40 (not reported)	

* Value reported for all samples investigated.

4. CONCLUSION

The results show that Cu, Fe, Mo and Zn can be successfully isolated from the geological matrix using six steps in a single column, and that the resulting purity is sufficient for direct analysis with correction by SSB employing MC-ICPMS. It can be applied to different types of geological samples, which have a diverse matrix, most of them with high concentrations of iron and low levels of the metals studied, and one with high calcium level and very low levels mainly of Mo (Limestone).

The results of the comparison of the isotopic compositions of Cu and Mo obtained for granodiorite, with respect to data reported in the literature, show that the simpler and multi-element method developed in this study can be safely used within the necessary limits of accuracy as a multi-proxy tool in isotope geochemistry.

The precision and accuracy of the measured isotope ratios are comparable to the analytical uncertainties reported by other authors in

similar investigations. Therefore, the data obtained suggest that the analytical method applied in this study provides accurate and reliable measurements of Cu, Zn and Mo isotopes for different geological samples; and, the separation methods and instrumental corrections can be simplified without damaging the reliability and precision of the data.

It is expected that this work will contribute to the advances of studies related to the isotopic geochemistry of transition metals and their applications as local and global proxies in paleo-environmental, biogeochemical and archaeological studies, among others.

Although limited in scope, this study report the first data for Cu, Zn and Mo isotopic signature of surficial sediments from Amazon River Basin, and reveal significant variation in $\delta^{65/63}\text{Cu}$ (+1.51 to +0.95 ‰), $\delta^{66/67}\text{Zn}$ (+0.32 to +0.70 ‰) $\delta^{98/95}\text{Mo}$ (+0.31 to -0.23 ‰) between samples collected from Xingu and Amazon River.

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