THE METHOD FOR Cu AND Zn ISOTOPE RATIO DETERMINATION BY MC ICP-MS USING THE AG MP-1 RESIN

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ABSTRACT. The isotopic composition of copper is of great interest for researchers in various fields of science, geochemistry and hydrology in particular, wherein the consideration is being given to the variations in the isotopic composition of the Earth's crust, extraterrestrial matter, and water basins, as well as to the origin and transfer of matter. Zn isotopes appear to be promising for identifying the sources and pathways of the environmental pollution. The aim of this study involves the refinement and validation of the zinc and copper isotopic ratio determination methodology covering the whole process from sample digestion to MC ICP-MS measurements. For this reason, as well as to assess the suitability of the methodology for the analysis of environmental samples, Zn and Cu isotopic analysis of the BHVO-2, BCR-2 and AGV-2 USGS certified reference materials has been performed. The method for determination of Cu and Zn stable isotope ratios by multi-collector inductively coupled plasma mass spectrometry in environmental samples is developed. The application of the AG MP-1 resin with optimized layer parameters (resin bed height 3.5 cm, diameter 1 cm) provides the high-purity Cu and Zn fractions. The method is characterized by high throughput and adequate analytical figures of merit when using the standard-sample bracketing technique for mass bias correction. The procedural blanks related to chemical dissolution and ion exchange procedures are lower than 1 and 3 ng for Cu and Zn, respectively, assuring no blank effect on the isotopic composition of samples. The accuracy and precision obtained for Cu and Zn isotope measurements in the BHVO-2, BCR-2 and AGV-2 geological certified reference materials demonstrate good agreement with the reference values published.

SHORT COMMUNICATION

МЕТОДИКА ОПРЕДЕЛЕНИЯ ИЗОТОПНЫХ ОТНОШЕНИЙ Cu И Zn МЕТОДОМ МК ИСП-МС С ИСПОЛЬЗОВАНИЕМ СМОЛЫ AG MP-1

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АННОТАЦИЯ. Изотопный состав меди представляет большой интерес для исследователей в различных областях науки, в частности в геохимии и гидрологии, где рассматриваются вариации изотопного состава земной коры и внеземного вещества, водных бассейнов, а также вопросы происхождения и процессы переноса вещества. Изотопы Zn перспективны для определения источников и путей загрязнения окружающей среды. Целью данного исследования является уточнение и валидация методики измерения изотопных соотношений цинка и меди, охватывающей весь процесс – от разложения образца до измерений методом МК ИСП-МС. Для оценки пригодности методики анализа образцов окружающей среды был проведен изотопный анализ Zn и Cu в стандартных образцах BHVO-2, BCR-2 и AGV-2, сертифицированных Геологический службой США. Разработан метод определения отношений стабильных изотопов Cu и Zn с помощью мультиколлекторной масс-спектрометрии с индуктивно связанной плазмой в экологических пробах. Применение смолы AG MP-1 с оптимизированными параметрами слоя (высота слоя смолы 3.5 см, диаметр 1 см) обеспечивает получение фракций Cu и Zn высокой чистоты. Метод отличается высокой производительностью и удовлетворительными метрологическими характеристиками при использовании брекетинга для коррекции дискриминации ионов по массе. Процедурные бланки (холостые пробы), относящиеся к процедурам химического растворения и хроматографии, составляют менее 1 нг для Cu и 3 нг для Zn, что гарантирует отсутствие значимого влияния холостой (контрольной) пробы на изотопный состав образцов. Точность и прецизионность, полученные при измерениях изотопов Cu и Zn в сертифицированных геологических стандартных материалах BHVO-2, BCR-2 и AGV-2, демонстрируют хорошее согласие с опубликованными сертифицированными значениями.

КЛЮЧЕВЫЕ СЛОВА: изотопные отношения Cu и Zn; МК ИСП-МС; брекетинг; хроматография; смола AG MP-1

1. INTRODUCTION

The isotopic composition of copper is of great interest for researchers in various fields of science, geochemistry and hydrology in particular, wherein consideration is being given to the variations in the isotopic composition of the Earth's crust, extraterrestrial matter, and water basins, as well as to the origin and transfer of matter [Vanhaecke et al., 2009]. Environmental studies, closely related to these areas, use copper isotopes to reveal the sources and pathways of pollution migration in the areas of mining and copper production.

Recently, an increase in the number of studies aimed at determining natural and anthropogenic sources of pollution is observed [Vasic et al., 2012; Grebenshchikova et al., 2017; Gustaytis et al., 2018]. The sources of trace elements and metalloids in atmospheric emissions are evidently associated not only with natural processes, such as weathering of rocks, mineralization and dust storms, but also with industrial activities, i.e. smelting, metal processing, and other technological processes. Large volumes of smelting activity cause a significant spatiotemporal variability in the concentrations of heavy metals in the lower atmosphere [Melaku et al., 2008]. In this regard, Zn isotopes appear to be promising for identifying sources and pathways of the environmental pollution. However, the data on the δ^{66}Zn values in liquid and solid forms of precipitation have turned out to be largely insufficient [Novák et al., 2016; Voldřichová et al., 2014]. Moreover, there is an obvious potential for determination of zinc isotopic variations in environmental studies.

The analytical precision is of the utmost importance for isotope ratio measurement when subtle variations in the isotopic composition of a target element are to be discovered and quantified. Multicollector ICP MS (inductively coupled plasma mass-spectrometry) instrumentation can successfully compete in isotope ratio precision with thermal ionization mass spectrometry (TIMS) – the technique traditionally used for accurate and precise isotopic analysis of metallic elements [Vanhaecke et al., 2009].

Moreover, one of the advantages of MC ICP-MS is the possibility of plasma ionization of the elements with high ionization potential, such as copper, that cannot be analyzed in thermal ionization mass spectrometry [Moynier et al., 2017].

Due to the differences in the efficiency of ion extraction, transmission and detection as a function of an analyte mass, an isotope ratio measured by ICP-MS may be significantly biased from the corresponding true value. This phenomenon is referred to as mass discrimination (mass bias) and may reach several % per mass unit [Vanhaecke et al., 2009]. Various approaches have been developed for ICP-MS mass bias correction including the use of an external and internal standards.

The application of an external standard implies that the solution containing an isotopic standard of the target element (with an isotopic composition or at least an isotope ratio known) is measured, and a correction factor is calculated on the basis of the bias observed between the measured value and the true value of the isotope ratio of interest [Vanhaecke et al., 2009]. Bracketing (SSB, standard-sample bracketing) – a special case of correction using an external standard – implies that the measurement of each sample is preceded and followed by the measurement of an isotopic standard. Most of the copper isotopic ratios are obtained by MC ICP-MS using bracketing technique [Maréchal et al., 1999; Maréchal, Albarède, 2002; Mathur et al., 2005].

The first measurements of zinc and copper isotopic composition were performed by the thermal ionization mass-spectrometry (TIMS) in 1960–1970 (see the review by [Moynier et al., 2017] and the references therein). This method is considered suitable for measuring isotopes, predominantly in combination with the double spike technique. However, the majority of studies on zinc isotopic measurements consider the inductively coupled plasma ionization in combination with bracketing or double spike technique as the most applicable method of isotopic analysis. Moreover, in this case, the mass bias correction is viable using the method of internal normalization with copper as an internal standard.

Obtained isotopic ratios are commonly expressed as δ (‰) relative to NIST SRM 976 (Cu) and JMC-Lyon (Zn) standard reference materials with certified isotope ratios used for bracketing:

$$\delta^{65}Cu = \left[\frac{\left(\frac{^{65}Cu}{^{63}Cu}\right)_{sample}}{\left(\frac{^{65}Cu}{^{63}Cu}\right)_{NISTSRM976}} - 1 \right] \times 1000,$$

$$\delta^{66}Zn = \left[\frac{\left(\frac{^{66}Zn}{^{64}Zn}\right)_{sample}}{\left(\frac{^{66}Zn}{^{64}Zn}\right)_{JMCLyon}} - 1 \right] \times 1000.$$

The precision of copper and zinc isotopic ratio measurement depends not only on proper mass bias correction, but

also on the sample preparation quality, including the degree of analyte purification, the lowest possible level of control (blank) sample, and the analyte yield in solution. Due to the great influence of sample matrix on the mass bias, the target element needs to be isolated from the matrix for obtaining high-quality results and it is even necessary to match the concentration of the target element in the samples with the standards within ±30 % [Vanhaecke et al., 2009], which is done by the thorough calculation of sample masses and the subsequent dilution of samples and standards under similar conditions.

The procedure of target element isolation usually consists of one- or several-stage chromatographic separation of pure analyte fractions on ion-exchange resins [Maréchal et al., 1999; Maréchal, Albarède, 2002; Mathur et al., 2005; Borrok et al., 2007; Dirks et al., 2010]. However, the researchers noted the fractionation of transition metal isotopes over an ion-exchange column due to the fractionation between metals adsorbed on the resin and their aqueous ions in an eluate [Maréchal, Albarède, 2002]. Therefore, the use of chromatographic isolation procedures with a certain type of resins requires checking for the absence of such fractionation, for example, by comparing between the isotopic ratios of copper obtained by direct analysis and those obtained after the chromatographic separation [Mathur et al., 2005]. Besides, possible isobaric interferences in mass spectrometric measurements are to be monitored for Zn, ^{64}Ni in particular.

The aim of this study involves the refinement and validation of zinc and copper isotopic ratio measurement methodology covering the whole process from sample digestion to MC ICP-MS measurements. For this reason, as well as to assess the suitability of the methodology for the analysis of environmental samples, Zn and Cu isotopic analysis of the BHVO-2, BCR-2 and AGV-2 USGS certified reference materials was performed.

2. MATERIALS AND METHODS

The study was conducted in the cleanroom facilities (ISO 6, 7) of the Zavaritsky Institute of Geology and Geochemistry, Ural Branch of the Russian Academy of Sciences. The experiments involved the use of PFA (Savillex, USA) or PTFE (Nalgene, USA) labware. Double sub-boiling purification was applied to ACS grade hydrofluoric, nitric and hydrochloric acids in PFA and PTFE purification systems (Savillex, USA; Berghof, Germany). Arium®pro unit (Sartorius, Germany) was used for obtaining ultrapure deionized water (18.2 MΩ·cm⁻¹).

For Cu and Zn chromatographic separation, the AG MP-1 strongly basic anion exchange resin of analytical grade (Bio-Rad Inc., USA) was used. This macroporous resin is usually used in an ionic form whose selectivity for the functional group is lower than that for the sample ions to be exchanged. The sample ions are then exchanged onto the resin when introduced, and can be eluted by introducing an ion with higher affinity for the resin or a high concentration of an ion with equivalent or lower affinity. The resin was loaded into columns in an aqueous suspension form.

Table 1. Neptune Plus and ASX 110 FR instrumental parameters for Cu and Zn isotope measurements

Табл. 1. Операционные параметры Neptune Plus и ASX 110 FR при изотопном анализе Cu и Zn

Instrumental parameters		Cu Faraday Cup configuration		Zn Faraday Cup configuration	
Ar cooling	15 L min^{-1}	–	–	L2	^{64}Zn
Ar auxiliary	0.9 L min^{-1}	L1	^{63}Cu	–	–
Ar sample	1.08 L min^{-1}	C	^{65}Cu	C	^{66}Zn
Nebulizer flow	50 µL min^{-1}	–	–	H1	^{67}Zn
Wash time	60 sec	–	–	H2	^{68}Zn
Takeup time	50 sec	–	–	–	–
Torch power	1050 W	–	–	–	–
Sensitivity for ^{63}Cu(^{66}Zn)	15 V ppm^{-1}	–	–	–	–

PE (polyethylene) frits were placed both in the bottom of the column and over the resin bed to prevent the resin from stirring.

The column calibration procedure was performed using the "Multi-element calibration Standard 2" (Perkin Elmer, USA), which contained 31 elements including Cu and Zn. The measurement of elemental concentrations for elution curves was conducted by a NexION 300S (Perkin Elmer, USA) quadrupole ICP mass-spectrometer. The elemental concentration was measured in a 1.5 wt. % HNO$_3$ solution.

For SSB, the SRM 976 (NIST, USA) Cu and JMC-Lyon Zn isotope standards were used. The AGV-2 andesite and BHVO-2 and BCR-2 basalts (USGS, USA) geological certified reference materials [Novák et al., 2016] were used for assessing the analytical figures of merit of the whole analytical procedure, including the sample digestion and chromatographic stages.

The measurement of Cu and Zn isotope ratios was performed by the SSB technique using a MC ICP-MS Neptune Plus (Thermo Fischer, Germany) with an ASX 110 FR automatic sample introduction system (Teledyne CETAC, USA) fitted by a PFA micro-flow nebulizer (50 µL min^{-1}) connected to a quartz spray chamber. Measurement sequence was similar for both Cu and Zn: blank, bracketing standard (Cu NIST SRM 976 or Zn JMC-Lyon), 1 sample, bracketing standard. Each individual acquisition contained 60 ratios collected at 8-second integrations with each block of 10 measurements followed by a 30 second baseline measurement. Blank correction was obtained using a 3 wt. % HNO$_3$ washing solution with a configuration of 20 cycles with 8 s integration time. The main parameters and Faraday cup configuration are presented in Table 1.

Cu and Zn Chromatographic Isolation. The studies described in [Streletskaya et al., 2020] formed the basis for conducting the chromatographic separation experiments. Given that the separation effectiveness increases with the increasing of resin layer height, two chromatographic columns of different dimensions and materials were packed.

The first column was made of quartz with an inner diameter of 0.7 cm and a resin bed height of 9 cm. Alternative standard PP (polypropylene) columns (Bio-Rad Inc., USA) with an inner diameter of 1 cm and a resin bed height of 3.5 cm were used. Column calibration was carried out using a multi-element solution. An aliquot of a solution containing 10 µg of each element was evaporated, dissolved in 0.5 mL of 10M HCl, centrifuged at 6.000 rpm for 15 min, and then loaded onto a column pre-conditioned with 5 mL of 10M HCl. Further, the sequence of eluents for a 9 cm column was as followed: 2 mL 10M HCl, 18 mL 4M HCl, 10 mL 1M HCl, and 6 mL H$_2$O. A 3.5 cm column reagent sequence included 1 mL 10M HCl, 9 mL 4M HCl, 5 mL 1M HCl and 5 mL H$_2$O. A 1 mL step elution was performed so that the volume of collected portions for elemental analysis comprised 1 mL. In order to eliminate the effect of isotopic fractionation accompanying the chromatographic separation of copper and zinc, all fractions of these elements were collected. The obtained portions were evaporated to dryness and dissolved in 3 mL of 1.5 % HNO$_3$ for the subsequent concentration measurement by a NexION 300S.

The resin regeneration stage or column washing was also examined with the aim of providing the volume of reagents necessary and sufficient for reducing the content of Cu, Zn and other interfering elements in the eluate to the level that did not affect the analytical figures of merit for the Cu and Zn isotope ratio determination. For both types of columns, this stage involved 3×5mL of 4M HCl followed by 5 mL of deionized H$_2$O. The volume of analyzed portion was 5mL. The treatment procedure prior to the elemental analysis was the same as for column calibration.

Chemical Preparation of Reference Materials. For the assessment of the analytical figures of merit of the whole analytical procedure, 0.05 g of the AGV-2 andesite and BHVO-2 and BCR-2 basalts were sampled in Savillex PFA vials. Then 3 mL HNO$_3$ and 1 mL HF (both concentrated) were added. The vials were screwed up and placed in the drying furnace heated to 120 °C for 3 days. After evaporating to dryness, the samples were admixed with 1 mL HNO$_3$ and 3 mL HCl (concentrated) and underwent another evaporation. After that, the obtained residue was dissolved in 4 mL of concentrated HCl and dried. Prior to the chromatographic step, the sample was admixed with 0.5 mL of 10 M HCl placed into PP Eppendorf vial and centrifuged at 6.000 rpm for 15 min.

3. RESULTS AND DISCUSSION

The Calibration of Chromatographic Columns. Fig. 1 shows the elution curves obtained for multi-element solution with the concentration of elements equal to 1 ppm prior to chromatography (with two heights of the resin layer provided). As a result of the experiment, the heights of the resin layer, both 3.5 and 9 cm, provide an acceptable purification and mass yield of Cu and Zn. However, the application of higher resin bed provides almost total purification of Zn. Despite that, a 9 cm resin bed tends to accumulate a bigger amount of matrix elements, which can negatively affect the accessibility of exchange centers for analytes.
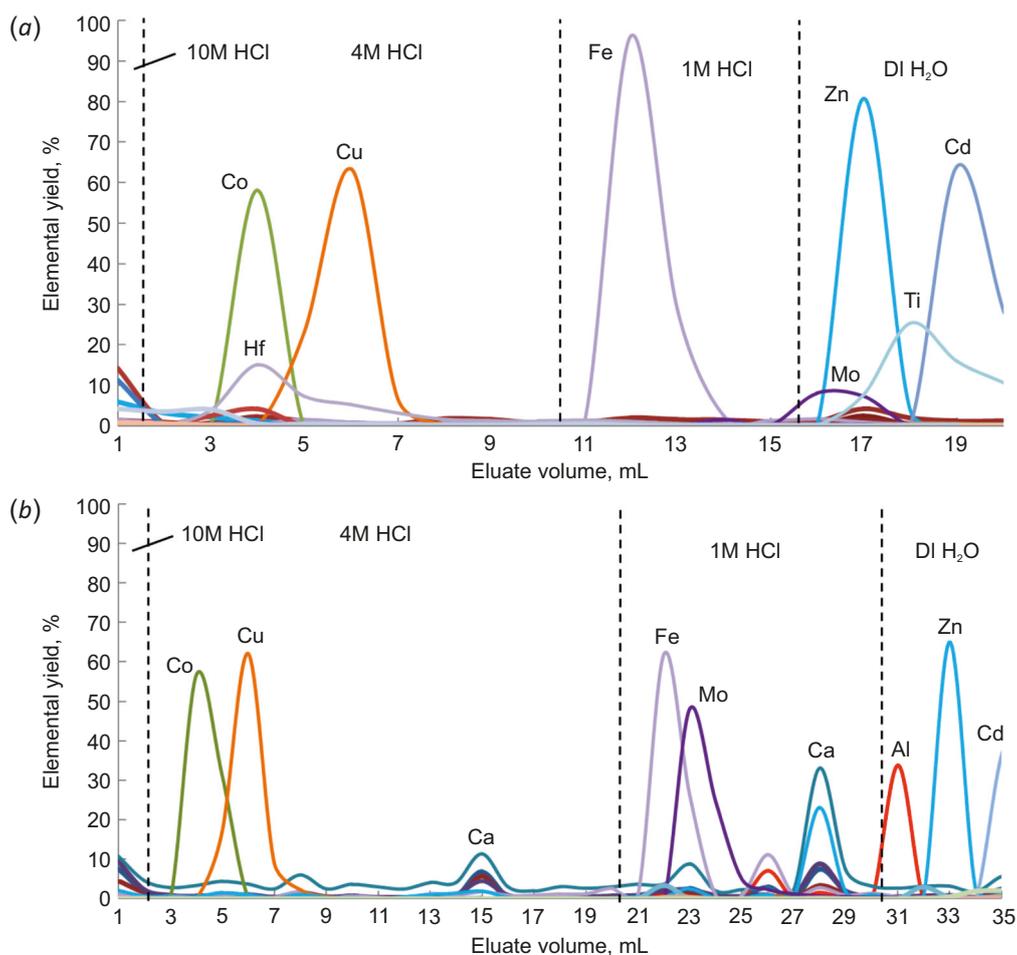
Fig. 1. Elution curves of a multi-element solution using the AG MP-1 resin bed of 3.5 (*a*) and 9 cm high (*b*).

Рис. 1. Кривые элюирования мультиэлементного раствора с использованием смолы AG MP-1 с высотой слоя 3.5 (*a*) и 9 см (*b*).
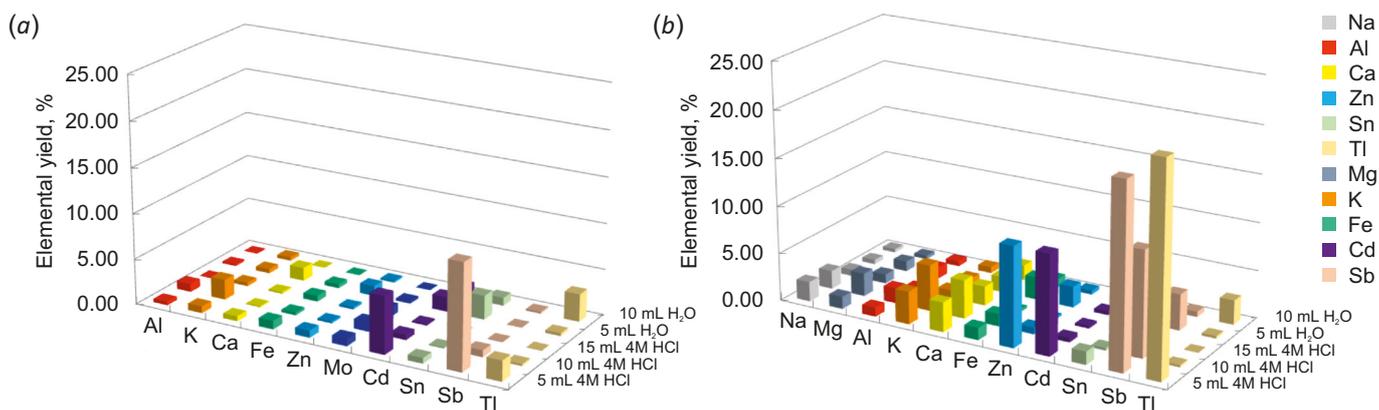

Fig. 2. Elemental yield in regenerative washing stage for the AG MP-1 resin bed of 3.5 (*a*) and 9 cm high (*b*) .

Рис. 2. Выход элемента в регенерирующей промывке смолы AG MP-1 с высотой слоя 3.5 (*a*) и 9 см (*b*).

Besides, the increased amount of accumulated elements results in extended time of resin regeneration prior to the next separation procedure.

Fig. 2 represents the elemental mass yield during the regenerative washing stage both for 3.5 and 9 cm resin beds. As was mentioned above, a higher (9 cm) resin bed retains a bigger amount of elements, resulting in the necessity for either repeated washing stage or enlarged volume of the reagents applied. Therefore, the decreased time of the whole chromatographic procedure, as well as the duration of regenerative washing stage, argues for an application of a 3.5 cm resin bed. The determined amount of molybdenum and thallium in Zn fraction causes no isobaric interferences during isotopic ratio measurement.

Table 2. Comparison of geological reference materials with $\delta^{65}Cu_{NIST976}$ and $\delta^{66}Zn_{JMC}$ values reported herein and stored in the GeoReM database

Табл. 2. Сравнение значений $\delta^{65}Cu_{NIST976}$ и $\delta^{66}Zn_{JMC}$ в геологических стандартных образцах, полученных в этой работе, с приведенными в базе данных GeoReM

CRM	$\delta^{65}Cu$, ‰	2SD	N*	$\delta^{66}Zn$, ‰	2SD	N*
BHVO-2 basalt in this study	0.14	0.04	5	0.20	0.08	8
BHVO-2 basalt in GeoRem	0.10	0.07	7	0.25	0.05	10
AGV-2 andesite in this study	0.12	0.04	5	0.21	0.06	8
AGV-2 andesite in GeoRem	0.10	0.04	6	0.29	0.06	4
BCR-2 basalt in this study	–	–	–	0.24	0.06	8
BCR-2 basalt in GeoRem	–	–	–	0.26	0.04	8

Note. *N is a number of measurements.
Примечание. *N – количество измерений.

The analysis of CRMs. Chromatographic preparation of CRM samples was performed according to the abovementioned scheme using the AG MP-1 resin with a 3.5 cm resin bed. Mass scanning prior to the analysis of Cu and Zn fractions obtained from geological reference materials confirmed the acceptable purity of the fractions obtained. No isobaric interferences in a quantity sufficient to affect the accuracy of isotopic ratio measurement were detected. The results of Zn and Cu isotopic ratio measurement of reference samples expressed as δ notations are presented in Table 2.

As can be seen from Table 2, the accuracy and precision obtained for Cu and Zn isotope ratios in geological CRMs (BHVO-2, BCR-2 and AGV-2) demonstrate good agreement with the values stored in the GeoReM database http://geo rem.mpch-mainz.gwdg.de/. The procedural blanks related to chemical dissolution and ion exchange procedures are lower than 1 and 3 ng for Cu and Zn, respectively, assuring no blank effect on the isotopic composition of the samples. Our analytical procedure can be used for the analysis of both geological and environmental samples, such as dust, sediments, and atmospheric aerosols and precipitation.

4. CONCLUSIONS

The present paper deals with the development of the method for $\delta^{65}Cu$ and $\delta^{66}Zn$ isotope ratio determination by MC ICP-MS in environmental samples. The calibration of chromatographic columns has indicated that the application of the AG MP-1 resin with optimized layer parameters (resin bed height 3.5 cm and diameter 1 cm) provides the high-purity Cu and Zn fractions. No isobaric interferences in a quantity sufficient to affect the accuracy of isotopic ratio measurement are detected. The method is characterized by high throughput and adequate analytical figures of merit when using the standard-sample bracketing technique for mass bias correction. For the method described, the accuracy and precision obtained for Cu and Zn isotope measurements in the BHVO-2, BCR-2 and AGV-2 geological CRMs demonstrate good agreement with the values stored in the GeoReM database.

5. CONTRIBUTION OF THE AUTHORS / ЗАЯВЛЕННЫЙ ВКЛАД АВТОРОВ

The authors contributed equally to this article.

Все авторы внесли эквивалентный вклад в подготовку публикации.

6. CONFLICT OF INTERESTS / КОНФЛИКТ ИНТЕРЕСОВ

The authors have no conflicts of interest to declare. All authors have read and agreed to the published version of the manuscript.

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