

Article

Cu Purification Using an Extraction Resin for Determination of Isotope Ratios by Multicollector ICP-MS

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Abstract: A new simple and quick method has been established for separation of Cu from solutions using an extraction chromatographic resin utilizing Aliquat[®] 336 (commercially available as TEVA[™] resin) and Cu(I). This method involves the use of a one milliliter column containing 0.33 mL TEVA[™] resin on 0.67 mL Amberchrom[®] CG-71C acrylic resin. Copper was adsorbed on the column by forming Cu(I) with 0.15% ascorbic acid in 0.05 mol·L⁻¹ HBr, while other major elements except Zn showed no adsorption. After removal of the major elements (Na, Mg, Al, P, K, Ca, Cr, Mn, Fe, Co and Ni), Cu was recovered using 2 mol·L⁻¹ HNO₃. The recovery yield and total blank were 102% ± 2% and 0.25 ng, respectively. To evaluate the separation method, Cu isotope ratios were determined by a standard-sample-standard bracketing method using multicollector inductively coupled plasma-mass spectrometry (ICP-MS), with a repeatability of 0.04‰ and 0.25‰ (SD), for the standard solution and the solutions from low S (<0.1% S) silicate standards, respectively.

Keywords: Cu separation; Cu(I); Cu isotope ratio; extraction resin; TEVA[™] resin; multicollector inductively coupled plasma source mass spectrometry; MC-ICP-MS

1. Introduction

Copper has two isotopes, ⁶³Cu and ⁶⁵Cu, and significant Cu isotope fractionation is observed in a variety of geological and biological materials (e.g., [1–3]). Copper isotopic analyses for samples are expressed as a permil difference from that of the ERM-AE647 (IRMM-647) Cu standard by the following equation in this paper:

$$\delta^{65}\text{Cu} = \left[\frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{ERM-AE647}}} - 1 \right] \times 1000 \quad (1)$$

Measurement of $^{65}\text{Cu}/^{63}\text{Cu}$ precisely and accurately requires separation of Cu from other major cations such as Na, Mg, Al, Fe and Ni, *etc.* This separation has previously been performed by anion exchange chromatography employing the Cu(II) chloro complex and the strong anion exchange resin, AG MP-1 [4]. Popular anion exchange resins, AG 1X8 and AG 1X4, are also used [5,6]. Many modified methods using these resins have been developed to achieve higher performance [2,7,8]. The flaw in using these resins resides in the weak affinity of Cu(II) for the resins, also affected by the matrix composition, although a very high recovery yield for Cu in the column chemistry (near 100%) is required to prevent isotopic fractionation [4]. Another approach for Cu purification involves the use of Cu(I), which is formed by reduction of Cu(II) by ascorbic acid [9]. Copper (I) has a higher affinity than Cu(II) for the anion exchange resins [10], because Cu(II) easily forms the Cu^{2+} -cation. Therefore, employing Cu(I) should be effective for measurements of Cu isotope ratios. Lerner *et al.* [11] recently revived this approach in a method in which Cu(I) was formed by reduction with ascorbic acid. Using this approach, a strong adsorption of Cu(I) on AG 1X8 resin was achieved.

Trioctylmethylammonium chloride (Aliquat[®] 336) works as an anion exchanger and is used in extraction chromatography (commercially sold as TEVA[™] resin) [12–14]. Recently, Makishima and Nakamura [15] and Makishima [16] successfully purified Zn and Fe, respectively, using a one milliliter column composed of 0.33 mL TEVA[™] resin on a 0.67 mL CG-71C resin bed. They exploited the acid resistance of the TEVA[™] resin [17] by using HNO_3 in the final step to recover Zn and Fe, which were strongly adsorbed on the resin. Based on this observation, the author hypothesized that the anionic character of TEVA[™] resin and Cu(I) could be applied to the separation of Cu. This paper documents the first application of TEVA[™] resin to the purification of Cu for isotope ratio measurements by multicollector inductively coupled plasma-mass spectrometry (MC-ICP-MS).

An advantage of the TEVA[™] resin column is that the column chemistry can be completed in <2 h, from sample loading to Cu collection. In order to demonstrate the applicability of the separation method for Cu developed in this study, Cu isotope ratios were measured by a standard-sample-standard bracketing method using MC-ICP-MS [1,18,19]. For evaluation of the column chemistry and mass spectrometry developed in this study, the author analyzed three USGS (the US Geological Survey) standard silicate reference materials, and six GSJ (Geological Survey of Japan) standard silicate reference materials.

2. Samples and Analytical Methods

2.1. Reagents and Silicate Samples

Here, a brief caution is first warranted regarding the high corrosive and toxic nature of HF, HCl, HNO_3 , HBr and HClO_4 . Inhalation or contact with skin and eyes should be avoided at all costs and these solutions should be at all times handled with protective glasses and gloves.

All experiments were performed in clean rooms and on clean benches with HEPA (High Efficiency Particulate Air) filtration [20]. Water and HF were purified as described elsewhere [20]. Electronic industry (EL) grade HCl and HNO_3 , TAMAPURE-AA-100 grade HBr and HClO_4 (Tama Chemicals Co., Ltd., Kawasaki, Japan), and analytical grade L(+)-ascorbic acid (Kanto Chemical Co. Inc., Tokyo, Japan) were used without purification. For each analytical session, the ascorbic acid solution was

freshly prepared by dissolution in H₂O, to be 30% (w/v). A 0.05 mol·L⁻¹ HBr solution with 0.15% (w/v), produced by addition of ascorbic acid, was prepared just before the column chemistry. In order to analyze the behavior of major and minor elements in the column (the column calibration), two multi-element standard solutions were used (Specpure[®], Nos. 42885 and 44270, Alfa Aesar, Lancashire, UK).

One mol·L⁻¹ ERM[®]-AE647 Cu solution (previously referred to as the IRMM-647 solution) was purchased from ERM[®] (European Reference Materials), and used as the Cu isotopic standard solution for MC-ICP-MS. TEVA[™] extraction resin (100–150 μm, Eichrom Technologies, LLC, Lisle, IL, USA) and Amberchrom[®] CG-71C (Rohm and Haas, Co., Philadelphia, PA, USA) were soaked and stored in water. The TEVA[™] resin and CG-71C were not reused.

Three USGS silicate reference materials, BHVO-1 (basalt), AGV-1 (andesite) and PCC-1 (peridotite), and six GSJ silicate reference materials, JB-1, JB-2, JB-3 (basalts), JA-1, JA-2 and JA-3 (andesites), were used as test samples.

2.2. TEVA[™] Resin Column and Silicate Sample Solution

The TEVA[™] resin column was prepared by packing 0.33 mL of TEVA[™] resin over 0.67 mL of CG-71C in a 1 mL polypropylene column (5 cm × 5 mm in diameter, Muromachi Technos Co., Ltd., Tokyo, Japan) [15,16]. The CG-71C resin was used for absorption of organic materials and control of the elution rate.

Silicate powder samples were digested by the normal sample digestion methods in the author's laboratory [21]. Briefly, samples were decomposed with HF-HClO₄ and dried to digest fluorides with HClO₄ [21], evaporated with HCl, and then diluted with 0.5 mol·L⁻¹ HNO₃. The final dilution was typically diluted ~250 times (for 5 mL solutions for 20 mg silicate samples). This solution was used to analyze the concentration of Cu by sector-type ICP-MS (ICP-SFMS; see Section 2.4). Then the sample solution containing 0.1 μg of Cu was dried and dried again with 0.6 mL of 8 mol·L⁻¹ HBr to change the sample into the bromide form.

2.3. Copper Purification by the TEVA[™] Resin Column

Details of Cu purification by the TEVA[™] column are shown in Table 1. The method is based on the high affinity of Cu(I) for the anion exchange resin [11]. The distribution coefficient is defined as the concentration of Cu(I) in the resin (w/v) over the concentration of Cu(I) in the co-existing solution (w/v). Also, the Cu bromo complexes have higher affinity to the anion exchange resin than the Cu chloro complex [10]. The resin bed was pre-washed with 6.4 mL of 2 mol·L⁻¹ HNO₃ and 1.6 mL of water, followed by 3.2 mL of 0.05 mol·L⁻¹ HBr. Then, the resin bed was conditioned with 3.2 mL of 0.05 mol·L⁻¹ HBr containing 0.15% (w/v) ascorbic acid.

The sample containing 0.1 μg of Cu was dissolved with 0.1 mL of 0.05 mol·L⁻¹ HBr containing 0.15% ascorbic acid and loaded onto the column. The adsorption of Cu is not particularly rapid, thus the column was left for 30 min (see Section 3.1). Then the major elements (Na, Mg, Al, P, Ca, Cr, Mn, Fe, and Ni) were washed away by addition of 4.8 mL of 0.05 mol·L⁻¹ HBr containing 0.15% ascorbic acid. Subsequently, the resin was washed with 0.8 mL of water to remove ascorbic acid. Finally, Cu was collected by addition of 6.4 mL of 2 mol·L⁻¹ HNO₃. The Cu fraction was dried for 12 h on a hot plate at 120 °C, in a clean fume hood, with addition of one drop of HClO₄ to decompose residual

organic materials. Finally, for complete removal of HClO_4 from the wall of the beaker, the dried sample was heated at $195\text{ }^\circ\text{C}$ for 6 h, then re-dissolved with 1 mL of $0.5\text{ mol L}^{-1}\text{ HNO}_3$.

Table 1. Chemical procedure for Cu purification using TEVA resin column.

Washing	$2\text{ mol}\cdot\text{L}^{-1}\text{ HNO}_3$	6.4 mL
	water	1.6 mL
	$0.05\text{ mol}\cdot\text{L}^{-1}\text{ HBr}$	3.2 mL
Conditioning	$0.05\text{ mol}\cdot\text{L}^{-1}\text{ HBr}$ with 0.15% ascorbic acid	3.2 mL
	Loading the sample (leave 30 min)	$0.05\text{ mol}\cdot\text{L}^{-1}\text{ HBr}$ with 0.15% ascorbic acid
Removing major elements	$0.05\text{ mol}\cdot\text{L}^{-1}\text{ HBr}$ with 0.15% ascorbic acid	4.8 mL
	water	0.8 mL
	Collecting Cu	$2\text{ mol}\cdot\text{L}^{-1}\text{ HNO}_3$

2.4. Measurements of Cu, Distribution Coefficients, and Major Elements (Elution Curves)

For measurements of the concentration of Cu, the distribution coefficient of Cu (Section 3.1), and major element measurements (Section 3.2), a sector-type ICP-MS, ELEMENT housed in the Pheasant Memorial Laboratory (PML) was used. Middle and high mass resolutions ($M/\Delta M = \sim 3000$ and ~ 7000) were used. Details of analytical conditions were described in Makishima and Nakamura [22].

2.5. Measurement of Cu Isotope Ratios

For evaluation of the Cu separation method developed in this study, isotope ratios of Cu were measured by MC-ICP-MS, NEPTUNE (Thermo Fisher Scientific Inc., Waltham, MA, USA) housed in the Pheasant Memorial Laboratory (PML). Details of the MC-ICP-MS operation conditions for Cu are shown in Table 2. The $0.5\text{ mol}\cdot\text{L}^{-1}\text{ HNO}_3$ solution was used as carrier and washing solution. Gains of amplifiers of each Faraday cup were calibrated once per analytical session (typically once a day). The Cu isotope ratios were obtained by a standard-sample-standard bracketing method. A drift of Cu isotope ratios was observed ($\sim 1 \times 10^{-2}\text{‰}\cdot\text{h}^{-1}$). The sample solution containing Cu of $0.1\text{ }\mu\text{g}\cdot\text{mL}^{-1}$ yielded $\sim 2 \times 10^{-10}$. A signal for $^{65}\text{Cu}^+$.

In most previous studies [2,4,6–8,11,17,21,22], the standard-sample-standard bracketing method for Cu was combined with mass discrimination correction by Zn. However, in this study, only the standard-sample-standard bracketing was used. The repeatability using the $0.1\text{ }\mu\text{g}\cdot\text{mL}^{-1}$ of Cu standard solution was 0.035‰ (SD, $n = 68$), suggesting that the simple standard-sample-standard bracketing method in this study was sufficiently precise to evaluate the new column chemistry developed.

Table 2. Multicollector inductively coupled plasma-mass spectrometry (MC-ICP-MS) operating conditions.

1. Sample introduction and ICP conditions									
Nebulizer	Micro-flow PFA nebulizer, PFA-50 (Elemental Scientific, Omaha, NE, USA), self-aspiration (flow rate: $\sim 50 \text{ } \mu\text{L} \cdot \text{min}^{-1}$)								
Plasma power	1.2 kW (27.12 MHz)								
Torch	Quartz glass torch with a sapphire injector								
Plasma Ar gas flow rate	$15 \text{ L} \cdot \text{min}^{-1}$								
Auxiliary Ar gas flow rate	$0.80 \text{ L} \cdot \text{min}^{-1}$								
Nebulizer Ar gas flow rate	$0.90 \text{ L} \cdot \text{min}^{-1}$								
2. Desolvator conditions									
Desolvator	ARIDUS II (CETAC Technologies, Omaha, NE, USA)								
Spray chamber temperature	110 °C								
Desolvator temperature	160 °C								
Sweep gas (Ar)	$8\sim 9 \text{ L} \cdot \text{min}^{-1}$								
3. Interface									
Sampling cone	Made of Ni								
Skimmer cone	Made of Ni (X-skimmer)								
4. Data acquisition conditions									
Resolution	$M/\Delta M = \sim 500$								
Washing time	480 s after measurement								
Uptake time	90 s								
Background data integration	4 s for 1 scan, 20 scans in one run Background was measured at the same mass with aspirating HNO_3								
Sample data integration	4 s for 1 scan, 20 scans in one run								
5. Cup configuration									
	L4	L3	L2	L1	C	H1	H2	H3	H4
				^{63}Cu		^{65}Cu			

3. Results and Discussion

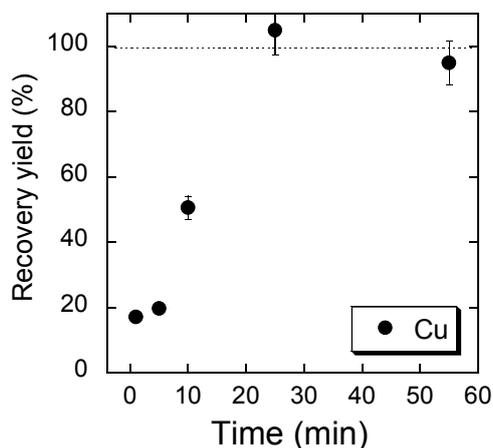
3.1. Kinetic Effects of Adsorption of Cu(I)

Kinetic effects during adsorption can be significant in TEVATM resin column chemistry [17], thus we tested for kinetic effects during the adsorption of Cu(I). For this consideration, the Cu standard solutions were loaded onto the TEVATM column at the same conditions as for the samples and left for 0, 5, 10, 25 and 55 min, respectively. Recovery yields for each of these differing loading times were then determined.

Analytical results are shown in Figure 1. Yields for Cu were $\sim 20\%$ for the 0 and 5 min loads, $\sim 50\%$ for the 10 min load time, and $\sim 100\%$ for the 25 and 55 min load time. Therefore, to achieve $\sim 100\%$ adsorption of Cu in the TEVATM column chemistry, it is necessary to wait for at least 25 min after

sample loading and we opted for a 30 min wait after each sample loading (Table 1). Based on the testing, 6.4 mL of $2 \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$ is sufficient to recover all Cu from the TEVATM resin column.

Figure 1. The sample adsorption time (min) after sample loading vs. the recovery yield (%) of Cu. Error bars are the accuracy of $\sim 7\%$ in inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) measurement. The dotted horizontal line shows 100% yield.



3.2. Elution Curves for Cu, Mg, and Zn Using the TEVATM Column and the Effects of Coexisting Zn

Elution curves for Mg, Zn, and Cu on the TEVATM resin column are shown in Figure 2. For this figure, the BHVO-1 solution added with Cu and Zn was used. In this figure, other major elements such as Na, Al, P, K, Ca, Cr, Mn, Fe, Co, and Ni are represented by the Mg elution curve. Based on these elution curves, the major elements in the silicate samples are effectively separated from Cu by the TEVATM column chemistry.

Zinc shows a weak affinity for the TEVATM resin in this condition and approximately 5% of the total amount of Zn remains in the Cu fraction. To determine the effects of the presence of this Zn on the Cu isotope ratios, varying amounts of Zn (0.1 , 0.2 , and $0.5 \mu\text{g} \cdot \text{mL}^{-1}$) were added to $0.1 \mu\text{g} \cdot \text{mL}^{-1}$ Cu standard solution, ERM-AE647, and the Cu isotope ratios were then determined. When the Zn yield of 5% is taken into account, initial Zn:Cu ratios correspond to 20, 40 and 100, respectively, in these experiments. The analytical results are shown in Figure 3. As shown in this figure, with up to $0.5 \mu\text{g} \cdot \text{mL}^{-1}$ of Zn, isotope ratios of Cu were within the 2SD range ($\pm 0.07\%$) of the Cu standard solution. Therefore, no effect of Zn was observed for Zn:Cu of up to 100 in measurement of the Cu standard. It is suggested that, except for unusual samples with a very high Zn:Cu ratio of >100 , the TEVATM resin column chemistry developed in this study can be applied for the Cu isotope ratio measurement by MC-ICP-MS. Extreme samples with Zn:Cu >100 could include sulfides such as sphalerite (ZnS).

The elution curve for S is not clear and Pribil *et al.* [23] demonstrated an effect of SO_4^{2-} on Cu isotope ratios by MC-ICP-MS, especially when $\text{SO}_4^{2-}:\text{Cu}$ was >50 . In the case when the Cu concentration is $100 \mu\text{g} \cdot \text{g}^{-1}$ in the sample, the S content is 0.1%. Sulfur contents this high are unusual for silicate samples, therefore, the effects of S can be neglected for usual silicate samples in this study. However, Sulfur could affect the analyses of sulfides such as chalcopyrite (CuFeS_2) in the method of

this study. In this sample digestion technique, although most S is likely expelled as H₂S during the sample digestion procedure [24], the effects of S could not be neglected in the analysis of sulfides.

Figure 2. Elution curves of Cu, Mg, and Zn for the TEVATM column. The horizontal axis shows the total eluent volume (mL). The vertical axis indicates the fraction (%) of each element compared to the total amount of the element loaded onto the column. Note the logarithmic scale for the vertical axis. Behaviors of Na, Al, P, K, Ca, Cr, Mn, Fe, Co, and Ni were similar to that of Mg, which has no affinity for the TEVATM resin. Zinc has a weak affinity for the TEVATM resin column in 0.05 mol L⁻¹ HBr with 0.15% ascorbic acid, thus, 5% of Zn is recovered with Cu. The horizontal arrows at the top of the figure show the eluents for washing of the major elements and the Cu fraction. “L” indicates the sample loading solution (0.1 mL). Note that the eluent volumes for each step are not the same.

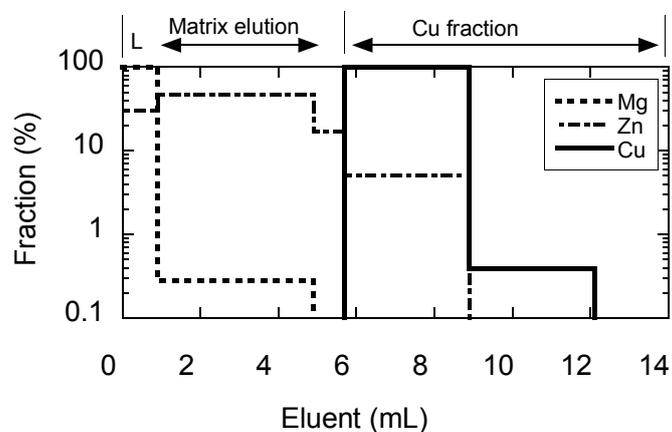
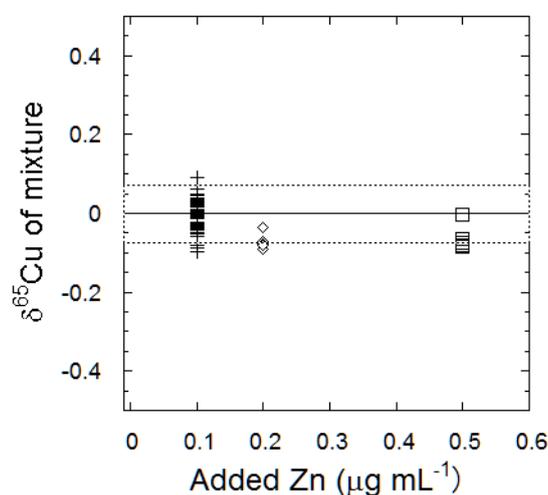


Figure 3. Analytical results of the mixing experiment of Cu with Zn. The horizontal axis shows the Zn concentration ($\mu\text{g}\cdot\text{mL}^{-1}$) in the $0.1\cdot\mu\text{g}\cdot\text{mL}^{-1}$ Cu standard solution, ERM-AE647. The vertical axis indicates the $\delta^{65}\text{Cu}$ of the mixture. The plus sign, diamond, and square represent the Zn concentration of 0.1 ($n = 78$), 0.2 ($n = 7$) and 0.5 ($n = 5$) $\mu\text{g}\cdot\text{mL}^{-1}$, respectively. The dotted lines indicate a $\pm 2\text{SD}$ error range ($\pm 0.070\text{‰}$) for the $\delta^{65}\text{Cu}$ of the Cu standard solution without any Zn addition.



3.3. Mass Fractionation, Recovery Yield, and Blank of the TEVA™ Resin Column Chemistry

I measured the Cu isotope ratios and yields for the Cu standard solution, ERM-AE647, with $0.1 \mu\text{g}\cdot\text{mL}^{-1}$ separated through the TEVA™ column, as a test of whether any mass fractionation is caused by the TEVA™ resin column chemistry or impurities introduced during the column chemistry (organic materials, *etc.*). These tests resulted in $\delta^{65}\text{Cu}$ of $0.02\text{‰} \pm 0.06\text{‰}$ ($n = 5$; SD). The standard deviation for these tests was slightly larger than for the measurement of the pure standard solution of 0.035‰ . It is suggested that the mass fractionation induced by the column chemistry or organic materials produced errors of up to 0.06‰ . However, the $\delta^{65}\text{Cu}$ values only slightly deviated from those for the standard solution ($\delta^{65}\text{Cu} = 0.02\text{‰}$), with the offset falling within errors. Therefore, we conclude that the TEVA™ column chemistry does not produce Cu isotope fractionation. The recovery yields determined from the signal intensity of the experiments using MC-ICP-MS were $102\% \pm 2\%$ ($n = 5$; SD). Thus, there are no losses of Cu during the column chemistry, removing the possibility of isotopic fractionation related to incomplete yields.

The blank of the column chemistry was 0.25 ng ($n = 11$). This level of Cu blank is similar or better than that reported in previous studies (0.2 ng [11], 0.5 ng [7] and 1.5 ng [6]). As only $0.1 \mu\text{g}$ (100 ng) of Cu are analyzed in this study, these levels of blank can be neglected.

3.4. Merits of the New Cu Column Chemistry

In this study, an HBr-ascorbic acid mixture is used instead of an HCl-ascorbic acid mixture [11]. This is because the stability and affinity for the Cu bromo complex are higher than for the chloro complex [10]. Another advantage of the Cu bromo complex is that it decomposes easily when reacting with HNO_3 , forming Br_2 [24].

As mentioned in the Introduction, the TEVA™ resin is resistant to oxidation [17]. Thus $2 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ can be used to recover Cu. There are three reasons to use HNO_3 : (i) HNO_3 easily decomposes the Cu bromo complex; (ii) Cu(I) is oxidized into Cu(II), which has very low adsorption onto the anion exchange resin; and (iii) NO_3^- is a stronger eluting anion than Cl^- . Therefore, NO_3^- removes Cu(I)-chloro or bromo complex out of the resin more efficiently than Cl^- .

Larner *et al.* [11] used 15 mL of $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ $-0.01\% \text{ H}_2\text{O}_2$ for recovery of Cu. In that study, additional H_2O_2 was added to oxidize Cu(I) to Cu(II). However, for the reasons provided above, $2 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ is more efficient for recovery of Cu than $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$. Larner *et al.* [11] could not use $2 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$, because AG 1X8 was damaged by $2 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ and, as a by-product, also the organic materials form from the resin. In contrast, the TEVA™ resin is more resistant to oxidation, therefore, use of the TEVA™ resin as in this study is preferable to the use of AG 1X8 when an oxidation reaction is involved.

The TEVA™ resin column chemistry has another advantage relative to the previously employed methods. The flow rate of the column is $0.3 \text{ mL}\cdot\text{min}^{-1}$, requiring less than two hours for separation of Cu including the time to wash the resin bed. The method of Larner *et al.* [11] requires $\sim 4 \text{ h}$ (this does not include column washing steps) with their flow rate of $\sim 0.2 \text{ mL}\cdot\text{min}^{-1}$ and 52 mL of total elution, the latter being far greater than the $\sim 12 \text{ mL}$ of this study.

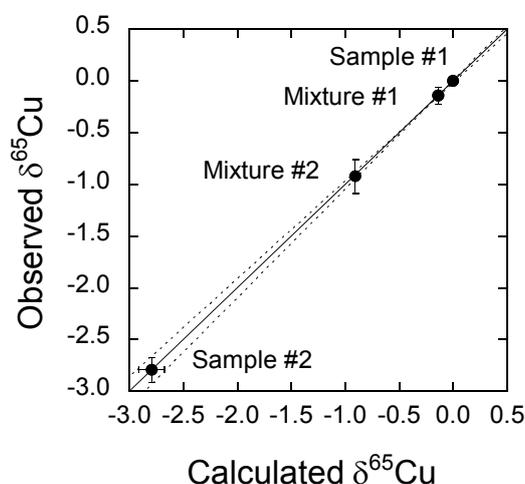
3.5. Evaluation of the Accuracy of the Cu Isotope Ratio Measurements

It is difficult to evaluate the accuracy in stable isotope mass spectrometry for less popular elements such as Cu, because there are few standard materials for which accurate isotope compositions are available. In order to examine the accuracy of the methods for analyses of samples with widely varying isotope ratios and matrix elements, we synthesized samples by mixing two samples with very different compositions. The measured isotope ratios of the mixture were then compared with calculated isotope ratios. These mixing tests were previously undertaken in studies of Tl and Zn isotopes, in both cases also to evaluate the accuracy of the method [15,25].

Table 3. Analytical results of mixing experiments.

	Calculated		Observed		<i>n</i>
	$\delta^{65}\text{Cu}$	SD (%)	$\delta^{65}\text{Cu}$	SD (%)	
Mixture #1	-0.14	0.01	-0.14	0.09	4
Mixture #2	-0.91	0.06	-0.92	0.16	4

Figure 4. Analytical results of the mixing experiments. The horizontal and vertical axes are the calculated and observed $\delta^{65}\text{Cu}$ values, respectively. The line connecting Sample #1 and #2 has a slope = 1. The dotted lines indicate the combined errors of the isotope measurements for Samples #1 and #2. Error bars are SD (%).



For this test, we used the Allende meteorite solution showing $\delta^{65}\text{Cu} = -2.80 \pm 0.12$ ($n = 4$) and the Cu isotope standard solution, ERM-AE647 of $\delta^{65}\text{Cu} = 0$. Two mixtures with differing proportions were produced and for each mixture we produced four samples. For each mixture, 0.4 mL of $8 \text{ mol}\cdot\text{L}^{-1}$ HBr were added, then the resulting solution was dried, passed through the TEVA™ resin column, and the Cu isotope ratio was determined by MC-ICP-MS. The measured $\delta^{65}\text{Cu}$ values of the two mixtures are shown in Table 3 and Figure 4, along with the calculated values for each mixture. The error in the calculation for each mixture was based on a concentration uncertainty of $\sim 5\%$ of the two starting solutions, and no other errors were taken into account. Table 3 and Figure 4 demonstrate that the measured isotope ratios of the mixtures are consistent with the calculated ratios, within error, although the two mixtures had very different major element compositions and isotope ratios. Therefore, it is

concluded that the Cu isotope ratios are not affected by the TEVA™ resin column chemistry and should be regarded as accurate isotope ratios.

3.6. Repeatability of Cu Isotope Ratios in Silicate Reference Materials

Analytical results for the three USGS and six GSJ silicate reference materials, using the new methods, are provided in Table 4. As also noted by Archer and Vance [2], the number of Cu isotope ratios of silicate reference materials is very limited, making it difficult to evaluate the accuracy of the isotope ratios obtained in this study. Obviously, future studies should in part be aimed at providing Cu isotope compositions of the same silicate reference materials.

Table 4. $\delta^{65}\text{Cu}$ values of US Geological Survey (USGS) and Geological Survey of Japan (GSJ) silicate reference materials. Note that $\delta^{65}\text{Cu}$ values are based on ERM-AE647.

Sample	$\delta^{65}\text{Cu}$	SD	<i>n</i>
	Average	(‰)	
BHVO-1	−0.44	0.07	3
AGV-1	−0.64	0.47	3
PCC-1	−0.71	0.50	3
JB-1	0.83	0.06	5
JB-2	1.01	0.01	3
JB-3	−0.75	0.43	3
JA-1	0.86	0.17	3
JA-2	−0.33	0.04	3
JA-3	0.11	0.06	3

In this study, repeatability, expressed as the standard deviation (SD) of actual silicate sample analyses, was 0.01‰–0.50‰ (see Table 4). The average of the SD is 0.25‰, thus we consider this to be the repeatability for measurements of $\delta^{65}\text{Cu}$ for silicate samples using this new method.

4. Conclusions

Using an extraction resin, TEVA™, a new column chemistry for the separation of Cu was established for isotope ratio determinations by MC-ICP-MS. Copper forms Cu(I) with 0.15% ascorbic acid in 0.05 mol L^{−1} HBr, with high adsorption onto the TEVA™ resin, while other major elements show no adsorption. The Cu can then be recovered using 2 mol·L^{−1} HNO₃. The recovery yields and total blank were 102% ± 2% (*n* = 5; SD) and 0.25 ng, respectively.

For the evaluation of the separation method, Cu isotope ratios were measured by a standard-sample-standard bracketing method employing MC-ICP-MS. Repeatability of the measurements of the isotope compositions of the Cu standard solution and the standard silicate reference materials were 0.04 and 0.25‰ (SD), respectively. The accuracy of the isotope compositions of these samples obtained using this method cannot at present be fully evaluated because of the scarcity of analyses from other laboratories.

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Conflicts of Interest

The author declares no conflict of interest.

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