

# Absolute Isotopic Abundance Ratio and the Atomic Weight of a Reference Sample of Copper

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An absolute value for the isotopic abundance ratio of a reference sample of copper has been obtained by thermal emission mass spectrometry. Samples of known abundance ratio, prepared from nearly pure separated copper isotopes, were used to calibrate the mass spectrometers. The results yield an absolute value of  $\text{Cu}^{63}/\text{Cu}^{65} = 2.2440 \pm 0.0021$  and an atomic weight of  $63.54555 \pm 0.00040$  ( $C^{12}=12$ ). The indicated uncertainties are overall limits of error based on 95 percent confidence limits for the mean and on allowances for the effects of known sources of possible systematic error.

A companion study of the  $\text{Cu}^{63}/\text{Cu}^{65}$  ratio in natural materials has shown that there is significant variation in some rare secondary minerals.

## 1. Introduction

The presently accepted value for the atomic weight of copper [1]<sup>1</sup> (63.54) is based on the revised chemical determinations by Hönigschmid and Johannsen [2] in 1944, and by Ruer and Bode [3] in 1924. The abundance ratios determined by many mass spectroscopists were not used because the instruments had not been calibrated adequately. In the present work, this difficulty is resolved by the use of calibration samples of known isotopic composition prepared from nearly pure separated copper isotopes. A companion study [4] of terrestrial and meteoritic samples showed that there are no significant isotopic variations in meteorites and primary copper ores, which constitute the bulk of the recoverable copper in the earth's crust. However, some rare secondary copper minerals show gross isotopic variation. The observed range is from 0.3 percent enrichment to 1.0 percent depletion in  $\text{Cu}^{63}$ .

## 2. Experimental Procedure

### 2.1. Instrumentation

The thermal ionization mass spectrometers used to compare the isotopic abundance ratios of the reference and terrestrial samples with those of the calibration samples are two nearly identical 12-in. radius of curvature, single-focusing instruments with 68-deg analyser tubes and 60-deg magnet pole pieces. The measuring circuit of instrument No. 4 was a d-c collector into a Cary V.R.E. that drove an expanded-scale recorder. The measuring circuit of instrument No. 3 included a 12-stage ion multiplier, which was necessary to do the analysis on the separated iso-

topes. The ion source used was a triple filament source with approximately 200  $\mu\text{g}$  of copper electroplated on each side filament. The  $\text{Cu}^+(63)$  ion current was nominally adjusted to  $5 \times 10^{-13}$  A, and data were taken only on a growing or constant ion signal. Tests showed that, in such cases, the ratio was independent of time. However, decaying signals showed a strong ratio variation with time and all such runs were rejected.

### 2.2. Purification of the Separated Isotopes

Electromagnetically separated copper isotopes in the form of copper oxide were obtained from the Isotopes Division, Oak Ridge National Laboratory of the Union Carbide Nuclear Company. The  $\text{Cu}^{63}\text{O}$  and the  $\text{Cu}^{65}\text{O}$  were designated Series IW, Lot Number 1064(a) and Series IW, Lot Number 1065(a), respectively. The certificate of analysis accompanying each sample indicated a high degree of chemical purity. They were further purified at the National Bureau of Standards by electrodeposition to insure removal of impurities except those which are deposited with copper.

Each isotope sample was treated as follows: The copper oxide (about 1.2 g) was dissolved in 100 ml of a solution containing 2 ml of concentrated sulfuric acid and 2 ml of concentrated nitric acid. The copper was slowly electrodeposited from an unstirred solution onto a small platinum-gauze electrode. The deposit was then stripped from the electrode with dilute nitric acid and analyzed by quantitative emission spectrography for the elements which could have electrodeposited with copper [5] or which are common impurities in copper. Quantitative values or limits of detection were determined for 18 elements. On this basis the  $\text{Cu}^{63}$  was estimated to be 99.999 percent pure Cu and the  $\text{Cu}^{65}$  was estimated to be 99.996 percent pure Cu, the principal impurities being silver and platinum in each case.

Figures in brackets indicate the literature references at the end of this paper.

### 2.3. Copper Concentration of the Separated Isotope Solutions

The solutions of  $\text{Cu}^{63}$  and  $\text{Cu}^{65}$  were each transferred to 50 ml Erlenmeyer flasks, diluted to 45 ml, and thoroughly mixed by swirling for several minutes. Each flask was then sealed with a No. 35 rubber serum septum and allowed to stand overnight in the case of a semi-microbalance to insure thermal equilibrium. The flask and contents were then weighed on the semi-microbalance with an accuracy of  $\pm 0.02$  mg. Samples were taken by inserting a stainless steel needle attached to a glass hypodermic syringe through the rubber septum and withdrawing the desired amount of solution. A second needle which just punctured the septum served as a vent. The syringe and needle were washed with distilled water and the washings were combined with the bulk of the sample. The weight of the sample withdrawn was determined from the weight of the flask before and after removal of the sample.

Four samples of from 5 to 6 g each were withdrawn from each solution of the separated isotopes and transferred to 22-ml vials by this method. After reduction of the volume to about 10 ml by evaporation on a steam bath, the bulk of the copper content was determined by the following procedure, which is a modification of the electrolytic method described by Wilson and Wilson [6]. One-half milliliter of a diluted acid mixture containing 0.1 ml of  $\text{HNO}_3$  and 0.1 ml of  $\text{H}_2\text{SO}_4$  was added to the solution in the vial which also served as the electrolysis cell. A stopper for the vial was prepared from an inverted rubber serum septum; a small glass tube, which served as a vent, was inserted through a hole in the septum. The lead of a small platinum-gauze cathode was inserted through the vent tube and a platinum-wire anode was inserted at the edge of the stopper. The copper in each solution was electrodeposited from the unstirred solutions onto the cathode by adjusting the voltage so that the current was about 0.1 A and allowing the electrolysis to continue overnight. Without interrupting the current, the vial was unstoppered and the septum, tube, and sides of the vial were washed with distilled water. The septum was replaced and the electrolysis was continued for another 4 hr. The vial was again unstoppered and the electrodes were withdrawn from the solution without interrupting the current. The cathode was rinsed with distilled water while it was being withdrawn to prevent re-solution of copper, dipped into absolute ethanol, and dried for 1 min at  $100^\circ\text{C}$ . The electrode was allowed to stand for 2 hr at room temperature to attain thermal equilibrium and weighed on a microbalance with an accuracy of  $\pm 0.002$  mg. The copper was then stripped from the electrode with dilute (1+9)  $\text{HNO}_3$  after which it was washed, dipped in ethanol, and dried for 1 min at  $100^\circ\text{C}$ . After standing at room temperature for 2 hr, the stripped electrode was weighed on the microbalance. The weight of copper was determined from the difference in weights.

The copper remaining in the electrolyte and washings was determined by the sodium diethyldithiocarbamate method [7] in the following manner: The solution was transferred to a 125 ml separatory funnel and two drops of 0.01 percent thymol blue solution and 5 ml of a 20 percent ammonium citrate solution were added. Dilute ammonium hydroxide (1 + 3) was added until the color of the indicator changed to pale blue ( $\text{pH}$  9.0–9.2). One milliliter of a 0.1 percent aqueous solution of sodium diethyldithiocarbamate and exactly 5 ml of carbon tetrachloride were then added and the solution was shaken for 2.0 min. The carbon tetrachloride layer, which contained copper diethyldithiocarbamate, was drained into a 1-cm cell. The transmittancy of the carbon tetrachloride solution was measured at 440 nm ( $m\mu$ ) on a Beckman DU Spectrophotometer, and compared to a reference curve.

The total amount of copper present in the sample was calculated from the two determinations. The weight of the electrodeposited copper was corrected for platinum and silver which would have deposited with the copper, and the total weight was corrected for air buoyancy. In a typical determination, the electrodeposited copper amounted to 0.190740 g, while 0.000018 g was found in the residual electrolyte.

This procedure was first applied to the determination of known amounts of copper to evaluate its reliability. Pure copper in the form of rods was obtained commercially. Quantitative spectrographic analysis showed that the copper was about 99.998 percent pure. However, of the impurities found, silver and platinum would electrodeposit with the copper; hence the apparent purity for this purpose was considered to be 99.999 percent.

A sample of the rod weighing about 1 g was pickled successively in dilute  $\text{HCl}$  and in dilute  $\text{HNO}_3$ , rinsed in distilled water, and finally in ethanol. The sample was dried, weighed on a microbalance to  $\pm 0.001$  mg, and transferred to an Erlenmeyer flask which had been weighed on a semi-microbalance along with a rubber septum. The copper was dissolved in dilute nitric acid, diluted to 45 ml with distilled water, and thoroughly mixed. The flask was then stoppered with the septum, allowed to reach thermal equilibrium, and weighed. From the weight of the copper and the weight of the solution, the concentration of copper was calculated. Four weighed samples were withdrawn and the copper determined by the method described.

This procedure was repeated on four additional samples of the copper for a total of 20 determinations. The copper recovered ranged from 99.984 to 100.014 percent of the calculated amounts for samples of from 0.10 to 0.26 g. The standard deviation of an individual determination is estimated to be  $1.5 \times 10^{-5}$  g.

Results for the determination of the copper content of the isotope solutions are tabulated in table 1. The standard deviation of the individual determination is estimated to be  $2.6 \times 10^{-6}$  g/g sol. Average values of 0.0211654 g  $\text{Cu}(\text{vac})/\text{g}$  sol for solution 63

and 0.0210895 g Cu(vac)/g sol for solution 65 were obtained with a standard deviation of  $1.3 \times 10^{-6}$  g/g sol.

TABLE 1. Concentration of solution Cu<sup>63</sup> <sup>a</sup>

Sample	Wt. sol.	Wt. Cu <sup>b</sup>	g Cu(vac)/g sol.
	<i>g</i>	<i>g(vac)</i>	
1.....	5.58000	0.118085	0.0211622
2.....	5.48942	.116189	.0211660
3.....	5.66492	.119903	.0211659
4.....	5.95065	.125960	.0211674
			Ave. 0.0211654
			Std error 0.0000013

Concentration of solution Cu<sup>65</sup> <sup>c</sup>

1.....	5.69855	0.120180	0.0210896
2.....	5.66517	.119486	.0210913
3.....	5.77382	.121754	.0210873
4.....	5.72793	.120800	.0210896
			Ave. 0.0210895
			Std error 0.0000013

<sup>a</sup> Purity taken as 99.999 percent from spectrographic analysis.  
<sup>b</sup> Corrected for Pt and Ag in the copper.  
<sup>c</sup> Purity taken as 99.996 percent from spectrographic analysis.

## 2.4. Isotopic Analysis of the Solutions of the Separated Isotopes

The isotopic analysis of the separated isotopes was not done until all the purification chemistry had been completed. To insure against possible bias effects all samples were run at the same total copper signal intensity. Thus, the large ratios encountered in the separated isotope solutions necessitated the use of an ion-multiplier to make the depleted isotope signals measurable.

The isotopic compositions of the separated isotopes used in the preparation of the calibration samples are given in table 2. These results have been corrected for both the discrimination of the ion multiplier and the discrimination from the mode of ionization used, using the average correction factors (cf) given in table 4.

TABLE 2. Isotopic composition of purified separated copper isotopes used in calibration samples

Isotope	Isotopic composition* (Atom %)
Cu <sup>63</sup> .....	Cu <sup>63</sup> =99.8398 ± 0.002
	Cu <sup>65</sup> =0.1602 ± 0.002
Cu <sup>65</sup> .....	Cu <sup>63</sup> =0.3575 ± 0.002
	Cu <sup>65</sup> =99.6425 ± 0.002

\*The limits set on the isotopic composition of the separated isotopes have been expanded to include a liberal estimate of possible bias.

## 2.5. Preparation of the Calibration Samples

Nine calibration samples were prepared by mixing weighed portions of the Cu<sup>63</sup> solution and the Cu<sup>65</sup> solution to produce ratios of approximately 0.5 Cu<sup>63</sup> to 1 Cu<sup>65</sup> up to approximately 3 Cu<sup>63</sup> to 1 Cu<sup>65</sup> on

an atomic basis. Calibration samples 1 through 7 and all of the samples for the determination of the copper concentration were withdrawn on the same day. Calibration samples 8 and 9 were withdrawn 3 days later and required a correction in the copper concentration because of a slight loss of water through the rubber septum. The mixing data of the calibration samples is given in table 3. Each calibration sample was analyzed three times, with as many analyses done on the reference sample as the total number of analyses done on the calibration samples.

The calculated isotopic ratio,  $\pi$ , for each calibration sample was obtained from

$$\pi = \frac{g_1(1-f_1) + g_2(1-f_2)}{g_1f_1 + g_2f_2} \frac{A}{B}$$

where  $A$  and  $B$  denote the atomic weights of copper in the Cu<sup>63</sup> solution and the Cu<sup>65</sup> solution respectively, and are given as

$$\begin{aligned} A &= M_2 - (M_2 - M_1)(1-f_1) = 62.93275 \\ B &= M_2 - (M_2 - M_1)(1-f_2) = 64.920642 \\ M_1 &= \text{nuclidic mass Cu}^{63} = 62.929594 \\ M_2 &= \text{nuclidic mass Cu}^{65} = 64.927786 \\ g_1 &= \text{weight of copper from Cu}^{63} \text{ solution} \\ g_2 &= \text{weight of copper from Cu}^{65} \text{ solution} \\ f_1 &= \text{fraction of } ^{65} \text{ in Cu}^{63} \text{ solution} = 0.001602 \\ 1-f_1 &= \text{fraction of } ^{63} \text{ in Cu}^{63} \text{ solution} = 0.998398 \\ f_2 &= \text{fraction of } ^{65} \text{ in Cu}^{65} \text{ solution} = 0.996425 \\ 1-f_2 &= \text{fraction of } ^{63} \text{ in Cu}^{65} \text{ solution} = 0.003575 \end{aligned}$$

The values of  $g_1$ ,  $g_2$ , and  $\pi$  are tabulated in table 3.

TABLE 3. Calibration samples

Sample	Solution Cu <sup>63</sup>		Solution Cu <sup>65</sup>		Isotopic ratio $\pi$
	Wt. sol. W <sub>1</sub>	Wt. Cu g <sub>1</sub>	Wt. sol. W <sub>1</sub>	Wt. Cu g <sub>1</sub>	
1.....	2.86377	0.0606128	0.99595	0.0210041	2.97217
2.....	2.09804	.0444059	.91834	.0193673	2.36453
3.....	2.10181	.0444856	.93224	.0196605	2.33361
4.....	2.13417	.0451706	.97065	.0204705	2.27608
5.....	2.12148	.0449020	1.04038	.0224599	2.06319
6.....	1.63190	.0218406	1.04034	.0219403	1.03082
7.....	1.05286	.0222842	2.12004	.0447106	5.1833
8.....	<sup>a</sup> 2.08309	.0441042	<sup>b</sup> 0.95677	.0201798	2.25448
9.....	<sup>a</sup> 2.08161	.0440729	<sup>b</sup> 0.97185	.0204979	2.21810

Concentration of Solution 63=0.0211654 g Cu(vac)/g Sol  
 Concentration of Solution 65=0.0210895 g Cu(vac)/g Sol

<sup>a</sup> Withdrawn 3 days after 1 through 7. Concentration of solution changed to 0.0211725 g Cu(vac)/g sol.

<sup>b</sup> Withdrawn 3 days after 1 through 7. Concentration of solution changed to 0.0210916 g Cu(vac)/g sol.

## 3. Results and Discussion

Table 4 summarizes the isotopic abundance ratio Cu<sup>63</sup>/Cu<sup>65</sup> measurements for both the calibration samples and the reference sample. Table 5 summarizes the atomic weight calculations for the reference sam-

TABLE 4. Calculated and observed isotopic ratios of the calibration samples and the observed ratio of the reference sample

Instr. No. 3			
Mixture	Calc ratio	Obs ratio	CF(Calc/obs)
1 <sup>a</sup> -----	2.9722	3.0514	0.97402
2-----	2.3645	2.4251	.97504
5-----	2.0632	2.1188	.97374
7-----	.51833	.53244	.97350
9-----	2.2181	2.2762	.97449
			Avg. .97416
Reference sample avg. 2.3039 <sup>b</sup>			
Corrected ratio=2.2443			
Instr. No. 4			
1-----	2.9722	3.0131	0.98642
3-----	2.3336	2.3661	.98627
4-----	2.2761	2.3062	.98694
6-----	1.0308	1.0457	.98580
8-----	2.2545	2.2876	.98552
			Avg. .98619
Reference sample avg. 2.2752			
Corrected ratio=2.2437			

<sup>a</sup> All calculations were done before rounding off.  
<sup>b</sup> Instrument equipped with ion multiplier.

TABLE 5. Summary calculations of the atomic weight of copper in the reference sample

Corrected isotopic ratio-----	Cu <sup>63</sup> /Cu <sup>65</sup>	=2.2440 ±0.0021*
Corrected isotopic composition, atom percent.	Cu <sup>63</sup> Cu <sup>65</sup>	=69.174±0.020* =30.826±0.020*
Nuclidic masses (C <sup>12</sup> =12)-----	Cu <sup>63</sup> Cu <sup>65</sup>	=62.929594 ±0.000006 [8] =64.927786 ±0.000006 [8]
Atomic weight Cu (unified table, C <sup>12</sup> =12)---		=63.54555 +0.00040*
Uncertainty components		
95% confidence limit of ratio determination.	±0.00024	
Possible systematic error in composition of separated isotopes.	±0.00004	
Possible systematic error in synthetic ratios.	±0.00012	
	±0.00040*	

\*The indicated uncertainties are overall limits of error based on 95 percent confidence limits for the mean and allowances for effects of known sources of possible systematic error.

ple which was a commercial sample of copper metal. The observed variation in the isotopic ratio for rare secondary minerals makes it necessary to include a variance component for natural variation in the overall uncertainty statement for terrestrial copper. A very large number of mineral samples has been analyzed in an effort to define the limits of variation. The most significant conclusion reached was that a microsample of a secondary mineral might show very large deviations from the average but that all the bulk samples showed little or no variation. If these conclusions are accepted it is not necessary to include the maximum range as the uncertainty in the atomic weight. The value  $63.5455 \pm 0.001$  includes a very liberal range of variation for bulk or processed copper. A complete discussion of the effect of the variation on the atomic weight will be published with the mineral survey [4].

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