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Absolute isotopic composition and atomic weight of zinc

Tsing-Lien Chang[a,]*, Mo-Tian Zhao[b], Wen-Jun Li[c], Jun Wang[b], Qiu-Yu Qian[a]

[a]*Department of Chemistry, Peking University, Beijing 100871, People's Republic of China*
[b]*National Research Centre for Certified Reference Materials, Beijing 100013, People's Republic of China*
[c]*Beijing University of Science and Technology, Beijing 100039, People's Republic of China*

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Abstract

Gravimetric synthetic mixtures prepared from highly enriched isotopes of zinc in the form of oxides of well defined purity were used to calibrate a thermal ionization mass spectrometer. Measurements on natural zinc samples yielded an absolute isotopic composition of 48.27 (21) at. % ^{64}Zn, 27.98 (5) at. % ^{66}Zn, 4.10 (1) at. % ^{67}Zn, 19.02 (8) at. % ^{68}Zn, and 0.63 (1) at. % ^{70}Zn, and the atomic weight of zinc as 65.409 (6) both with an uncertainty given on the basis of 95% confidence limit. (Int J Mass Spectrom 208 (2001) 113–118) © 2001 Elsevier Science B.V.

Keywords: Zinc; Isotopic abundance; Atomic weight; Mass spectrometry

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1. Introduction

The current value of the atomic weight of zinc was recommended as 65.39 (2) in 1983 [1], whereas the best measurement of the isotopic composition was made by Rosman in 1972 yielding 65.396 (5) [2,3], the value within the parentheses denoting the uncertainty of the last figure (such notation is to be used throughout this article). In this study we used three separated isotopes ^{64}Zn, ^{66}Zn, and ^{68}Zn to carry out a calibration measurement. Zinc is a pentanuclidic element. Its interfering isobars are shown in Table 1.

Since Rosman has thoroughly examined the various occurrences of terrestrial zinc materials and found no evidence of isotopic fractionation [2], no attempt was made to collect a number of such samples to look for any such phenomenon.

2. Experimental

2.1. Isotopic materials

Separated isotopes of 97.3 at. % ^{64}Zn (sample A), 96.1 at. % ^{66}Zn (sample B) and 98.5 at. % ^{68}Zn (sample C) were purchased from the Beijing Institute of Atomic Energy, China. The procedure of purification was based on a trial experiment, in which 0.25 g of 99.99% ZnO was first dissolved in 30 mL 0.4 mol L^{-1} HCl (all reagents used in this work were of analytical grade). The mixture was doped with 0.5% each of Fe, Ni, Cu, Mg, and Ca. Then 5 mL of saturated H_2S solution was added. After standing for 30 min the mixture was filtered. After the filtrate was

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* Corresponding author.

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Table 1
Interfering isobars of zinc

Mass no.	64	66	67	68	70
Element (natural abundance, at. %)	Ni (0.91) Zn (48.6)	Zn (27.9)	Zn (4.1)	Zn (18.8)	Zn (0.60) Ge (20.5)

warmed to 50 °C, a solution of 1 mol L^{-1} NH_4HCO_3 was added dropwise till no more precipitate was formed. After standing for 30 min, the mixture was filtered and washed. Then the precipitated $ZnCO_3$ was dried, and heated in a muffle furnace at 800 °C. A current of dry nitrogen was passed to the bottom of the furnace to remove the decomposition product CO_2 so as to prevent it from contaminating the formed ZnO. The product ZnO was in the form of pure white powder of a 88% yield. Final analysis by inductively coupled plasma mass spectrometry showed that these impurities were reduced to 0.006% Fe, 0.010% Ni, 0.003% Cu, 0.0026% Mg, and 0.0045% Ca. We concluded that these elements after purification were insignificant. After allowing the presence of various possible impurities in minute amounts, the three isotopic samples A, B, and C were assessed as 99.98 (2)% pure.

2.2. Mass spectrometric measurement

A solid source thermal ionization mass spectrometer (model Finnigan MAT-261) was used. It was provided with five Faraday cups and a secondary electron multiplier. The specifications were given in our previous article [4]. In the ion source we utilized the single filament insert. A filament made of rhenium was 8 mm long, 1 mm wide, and 0.04 mm thick. It was first cleaned by acetone, degassed in a vacuum at 10^{-7} mbar, and then heated with a current gradually increasing from 2 A, through 3, 4, 5 A up to 5.5 A each time for 25 min. Since zinc possesses a high ionization potential of 9.3942 eV [5], a silica gel–phosphoric acid technique was employed as an enhancing agent in order to increase the ionization efficiency. An aliquot of silica gel was placed on the rhenium filament by a microloading device and dried by passing a current. Then another aliquot of the HNO_3 solution containing 10 μg Zn was added onto the dry gel. The mixture was dried electrically and an aliquot of phosphoric acid was spread on it. This was again heated until the vapor appeared. Then the heating current was kept at this strength until the loaded material appeared completely dry and formed a uniform layer. Thereafter the loaded layer was heated until it appeared dull red when the heating was terminated.

After the filament inserts were placed into the ion source, the latter was evacuated down to 10^{-8} mbar. During the initial heating of the filament, a signal of $^{39}K^+$ was first adopted as the monitor mass. Then the major peak $^{64}Zn^+$ was used as the pilot signal for further heating. An on-line HP-9836 computer was used to monitor the various electric parameters to adjust the cups' positions to attain optimum coincidence of peak shapes through matching the computer graphs. In this way the peaks of all ion beams could be normalized to 100% scale. Such a procedure ensured the perfect position of the cups to completely collect all the ion beams simultaneously. In short, the loading technique and the measuring program were kept identical during the measurement of all the samples in this work, so that the fractionation effect due to the mass discrimination was minimized.

Finally the filament was heated with a current increasing very slowly to about 4 A, whence the ion beam of the pilot signal $^{64}Zn^+$ was adjusted to 10^{-11} A. The measured isotopic ratios were recorded by the computer. The multicollection system simultaneously collected all the ion beams. One loading on each filament represented a single measurement. Each measurement contained 5 sets, and each set comprised 10 readings of isotopic ratios, altogether yielding a mean ratio. The measurement was repeated in several replicates to form the mean of mean ratios. There were 5 replicates for each of samples A, B, and C, 3 replicates for each of the mixes AB and BC, and 10 replicates for each of three natural samples.

The results of measurement for samples A, B, and C are shown in Table 2, from which the isotopic

Table 2
Measured isotopic ratios of samples A, B, and C (5 replicates, 1*s*)

Sample	A	B	C
^{64}Zn/^{66}Zn	72.308 (94)	0.014 564 (79)	1.0087 (90)
^{67}Zn/^{66}Zn	0.0986 (20)	0.008 318 (15)	0.3447 (13)
^{68}Zn/^{66}Zn	0.3076 (21)	0.016 478 (15)	163.23 (47)
^{70}Zn/^{66}Zn	0	0.000 374 (37)	0.1468 (73)

composition of these samples can be readily calculated as given in Table 3.

2.3. Solutions A, B, and C

About 210–230 mg of each purified sample of the three separated isotopes in the form of oxide was accurately weighed on a microbalance with calibrated weights. The weightings were corrected for air buoyancy. This weighing technique was to be applied to other cases in preparing the primary and mixed solutions as stated in the following. Then each sample was carefully dissolved in 0.2 mol L^{-1} HNO$_3$. These resulting solutions were weighed on a balance. The data for the preparation of these solutions are shown in Table 4.

2.4. Mixed solutions AB and BC

Portions of the solutions A and B, and B and C were weighed and then combined to form a series of AB and BC mixes. The isotopic concentration of each series of mixes was calculated as shown in Table 5. Then we measured the isotopic ratio $R_{64/66}$ for the AB mixes, and $R_{66/68}$ for the BC mixes separately to find the correction factors $K_{64/66}$ and $K_{66/68}$.

Table 3
Isotopic composition of zinc in samples A, B, and C (1*s*)

Isotope	at. % in sample A	at. % in sample B	at. % in sample C
64	98.092_3 (258)	1.4007 (78)	0.6086 (72)
66	1.3566 (18)	96.1785 (135)	0.6034 (18)
67	0.1338 (29)	0.8000 (16)	0.2080 (14)
68	0.4173 (34)	1.5848 (17)	98.491_4 (573)
70	0	0.0360 (36)	0.0886 (47)

Table 4
Solutions of separated isotopes A, B and C

Sample	A	B	C
Compound	^{64}ZnO	^{66}ZnO	^{68}ZnO
Purity (%)	99.98 (2)	99.98 (2)	99.98 (2)
Weight (mg)	214.100	217.107	228.656
Net weight (mg)	214.057	217.064	228.610
Weight of solution (g)	29.987 00	33.370 79	33.147 58

2.5. AB mixed solutions

The following formula [6] serves to calculate the correction factor K, which in the present case stands for $K_{64/66}$:

$$K = \frac{W_A C_A (R_A - R_{AB}) - W_B C_B (R_{AB} - R_B)}{W_B C_B R_A (R_{AB} - R_B) - W_A C_A R_B (R_A - R_{AB})}$$

W_A and W_B are the weights of solutions A and B, that form the AB mix, whereas R_{AB} is the measured $R_{64/66}$ (these are variables). $R_A = 72.3082$, $R_B = 0.014\,56$, both being derived from Table 3; C_A and C_B are given in Table 5 (these are constants). We can calculate the correction factor $K_{64/66} = 0.986\,77\ (64)$ as listed in Table 6.

As the $K_{64/66}$ now ascertained differs from one by 1.3%, it is pertinent to carry out an iterative calculation. Since the values of C_A and C_B are calculated from R_A and R_B, these latter, if replaced by KR_A and KR_B, will cause C_A and C_B to have new values. Thereby a new $K_{64/66}$ is obtained as 0.986 91.

2.6. BC mixed solutions

For the BC mixed solutions, the isotopic ratio $B_{66/68}$ was measured to find the correction factor $K_{66/68}$ by applying the following formula:

$$K_{66/68} = \frac{W'_B C'_B (R'_B - R'_{BC}) - W'_C C'_C (R'_{BC} - R'_C)}{W'_C C'_C R'_B (R'_{BC} - R'_C) - W'_B C'_B R'_C (R'_B - R'_{BC})}$$

In the calculation, W'_B and W'_C are the weights of solutions B and C, that form the BC mix, whereas R'_{BC} is the measured $R_{66/68}$ (these are variables). $R'_B = 60.6870$ and $R'_C = 0.006\,126$, both being derived from Table 3; C'_B and C'_C are given in Table 5

Table 5
Isotopic concentration of A, B, and C solutions

Sample	A	B	C
Atomic weight	63.976 921	65.939 192	67.888 166
ZnO mol weight	79.976 321	81.938 592	83.887 566
Total μmol Zn	2676.507	2649.101	2725.198
For AB mixes			
at. % (^{64}Zn + ^{66}Zn)	99.448 9	97.579 2	
μmol (^{64}Zn + ^{66} Zn)	2661.757	2584.971	
μmol (^{64}Zn + ^{66}Zn) g^{-1} soln.	88.763 70 (C_A)	77.462 10 (C_B)	
For BC mixes:			
at. % (^{66}Zn + ^{68}Zn)		97.763 3	99.094 8
μmol (^{66}Zn + ^{68}Zn)		2589.848	2700.530
μmol (^{66}Zn + ^{68}Zn) g^{-1} soln.		77.608 24 (C'_B)	81.469 90 (C'_C)

(these are constants). We can calculate the correction factor $K_{66/68} = 0.986\ 78\ (10)$ as shown in Table 7.

The iterative calculation for the true $K_{66/68}$ is similar to the above case of AB and yields 0.986 75.

2.7. Terrestrial samples of zinc

Only three samples of zinc were purchased in China, and from Germany and UK as follows: (1) 99.99% Zn, Shanghai Chemicals Corp., China; (2) 99.97% Zn, E. Merck, Germany; (3) 99.9% Zn, B.D.H., UK.

All the samples were converted into $Zn(NO_3)_2$ with a concentration of 9.5 mg Zn mL^{-1} in 0.2 mol L^{-1} HNO_3 for the use as the loading material. Mass spectrometric measurement of the four isotopic ratios yielded the results as listed in Table 8.

Then by applying the following correction factors:

$$K_{64/66} = 0.986\ 83$$

$$K_{67/66} = K_{68/66}^{1/2} = 1.006\ 65$$

$$K_{68/66} = K_{64/66}^{-1} = 1.013\ 35$$

$$K_{70/66} = K_{64/66}^{2} = 1.026\ 87$$

which result from $K_{64/66} = 0.986\ 83$, being the mean of $K_{64/66} = 0.986\ 91$ and $K_{66/68} = 0.986\ 75$ (iterative values). We can calculate the mean absolute isotopic composition of zinc $(2s)$ as shown below:

48.268 (214) at. % ^{64}Zn

Table 6
Measured $R_{64/66}$ of AB mixed solutions, (3 replicates) and $K_{64/66}$ $(1s)$

Mix no.	Weight of solution A W_A (mg)	Weight of solution B W_B (mg)	$R_{64/66}$	$K_{64/66}$
1	606.938	1034.856	0.689 59	0.986 45
2	660.783	491.784	1.543 43	0.985 90
3	1333.238	869.283	1.752 30	0.987 22
4	1088.921	504.880	2.433 96	0.987 50
5	1265.871	738.614	1.952 29	0.986 48
6	909.948	655.652	1.590 05	0.987 60
7	1118.449	930.047	1.384 62	0.986 91
8	1159.244	673.324	1.961 63	0.986 09
Mean				0.986 77
1 s				0.000 64

Table 7
Measured $R_{66/68}$ of BC mixed solutions (3 replicates) and $K_{66/69}$ $(1s)$

Mix No.	Weight of solution B W'_B (mg)	Weight of solution C W'_C (mg)	$R_{66/68}$	$K_{66/68}$
1	1018.266	725.494	1.3179 (2)	0.986 68
2	1117.020	713.405	1.4655 (5)	0.986 90
3	1152.971	798.231	1.3552 (11)	0.986 71
4	1093.887	794.478	1.2933 (13)	0.986 83
Mean				0.986 78
1s				0.000 10

Table 8
Measured isotopic ratios of zinc in the terrestrial samples, 10 replicates ($1s$)

Sample	$R_{64/66}$	$R_{67/66}$	$R_{68/66}$	$R_{70/66}$
1	1.7514 (86)	0.145 70 (31)	0.6699 (33)	0.021 91 (14)
2	1.7460 (57)	0.145 68 (31)	0.6720 (19)	0.021 98 (43)
3	1.7479 (37)	0.145 60 (21)	0.6713 (14)	0.021 97 (18)

27.975 (51) at. % ^{66}Zn

4.102 (14) at. % ^{67}Zn

19.024 (82) at. % ^{68}Zn

0.631 (6) at. % ^{70}Zn

2.8. Atomic weight of zinc and error analysis

By multiplying the isotopic abundances (in atomic fraction) each by the known atomic mass of nuclide [7], we obtain the atomic weights of three samples of zinc ($2s$): (1) 65.4066 (84); (2) 65.4104 (61); (3) 65.4091 (44).

Table 10
Atomic weight values of zinc by various authors

Year	Atomic weight	Author	Reference
1948	65.387 (5)	Leland and Nier	[8]
1948	65.3859 (3)	Hess Jr. et al.	[9]
1949	65.393 (3)	Hibbs	[10]
1959	65.3598 (6)	Okamoto et al.	[11]
1971	65.377 (3)	Marinenko and Foley[a]	[12]
1972	65.396 (5)	Rosman	[2]
1990	65.376	Loss et al.	[13]
2001	65.409 (6)	This work	

[a] By chemical method.

Therefore, the mean atomic weight of zinc is

$$A_r(\mathrm{Dy}) = 65{,}4087(63)$$

The error analysis of the complete experiment was carried out. However, only the details for sample (3) are shown as an example in Table 9.

3. Conclusion

Since 1948 the atomic weight of zinc has been determined by various authors as shown in Table 10.

Table 9
Summary of the calculation of the atomic weight of zinc (sample 3)

Parameter	Value	Mass spectrometric analytical error $2S_m$, $\pm\ 10^{-3}$	Possible error in chemical analysis $2S_c$, $\pm 10^{-4}$	Possible bias in separated isotope ratio B, $\pm 10^{-4}$	Overall limit of error[a] $\pm[2(S_m^2 + S_c^2)^{1/2} + B]$, $\pm 10^{-3}$
Isotopic ratio					
^{64}Zn/^{66}Zn	1.724 87	2.38	5.00	6.55	3.10
^{67}Zn/^{66}Zn	0.146 56	0.135	0.418	0.555	0.197
^{68}Zn/^{66}Zn	0.680 22	0.905	1.93	2.55	1.18
^{70}Zn/^{66}Zn	0.022 56	0.115	0.063	0.084	0.124
at. %					
^{64}Zn	48.258 7	114	240	319	148.4
^{66}Zn	27.978 2	27.5	58.0	76.2	35.7
^{67}Zn	4.100 6	7.83	20.2	26.8	10.8
^{68}Zn	19.031 4	44.1	93.5	124	57.5
^{70}Zn	0.631 1	3.84	3.07	4.07	4.26
Atomic weight	65.409 1	2.283[b]	4.79	6.37	2.97
		0.078[b]	0.202	0.268	0.108
		0.882[b]	1.87	2.47	1.149
		0.154[b]	0.123	0.163	0.171

[a] For the uncertainty in the value of atomic weight, an item B_n, $\pm 2 \times 10^{-6}$ (possible bias in isotopic mass) is added.

[b] The four components pertain to four ratios.

Now that our new value $A_r(\mathrm{Zn}) = 65.4087$ (63) results from a calibrated measurement using gravimetric synthetic mixtures of three separated isotopes of zinc, it is superior to all the others.

The atomic weight of zinc, if calculated from the raw data of this experiment is 65.392, which agrees with the known uncalibrated measurements. Thus the calibration increases the value of $A_r(\mathrm{Zn})$ by 0.017, which comes from the correction factors $K_{64/66} = K_{66/68} = 0.986\,83$.

Finally, it is to be noted that the BDH's reagent of 99.9% Zn in form of small granules (natural sample 3) might serve as a laboratory standard of zinc for the use in isotope dilution analysis.

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