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Absolute isotopic composition and atomic weight of germanium

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Abstract

Gravimetric synthetic mixtures prepared from highly enriched isotopes of germanium in the form of oxides of well defined purity were used to calibrate a thermal ionization mass spectrometer. Measurements on natural germanium samples yielded an absolute isotopic composition of 20.38(10) at. % ^{70}Ge, 27.34(9) at. % ^{72}Ge, 7.75(5) at. % ^{73}Ge, 36.71(9) at. % ^{74}Ge, and 7.82(4) at. % ^{76}Ge, and the atomic weight of germanium as 72.639(7) both with an uncertainty given on the basis of 95% confidence limit. No isotopic fractionation was found in terrestrial normal germanium materials. (Int J Mass Spectrom 189 (1999) 205–211) © 1999 Elsevier Science B.V.

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1. Introduction

The current atomic weight of germanium A_r(Ge) = 72.61(2) was recommended in 1985 [1], the value within the parentheses denoting the uncertainty of the last figure (such denotion is to be used throughout this paper). It is the mean of the chemically and mass spectrometrically determined atomic weights, 72.592 and 72.628, respectively [2,3]. The large discrepancy between the two values remains unexplained. Reviews written by Peiser et al. [2] and De Laeter et al. [4] also called for a calibrated mass spectrometric measurement to solve the problem.

Germanium has five stable isotopes. The interfering isobars are shown in Table 1. It is suitable to utilize the two major isotopes, ^{72}Ge and ^{74}Ge for calibration.

2. Experimental

2.1. Isotopic materials

Two samples of germanium oxides with isotopic abundance of 94.7 at. % ^{72}Ge in one (A) and 97.7 at. % ^{74}Ge in the other (B) were bought in 1992 from the Medgenix Co., Düsseldorf, Germany. Impurity analysis as performed by either inductively coupled plasma (ICP) mass spectrometry or ICP atomic emission spectra indicated <20 μg Zn and 10 μg Pb per gram GeO_2 in sample A, and 150 μg Zn and 17 μg Pb per gram GeO_2 in sample B. Zn and Pb were present in the form of oxides. Other impurities were below the detection limit in both samples as shown in Table 2. Therefore, the chemical purity was 99.999% GeO_2 in sample A, and 99.980% GeO_2 in sample B. The error assessed is 0.02%.

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Table 1
Interfering isobars

Mass no.	70	72	73	74	76
Element (natural abundance, at. %)	Zn (0.6) Ge (20.5)	Ge (27.4)	Ge (7.8)	Ge (36.5) Se (0.9)	Ge (7.8) Se (9.0)

Table 3
Isotopic ratio data of sample A

Replicate	^{70}Ge/^{72}Ge	^{73}Ge/^{72}Ge	^{74}Ge/^{72}Ge	^{76}Ge/^{72}Ge
1	0.014 556	0.009 122	0.027 282	0.005 890
2	0.014 227	0.009 210	0.027 184	0.005 882
3	0.014 330	0.009 369	0.027 230	0.005 769
4	0.014 243	0.009 207	0.027 278	0.005 865
5	0.014 478	0.009 231	0.027 216	0.005 854
6	0.014 754	0.009 186	0.027 166	0.005 684
Mean	0.014 431	0.009 221	0.027 226	0.005 824
1*s*[a]	0.000 205	0.000 082	0.000 048	0.000 081

[a] Standard deviation.

Furthermore, both samples were examined on an x-ray diffractometer of Rigaku DMOX-2400 model made in Japan, and found exclusively to be hexagonal in crystalline form. So they are soluble in water. They were dried at 110 °C for 2 h before use.

2.2. Mass spectrometric measurement

The mass spectrometer used was a VG-354 model made in England. The electromagnetic parameters and other working conditions were: accelerating potential 7 kV, magnet current 2.3–2.5 A, working potential of the Daly multiplier from -20 to -23 kV, supplying potential of the photoelectric multiplier 1 kV, vacuum in the ion source better than 6×10^{-7} mbar, and vacuum in the analytical line better than 10^{-8} mbar.

Since germanium possesses a rather high ionization potential, that is, 7.899 eV [5], the emission of Ge^+ ion is difficult, thus necessitating the use of triple rhenium filaments. The two lateral filaments were loaded each with about 10 μg Ge in the form of the aqueous solution of germanic acid mixed with 0.1 mg boric acid as an enhancing agent. After the loading was dried, the filaments were heated to dark red with a current of 2.5–3 A in air. Then the triple filaments were put into the ion source for isotopic ratio measurement. There were 16 bead positions in one barrel.

Before the Ge^+ peaks were measured, the central filament was heated to about 4 A in a few minutes, and the peak of $^{187}Re^+$ was adjusted to 1×10^{-13} A as a temperature monitor for 2000 °C. As the side filaments were heated gradually up with a current from zero to 2.5 A, the field scan began. The Ge^+ peaks generally appeared at about 1 A. When the aiming current reached 3×10^{-13} A, the on-line computer HP9836 began to record the data of the intensities of every Ge^+ peak. Using the peak-jump method and the Daly multiplier [6], the four isotopic ratios of samples A and B were measured. Great care was taken in cleaning the concerned parts of the ion source to eliminate contamination before a new measurement for the sample with a different isotopic composition. Throughout the measurement, the electromagnetic parameters and other working conditions were kept constant.

The result of measurement is shown in Tables 3 and 4, which contain 6 replicate loadings of sample A

Table 2
Impurities below the detection limit in both samples

Element	μg g^{-1} GeO$_2$
Si Al Fe Ca Mg Na Li B V Sr	<50
Se	<20
Ti Mn Ni Cu	<10
Ba Co Rb Nb Ag Cd In Sn Sb Cs La Ce Hg Tl Bi	<5

Table 4
Isotopic ratio data of sample B

Replicate	^{70}Ge/^{74}Ge	^{72}Ge/^{74}Ge	^{73}Ge/^{74}Ge	^{76}Ge/^{74}Ge
1	0.000 313	0.000 643	0.005 604	0.016 772
2	0.000 364	0.000 685	0.005 516	0.017 579
3	0.000 364	0.000 647	0.005 433	0.017 384
4	0.000 406	0.000 613	0.005 437	0.017 299
5	0.000 319	0.000 652	0.005 516	0.016 481
6	0.000 304	0.000 683	0.005 732	0.016 998
7	0.000 264	0.000 585	0.005 437	0.016 114
8	0.000 308	0.000 634	0.005 463	0.016 184
Mean	0.000 330	0.000 643	0.005 517	0.016 851
1*s*	0.000 037	0.000 027	0.000 085	0.000 454

Table 5
Isotopic composition of germanium in samples A and B

Isotope	at. % in sample A (1*s*)	at. % in sample B (1*s*)
70	1.366 (19)	0.032 (4)
72	94.634 (22)	0.063 (3)
73	0.873 (8)	0.539 (8)
74	2.576 (4)	97.719 (44)
76	0.551 (8)	1.647 (44)

and 8 of sample B, respectively. Fifty readings of each of the four isotopic ratios with automatic reduction of background were recorded for every replicate, and the mean ratios are given in the tables. The ratios of the replicates serve to produce the final means, which appear with the respective errors in the bottom rows of the tables. From these mean ratios the isotopic composition of samples A and B can be calculated. The results are listed in Table 5, in which each value is provided with an error. The error calculation throughout the work is carried out according to the generally employed statistical treatment of errors. All experimental errors are given with 1*s* (standard deviation).

2.3. Primary standard solutions

The samples A ($^{72}GeO_2$) and B ($^{74}GeO_2$) each about 250 mg were dissolved separately in two small beakers each containing 12 mL 0.3 mol L^{-1} NaOH (all chemicals in this work used were of guaranteed grade and water was bidistilled) with heating on a water bath about 10 min. When cool it was acidified with 5 mL 1.6 mol L^{-1} HNO_3. Then each solution was transferred into a volumetric flask, and small portions of the HNO_3 solution were employed to rinse the beaker successively for 10 times to assure that no germanium was left in it.

Table 6
Standard solutions A and B

Sample	A	B
Compound	$^{72}GeO_2$	$^{74}GeO_2$
Purity (%)	99.999	99.980
Weight (mg)	245.633	250.551
Net weight (mg)	245.631	250.501
Weight of solution (g)	34.578 89	36.309 36

Table 7
Isotopic concentration of standard solutions

Sample	A	B
Atomic weight	71.977 1	73.946 2
GeO_2 mol weight	103.975 9	105.945 0
Total μmol Ge	2362.384	2364.444
at. % ($^{72}Ge + ^{74}Ge$)	97.210 6	97.781 9
μmol ($^{72}Ge + ^{74}Ge$)	2296.488	2311.998
μmol ($^{72}Ge + ^{74}Ge$) g^{-1} soln.	66.413 01 (C_A)	63.674 99 (C_B)

The sample and the solution were accurately weighed with the technique, that included the correction for air buoyancy as described in our recent article on A_r(Er) [8]. The weighing data are given in Table 6.

The isotopic concentrations of ($^{72}Ge + ^{74}Ge$), C_A and C_B, in the two standard solutions resulting from the calculation by using the concerned isotopic masses [7] are shown in Table 7. These, together with R_A and R_B defined as

$$R_A = R_{72/74\ \text{sample A}} = 36.7296$$
$$R_B = R_{72/74\ \text{sample B}} = 0.000\,643$$

are useful in the calculation of the correction factor $K_{72/74}$ (see Sec. 2.5).

2.4. Mixed standard solutions

Portions of solutions A and B were accurately weighed and thoroughly mixed in preparation for a series of mixed standard solutions. The weighing data designated by W_A and W_B are shown in Table 8, which

Table 8
Observed $R_{72/74}$ of mixed standard solutions and the correction factor $K_{72/74}$

Mix no.	Weight of solution A W_A (mg)	Weight of solution B W_B (mg)	$R_{72/74}$ (1*s*)	$K_{72/74}$
1	1042.506	1077.821	0.970 63 (82)	0.986 16
2	824.467	561.662	1.458 60 (80)	0.982 01
3	1179.071	1438.156	0.830 16 (92)	0.981 14
4	980.541	1448.020	0.687 25 (64)	0.983 00
5	774.274	1403.191	0.561 94 (60)	0.983 26
6	829.465	1275.212	0.658 91 (137)	0.985 73
Mean				0.983 55
1*s*				0.002 01

Table 9
Corrected values of C_A and C_B resulting from iterative calculation

Ordinal no. of iteration	C_A (μmol g^{-1} soln.)	C_B (μmol g^{-1} soln.)	$K_{72/74}$
0	66.413 01	63.674 99	0.983 37
1	66.410 15	63.660 47	0.983 55
2	66.410 23	63.660 60	0.983 55
3	66.410 23	63.660 60	0.983 55

Table 10
True isotopic composition and the atomic weight of germanium of samples A and B

Sample	A	B
at. % ^{70}Ge	1.342 5	0.031 2
at. % ^{72}Ge	94.590 1	0.061 8
at. % ^{73}Ge	0.879 5	0.534 5
at. % ^{74}Ge	2.618 4	97.698 6
at. % ^{76}Ge	0.569 5	1.673 9
Atomic weight	71.979 18	73.946 84

contains also the corresponding $R_{72/74}$ observed by means of mass spectrometric measurement, each value being the mean of five through seven replicates.

2.5. Correction factors

In order to find the correction factor, $K_{72/74}$ for the mass discrimination effect, we apply the following formula:

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

the derivation of which was given in our previous paper [9]. In the calculation, K denotes $K_{72/74}$ of each mix, R_A and R_B denote $R_{72/74}$ of samples A and B (Tables 3 and 4). These four values are all constants for each mix. On the other hand, R_{AB}, denoting $R_{72/74}$ as well as W_A and W_B, varies in each mix (Table 8). Thus we obtain six values of $K_{72/74}$.

As the $K_{72/74}$ now ascertained differs from one by 1.6%, 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, the latter, if replaced by KR_A and KR_B, will change C_A and C_B into C'_A and C'_B. In this way, C'_A and C'_B obtained by the first iteration will enter into the second iteration to yield C''_A and C''_B, and so on. Such iterative calculations furnish converging values of C_A and C_B, as well as that of $K_{72/74}$ at the second and third iterations as shown in Table 9. Further, the true isotopic composition and the atomic weight of samples A and B correspondingly obtained are shown in Table 10.

As there were numerous impurities in samples A and B below the detection limit, if an allowance of 200 μg oxide per gram GeO_2 is made, we have the chemical purity 99.979% for sample A, and 99.960% for sample B. This may raise the value of $K_{72/74}$ by 0.000 08. The effect is only to be noted, and not to be regarded as basis for correction.

From the value of $K_{72/74}$, the other correction factors can be calculated by means of the exponential rule [8] as follows:

$$K_{70/74} = K^2_{72/74} = 0.967\ 37$$

$$K_{72/74} = 0.98355$$

$$K_{73/74} = K^{1/2}_{72/74} = 0.991\ 74$$

$$K_{76/74} = K^{-1}_{72/74} = 1.016\ 73$$

2.6. Terrestrial germanium samples

Five germanium samples were collected from America, Europe and Asia for isotopic analysis: (1) 99.999% GeO_2, electronic grade, Acros Co., USA; (2) 99.999% Ge powder, Fluka Co., Switzerland; (3) 99.99% GeO_2, Ditto; (4) 99.99% Ge powder, Shanghai Chemicals Supply Station, China; (5) 99.99% GeO_2, Ditto.

Table 11
Isotopic ratios observed for the natural germanium samples

Sample	$R_{70/74}$	$R_{72/74}$	$R_{73/74}$	$R_{76/74}$
1	0.573 32	0.755 93	0.212 90	0.209 70
2	0.575 05	0.759 87	0.213 34	0.209 52
3	0.572 43	0.758 39	0.212 83	0.209 78
4	0.575 34	0.759 45	0.213 57	0.209 18
5	0.573 67	0.752 40	0.212 25	0.209 18

Table 12
Summary of the calculation of the atomic weight of germanium (sample 1)

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					
^{70}Ge/^{74}Ge	0.554 610	1.56	1.64	2.96	1.86
^{72}Ge/^{74}Ge	0.743 497	2.75	2.16	3.90	3.14
^{73}Ge/^{74}Ge	0.211 143	0.563	0.609	1.10	0.676
^{76}Ge/^{74}Ge	0.213 211	0.514	0.600	1.08	0.625
at. %					
^{70}Ge	20.374 5	64.5	67.8	122	77.1
^{72}Ge	27.310 7	90.3	71.0	128	103
^{73}Ge	7.755 5	38.4	41.5	75.0	46.1
^{74}Ge	36.729 1	72.6	67.6	122	85.1
^{76}Ge	7.830 2	34.9	40.8	73.4	42.5
Atomic weight	72.640 3	2.58[b]	2.71	4.88	3.08
		1.81[b]	1.42	2.56	2.07
		0.383[b]	0.414	0.748	0.460
		0.698[b]	0.816	1.47	0.850

[a] For the uncertainty in the value of atomic weight, an item B_n, $\pm 1 \times 10^{-6}$ (possible bias in isotopic mass) is added.

[b] The four components pertain to the four ratios.

Each Ge sample was heated in dilute NaOH with an addition of H_2O_2, and the resulting solution was acidified with HNO_3. 10 μg Ge was loaded onto each lateral filament as described in Sec. 2.2. Then the four ratios of the five isotopes of germanium were measured as described in Sec. 2.2. For each sample, five through twelve replicate loadings were made, and each value of the four ratios with an average error of 0.28% ($1s$) is shown in Table 11. Then the four ratios of each sample are corrected by the respective K's as given in Sec. 2.5.

2.7. Absolute isotopic composition and the atomic weight

The final error analysis for the absolute isotopic composition and atomic weight of each terrestrial germanium sample is carried out as shown in Table 12, where only the data of sample (1) are listed, just making it not cumbersome. However, Table 13 gives completely the atomic weight of the five samples with the respective overall limit of error.

The absolute isotopic composition of germanium ($2s$) is as follows: 20.382(97) at. % ^{70}Ge, 27.338(91) at. % ^{72}Ge, 7.754(48) at. % ^{73}Ge, 36.708(85) at. % ^{74}Ge, 7.818(41) at. % ^{76}Ge; and the atomic weight of germanium ($2s$) is

$$A_r(\mathrm{Ge}) = 72.6390(69)$$

3. Conclusion

Since 1947 the atomic weight of germanium, as determined by various authors making mass spectrometric measurements of the four isotopic ratios,

Table 13
Atomic weight of germanium (five samples)

Sample	Atomic weight	Overall limit of error ($2s$)
1	72.6403	±0.006 46
2	72.6374	±0.005 46
3	72.6406	±0.006 35
4	72.6368	±0.010 46
5	72.6401	±0.005 99

Table 14
Atomic weight values of germanium by various authors

Year	Atomic weight	Author	Note	Reference
1947	72.630 (6)	Hess et al.		[10]
1949	72.626 (2)	Hibbs et al.		[11]
1951	72.634 (1)	Graham et al.		[12]
1952	72.624 (7)	Dibeler		[13]
1953	72.631 (6)	Reynolds		[14]
1963	72.604 (1)	Shima		[15]
1986	72.591 (1)	Green et al.	Double spike	[16]
1997	72.639 (3)	Chang and Qiao	Subst. calibr.	[17]
1999	72.639 (7)	This work	Calibrated	

yielded results as shown in Table 14. The new value found in this work is superior to all the others, because it originates from the calibrated measurement on gravimetric synthetic mixtures of highly enriched isotopes, which method is more satisfactory than that of the double spike [2].

Note: The atomic weight of germanium found in this work, if not calibrated, is A_r(Ge) = 72.614, which agrees with the average of the previous seven uncalibrated values 72.620. Calibration will raise the uncalibrated value by 0.025. The magnitude of increment depends on the $K_{72/74} = 0.98355$. This K value is close to those factors $K_{M/(M+2)}$, where M denotes the mass number of the isotope of three preceding elements with the atomic number less by 4, 3 or 1 than that of germanium as shown as follows:

Ni [18]	$K_{58/60}$	0.9843;	0.9854
	$K_{60/62}$	0.9846;	0.9855
Cu [19]	$K_{63/65}$	0.9742;	0.9862
Ga [20]	$K_{69/71}$	0.9859;	0.9858
Ge	$K_{72/74}$	0.9836	

The two values for each mass-pair were obtained by two different operators.

As to the atomic weight values of germanium determined by the chemical methods in 1924–1936, at a time when isotopic separation occurring in a fractionation column was not yet known, a four-stage Hempel column of considerable height as used by Baxter and Cooper [21] would certainly cause the enrichment of lighter isotopes of germanium and chlorine in the top-fractions of germanium chloride as the distillate. Evidence of such isotopic separation was indicated by the data listed in Tables IV, V, and VI of [21] (pp. 1062–1064). The two methods employed in analysis: (1) $GeCl_4$/4Ag and (2) $GeCl_4$/4AgCl yielded distinctly different results. Method (1) resulted in an atomic weight as 72.602, whereas method (2), 72.612. This is because they met with the enrichment of lighter isotopes of both germanium and chlorine in (1), whereas only the lighter isotopes of germanium in (2), where four chlorine atoms in both numerator and denominator counterbalanced each other in the isotopic effect. If no isotopic fractionation occurred, the atomic weight would further increase by, say, 0.01, depending on the extent of separation of the five germanium isotopes. The trend of the isotopic effect can be illustrated approximately by the following scheme:

A_r(Ge) = ~72.622

↓ effect of the enrichment of lighter Ge isotopes

72.612

↓ + effect of the enrichment of ^{35}Cl

72.602

(The atomic weight values mentioned in this paragraph is on the scale O = 16. The value will decrease by 0.003 when scaled to ^{12}C = 12.)

Furthermore, it is to be noted that the experimental error involved in the chemical method is much larger than that in mass spectrometry.

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References

[1] IUPAC Commission on Atomic Weights and Isotopic Abundances, Pure Appl. Chem. 68 (1996) 2339.
[2] H.S. Peiser, N.E. Holden, P. De Bièvre, I.L. Barnes, Pure Appl. Chem. 56 (1984) 695.
[3] P. De Bièvre, M. Gallet, N.E. Holden, I.L. Barnes, Phys. Chem. Ref. Data 13 (1984) 809.
[4] J.R. De Laeter, P. De Bièvre, H.S. Peiser, Mass Spectrom. Rev. 11 (1992) 193.
[5] Handbook of Chemistry and Physics, 71st ed., D.R. Lide (Ed.), CRC, Boston, 1990–1991, p. 10-210.
[6] N.R. Daly, Rev. Sci. Instrum. 31 (1960) 264.
[7] G. Audi, A.H. Wapstra, Nucl. Phys. A 565 (1993) 1.
[8] T.L. Chang, M.T. Zhao, W.J. Li, J. Wang, Q.Y. Qian, Int. J. Mass Spectrom. Ion Processes 177 (1998) 131.
[9] T.L. Chang, Q.Y. Qian, M.T. Zhao, J. Wang, Int. J. Mass Spectrom. Ion Processes 123 (1993) 77.
[10] D.C. Hess, M.G. Inghram, R.J. Hayden, Report No. ANL-4082 Argonne National Lab, Argonne, IL, 1947, p. 6.
[11] R.F. Hibbs, J.W. Redmond, H.R. Gwinn, W.D. Harman, Phys. Rev. 75 (1949) 533.
[12] R.P. Graham, J. Macnamara, I.H. Crocker, R.B. MacFarlane, Can. J. Chem. 29 (1951) 89.
[13] V.H. Dibeler, J. Res. Natl. Bur. Stand. 49 (1952) 235.
[14] J.H. Reynolds, Phys. Rev. 90 (1953) 1047.
[15] M. Shima, J. Geophys. Res. 68 (1963) 4289.
[16] M.D. Green, K.J.R. Rosman, J.R. De Laeter, Int. J. Mass Spectrom. Ion Processes 68 (1986) 15.
[17] T.L. Chang, G.S. Qiao, Chin. Chem. Lett. 8 (1997) 837.
[18] J.W. Gramlich, L.A. Machlan, I.L. Barnes, P.J. Paulsen, J. Res. Natl. Inst. Stand. Technol. 94 (1989) 347.
[19] W.R. Shields, T.J. Murphy, E.L. Garner, J. Res. Natl. Bur. Stand. A 68A (1964) 589.
[20] L.A. Machlan, J.W. Gramlich, L.J. Powell, G.M. Lambert, J. Res. Natl. Bur. Stand. 91 (1986) 323.
[21] G.P. Baxter, W.C. Cooper, J. Phys. Chem. 28 (1924) 1049.