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锗原子量的新测定

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〔摘要〕用两种高富集锗同位素配制的标准混合溶液系列, 以标定一台MAT-262热电离质谱仪, 求得4个同位素丰度比的校准因数, 从而测得5种天然锗样品的4个同位素丰度比的真值。由此计算天然锗5种同位素的丰度值如下:

20.37±0.05 原子% ^{70}Ge
27.38±0.04 原子% ^{72}Ge
7.76±0.05 原子% ^{73}Ge
36.66±0.05 原子% ^{74}Ge
7.83±0.05 原子% ^{76}Ge

再各乘以已知的原子质量, 得出锗原子量的新值为:

$$A_r(\mathrm{Ge}) = 72.639 \pm 0.004$$

这些精确数值的置信度为95%。优于文献上所有已知的相应值。

关键词: 锗 原子量 同位素丰度 质谱

Redetermination of the Atomic Weight of Germanium

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Abstract

A MAT-262 thermal ionization mass spectrometer was calibrated by using

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the gravimetric synthetic mixtures of highly enriched germanium isotopes in the form of oxides with known chemical purity. Measurements on natural germanium samples yielded an absolute isotopic composition of 20.37(5) at. % ^{70}Ge, 27.38(4) at. % ^{72}Ge, 7.76(5) at. % ^{73}Ge, 36.66(5) at. % ^{74}Ge and 7.83(5) at. % ^{76}Ge, and the atomic weight of germanium as 72.639(4) both with an uncertainty given on the basis of 95% confidence limit.

Key Words: germanium, atomic weight, isotopic abundance, mass spectrometry

1 Introduction

Recently our research group reported the absolute isotopic composition of germanium, and its atomic weight as 72.639(7)[1], where the figure within the brackets indicates the uncertainty of the third decimal (notation like this will be used throughout this paper). Now that the rounded value 72.64(1) has been adopted by the IUPAC Commission on Atomic Weights and Isotopic Abundances in 1999 to revise the current value 72.61(2) by an increment so large as 0.03, such a conspicuous change in Ar(E) is a rare event in the contemporary history of atomic weight determinations. The importance of this problem has encouraged us to use a more sensitive thermal ionization mass spectrometer of Finnigan MAT-262 to repeat the isotopic ratio measurement by utilizing the solution samples already prepared in Ref[1].

These samples consisted of 2 primary standard solutions, 8 mixed standard solutions (2 of which had not been measured in the previous work) and 5 solutions prepared from terrestrial germanium materials. In this way, we obtained the same value of the atomic weight of germanium but with a smaller uncertainty.

2 Experimentals

2.1 Mass spectrometric measurement

The Finnigan MAT-262 is an automatic thermal ionization mass spectrometer provided with six Faraday cups, a secondary electron multiplier and a retarding potential quadrupole (RPQ) ion counter, the latter being suitable for measuring the isotopic abundance ratio down to 10^{-5}. The instrument is designed to measure either positive or negative ions. The online computer is Legend 586 LX-P5/100 PCI system with the color graphics software package written in HT BASIC (version 4.4).

The double filament rhenium technique was adopted for measuring germanium ions. After being degassed in vacuum the sample filament was loaded with 3 μL of a saturated solution of boric acid (guaranteed reagent) and then heated with a current of 0.7 A. Thereafter 10 μL of the sample solution containing about 47 μg Ge was carefully loaded onto the liquid layer. When the mixed solution evaporated almost to dryness, the current was lowered to 0.5 A so as to make the loaded film drying up slowly. After the sample magazine was laid into the ion source, the measuring system was evacuated down to 5×10^{-8} mbar. Then the ionization filament was heated up with a current increasing slowly till it reached 4.8 A. Thereafter the sample filament was similarly heated till it reached 0.5 A. After 1 hr the current for the two filaments was increased alternately till the sample filament reached 700℃, and the ionization filament about 2250℃. At this stage the major Ge^+ beam attained about 10^{-12} A. The emission of the ion beam could be kept constant for more than 1 hr.

In the case of samples A and B, the major peak $^{72}G^+$ or $^{74}G^+$ was collected by the Faraday cup, whereas the small peaks were measured by the RPQ. For the eight mixed standard solutions, where only the abundance ratio of $^{72}Ge/^{74}Ge$ needed measuring, two Faraday cups were used for simultaneous collection. In the case of five natural samples of germanium, simultaneous collection of the ion beams of four lighter isotopes by Faraday cups was adopted, but the $^{76}Ge^+$ beam was recorded separately by means of peak-jumping for the sake of avoiding dispersion.

For each sample to be measured, five through ten replicate loadings were made, and for each loading 100 ratios were recorded together with a mean ratio. All those mean ratios form the grand mean of the sample, which is shown in the data tables of this paper.

2.2 Gravimetric synthetic mixtures of highly enriched germanium isotopes

The isotopic composition of samples A and B was first determined by measuring the four ratios of the five isotopes of germanium as shown in Table 1, whereas Table 2 gives the isotopic composition of germanium in each sample. From the latter the concentration of ($^{72}Ge+{}^{74}Ge$) in both primary standard solutions A and B, that is C_A and C_B, can be calculated as described in Ref[1]. The results are given in Table 3.

Table 1 Observed isotopic ratios of germanium in samples A and B (1s)

Sample A 8 replicates		Sample B 6 replicates	
Mass pair	Abundance ratio	Mass pair	Abundance ratio
70/72	0.01502(10)	70/74	0.000301(12)
73/72	0.00931(7)	72/74	0.000609(5)
74/72	0.02738(15)	73/74	0.00551(3)
76/72	0.00594(9)	76/74	0.01623(20)

Table 2 Isotopic composition of germanium in samples A and B(1s)

Isotope	At% in sample A	At% in sample B
70	1.420(10)	0.0294(12)
72	94.549(40)	0.0595(5)
73	0.880(7)	0.539(3)
74	2.589(14)	97.785(20)
76	0.562(9)	$1.587_1(19_4)$

Table 3 Concentration of (^{72}Ge+ ^{74}Ge) in standard solutions A and B

Sample	A	B
Atomic weight	71.9767	73.9452
GeO_2 mol weight	103.9755	105.9440
Total μmol Ge	2362.393	2364.466
At% (^{72}Ge+ ^{74}Ge)	97.1380	97.8447
μmol% (^{72}Ge+ ^{74}Ge)	2294.781	2313.505
μmol(^{72}Ge+ ^{74}Ge) g^{-1} soln.	66.36364(C_A)	63.71649(C_B)

Portions of solutions A and B, weighed accurately as W_A and W_B, were mixed to form eight mixed standard solutions W_A and W_B for mixes Nos 1 through 6 are given in Ref[1], whereas these for Nos 7 and 8 are shown in the footnotes of Table 4. Then the isotopic ratio $R_{72/74}$ of each mix was determined, and from that the correction factor for the instrumental bias, $K_{72/74}$, can be calculated by means of the formula[1]:

$$K=\frac{W_AC_A(R_A-R_{AB})-W_BC_B(R_{AB}-R_B)}{W_BC_BR_A(R_{AB}-R_B)-W_AC_AR_B(R_A-R_{AB})}$$

where Ca and C_B (see Thble 3), $R_A = 36.523$ and $R_B = 0.000609$ (see Table 1) are all constant, whereas W_A, W_B and $R_{AB} = R_{72/74}$ vary in each mix. Thus we obtained eight values of $K_{72/74}$ with the mean as 0.99148(100). Iteration yielded the true value of C_A and C_B as 66.36245 and 63.70947 μmol per gram solution respectively. From those we obtained the true $K_{72/74} = 0.99158(100)$. Besides, the true isotopic composition and the atomic weight of samples A and B are listed in Table 5. The K's for other isotopic ratios as calculated by means of the exponential rule are $K_{70/74} = 0.98323$, $K_{73/74} = 0.99578$ and $K_{76/74} = 1.00849$.

Table 4　Observed $R_{72/74}$ of mixed standard solutions and the correction factor $K_{72/74}$ (1s)

Mix No.	$R_{72/74}$	$K_{72/74}$
1	0.96268(104)	0.99277
2	1.44499(200)	0.98986
3	0.82086(100)	0.99087
4	0.68059(119)	0.99113
5	0.55658(86)	0.99120
6	0.65340(74)	0.99248
7[a]	0.55636(29)	0.99246
8[b]	0.63462(44)	0.99110
Mean		0.99148(100)
Iteration		0.99158(100)

[a] $W_A = 874.025$ mg; $W_B = 1582.652$ mg　[b] $W_A = 1106.263$ mg; $W_B = 1754.442$ mg

Table 5 True isotopic composition and the atomic weight of germanium in samples A and B(1s)

Sample	A	B
At. % ^{70}Ge	1.408(14)	0.0289(13)
At. % ^{72}Ge	94.527(46)	0.0590(6)
At. % ^{73}Ge	0.884(8)	0.537(3)
At. % ^{74}Ge	2.610(17)	97.775(26)
At. % ^{76}Ge	0.571(10)	1.6001(210)
Atomic weight	71.9778	73.9455

2.3 Isotopic composition of terrestrial samples of germanium

The five samples described in Ref[1]. were analyzed for the four ratios of germanium isotopes. The results are shown in Table 6. These observed ratios when multiplied by the respective correction factors yielded the true ratios, from which the isotopic compositions were readily calculated and are given is Tables 7 and 8. The former shows the complete calculation for sample 1 as an example with the overall limit of error, whereas the latter, the isotopic composition of all the terrestrial germanium samples together with the mean isotopic composition. Again, no isotopic fractionation in natural was found. In addition, Table 9 gives the five values of the atomic weight of germanium and also the mean.

Table 6 Observed isotopic ratios of germanium in terrestrial samples(1s)

Sample	No. of replicates	$R_{70/74}$	$R_{72/74}$	$R_{73/74}$	$R_{76/74}$
1	8	0.5649(6)	0.7537(10)	0.2125(6)	0.2123(10)
2	9	0.5651(7)	0.7525(5)	0.2125(7)	0.2115(9)
3	9	0.5660(14)	0.7545(14)	0.2132(11)	0.2118(7)
4	8	0.5652(18)	0.7526(10)	0.2124(9)	0.2123(15)
5	6	0.5646(5)	0.7531(5)	0.2121(11)	0.2118(6)

Table 7 Summary of the calculation of the atomic weight of germanium (sample 1)

Parameter	Value	Mass spectrometric analytical error $2S_m$, ±10^{-3}	Possible error in chemical analysis $2S_c$, ±10^{-4}	Possible bias in separated isotope ratio B, ±10^{-4}	Overall limit of error[a] $[2(S_m^2+S_c^2)^{1/2}+B]$, ±10^{-3}
Isotopic ratio					
$^{70}Ge/^{74}Ge$	0.555427	0.613	1.63	2.82	0.916
$^{72}Ge/^{74}Ge$	0.747354	0.899	2.17	3.77	1.30
$^{73}Ge/^{74}Ge$	0.211603	0.478	0.613	1.06	0.588
$^{76}Ge/^{74}Ge$	0.214072	0.711	0.612	1.06	0.820
At. %					
^{70}Ge	20.3568	25.3	67.3	117	37.9
^{72}Ge	27.3911	29.4	71.2	123	42.5
^{73}Ge	7.7554	32.6	41.7	72.2	40.0
^{74}Ge	36.6508	36.3	67.5	117	48.6
^{76}Ge	7.8459	48.2	41.5	71.9	55.6
Atomic weight	72.6395	1.012[b]	2.69	4.66	1.51
		0.589[b]	1.42	2.47	0.853
		0.325[b]	0.416	0.720	0.400
		0.965[b]	0.831	1.44	1.11

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

[b] The four components pertain to the four ratios

Table 8 Isotopic composition of germanium with overall limit of error in brackets

Sample	At. % ^{70}Ge	At. % ^{72}Ge	At. % ^{73}Ge	At. % ^{74}Ge	At. % ^{76}Ge
1	20.3568(379)	27.3911(425)	7.7554(400)	36.6508(486)	7.8459(556)
2	20.3791(378)	27.3639(342)	7.7606(419)	36.6752(440)	7.8212(483)
3	20.3808(527)	27.3991(479)	7.7750(587)	36.6226(565)	7.8225(416)
4	20.3750(673)	27.3580(422)	7.7555(504)	36.6615(652)	7.8500(819)
5	20.3602(362)	27.3849(352)	7.7464(700)	36.6738(482)	7.8347(427)
Mean	20.370(46)	27.380(40)	7.759(52)	36.656(53)	7.835(54)

Table 9 Atomic weight of germanium with overall limit of error in brackets

Sample	Atomic weight
1	72.63951(387)
2	72.63862(358)
3	72.63773(448)
4	72.63953(567)
5	72.63937(371)
Mean	72.6390(43)

3 Conclusion

The atomic weight of germanium redetermined in this work as Ar(Ge) = 72.6390 (43) confirms the previously determined value 72.6390 (69). Contribution of this new measurement is the distinctly smaller uncertainty. The comparison with other known values given by various authors was already made in Ref[1]. Besides, Kipphardt et al. recently published a value of 72.628 (19), which was obtained by measurement without using separated isotopes for calibration.

It might be interesting to note that though different models of mass spectrometers possess different instrumental bias (in our case, $K_{72/74}$ = 0.99158 vs 0.98355), the final value of Ar(Ge) as ascertained is the same within experimental error as it ought to be.

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