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Publisher's version / Version de l'éditeur:

https://doi.org/10.1021/ac100439j Analytical Chemistry, 82, 10, pp. 4188-4193, 2010-04-27

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Resolving the germanium atomic weight disparity using multicollector ICP-MS

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ABSTRACT

Two most recent mass spectrometric measurements of natural isotopic composition germanium gave discordant Ge atomic weight values of 72.6276(64)_{*k*=2} and 72.6390(69)_{*k*=2}, respectively, a decade ago. Each measurement was performed with a different mass spectrometry platform, gas source isotope ratio mass spectrometry and thermal ionization mass spectrometry, respectively. Herein we report results obtained by multicollector inductively coupled plasma mass spectrometry yielding an atomic weight of germanium 72.6296(19)_{*k*=2} which is in support of the upcoming 2009 Standard Atomic Weight adjustment by IUPAC. Germanium isotope ratios were calibrated using a regression mass bias correction model and NIST SRM 994 gallium isotopic reference material. In this model, no assumptions are made regarding the mass bias differences between gallium and germanium or between the isotopes of germanium. Isotope ratios of 0.5620(21), 0.7515(16), 0.2125(7) and 0.2121(12) were obtained for $n(^{70}\text{Ge})/n(^{74}\text{Ge})$, $n(^{72}\text{Ge})/n(^{74}\text{Ge})$, $n(^{73}\text{Ge})/n(^{74}\text{Ge})$ and $n(^{76}\text{Ge})/n(^{74}\text{Ge})$, respectively, with expanded uncertainties (k = 2) estimated in accordance with the ISO/BIPM Guide to the Expression of Uncertainty in Measurements.

INTRODUCTION

Determination of the atomic weight of germanium has always been somewhat of a challenge – uncertainties as to its precise atomic weight appeared even before the discovery of this element in 1886. In 1864 John Newlands predicted the existence of germanium as a mean of the triad Si–?–Sn with an atomic weight of 73.¹ De Boisbaudran² surmised the existence of an element having atomic weight 72.28 and Mendeleyev's predictions of the atomic weight for ekasilicon varied from 70 (1869) to 72 (1871).^{3,4} (A common misconception is that Mendeleyev was first to predict the existence of this element in 1869.)

Early mass spectrometric measurements of germanium using thermal ionization mass spectrometry gave the average atomic weight value 72.63 whereas the average atomic weight determined by chemical methods was 72.59.^{5,6} Since these mass spectrometric measurements were not calibrated, the Commission on Atomic Weights recommended the 'chemical' value in 1961.⁵ The first fully calibrated germanium isotope ratio measurements appeared only a decade ago, in 1999, and the atomic weights derived were discordant: 72.6276(64) and 72.6390(69).^{7,8} These two measurements were undertaken with different mass spectrometry platforms: gas source isotope ratio mass spectrometry (GSMS) and thermal ionization mass spectrometry (TIMS), respectively and both analysed high-purity germanium standards. Hence, the difference in results is likely due to the measurement process. The Commission on Isotopic Abundances and Atomic Weights sided with the value of Chang et al.⁷ and recommended the 1999 Standard Atomic Weight 72.64(1).⁹ However, at its 2009 Vienna meeting, the Commission reconsidered its previous decision and chose the value of Kipphardt et al.⁸ resulting in the 2009 Standard Atomic Weight of germanium 72.63(1) which will be soon released.¹⁰ This action was supported by the reevaluation of the historical (1950s) crystallographic data by John Arblaster, A_r (Ge) = 72.625(2).¹⁰ However, crystallographic data provide only atomic weight of Ge and no isotopic composition. To help resolve the lingering atomic weight dilemma between the results of Chang et al.⁷ and Kipphardt et al.⁸, we report absolute isotope ratio measurements of germanium using a mass spectrometry platform that is different from

these two studies – a multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS).

Traditionally TIMS has been the technique of choice for achieving the highest accuracy and precision for isotope ratio measurements despite the investment of extensive sample preparation and long measurement time necessary to achieve reliable data.¹¹ Recent developments in MC-ICP-MS has brought a new dimension to this field. In addition to its simple and robust sample introduction, high sample throughput and high mass resolution, the relative precision of the isotope ratio measurements can be as low as ten parts per million, which is comparable to TIMS. However, the much larger mass bias observed with MC-ICP-MS has to be recognized and properly corrected for to achieve accurate isotope ratio measurements. Such a task, however, remains a challenge in analytical chemistry. To date, there is a limited number of applications of MC-ICP-MS for germanium isotope ratio measurements and all of these studies circumvent the challenges of absolute isotope ratio determination by reporting isotope ratios relative to an arbitrary standard (delta scale).¹²⁻¹⁵ In this study we have undertaken absolute isotope amount ratio measurements of the Sigma-Aldrich germanium standard by MC-ICP-MS using a state-of-the-art regression mass bias correction model based on the utilization of temporal drift between the measured Ge and Ga isotope ratios in their log space without any untestable assumptions.

EXPERIMENTAL SECTION

Instrumentation. A Thermo Fisher Scientific Neptune MC-ICPMS (Bremen, Germany) equipped with nine Faraday cups and a combination of cyclonic and Scott-type spray chambers with a self-aspirating nebulizer MCN50 (Elemental Scientific, Omaha NE, USA) made from perfluoroalkoxy polymer and operating at 50 μ L min⁻¹ was used in all measurements. The plug-in quartz torch with sapphire injector was fitted with a platinum guard electrode. Low resolution mode was employed to perform isotope ratio measurements. Optimization of the Neptune was performed as recommended by the manufacturer and typical operating conditions are summarized in Table 1. The gain on each Faraday cup was monitored daily to ensure correction for its efficiency.

Reagents and solutions. Reagent grade nitric acid (Fischer Scientific Canada, Ottawa ON, Canada) was purified in-house prior to use by sub-boiling distillation of reagent grade

feedstock in a quartz still. Environmental grade HF was purchased from Anachemia Science (Montreal QC, Canada). High-purity (18 M Ω cm) deionized water was obtained from a NanoPure mixed bed ion exchange system fed with reverse osmosis domestic feed water (Barnstead/Thermolyne Corp, Iowa, USA). Gallium metal isotopic reference material, NIST SRM 994, was purchased from the National Institute of Standards and Technology (Gaithersburg MD, USA). A 2000 µg g⁻¹ stock solution of SRM 994 was prepared by quantitative dissolution of Ga in warm concentrated nitric acid and then diluted with water. A 2500 µg g⁻¹ stock solution of germanium was prepared by quantitative dissolution of high purity Ge metal (99.999%, Sigma-Aldrich, Oakville ON, Canada) in a mixture of HNO₃ and HF followed by diluted with water.

Sample preparation and analysis. Sample preparation was conducted in a Class-100 clean room. Replicate solutions of 4 μ g g⁻¹ Ge were prepared by diluting the Ge stock solution in 2% HNO₃ followed by spiking with the gallium stock solution, yielding a mass fraction of 500 ng g⁻¹ for Ga.

Samples were introduced into the plasma in a self-aspiration mode at a flow rate of 50 μ L min⁻¹. Intensities of Ge and all other measured isotopes of interest (see below) obtained from a blank solution of 2 % HNO₃ were subtracted from those of all samples. A static run was employed to collect ⁶⁹Ga, ⁷⁰Ge, ⁷⁰Ge, ⁷¹Ge, ⁷²Ge, ⁷³Ge, ⁷⁴Ge and ⁷⁶Ge isotopes simultaneously using the Faraday cup configuration shown in Table 1. Ten to thirteen measurements were made on each sample solution. The duration of each session of measurements was on the order of 10-13 h. Data sets reported here were collected between September and December of 2009. As no significant amounts of Zn and Se were found in the diluted Ge solutions there was no need for corrections of minor isobaric interferences from ⁷⁰Zn on ⁷⁰Ge or ⁷⁴Se on ⁷⁴Ge. Data acquisition parameters are summarized in Table 1.

Table <u>1. MC-ICP-MS operating conditions</u>

Instrument settings			
Reflected forward power	1250 W		
Plasma gas flow rate	15.0 L Ar min ⁻¹		
Auxiliary gas flow rate	1.00 L Ar min ⁻¹		
Carrier gas flow rate	1.080 L Ar min ⁻¹		
Sampler cone depth (H, Ni)	1.1 mm		
Skimmer cone depth (Ni)	0.8 mm		
Lens settings	Optimized for maximum analyte signal intensity		
Data acquisition parameters			
Faraday cup configuration	L3 (⁶⁹ Ga), L2 (⁷⁰ Ge), L1 (⁷¹ Ge), C (⁷² Ge), H1 (⁷³ Ge), H2 (⁷⁴ Ge), H3 (⁷⁶ Ge)		
	$(^{73}Ge), H2 (^{74}Ge), H3 (^{76}Ge)$		
Mass resolution	(⁷³ Ge), H2 (⁷⁴ Ge), H3 (⁷⁶ Ge) ~300		
Mass resolution Sensitivity	(⁷³ Ge), H2 (⁷⁴ Ge), H3 (⁷⁶ Ge) ~300 6.2 V for ⁷² Ge at 1 μg Ge g ⁻¹		
Mass resolution Sensitivity Blank signal (2% HNO ₃)	(⁷³ Ge), H2 (⁷⁴ Ge), H3 (⁷⁶ Ge) ~300 6.2 V for ⁷² Ge at 1 μ g Ge g ⁻¹ 1.6 mV for ⁷² Ge		
Mass resolution Sensitivity Blank signal (2% HNO ₃) Signal integration time	(⁷³ Ge), H2 (⁷⁴ Ge), H3 (⁷⁶ Ge) ~300 6.2 V for ⁷² Ge at 1 μ g Ge g ⁻¹ 1.6 mV for ⁷² Ge 33.5 s		

RESULTS AND DISCUSSION

Mass bias correction. Internal mass bias correction for determination of isotope ratios using MC-ICP-MS commonly employs a pair of isotopes of another "suitable" or reference element and the Russell equation.¹¹ Among such pairs of elements are Hg-Tl,¹⁶ Pb-Tl,¹⁷ Sr-Zr¹⁸ or B-C¹⁹. The Russell equation equates to the following:²⁰⁻²¹

$$R_{i,j} = r_{i,j} \left(\frac{m_i}{m_j}\right)^{-f}.$$
(1)

Here $R_{i,j} = n({}^{i}E)/n({}^{j}E)$, $r_{i,j}$ is the measured (uncorrected) isotope ratio, f is the fractionation function and m_i , m_j are the nuclide masses. Throughout the manuscript we use the notation $R_{i,j} = n({}^{i}E)/n({}^{j}E)$ where E is the element of interest. Assuming identical mass bias for two elements, say $f_{Ga} = f_{Ge}$, Eq. 1 is then used to calibrate (correct) the isotope ratio ($r_{i,j}$) if the isotope ratio $(R_{k,l})$ is known for the reference element:¹⁶⁻¹⁹

$$\boldsymbol{R}_{i,j} = \boldsymbol{r}_{i,j} \left(\frac{\boldsymbol{R}_{k,l}}{\boldsymbol{r}_{k,l}} \right)^{\frac{\ln m_i - \ln m_j}{\ln m_k - \ln m_l}}$$
(2)

In the recent years, however, it has been recognized that the isotope fractionation behavior, *i.e.* the value of *f* in MC-ICP-MS differs from element to element.¹¹ Consequently, the isotope ratios derived in this manner can be erroneous. Errors of up to half a per cent have been noted when the 202 Hg/ 200 Hg ratio is calibrated *via* 205 Tl/ 203 Tl using Eq. 2. $^{22-23}$ Besides, the 'corrected' isotope ratios using the Eq. 2 can be concentration dependent, which clearly invalidates the use of such a correction model for high precision measurements.²³

The performance 'ceiling' of the thirty-year old Russell equation (Eq. 2) is now clearly realized; in the Ga-Ge system, for example, it is able to correct isotope ratios of germanium only to the second decimal digit. With absolute values of isotope ratios being of interest, an alternative approach was employed. To wit, the employed process of Ge isotope ratio determination is described by simultaneously measuring the temporal drift of the Ge and Ga isotope signals. The intercept and slope of the observed log-linear regressions between the measured (uncorrected) isotope ratios of ${}^{i}\text{Ge}/{}^{74}\text{Ge } vs$. ${}^{69}\text{Ga}/{}^{71}\text{Ga}$ forms the basis for calibration of germanium isotope ratio measurement results.¹¹

The principle of the regression model can be obtained through a series of mathematical transformations, free of any untestable. First, the isotope ratio correction factor (K) is introduced here as a factor that links the observed isotope ratios (r) with the unbiased estimates of the isotope ratios (R):

$$R_{i/74}^{Ge} = K_{i/74}^{Ge} \cdot r_{i/74}^{Ge}$$

$$R_{69/71}^{Ga} = K_{69/71}^{Ga} \cdot r_{69/71}^{Ga}$$
(3)

The above expression holds no assumptions for it is merely a definition of the correction factors. The multiplicative relation between the variables K and r can be turned into an additive by the use of logarithms:

$$\ln R_{i/74}^{Ge} - \ln r_{i/74}^{Ge} = \ln K_{i/74}^{Ge}$$

$$\ln R_{69/71}^{Ga} - \ln r_{69/71}^{Ga} = \ln K_{69/71}^{Ga}$$
(4)

Rearrangement of this expression leads to a log-linear regression between the measured isotope ratios of Ge and Ga:

$$\ln r_{i/74}^{\text{Ge}} = \underbrace{\ln R_{i/74}^{\text{Ge}} - \frac{\ln K_{i/74}^{\text{Ge}}}{\ln K_{69/71}^{\text{Ga}}} \ln R_{69/71}^{\text{Ga}}}_{\text{intercept, } a_i} + \underbrace{\frac{\ln K_{i/74}^{\text{Ge}}}{\ln K_{69/71}^{\text{Ga}}} \cdot \ln r_{69/71}^{\text{Ga}}}_{\text{slope, } b_i}$$
(5)

As evident from Figure 1, the measured drift of the ${}^{i}\text{Ge}/{}^{74}\text{Ge}$ and ${}^{69}\text{Ga}/{}^{71}\text{Ga}$ isotope ratios shows well-defined log-linear relationships over a measurement session of 10-13 h in accordance with the Eq. 5. The corresponding intercept (a_i) and slope (b_i) of the log-linear regression is calculated using the least squares approach and these estimates are then used to obtain the mass-bias corrected isotope ratios for germanium, $n({}^{4}\text{Ge})/n({}^{74}\text{Ge}) = R_{i/74}^{\text{Ge}}$, by algebraic rearrangement of Eq. 5:²⁴

$$R_{i/74}^{\text{Ge}} = \left(R_{69/71}^{\text{Ga}} \right)^{b_i} \cdot e^{a_i}$$
(6)

No significant difference in Ge isotope ratios was observed in subsequent experiments with Ge mass fraction in the analyzed solutions from 0.2 to 5 μ g g⁻¹. Once the germanium isotope amount ratios are obtained, Eq. 7 and 8 were used to obtain isotopic abundances and atomic weight of germanium, respectively:²⁵

$$x_{i} = \frac{R_{i/74}^{\text{Ge}}}{\sum_{j} R_{j/74}^{\text{Ge}}}$$
(7)

$$A_{\rm r}({\rm Ge}) = \sum_{i} m_i x_i \tag{8}$$

This isotope ratio calibration model, also known as the external empirical normalization, was first introduced by Maréchal *et al.*²⁶ for determination of the Zn isotope ratio using Cu as a reference element and has been most recently used for the determination of Hg isotope ratios *via* Tl.²² The logic and validation of this measurement process has been described in detail elsewhere.²⁴⁻²⁶ As the model has now been succesfully employed for the analysis of

Cu-Zn²⁶, Hg-Tl²² and Pb-Tl²⁷, we believe that it can be applicable for high-precision absolute isotope ratio measurements of any other element. Moreover, the universal applicability of this model is also strongly supported by the lack of untestable assumptions in its mathematical framework.²⁴

In this work, the NIST certified value²⁸ of 1.50676(39)_{95%} was used for $R_{69/71}^{Ga}$ to obtain the mass bias corrected $R_{i/74}^{Ge}$.



ln (Ga⁶⁹/Ga⁷¹)

Figure1. Temporal drifts of the germanium and gallium isotope ratios during a 13 h measurement session. The log-linear regression plots are the basis for calibrating germanium isotope ratios *via* the $n({}^{69}\text{Ga})/n({}^{71}\text{Ga})$ certified reference value (NIST SRM 994).

Spectral interferences. Potential spectral interferences from ⁴⁰Ar²⁹Si⁺, ⁷⁰Zn⁺, ⁴⁰Ar²⁰Si⁺, ³⁶Ar³⁵Cl⁺, ³⁶Ar³⁵Cl⁺, ³⁶Ar³⁵Cl⁺, ³⁶Ar³⁵Cl⁺, ³⁶Ar³⁵Cl⁺, ³⁶Ar³⁶Ar⁺, ⁷⁶Se⁺, and ³⁶Ar⁴⁰Ar⁺ on both Ga and Ge isotopes could occur in samples containing these elements which would degrade the accuracy of calculated Ge isotope ratios and require elimination or correction. Semiquantitative analysis of Ge sample solutions revealed that the mass fraction of such interfering elements as Zn and Se was less than 5 pg g⁻¹. Such concentrations are insignificant to form isobaric interferences since the mass fraction of Ga and Ge in the samples was 0.25 to 5 μ g g⁻¹, respectively. No significant Si was found in the test solutions. Argon dimer and its associated polyatomic interferences were corrected by subtracting intensities measured from a 2% HNO₃ solution which was used for sample preparation. In general, measured intensities for Ga and Ge isotopes in the 2% HNO₃ solution were at least three to four orders of magnitude lower than those obtained from germanium samples, confirming insignificant contributions from Ar₂⁺ or its associated interferences.

Uncertainty evaluation. Uncertainty propagation of the mass bias corrected germanium isotope ratios (Eq. 6) was done in accordance with the ISO/BIPM "Guide to the Expression of Uncertainty in Measurement". ²⁹ The full uncertainty evaluation framework for isotope ratio, isotopic abundance and atomic weight measurement results is described in great detail elsewhere.^{22, 24}

Because the uncertainty associated with NIST SRM 994 Ga, $n({}^{69}\text{Ga})/n({}^{71}\text{Ga}) = 1.50676(39)_{k=2}$, has to be incorporated in the overall germanium isotope ratio measurement uncertainty, the uncertainty of $R_{i/74}^{\text{Ge}}$ can be evaluated only by means of error propagation. Note also that the regression parameters a_i and b_i in Eq. 6 cannot be considered independent variables. Instead, these are perfectly anti-correlated variables, *i.e.* $\rho(a_i, b_i) = -1$. ^{22, 24} Therefore, the conventional variance propagation of the Eq. 6 leads to the following:

$$u^{2}(R_{i/74}) = \left(b_{i}R_{i/74} \cdot \frac{u(R_{\text{Ga}})}{R_{\text{Ga}}}\right)^{2} + R_{i/74}^{2}(u_{a} - \ln R_{\text{Ga}} \cdot u_{b})^{2}$$
(9)

To account for the correlation between the isotope ratios,³⁰⁻³¹ germanium isotope ratio covariance matrix was evaluated from Eq. 6 using the variance-covariance propagation of the uncertainty contributions from the isotope ratio of gallium and the Ge-Ga regression parameter estimates:

$$\sum_{R} = \mathbf{J}_{R} u_{R_{\text{Ga}}}^{2} \mathbf{J}_{R}^{T} + \mathbf{J}_{reg} \sum_{reg} \mathbf{J}_{reg}^{T}, \qquad (10)$$

where

$$\mathbf{J}_{R} = \left[\frac{\partial R_{i/74}}{\partial R_{Ga}}\right] = \frac{1}{R_{Ga}} \begin{bmatrix} b_{70} \cdot R_{70/74} \\ \vdots \\ b_{76} \cdot R_{76/74} \end{bmatrix},$$
(11)

and

$$\mathbf{J}_{reg} = \begin{bmatrix} \frac{\partial R_{i/74}}{\partial a_i} & \frac{\partial R_{i/74}}{\partial b_i} \end{bmatrix} = \begin{bmatrix} \frac{76}{\bigoplus_{i=70}} R_{i/74} & \ln R_{\mathrm{Ga}} \bigoplus_{i=70}^{76} R_{i/74} \end{bmatrix}.$$
(12)

Here \oplus is a matrix direct sum operator. As an example,

$$\bigoplus_{i=1}^{3} R_{i} = \begin{bmatrix} R_{1} & 0 & 0 \\ 0 & R_{2} & 0 \\ 0 & 0 & R_{3} \end{bmatrix}$$
(13)

Noting again that the estimates of the individual regression intercepts and slopes are perfectly anti-correlated,^{22, 24}

$$\Sigma_{reg} = \begin{bmatrix} \bigoplus_{i}^{1} u_{a_i}^2 & -\bigoplus_{i}^{1} u_{a_i} u_{b_i} \\ -\bigoplus_{i}^{1} u_{a_i} u_{b_i} & \bigoplus_{i}^{2} u_{b_i}^2 \end{bmatrix}.$$
(14)

The uncertainty of isotope abundance measurement results is obtained from the isotope ratio covariance matrix:

$$\boldsymbol{\Sigma}_{\boldsymbol{X}} = \mathbf{J}_{\boldsymbol{X}} \boldsymbol{\Sigma}_{\boldsymbol{R}} \mathbf{J}_{\boldsymbol{X}}^{T} \tag{15}$$

where

$$\mathbf{J}_{x} = \begin{bmatrix} \frac{\partial R_{70/74}}{\partial x_{70}} & \cdots \\ \vdots & \frac{\partial R_{76/74}}{\partial x_{76}} \end{bmatrix}$$
(16)

Last, the uncertainty of atomic weight measurement result was calculated as follows:^{22, 24}

$$u_{A_{\rm r}({\rm Ge})}^2 = \vec{x}^T \cdot \sum_m \cdot \vec{x} + \vec{m}^T \cdot \sum_x \cdot \vec{m}$$
(17)

where $\vec{x} = [x_{70}, ..., x_{76}]^T$ and $\vec{m} = [m_{70}, ..., m_{76}]^T$. Using this approach, each regression plot yields a set of Ge isotope ratios, isotope abundances and atomic weight with the corresponding uncertainties for each estimate. The average of all regression experiment results is then obtained which serves as the property value for all measurands. The combined uncertainty of the grand mean, u_c , was obtained by combining the uncertainties of the individual estimates and the variations between these means as per recent guidelines of NIST—the Type B model of the bias method.³² The following equation was used:

$$u_{\rm c} = \sqrt{s_{\rm m}^2 + \frac{1}{p} \sum u_i^2}$$
(18)

where s_m is the standard deviation of the *p* means (*p* = 12) and u_i is the uncertainty of the individual measurand estimates, i = [1...p].

Results. For the determination of germanium isotope ratios, replicate sample solutions of 4 μ g g⁻¹ Ge and 0.50 μ g g⁻¹ Ga were prepared and each was measured under the optimized experimental conditions in a 10-13 h measurement session. During the three-month period between September and December 2009, many sets of isotope ratio log-linear regressions were acquired for ⁷⁰Ge/⁷⁴Ge, ⁷²Ge/⁷⁴Ge, ⁷³Ge/⁷⁴Ge and ⁷⁶Ge/⁷⁴Ge *vs*. ⁶⁹Ga/⁷¹Ga, each yielding the respective intercept and slope. Depending on the daily operating conditions and stability of the instrument, data sets with poor linearity between Ge isotope ratios and ⁶⁹Ga/⁷¹Ga in their log space could obtained due to unexplained variations in ln $K_{69/71}^{Ge}$ / ln $K_{69/71}^{Ge}$ during the measurement session. Thus, only twelve sets of high-quality

isotope ratio log-linear regressions with high coefficient of determination ($r^2 \ge 0.99$) for all isotope ratios were selected for calculation of the final result. The mass bias corrected Ge isotope ratios were then obtained from Eq. 6 followed by the calculation of the isotopic abundances and the atomic weight using Eq. 7 and 8, respectively.

Mass number,	Nuclide mass, ^b	Isotope amount ratio,	Isotopic abundance,
A	т	$n(^{A}\text{Ge})/n(^{74}\text{Ge})$	x_A
70	69.924 247(2)	0.5620(21)	0.205 26(46)
72	71.922 076(4)	0.7515(16)	0.274 46(15)
73	72.923 459(4)	0.2125(7)	0.077 60(25)
74	73.921 178(4)	1.0000(exact)	0.365 23(63)
76	75.921 403(4)	0.2122(12)	0.077 45(35)
	Atomic weight $A_r(Ge) = 72.6296(19)$		

Table 2. Results for germanium isotope ratios, isotopic abundances and atomic weight^a

a. Values are presented in a concise notation whereby the expanded uncertainty is given in parenthesis next to the least significant digits to which it applies; for example, $x_{70} = 0.205 \ 26(46)$ is the concise form of the expression $x_{70} = 0.20526 \pm 0.00046$. It is intended that the expanded uncertainty encompasses every aspect that reasonably contributes to the uncertainty of the property value. A coverage factor of two (2) was applied.

b. Atomic masses used for calculation are from the 2003 Atomic mass evaluation.³²

The atomic weight of 72.6296(19)_{k=2} obtained by MC-ICP-MS in this study using the regression mass bias correction model is in a good agreement with the value of 72.6276(64)_{k=2} obtained by Kipphardt *et al.*⁸ (GSMS) but is significantly different from 72.6390(69)_{k=2} reported by Chang *et al.*⁷ (TIMS). In our view, the results obtained by Chang *et al.* appear in error largely due to the external calibration of the mass bias. Note that previous studies of germanium isotopic composition have showed no measurable

variations in high purity Ge materials at the level of precision attained in this work.^{7,8,33} However, small variations of ⁷⁰Ge/⁷⁴Ge ratio spanning from –4.0 to +3.0 per mill relative to Sigma-Aldrich Ge standard have been documented in various geological and environmental samples.^{13-15, 34} Since the atomic weight of Ge in this study was measured for the same Sigma-Aldrich Ge material, the observed *relative* natural variations can be readily compared to the measurement uncertainty reported in this work. As shown in Figure 2, the expanded measurement uncertainty of the Ge atomic weight in this material effectively covers the observed variations of Ge isotope ratios.



Sigma-Aldrich Ge material. Range of natural variations, depicted as shaded bowtie, is compiled from Luais $(2007)^{34}$, Siebert *et al.* $(2006)^{13}$, Rouxel *et al.* $(2006)^{14}$ and Hirata *et al.* $(1997)^{15}$.

To achieve utmost transparency of the measurement results, this manuscript is accompanied by an electronic supplementary data file (Microsoft Excel) containing all raw data and calculations contributing to the final germanium isotope ratios, isotopic composition and atomic weight.

CONCLUSIONS

A precise and accurate method was employed for absolute germanium isotope ratio measurements wherein isotopic abundances and atomic weight were calibrated using a regression mass bias correction model. The atomic weight of $72.6296(19)_{k=2}$ obtained in this study agrees with the $72.6276(64)_{k=2}$ by Kipphardt *et al.*⁸ and is in support of the 2009 Standard Atomic Weight of germanium, 72.63(1).¹⁰ Whereas TIMS has been historically the authoritative technique for determining accurate isotopic composition of the elements, MC-ICP-MS was paramount in resolving the recent controversy regarding the atomic weight of zinc.³⁵ Likewise, with this account, we believe that the existing disparity in the atomic weight of germanium will be resolved.

ACKNOWLEDGEMENT

Authors thank Ralph Sturgeon and Zoltán Mester for their valuable comments and discussion which have helped to improve this manuscript.

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