Absolute isotopic composition and atomic weight of selenium using multi-collector inductively coupled plasma mass spectrometry

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ABSTRACT

The isotopic composition of selenium was measured with high precision using a collision cell multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). Gravimetric synthetic mixtures prepared from three highly enriched isotope of ^{76}Se, ^{78}Se and ^{82}Se with well defined purity were used to calibrate a MC-ICP-MS. Measurements of seven various natural selenium materials including Se NIST SRM 3149 yielded the absolute isotopic composition (in at.%) of ^{74}Se 0.8623(38), ^{76}Se 9.228(10), ^{77}Se 7.5975(50), ^{78}Se 23.693(12), ^{80}Se 49.800(17) and ^{82}Se 8.8188(85). The new atomic weight of selenium was calculated as 78.9711(9).

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1. Introduction

Selenium comprises six isotopes, including ^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se and ^{82}Se. Because of the large number of selenium isotopes with a total percentage mass difference between ^{76}Se and ^{82}Se of 7%, and with the numerous microbial or abiotic redox transformations, Se isotopes are potentially excellent tracers of biogeochemical processes and environmental sources. However, it is an arduous job for obtaining accurate measurement result of isotope compositions of Se due to its high ionization potential (9.75 eV) and various influences occurred during the measurement process as well. In addition, the isotope certified reference material of Se is unavailable at present.

Current atomic weight of Se which based on the chemical determination by Hönigschmid and Gönhardt [1,2] has remained unchanged at a value of 78.96 since 1961 [3]. In 1969, Commission on Atomic Weights and Isotopic Abundances (CAWIA) assigned an uncertainty of 0.03 to this value [4]. In recent years, mass spectrometric methods were used for the determination of the atomic weight of Se. Wachsmann and Heumann [5] reported the Se isotopic abundances obtained using negative ionization thermal ionization mass spectrometry (TIMS), the result of which was accepted as the "best measurements" with "1s N" by IUPAC. The calculated atomic weight 78.9594(8) yielded from their noncorrected data, was in good agreement with that of the existing value [6]. In addition, natural variations of Se isotopic composition were established

by Krouse and Thode using high-precision differential methods of measurements [7], the result of which was that the annotation "r" was added by CAWIA in 1999 [8].

More recently, isotopic composition determination of Se has been carried out mainly by using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), which leads to the higher sensitivity and better measurement precision when compared with using TIMS. However, the use of MC-ICP-MS also results in much more interfering species on Se isotopes and greater mass discrimination effects. To address this spectral interferences problem, a number of approaches have been employed. One popular approach is to couple special sample introduction system with a MC-ICP-MS. Rouxel et al. [9] used a continuous flow hydride generator to introduce the analyte into the plasma torch yielded the external precision of 0.025% for isotope ratio ^{82}Se/^{76}Se. Elwaer and Hintlemann [10,11] compared different sample introduction techniques and proved that a hydride generation system was the most suitable method yielding the maximum sensitivity and best precision for Se isotope ratio measurement. Introduction of collision gases into a hexapole collision cell was reported as an effective approach to reduce the interfering species, especially the dimer of Ar to background levels (<1 mV) [12–14].

Correction of mass discrimination effect greatly affected the accurate measurement of Se by MC-ICP-MS. Given the lacking of certified reference materials of Se isotope, Sr is normally used to correct the mass discrimination as internal standard [9,11]. However, the weakness of this method is that Sr and Se may behave differently in both plasma and interface because of the different elemental specialties [9]. Double-spike technique is widely used for the mass discrimination correction described in many

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literatures [10,15,16]. However, it is not an ideal method for correcting different isotope ratios due to the fact that a bias is generated when the same normalized correction factor is applied to correct mass discrimination of all isotope ratios [17–19].

In this paper, Se isotopic composition was accurately measured using GV Isoprobe hexapole collision cell MC-ICP-MS. The interfering species were eliminated by using the mixture of collision gases Ar and H_2. The mass discrimination effects were corrected by using two series of synthetic isotope mixtures, which were gravimetrically prepared with purified enriched isotope materials of ^{76}Se, ^{78}Se and ^{82}Se. The linear relationship between normalized mass discrimination factors and corresponding average mass was used to calculate other mass discrimination factors. Finally, a rigorous assessment of the measurement uncertainty was carried out to obtain the accurate values of isotopic composition and atomic weight of Se.

2. Materials and methods

2.1. Purification of Se isotope materials

^{76}Se, ^{78}Se and ^{82}Se isotope materials with enrichment degrees of more than 99% were purchased from Cambridge Isotope Laboratory (USA). Based on the difference of elemental vapor pressures, three enriched isotope materials were further purified separately by sublimation in a specially designed vacuum vessel at a pressure of 10^{-5} mbar [20]. A maximum of 0.3 g Se material was purified in each purification process. The sublimation for Se took place at about 250 °C with the sublimation rate around 3–5 mg min^{-1}. During the purification process gaseous traces like CO_2 and water vapor, trace non-metallic and metallic elements were successfully removed from these Se materials. Measurements of impurity amounts in the refined enriched isotope materials were carried out with an ICP-MS (Thermo Elemental II). The measurement results showed that the total amount of impurities lowered than 100 μg g^{-1} after purification [20]. In particular, As, Ni and Ge, potential interference on ^{74}Se and ^{76}Se isotopes measurement, were not detected in these purified materials.

2.2. Preparation of primary solutions of enriched ^{76}Se, ^{78}Se and ^{82}Se

Each purified enriched isotope material was carefully weighed with a UMX2 balance (Mettler Toledo, the balance permits estimation to 0.1 μg). The weight pertained to the difference between the weighing beaker and after it into which the sample was added. Buoyancy correction was implemented for all weighing data. The weighed sample in the beaker was dissolved using 1.6 mol L^{-1} HNO_3, then the solution was transferred into the volumetric flask with a dropper. Acid were then used to rinsing the beaker and the solution were combined into the same volumetric flask. Finally, the primary solution was weighed with the XP205 balance (Mettler Toledo). All the data of the primary solutions A (^{76}Se), B (^{78}Se) and C (^{82}Se) are reported in Table 1.

Table 1
Primary solutions A, B and C.

Sample	A	B	C
Enriched isotope	^{76}Se	^{78}Se	^{82}Se
Purity (%)	99.99(1)	99.99(1)	99.99(1)
Weight (mg)	253.9610(1)	414.9886(1)	156.7608(1)
Concentration (μmol g^{-1})	65.346(7)	63.798(6)	60.785(6)

The combined standard uncertainties u_c are given in parentheses.

2.3. Preparation of the synthetic isotope mixtures

Portions of primary solutions A and B, A and C were accurately weighed and thoroughly mixed to develop two series of Se isotope mixtures respectively. There were six isotope mixtures solutions in each series. The isotope ratios were calculated based on the following Eqs. (1) and (2). The weighting data and calculation values of isotope ratios of these mixtures are listed in Table 2.

$$R_{AB} = \frac{W_A C_A f_A{}^a + W_B C_B f_B{}^a}{W_A C_A f_A{}^b + W_B C_B f_B{}^b} \tag{1}$$

$$R_{AC} = \frac{W_A C_A f_A{}^a + W_C C_C f_C{}^a}{W_A C_A f_A{}^c + W_C C_C f_C{}^c} \tag{2}$$

where W refers to weight of the solution A, B and C; C refers to concentration of the solution A, B and C (shown in Table 1); f^a, f^b and f^c are the isotopic abundance of 76, 78 and 82 in the solution A, B and C respectively (shown in Table 6).

2.4. Mass spectrometric measurement

The hexapole collision cell MC-ICP-MS (Isoprobe, GV Instruments) was used to measure the isotope ratios of Se in three enriched isotope materials, synthetic isotope mixtures and natural materials respectively. Nine Faraday cups were used to collect all Se isotopes simultaneously. The instrument was equipped with a set of hexapole collision cell, by which the interfering species based on Ar could be reduced to less than 0.1 mV when the mixture of Ar and H_2 (Ar/H = 6.7) was introduced as a collision gas. Under this condition, the vacuum of the analyser could maintain pressures in the 10^{-8} mbar range, and the signal intensity of ^{80}Se$^+$ in 400 ng g^{-1} natural solution could reach 1 V. However, the use of H_2 in the hexapole collision cell resulted in the formation of 8% of Se hydride SeH$^+$, which required a correction for observed Se isotope ratios before the correction of mass discrimination. A designed experiment showed that the signals occurred at m/z 81 was caused by ^{80}Se^{1}H$^+$. Therefore based on evaluating the rate of hydride formation with the ratio ^{80}Se/^{80}Se^{1}H at m/z 80 and 81, Se hydride interference on each Se isotope were corrected using the Eqs. (3)–(9). The corrections of SeH$^+$ were performed automatically during the isotope ratio data acquiring and reprocessing according to the setting software program.

$$r = R_{81/80} \tag{3}$$

$$I_{74corr} = I_{74meas}(1 + r) \tag{4}$$

Table 2
Isotope ratios of Se in series of AB and AC.

Sample	Weight of solution A(g)	Weight of solution B(g)	(^{76}Se/^{78}Se)$_{calc}$	Sample	Weight of solution A(g)	Weight of solution C(g)	(^{76}Se/^{82}Se)$_{calc}$
Mix-AB-1	0.30877(1)	1.51345(1)	0.20910(3)	Mix-AC-1	0.30242(1)	1.50773(1)	0.21658(3)
Mix-AB-2	0.49040(1)	1.39082(1)	0.36130(5)	Mix-AC-2	0.50295(1)	0.99514(1)	0.54426(8)
Mix-AB-3	0.52895(1)	1.39018(1)	0.38987(6)	Mix-AC-3	1.02588(1)	1.07494(1)	1.02685(15)
Mix-AB-4	0.51197(1)	1.30941(1)	0.40063(6)	Mix-AC-4	1.02793(1)	1.03243(1)	1.07123(15)
Mix-AB-5	0.52605(1)	0.52950(1)	1.01774(15)	Mix-AC-5	1.02155(1)	0.94804(1)	1.15925(16)
Mix-AB-6	0.99126(1)	0.49240(1)	2.06199(30)	Mix-AC-6	1.00754(1)	0.66473(1)	1.63022(23)

The combined standard uncertainties u_c are given in parentheses.

Table 3
Measurement conditions of Se isotope ratio with MC-ICP-MS.

Parameters	
RF power (W)	1350
Plasma Ar gas flow (L min^{-1})	13.5
Auxiliary Ar gas flow (L min^{-1})	1.05
Nebulizer Ar gas flow (L min^{-1})	1.10
Nebulizer type	μ-Flow PFA-ST
Typical sample uptake rate (μL min^{-1})	100
Sampling cone material	Nickel
Skimmer cone material	Nickel
Ar collsion flow rate (mL min^{-1})	1.0
H$_2$ collision flow rate (mL min^{-1})	0.15
Block	3
Cycle	10
Mass assignment to detectors	9 Faraday cups
^{82}Se	H6
^{80}Se^{1}H	H5
^{80}Se	H4
^{78}Se^{1}H	H3
^{78}Se	H2
^{77}Se	H1
^{76}Se	Ax
^{75}As	L1
^{74}Se	L2

$$I_{76corr} = I_{76meas}(1 + r) \tag{5}$$

$$I_{77corr} = (I_{77meas} - I_{76meas}r)(1 + r) \tag{6}$$

$$I_{78corr} = (I_{78meas} - (I_{77meas} - I_{76meas}r)r)(1 + r) \tag{7}$$

$$I_{80corr} = I_{80meas}(1 + r) \tag{8}$$

$$I_{82corr} = I_{82meas}(1 + r) \tag{9}$$

Where I_{corr} and I_{meas} are the corrected signal intensity and the measured signal intensity of each isotope respectively.

The instrument background signal on each Faraday collector was measured before each Se sample analysis by using 2% HNO$_3$ and then subtracted automatically from the corresponding signal in the Se sample based on the setting measurement program. NiO$^+$ interferences resulting from nickel cones at m/z 74 and 76 were also observed at the background level but did not exceed 0.05 mV level. In order to avoid cross contamination caused by different isotope samples, the instrument background was rinsed with 2% HNO$_3$ for at least 15 min between samples. The measurement parameters and Faraday cups arrangement are listed in Table 3.

The measurements of all samples (enriched isotope materials, synthetic isotope mixtures and natural materials) were performed over two consecutive days. Constance current gain corrections cross calibrated the gains for each amplifier was performed at the beginning of each day's session. The analytical sequences applied are described in Fig. 1.

3. Results and discussion

3.1. Calculation of the correction factors of mass discrimination

Two series of synthetic isotope mixtures were analyzed for investigating the mass discrimination of the MC-ICP-MS. The correction factors (K) of mass discrimination were calculated by Eq. (10). The data are listed in Table 4.

$$K = \frac{R_{calc}}{R_{meas}} \tag{10}$$

where R_{calc} is the calculated isotope ratio with Eqs. (1) or (2), R_{meas} is the measured isotope ratio.

Mass bias effect caused in MC-ICP-MS is very different from that in TIMS [21–23], and researches [24,25] prove that both K factors and normalized correction factors (β) of different isotope ratios are different in MC-ICP-MS. The relationship between β and K can be described with the Eq. (11). It was found [18,19] that β appears to be linearly correlated with the corresponding isotope pair mass average in MC-ICP-MS, which was confirmed in our experiment (shown in Fig. 2). It was adapted for calculating the correction factors of other Se isotope ratios. The correction factors of all the Se isotope ratios are shown in Table 5.

$$\beta = \frac{Ln\ K}{Ln(M_i/M_j)} \tag{11}$$

where M_i and M_j are the nuclear mass of isotope i and j respectively.

3.2. Stability of the instrument over time

Since it took two days to finish the measurement of all samples, the stability of the MC-ICP-MS was quite important for obtaining ideal data. For the purpose of testing the stability of the MC-ICP-MS two experiments were designed. Firstly, Se isotope ratios in natural Se-1 sample were monitored over a period of 5 h. The data were obtained under the measurement conditions listed in Table 3. The RSD of the average ratios of ^{82}Se/^{80}Se, ^{78}Se/^{80}Se and ^{76}Se/^{80}Se were 0.005%, 0.007% and 0.01% respectively. Secondly, the series of AB isotope mixtures were measured repeatedly over three days (the plasma was shut down after finishing the measurement in one day). The values of K(^{76}Se/^{78}Se) obtained in three days agreed within less than 0.01%. The experiments indicated that no obvious systematic drift of the instrument and fluctuation of the mass discrimination were observed over the period of the entire measurements.

3.3. Enriched ^{76}Se, ^{78}Se and ^{82}Se materials

The isotope ratios of three enriched isotope materials ^{76}Se, ^{78}Se and ^{82}Se were measured under the same instrument conditions and replicated three times. Meanwhile, AB and AC series isotope mixtures were used to calibrate the mass discrimination effect. The K factor values were calculated by an iteration cycle method (Eqs. (1), (2), (10) and (11)). The iteration continued until the relative
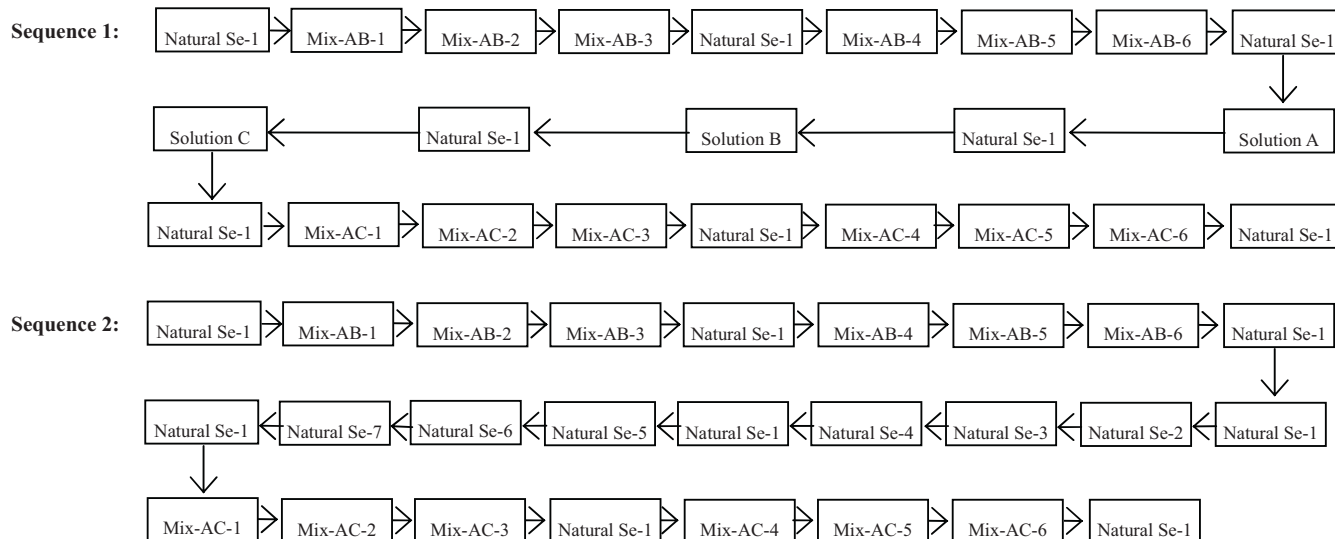
Table 4
Correction factors of series AB and AC.

Sample	(^{76}Se/^{78}Se)$^a_{meas}$	K(^{76}Se/^{78}Se) [b]	Sample	(^{76}Se/^{82}Se)$^a_{meas}$	K(^{76}Se/^{82}Se) [b]
Mix-AB-1	0.198174(3)	1.0551(2)	Mix-AC-1	0.183544(6)	1.1800(2)
Mix-AB-2	0.342135(7)	1.0560(1)	Mix-AC-2	0.462178(14)	1.1778(2)
Mix-AB-3	0.369466(12)	1.0552(2)	Mix-AC-3	0.871223(26)	1.1786(2)
Mix-AB-4	0.379647(11)	1.0553(2)	Mix-AC-4	0.908576(33)	1.1790(2)
Mix-AB-5	0.964234(26)	1.0555(2)	Mix-AC-5	0.983797(70)	1.1783(2)
Mix-AB-6	1.952121(33)	1.0563(2)	Mix-AC-6	1.384049(43)	1.1779(2)
Mean		1.0556(2)	Mean		1.1786(3)
$\beta_{76/78}$		-2.082(7)	$\beta_{76/82}$		-2.161(4)

[a] The standard deviations of the means (1s) are given in parentheses.
[b] The combined standard uncertainties u_c are given in parentheses.

Fig. 1. Measurement sequences of Se isotope mixtures, enriched isotope materials and natural Se samples.

difference between two consecutive K values was less than 10^{-7}. The corrected isotopic compositions of the three enriched isotope materials are shown in Table 6.

3.4. Absolute isotopic composition and atomic weight of Se

Five natural solid Se materials with high purity (over 99.999%) and two standard solutions of Se were collected for isotopic composition determination in this work. The details of the seven materials are listed in Table 7. All natural materials and two series of synthetic

Table 5
Correction factors of selenium isotope ratios.

Isotope ratio	β	K
$^{76}Se/^{74}Se$	−2.007 (16)	0.9479(4)
$^{76}Se/^{77}Se$	−2.064 (7)	1.0274(1)
$^{76}Se/^{78}Se$	−2.082(7)	1.0556(2)
$^{76}Se/^{80}Se$	−2.120 (2)	1.1149(2)
$^{76}Se/^{82}Se$	−2.161(4)	1.1786(3)

The combined standard uncertainties u_c are given in parentheses.

Table 6
Isotopic composition of the enriched isotope materials.

	Sample	A	B	C
	Enriched isotope	^{76}Se	^{78}Se	^{82}Se
^{74}Se		0.00031(2)	0.00002(3)	0.00011(5)
^{76}Se		0.99377(3)	0.000118(3)	0.000951(8)
^{77}Se		0.005796(1)	0.003739(2)	0.00014(2)
^{78}Se		0.000037(1)	0.99569(3)	0.00005(1)
^{80}Se		0.000015(1)	0.000414(1)	0.001201(1)
^{82}Se		0.00007(2)	0.000020(8)	0.99755(5)

The combined standard uncertainties u_c are given in parentheses.

Table 7
Details of seven natural selenium materials.

| Materials	Properties	Source
Natural Se-1	Se, black powder	ALDRICH 229865, Belgium
Natural Se-2	Selenium dioxide, White powder	ALDRICH 204315, USA
Natural Se-3	Selenium dioxide, White pieces	ACROS, USA
Natural Se-4	Selenium dioxide, White pieces	STREM, USA
Natural Se-5	Solution, 100 μg ml^{-1}	GBW(E) 080215, NIM, China
Natural Se-6	Solution, 10 mg g^{-1}	SRM 3149, NIST, USA
Natural Se-7	Se, gray pellet	ALDRICH 204307, USA
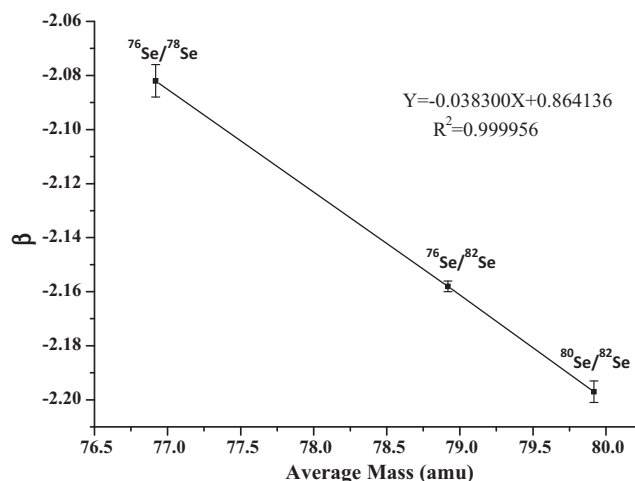
Fig. 2. Variation of β against the corresponding average atomic mass.

isotope mixtures were analyzed in one day and repeated for three times independently. The data of corrected isotope ratios of the seven natural materials are listed in Table 8. The absolute isotopic compositions and atomic weights with the expanded uncertainties (k = 2) of seven natural materials are reported in Table 9, which were calculated using the corrected isotope ratios. Furthermore, an atomic weight of $A_r(Se)$ = 78.9711(9) (k = 2) was obtained from the seven natural materials.

3.5. Uncertainty evaluation

Wieser and Berglund presented the recommendations for evaluation of isotope-ratio-measurement uncertainty in "Atomic weights of the elements 2007" (IUPAC Technical Report) [26]. According to this guideline and ISO GUM [27], all uncertainties reported in this paper were evaluated including random error and potential systematic errors.

For the uncertainty evaluation of Se isotope ratios, the internal precision, reproducibility of the measurement and K factors were taken into account. For the calculation of K factor, the uncertainty on the purities of the enriched isotope materials was the major contributor to the total budget by far 90%, followed by the uncertainty on the weighting of Se materials. In this study purifying of isotope

Table 8
Corrected isotope ratios of natural selenium.

Materials	^{76}Se/^{74}Se	^{76}Se/^{77}Se	^{76}Se/^{78}Se	^{76}Se/^{80}Se	^{76}Se/^{82}Se
Natural Se-1	10.728(19)	1.2146(3)	0.38928(18)	0.18508(16)	1.0443(14)
Natural Se-2	10.77(5)	1.2153(6)	0.38937(12)	0.18525(6)	1.0461(5)
Natural Se-3	10.690(8)	1.2143(3)	0.38955(9)	0.18538(5)	1.0472(4)
Natural Se-4	10.684(6)	1.21422(20)	0.38950(10)	0.18533(6)	1.0467(4)
Natural Se-5	10.67(3)	1.2164(4)	0.39023(12)	0.18586(12)	1.0500(9)
Natural Se-6	10.684(23)	1.2141(3)	0.38928(9)	0.18509(9)	1.0447(8)
Natural Se-7	10.70(3)	1.21435(25)	0.38924(13)	0.18512(10)	1.0454(3)
Average	10.705(27)	1.2147(4)	0.38950(16)	0.18530(14)	1.0463(11)

The combined standard uncertainties u_c are given in parentheses.

Table 9
Isotopic abundance and atomic weight of natural selenium.

Materials	$f(^{74}$Se)	$f(^{76}$Se)	$f(^{77}$Se)	$f(^{78}$Se)	$f(^{80}$Se)	$f(^{82}$Se)	Atomic weight
Natural Se-1	0.008594(40)	0.09220(12)	0.075917(74)	0.23685(12)	0.49815(22)	0.08829(12)	78.9720(11)
Natural Se-2	0.008583(84)	0.09230(4)	0.075941(89)	0.23699(10)	0.49803(16)	0.088155(60)	78.9715(6)
Natural Se-3	0.008635(14)	0.09231(4)	0.076022(22)	0.23696(8)	0.49793(12)	0.088150(45)	78.9706(3)
Natural Se-4	0.008638(12)	0.09229(4)	0.076012(24)	0.23694(8)	0.49796(12)	0.088167(40)	78.9707(4)
Natural Se-5	0.008667(51)	0.09249(8)	0.076045(25)	0.23703(16)	0.49767(18)	0.088093(84)	78.9693(8)
Natural Se-6	0.008630(33)	0.09220(6)	0.075949(40)	0.23685(14)	0.49812(16)	0.088253(76)	78.9717(6)
Natural Se-7	0.008617(44)	0.09221(8)	0.075942(39)	0.23690(10)	0.49812(16)	0.088207(38)	78.9715(6)
Average	0.008623(38)	0.09228(10)	0.075975(50)	0.23693(12)	0.49800(17)	0.088188(85)	78.9711(9)

The expanded uncertainties U are given in parentheses, $U = k \cdot u_c$, $k = 2$.

materials and weighing with high precision balances reduced the related uncertainties effectively. The systematic errors in the measurement caused by the corrections of blank, baseline, SeH$^+$, and the stability of the instrument were reflected in the internal precision and reproducibility of the measurement of the isotope ratios. The variability of mass discrimination resulted from the different synthetic isotope mixtures and the fluctuation of the mass discrimination during the measurement were reflected in the uncertainty of the corrected isotope ratio.

For the uncertainty evaluation of the Se atomic weigh, besides the sources of uncertainties mentioned above, the isotopic abundance variations in the seven natural materials were taken into account as well.

4. Conclusions

The absolute isotopic composition of Se was determined by collision cell MC-ICP-MS. The absolute mass spectrometry method described in this paper makes precise measurement of Se isotope ratios in high purity samples possible for the first time.

Special attentions were paid not only to the elimination of isobaric interferences with Se isotopes using the mixture of Ar and H$_2$ gases as collision gas, but also to correct the effect of Se hydride reasonably. Two series of synthetic isotope mixtures, which gravimetrically prepared with purified enriched isotope materials ^{76}Se, ^{78}Se and ^{82}Se were used to correct the MC-ICP-MS. The isotope discrimination correction factors were calculated based on the linearity relationship between β and corresponding average mass. The corrected isotope ratios were used to calculate the final isotopic abundances and atomic weight of Se. The new atomic weight of Se derived from these seven natural materials is A_r(Se) = 78.9711(9). Compared with the present values of isotopic composition and standard atomic weight of Se [6], the uncertainties are significantly improved. In this study, we also investigated the isotopic composition and atomic weight of Se in NIST SRM3149 (Se solution), which is commonly used for Se isotope research as the reference standard (the delta zero material) in recent years [10,16,28], the absolute isotopic composition of this sample is listed in Table 9, and the derived Se atomic weight is 78.9717(6).

On the basis of this study, some of the natural Se materials (Table 9) have the potential to be used as the isotope reference materials through the further stability testing and combined uncertainty evaluation for the reference material according to the ISO GUIDE 35.

References

[1] O. Hönigschmid, L. Gönhardt, Naturwissenschaften 32 (1944) 68.
[2] O. Hönigschmid, W. Kapfenberger, Z. Anorg. Allg. Chem. 212 (1933) 198.
[3] A.E. Cameron, E. Wichers, J. Am. Chem. Soc. 84 (1962) 4175–4197.
[4] Atomic weights of the elements 1969. Pure Appl. Chem. 21(1970) 91–108.
[5] M. Wachsmann, K.G. Heumann, Adv. Mass Spectrom. 11B (1989) 1828–1829.
[6] J.R. de Laeter, J.K. Böhlke, P. De Bièvre, H. Hidaka, H.S. Peiser, K.J.R. Rosman, P.D.P. Taylor, Pure Appl. Chem. 75 (2003) 683–800.
[7] H.R. Krouse, H.G. Thode, Can. J. Chem. 40 (1962) 367–375.
[8] T.B. Coplen, Atomic weights of the elements 1999, Pure Appl. Chem. 73 (2001) 667–683.
[9] O. Rouxel, J. Ludden, J. Carignan, L. Marin, Y. Fouquet, Geochim. Cosmochim. Acta 66 (2002) 3191–3199.
[10] N. Elwaer, H. Hintelmann, J. Anal. At. Spectrom. 23 (2008) 733–743.
[11] N. Elwaer, H. Hintelmann, J. Anal. At. Spectrom. 23 (2008) 1392–1396.
[12] G.C. Eiden, C.J. Barinaga, D.W. Koppenaal, J. Anal. At. Spectrom. 11 (1996) 317–322.
[13] J.J. Sloth, E.H. Larsen, J. Anal. At. Spectrom. 15 (2000) 669–672.
[14] K. Inagaki, A. Takatsu, A. Nakama, S. Eyama, T. Yarita, K. Okamoto, K. Chiba, Anal. Bioanal. Chem. 385 (2006) 67–75.
[15] K. Dideriksen, J.A. Baker, S.L.S. Stipp, Geochim. Cosmochim. Acta 70 (2006) 118–132.
[16] J.M. Zhu, T.M. Johnson, S.K. Clark, X.K. Zhu, Chin. J. Anal. Chem. 10 (2008) 1385–1390.
[17] C.R. Quétel, J. Vogl, T. Prohaska, S. Nelms, P.D.P. Taylor, P. De Bièvre, Fresenius J. Anal. Chem. 368 (2000) 148–155.
[18] D. Vance, M. Thirwall, Chem. Geol. 185 (2002) 227–240.
[19] E. Ponzevera, C.R. Quétel, M. Berglund, P.D.P. Taylor, P. Evans, R.D. Loss, G. Fortunato, J. Am. Soc. Mass Spectrom. 17 (2006) 1412–1427.
[20] T.X. Ren, X.Y. He, J. Wang, H. Lu, T. Zhou, Chem. Reagents 32 (2010) 747–749.

[21] T.X. Ren, H. Lu, J. Wang, X.Y. He, T. Zhou, Chin. J. Anal. Chem. 38 (2010) 1620–1624.
[22] C.P. Ingle, B.L. Sharp, M.S.A. Horstwood, R.R. Parrish, D.J. Lewis, J. Anal. At. Spectrom. 18 (2003) 219–229.
[23] H. Andreïn, I. Rodushkin, A. Stenberg, D. Malinovsky, D.C. Baxter, J. Anal. At. Spectrom. 19 (2004) 1217–1224.
[24] M.F. Thirlwall, R. Anczkiewicz, Int. J. Mass Spectrom. 235 (2004) 59–81.
[25] F. Wombacher, M. Rehkämper, J. Anal. At. Spectrom. 18 (2003) 1371–1375.
[26] E.W. Michael, M. Berglund, Pure Appl. Chem. 11 (2009) 2131–2156.
[27] Guide to the Expression of Uncertainty in Measurement, International Organisation for Standardisation, Geneva, Switzerland, 1995.
[28] J. Carignan, H.J. Wen, Chem. Geol. 242 (2007) 347–350.