

Novel Approach for the Accurate Determination of Se Isotope Ratio by Multicollector ICP-MS

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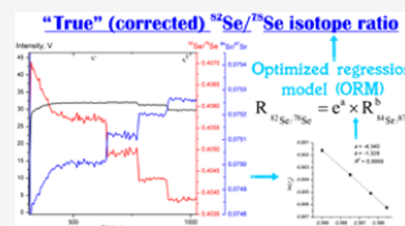
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ABSTRACT: In this work, a method for the accurate and precise determination of $^{82}\text{Se}/^{78}\text{Se}$ isotope ratio in natural samples of environmental and biological origin, using multicollector inductively coupled plasma mass spectrometry in a wet plasma mode without using neither hydride generation nor separation of Se, was developed. It was based on the optimized regression model with standard–sample bracketing (ORM–SSB) to efficiently correct instrumental isotopic fractionation/mass bias and matrix effects. In addition, three mass bias correction models of SSB alone, SSB combined with internal standard (IS–SSB), and ORM–SSB were compared for the Se isotope ratio measurements. NIST SRM 987 Sr was used as an internal standard, and the reproducibility of the results obtained with the proposed method was verified by measuring NIST SRM 3149 standard over different days (nine independent measurement sessions). Delta values of the $^{82}\text{Se}/^{78}\text{Se}$ isotope ratio were measured in selenium-enriched yeast-certified reference material SELM-1, natural selenomethionine samples, and model solutions of artificial seawater. Solutions obtained after thiol resin treatment were measured to demonstrate the applicability of the proposed method in eliminating matrix effects due to residual of thiol resin in the sample solutions. Among three mass bias correction models, ORM–SSB correction model proved to be the best to eliminate the matrix effects and instrumental drift. IS–SSB model offered also a good precision but was slightly less accurate. Both models showed good robustness against effects of different sample matrices. Finally, the SSB alone could not be recommended for Se isotope analysis as it produces inaccurate and imprecise results.



Selenium (Se) is an essential trace element for humans and many other organisms, responsible for healthy growth and normal physiological functioning. It has both toxicological and environmental interests because its range between beneficial and poisonous is very narrow.¹ In recent years, Se has received ongoing attention in the fields of geoscience,² environmental science,³ paleontology,⁴ botany,⁵ zoology,⁶ microbiology,^{7,8} medicine,⁹ animal husbandry,^{10,11} food,¹² nutrient sciences,¹³ and so on. Se isotopes can elucidate the biogeochemical cycling of this element and provide information on environmental changes in the deep history.^{2,14}

Selenium has six natural isotopes of masses 74, 76, 77, 78, 80, and 82 with mole fractions in naturally occurring samples of 0.889, 9.366, 7.635, 23.772, 49.607, and 8.731%, respectively. Due to common isotope-abundance variations in Se-containing materials of natural terrestrial origin, the standard atomic weight uncertainties have been assigned values that are much larger than analytical uncertainties.¹⁵ That is why the determination of Se isotope fractionation in natural samples is a challenging task.

Thermal ionization mass spectrometry (TIMS) was recognized as a gold standard for highly precise measurements of Se isotope ratios to investigate the natural fractionation of Se isotopes, as IUPAC accepted Se isotopic abundances were measured using this method.¹⁶ Nowadays, most investigations of Se fractionation in natural objects are carried out by using

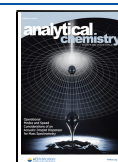
multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), which offers better precision and higher sensitivity in comparison with TIMS.¹⁷ Other methods like hexapole collision cell CC-ICP-MS and a double-focusing sector field SF-ICP-MS usually lack precision.¹⁸ That is why MC-ICP-MS has found numerous applications for various samples including yeasts,¹⁹ chondrites,²⁰ black shales,²¹ seawater,²² urban top soils,³ soils with specific fungi,²³ and different geological samples.^{4,24}

On the other hand, the application of MC-ICP-MS has two problems to deal with during the measurement of Se isotope ratios: (1) the presence of numerous isobaric interfering species, especially different argides, formed whenever argon was used as a plasma gas; and (2) Se has a relatively high first ionization potential (9.75 eV), which results in low ionization efficiency and consequently poor sensitivity for elemental analysis by ICP-MS. Moreover, the most abundant Se isotope (^{80}Se) is often overlooked due to interference from argon

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dimer. To solve the problem of isobaric interferences, two main approaches have been used. The first is to employ the collision cell technology.^{17,25} Most interferences, including dimers of Ar, can be eliminated in this method via the interaction with a collision gas (H₂ or Ar) in a hexapole collision cell. The reported precision is sufficient to investigate the fractionation of Se isotopes in natural samples.²⁶ The second approach, which is much more popular, is to couple MC-ICP-MS with a dedicated sample introduction system. Hydride generation (HG) system is the most commonly used for Se,^{3,4,19–25,27,28} providing the best possible matrix removal. The detailed comparison²⁹ of a hydride generation technique with other modes of sample introduction, e.g., multimode sample introduction system (MSIS),³⁰ confirmed that the coupled HG-MC-ICP-MS method yields the best precision and highest sensitivity for Se isotope analysis. It was found that mixing the gaseous hydrides evolved from a HG system with a small volume of methane increases the sensitivity even more.¹ Serious problems with maintaining the stability of the signal can occur when MC-ICP-MS is coupled with hydride generation as chemical form and oxidation state negatively affects the precision and sensitivity. Besides, there are hydride elements (Ge, As) that directly interfere with Se hydride²¹ or possible interelemental interferences causing matrix effects in the formation of hydrides^{31,32} leading to the necessity of additional sample treatment steps.

Due to intensive research into selenium isotopes in recent years, the application of selenium isotopic certified reference materials (CRMs) would have been the easiest way to correct the mass discrimination effect of the instrument. NIST standard reference material (SRM) 3149 was offered as the delta zero reference Se solution²⁶ and used by many researchers, but still there is no consensus about this. Efforts to develop other reliable CRMs were carried out,³³ but they have not gained wide approval from the scientific community yet. The gravimetric isotope mixture correction model is a great alternative with good precision, but it is very complex and expensive, so it has found application in Se isotope ratio determination only in one research,¹⁷ although the double-spike technique is the most widely employed for the isotopic fractionation correction during analysis of Se.^{3,20,23,24,27,28} Nevertheless, this method is not ideal for correcting Se isotope ratios because it does not take into account the possible mass-independent fractionation, and a bias is generated when the same normalized correction factor is used for all Se isotope ratios.¹⁷

The application of an internal standard (IS) of a different element, usually Sr, for the determination of Se isotope ratios is a common practice.^{25,30} Since both the analyte and IS are measured simultaneously in the same solution, the sample matrix effects may be limited.³⁴ As during the analysis of real samples, it is usually required that Se is separated from the matrix by means of commercially available ion-exchange resins to eliminate the adverse matrix effects. Thus, the application of IS may omit the necessity of the applying hydride generation system for matrix removal. However, this mass bias correction method received a lot of criticism since Sr and Se may behave differently in the ICP due to differences in elemental peculiarities.^{17,25} On the other hand, at least 2-fold improvement in the precision of isotope ratio measurements was achieved by the combination of standard–sample bracketing with internal standard normalization (IS–SSB) according to the Russell law^{35–37} compared to the corrected results from

SSB alone.³⁸ The drawback of this technique is that the corrected isotope ratios depend on the concentration, so the contents of both internal standard and analyte in the standard solution and the sample need to be matched for accurate results.

The regression model, which also uses a primary isotope reference material of a different element but is not derived from either the exponential or the Russell law, is one of the most state-of-the-art methods for instrumental fractionation correction.^{38,39} Initially proposed by Marechal et al.,⁴⁰ this model was modified and applied for the determination of absolute isotopic composition and atomic weight of Ge and In.^{41,42} Further development of the modified regression model led to the reduction of measurement time from 6–15 h to less than 30 min per session.^{33,43,44} By means of this optimized regression model (ORM), the absolute isotopic composition was re-established for such elements as Ir, Mo, Pb, Os, Lu, and Hf,^{39,43–47} and most of the results obtained were adopted by IUPAC as best atomic weight values (Ir, Hf, Ge, In). Moreover, after the primary validation of ORM,³⁹ it was additionally cross-validated with the expensive full gravimetric isotope mixture model, which on the contrary requires matrix matching.⁴⁴ The results from both models were in good agreement, proving that ORM is robust to matrix effects.

According to literature data, ORM has not been applied yet for the determination of Se delta values using the Neptune Thermo Fisher MC-ICP-MS instrument. As for multicollectors from the second of the two most popular manufactures,⁴⁸ Nu Instruments (Wrexham, U.K.), this mass bias correction model was not used at all for the determination of stable isotope ratio of any other element. Since ORM is a promising and relatively cheap way to correct both mass-dependent and mass-independent fractionations, its suitability for precise Se fractionation studies of natural samples is worth checking.

The objectives of this work were to develop a method for the accurate and precise determination of ⁸²Se/⁷⁸Se ratio in natural samples and to check the applicability of different mass bias correction models. The possibility of ⁸⁷Sr/⁸⁴Sr and ⁸⁶Sr/⁸⁴Sr ratios as an internal standard for the correction of mass discrimination and instrumental drift during isotopic analysis of ⁸²Se/⁷⁸Se was investigated. To the best of our knowledge, this is the first study for the detection of isotopic fractionation in natural samples using the MC-ICP-MS instrument “Plasma II” that applies ORM. Moreover, bromine and rubidium were also studied as alternative internal standards due to the following reasons: (1) they have a close atomic weight in relation to selenium and (2) they exist only in the form of two stable isotopes (⁷⁹Br, ⁸¹Br, and ⁸⁵Rb, ⁸⁷Rb), in contrast to strontium, which has four isotopes. The ORM will be compared with other mass bias correction models in terms of accuracy, precision, and especially robustness to matrix effects.

■ EXPERIMENTAL SECTION

Correction for Instrumental Isotopic Fractionation.

The main goal of the present study was to develop a new and simple method for the determination of Se isotope ratio without matrix separation and to compare the performance of three methods for measuring the δ value of the ⁸²Se/⁷⁸Se ratio: SSB, IS–SSB, and ORM–SSB.

The determination of isotopic changes using the SSB model was based on sequential measurements of the standard–sample–standard at a fixed (1300 W) radio-frequency (RF)

value. Such external calibration with a standard (NIST SRM 3149) provides the delta value, calculated according to eq 1

$$\delta\text{Se}(\text{‰}) = \left(\frac{\left(\frac{{}^{82}\text{Se}}{{}^{78}\text{Se}} \right)_{\text{sample}}}{\frac{\left(\frac{{}^{82}\text{Se}}{{}^{78}\text{Se}} \right)_{\text{std}(1)} + \left(\frac{{}^{82}\text{Se}}{{}^{78}\text{Se}} \right)_{\text{std}(2)}}{2}} - 1 \right) \times 1000 \quad (1)$$

IS–SSB relies on a simultaneous measurement of the isotope ratio of Se and Sr in the sample and the standard. Since the Sr isotope ratio is known, this element is used to correct the measured Se isotope ratio. The Russell law is applied with the following equation³⁸

$$R_{i/j} = r_{i/j} \times \left(\frac{m_i}{m_j} \right)^f \quad (2)$$

where R denotes the “true” (corrected) ratio, r is the measured ratio, m is the atomic mass of the isotope of interest, i and j in our particular case are isotopes ${}^{82}\text{Se}$ and ${}^{78}\text{Se}$, respectively, and f is the mass bias correction factor, calculated using the following equation⁴⁹

$$f = \frac{\ln\left(\frac{R_{k/l}}{r_{k/l}}\right)}{\ln\left(\frac{m_k}{m_l}\right)} \quad (3)$$

where k and l are isotopes ${}^{84}\text{Sr}$ and ${}^{87}\text{Sr}$, respectively. In this case, the sample and standard (NIST SRM 3149) are both spiked with Sr standard (NIST SRM 987) and measured alternately several times at a fixed (1300 W) RF power. Once true Se isotope ratios have been calculated for both the standard and sample, the delta value is then calculated according to eq 1.

The optimized regression model (ORM) relies on the observation of the correlated drift between isotope ratios of Se and Sr. A linear relation is observed between both measured ratios r in natural logarithmic coordinates and can be expressed as follows

$$\ln(r_{i/j}) = a + b \times \ln(r_{k/l}) \quad (4)$$

It is assumed that the true isotope ratio R is proportional to its measured ratio r , so eq 5 was deduced from the previous dependence to calculate the isotope ratios free from instrumental fractionation and independent from the assumption that different isotope pairs undergo the identical isotopic fractionation, as it is believed in the traditional internal standard model. In fact, this is the main advantage of ORM over the traditional internal standard method that it is free from this untested assumption. For more details about ORM and its theoretical explanation, one can check for some of our previous works^{38,41,42}

$$R_{i/j} = e^a \times R_{k/l}^b \quad (5)$$

Coefficient a is the intercept and b is the slope of the corresponding linear regression (eq 4), obtained using the least-squares fitting of experimental isotope ratio data. Here, Se standard (NIST SRM 3149) spiked with Sr standard (NIST SRM 987) was measured at four different plasma power values (1300, 1315, 1330, and 1345 W); next, $R_{i/j}$ was calculated, and exactly the same measuring scheme was applied for Se sample

spiked with Sr standard (NIST SRM 987). This sequence was repeated several times resulting in a few $R_{i/j}$ for the sample and the standard. Then, the $R_{i/j}$ values for the standards and samples measured alternately were put into eq 1 and the delta values were calculated. The experimental data sets were accepted only when the dependence $\ln(r_{i/j})$ vs $\ln(r_{k/l})$ was characterized with the squared linear correlation coefficient R^2 (coefficient of determination) higher than 0.9995.

As there is no value of the ${}^{84}\text{Sr}/{}^{87}\text{Sr}$ isotope ratio in NIST SRM 987 available, this ratio was calculated using eq 6 from the respective values of ${}^{84}\text{Sr}/{}^{86}\text{Sr}$ and ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratios, compiled by the GeoReM database, and used in further investigations. The average ${}^{84}\text{Sr}/{}^{86}\text{Sr}$ ratio value of 0.05655 supplied by GeoReM was also used in experiments

$$\frac{{}^{84}\text{Sr}}{{}^{87}\text{Sr}} = \frac{{}^{84}\text{Sr}}{{}^{86}\text{Sr}} \div \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}} = 0.05655 \div 0.71034 = 0.07961 \quad (6)$$

Sr isotopic composition varies in nature. Therefore, the sample must be as strontium free as possible for the IS–SSB and ORM–SSB methods to be used. However, our calculations and experience show that the Sr content reaching 1.1% of the Se content does not adversely affect the quality of the results.

Sample Preparation. To compare the accuracy and precision of three methods for measuring Se isotope ratios (SSB, IS–SSB, and ORM–SSB), five types of samples were prepared and investigated: NIST SRM 3149 (Se) spiked with NIST SRM 987 (Sr), artificial seawater diluted 500 times and spiked with NIST SRMs (987 and 3149), a matrix sample (elemental composition shown in Table 2) obtained by applying the full procedure of Se purification using commercial thiol resin (SiliaMetS Thiol R51030B, SiliCycle Inc., Quebec City, Quebec, Canada) spiked with NIST SRM (987 and 3149), selenium-enriched yeast-certified reference material SELM-1, and finally natural Se–methionine samples that have undergone microwave-assisted decomposition in a closed system. Because all sample types except the first one are characterized by a rather heavy matrix (approximate elemental composition shown in Tables 1–3), in this way the robustness of the three considered methods was examined as well.

Table 1. Composition of the Artificial Seawater

component	Na ⁺	Mg ²⁺	K ⁺	Cl [−]
concentration, g/kg	10.8	1.3	0.4	16.7

Samples with a Se concentration of 25 mg/kg were prepared by diluting the NIST SRM 3149 in 1% HNO₃ and spiking with the NIST SRM 987 solution to a total Sr content of 12 mg/kg.

The artificial seawater was prepared by an appropriate dilution of chloride salts of sodium, magnesium, and potassium (Sigma-Aldrich, Milwaukee, WI) with Milli-Q water. The solution obtained had concentrations of components as listed in Table 1. This artificial seawater was diluted 500 times and spiked with both NIST SRM 3149 and NIST SRM 987 to a total concentration of Se and Sr of 25 and 12 mg/kg, respectively.

The thiol resin was processed under similar experimental conditions, as in ref 50, and the model solution was prepared according to the following procedure: 5 mL of Milli-Q water was added to 1.0 g of thiol resin powder in a 15 mL tube and properly shaken with a Reax top Vortex mixer (Heidolph, Schwabach, Germany). The two phases were then separated by

Table 2. Composition of Blank Samples Obtained after the Treatment of Thiol Resin

analyte concentration, $\mu\text{g}/\text{kg}$	Se	Sr	Rb	Na	Mg	Al	Ca	Ni	Zn	Ba	Pb
	1	7	<0.2	450	107	207	483	0.3	10	77	3

Table 3. Elemental Composition of Selenomethionine and Selenized Yeast Samples^a

component	sample						
	Se-Met 1	Se-Met 4	Se-Met 6	Se-Met 7	Se-Met 8	SELM-1	
Na mg/kg	3.92	1.47	1.76	6.22	1.90	3.30	
Al $\mu\text{g}/\text{kg}$	26	11	22	19	14	26	
Mg $\mu\text{g}/\text{kg}$	26	<LOD	<LOD	142	<LOD	14 011	
Ca $\mu\text{g}/\text{kg}$	395	225	169	348	108	5362	
Sr $\mu\text{g}/\text{kg}$	2	1	1	2	1	8	
Ba $\mu\text{g}/\text{kg}$	14	3	19	2	5	4	
Cr $\mu\text{g}/\text{kg}$	<LOD	<LOD	<LOD	4	<LOD	6	
Mn $\mu\text{g}/\text{kg}$	1	<LOD	1	1	1	28	
Fe $\mu\text{g}/\text{kg}$	39	<LOD	<LOD	<LOD	88	416	
Co ng/kg	<LOD	<LOD	<LOD	87.0	<LOD	1800	
Ni $\mu\text{g}/\text{kg}$	<LOD	<LOD	<LOD	2.10	<LOD	1	
Cu $\mu\text{g}/\text{kg}$	8	4	6	8	<LOD	62	
Zn $\mu\text{g}/\text{kg}$	68	53	178	39	105	1060	
Cd ng/kg	89	46	46	49	<LOD	126	
Pb $\mu\text{g}/\text{kg}$	1	3	3	3	1	<LOD	
Tl ng/kg	15	6	5	9	<LOD	801	
Rb $\mu\text{g}/\text{kg}$	0.2	<LOD	<LOD	0.3	<LOD	216	
Se mg/kg	220	147	171	261	186	14.3	

^a<LOD means that the concentration was below the limit of detection. Uncertainty: standard deviation (SD) $\pm 7.5\%$.

centrifuging at 4200 rpm for 5 min in the centrifuge model 5804R (Eppendorf, Hamburg, Germany). The liquid phase was excluded, and the procedure was repeated twice with 5 mL of 6 M HCl solution and then again with 5 mL of Milli-Q water (2–3 times). The near-dry residue of thiol resin was treated with 1 mL of HNO₃ solution (1:1) and heated in a boiling water bath for 20 min to extract Se from the powder. Then, the mixture was filtered through a 0.22 μm filter and the supernatant was diluted to 50 mL with water and used as a matrix solution in further measurements. The corresponding model sample was prepared by spiking the matrix solution with 30 mg/kg of Se NIST SRM 3149 and 12 mg/kg Sr NIST SRM 987. Blank samples prepared according to the same procedure without adding the thiol resin powder were checked for Se and Sr contents by means of quadrupole ICP-MS (Perkin Elmer NexION 300D, Waltham, MA), and no more than 10 $\mu\text{g}/\text{kg}$ of each element was found (Table 2).

Natural Se–methionine samples were prepared in NRC Metrology labs. In brief, approximately 0.15 g of Se–methionine was put into the Teflon vessel and around 4 mL of concentrated HNO₃ was added. Next, microwave-assisted sample decomposition in a closed system (Ethos One Microwave Digestion System, Milestone, Sorisole, Italy) was done according to the following program: 20 min ramping to 220 °C and 48 bar and then holding for 15 min. The solutions were diluted to approximately 250 mg/kg Se and kept in the dark at room temperature. The elemental composition of samples obtained was also measured using quadrupole ICP-MS (Table 3). Samples were appropriately diluted (Se content ~ 25 mg/kg) and spiked with NIST SRM 987 (Sr) (~ 12 mg/kg) just before measurement.

A standard reference material SELM-1 (NRC, Canada) was prepared according to the procedure proposed by Far et al.¹⁹ Albeit, as in our experiment, the hydride generation system was

not applied, the sample digestion technique was modified: 0.3 g of SELM-1 powder was digested with a mixture of 2 mL of HNO₃ (65% w/w) and 2 mL of H₂O₂ (30% w/w) using the same program as for Se–methionine samples. The reduction step using concentrated HCl was not performed. After the digestion, the content of the Teflon vessel was transferred to a 50 mL test tube. The vessel was rinsed with water, combined with the colorless digest in the test tube, and made up to 50 mL. The content of Se and other elements in the obtained sample solution was also checked using quadrupole ICP-MS (Table 3). Before isotope measurements, the proper aliquot of the sample was spiked with NIST SRM 987 to supply a total Sr concentration of ~ 9 mg/kg.

MC-ICP-MS Analysis. Selenium isotope ratios were measured at the Biological and Chemical Research Center of the University of Warsaw using the “Plasma II” multicollector ICP mass spectrometer equipped with 16 Faraday cups (Nu Instruments, Wrexham, U.K.). Measurement of the most abundant selenium isotope ⁸⁰Se is affected by dimers of Ar; that is why two other isotopes (⁷⁸Se and ⁸²Se) both sufficiently abundant and measurable with high precision were chosen for isotope ratio measurements. In the first detector configuration, two of the Faraday collectors, L5 and H2, were set to register the signals from selenium 78 and 82 isotopes, respectively. As for the internal standard, strontium 84 and 87 isotopes were selected and their signals were registered on detectors H6 and H10, respectively. ⁸⁷Sr/⁸⁶Sr ratio cannot be measured on this particular spectrometer with a mass separation of 0.5 atomic mass unit due to technical limitations. Alternatively, the second cup configuration was also checked with isotope ⁸⁶Sr measured on detector H10 (Table 4).

The amplifier boards of the collectors were calibrated on a daily basis, using an internal 40 V reference signal. Fine-tuning of the MC-ICP-MS instrument was performed before each

Table 4. MC-ICP-MS Operating Parameters

MC-ICP-MS parameters	
RF power	1300 W
coolant flow (Ar)	13 L/min
auxiliary flow (Ar)	1.0 L/min
nebulizer gas flow (Ar)	36.0 psi
interface cones	nickel
measurement parameters	
resolution mode	~300
cup configuration 1	H10- ⁸⁷ Sr; H6- ⁸⁴ Sr; H2- ⁸² Se; L5- ⁷⁸ Se
cup configuration 2	H10- ⁸⁶ Sr; H8- ⁸⁴ Sr; H4- ⁸² Se; L4- ⁷⁸ Se
integration time	5.0 s

measurement session. All data sets reported in this paper were collected between April and June of 2020. Operating parameters for the MC-ICP-MS system are listed in Table 4.

All samples and standard solutions were introduced into the MC-ICP-MS instrument in wet plasma mode using a self-aspirating nebulizer. The optimum value of the plasma RF power P_0 that assures the stable signal and highest sensitivity^{34,44} was found to be 1300 W and then used in all further investigations. The nebulizer gas pressure was optimized at P_0 before every measurement. While increasing the RF power from the optimum value, the intensity of isotope signals (both Se and Sr) decreased; consequently, the P_{\max} value, which corresponds to the signal decrease by approximately 10%, was found to be 1345 W. Further increasing of RF power did not cause significant changes in Se and Sr isotope ratios, at the same time leading to severe signal instability. The RF power was increased from P_0 to P_{\max} at equal increments (15 W), which was enough to cause sufficient drift and shorten the measurement session time (less than 30 min) in comparison with previously reported analyses at a fixed RF power (up to 15 h).^{41,42} It is worth mentioning that all measurements were done in a time-resolved analysis (TRA) mode. TRA is a way of collecting and graphically presenting data that enables real-time observation of subtle signal changes. It is possible to follow any parameter vs time; thus, not only the intensities but also the isotope ratios can be constantly monitored. Moreover, before measuring a sample, a blank solution of 1% HNO₃ was measured not only at fixed P_0 but also after every increment of RF power using the same procedure, and then obtained intensities at the Se and Sr isotope masses were subtracted from the respective values of a sample measured at these RF powers. The continuous signal was measured with the integration time of 5 s for at least 20

replicates. It was found that longer integration (25–30 replications) caused improvement in precision.

RESULTS AND DISCUSSION

Se Isotope Measurements of NIST SRM 3149 and Artificial Samples. The results of Se isotope ratio measurements in standard reference material NIST SRM 3149 solutions, as well as in artificial seawater samples diluted 500 times and solutions obtained after thiol resin treatment, spiked with 25 mg/kg of SRM 3149, are shown in Table 5.

Figure 1 represents a typical experimental profile of Se isotope ratio measurement in a time-resolved analysis mode in solutions obtained after thiol resin treatment. One can notice that the signal achieved at P_0 and after each RF power increment was integrated only when its intensity and isotope ratios remained stable for at least 100 s (20 measurements). For this purpose, TRA proved to be a useful tool providing real-time information about the isotopic fractionation in measured samples. Furthermore, the application of a TRA mode has shown that an initial preconditioning needs to be carried out for a precise isotope ratio determination until stable signals are achieved. So, for this purpose, the samples were passed through the sample introduction system at least for 3–5 min (Figure 1 between 300 and 500, 1250 and 1500, 2500 and 2700 s). Coefficient of determination has a significant impact on precision of determination of the slope and increment values. The closer the coefficient is to 1, the better the precision. For this reason during the experiment, only parameters of curves (Figure 2) with coefficient of determination higher than 0.9995 were taken in further calculations according to eq 5.

According to our preliminary studies (data not shown), interfering effects of thiol resin matrices have a significant influence on the isotope ratio measurements using the standard–sample bracketing model leading to high uncertainties and incorrect δ values. The experimental data in Table 5 confirm that the SSB model is the least suitable method for Se isotope ratio determination due to the highest standard deviation observed and incorrect δ value. Indeed, this model produced delta values for Se in tested samples, which differ significantly from the expected value (0). This is accordingly to our previous observation that in wet plasma conditions SSB model is not suitable for accurate and precise measurements of Se isotope ratios in samples after Se separation on thiol resins.

As to the other two mass bias correction models, the processing of results with IS–SSB model leads to the lowest standard deviation in standard solutions; however, the

Table 5. $\delta^{82/78}\text{Se}$ Isotope Ratio Values Obtained in This Work after the Application of Different Mass Bias Correction Models

sample	SSB			IS–SSB			ORM–SSB			expected δ value
	δ , ‰	2SD	<i>n</i>	δ , ‰	2SD	<i>n</i>	δ , ‰	2SD	<i>n</i>	
NIST SRM 3149	0.06	0.38	11	−0.04	0.15	8	0.03	0.25	11	0
artificial seawater	−0.33	0.60	13	−0.09	0.19	14	−0.01	0.17	13	0
thiol resin	2.53	1.29	9	−0.37	0.31	9	0.00	0.17	9	0
Se-yeast	−2.2	0.42	4	−2.37	0.03	4	−2.83	0.29	4	
Se-Met 6	−1.74	2.76	4	−2.32	0.14	4	−2.43	0.24	4	
Se-Met 7	−0.38	4.08	3	−2.34	0.25	3	−2.54	0.10	3	
Se-Met 1	8.06	0.62	6	5.35	0.40	6	5.69	0.50	6	
Se-Met 8	−2.20	0.83	4	−2.37	0.05	4	−2.25	0.25	4	
Se-Met 4	−0.87	0.61	3	−2.50	0.25	3	−2.52	0.24	3	
SELM-1	1.74	0.48	3	−0.54	0.02	3	−0.68	0.02	3	−0.66 ¹⁹

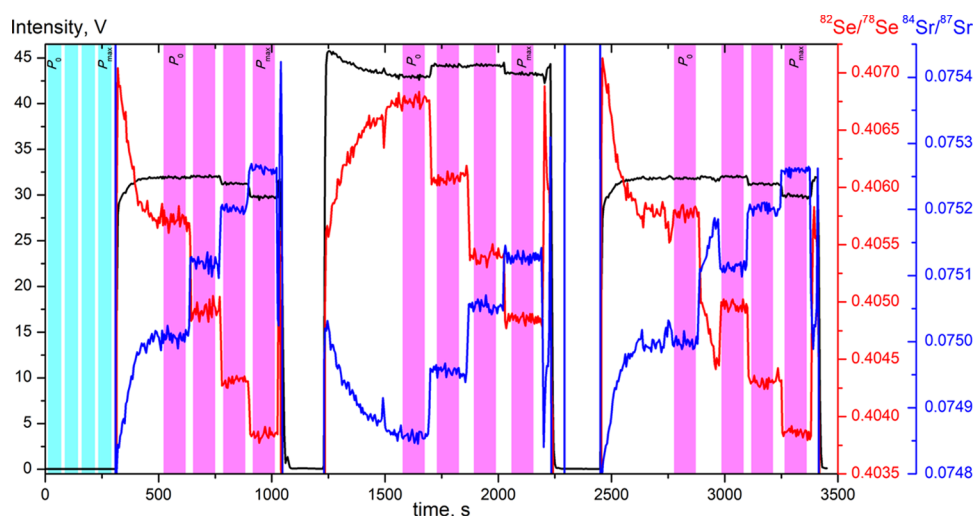


Figure 1. Se isotopic analysis in the solution obtained after thiol resin treatment—the signal in the middle corresponds to the sample solution; signals to the left and right refer to Se NIST SRM 3149 solution; and cyan and magenta areas represent the time periods when signals from blank and Se solutions, respectively, were integrated at specific RF powers. ^{78}Se is the source of the intensity signal (in black).

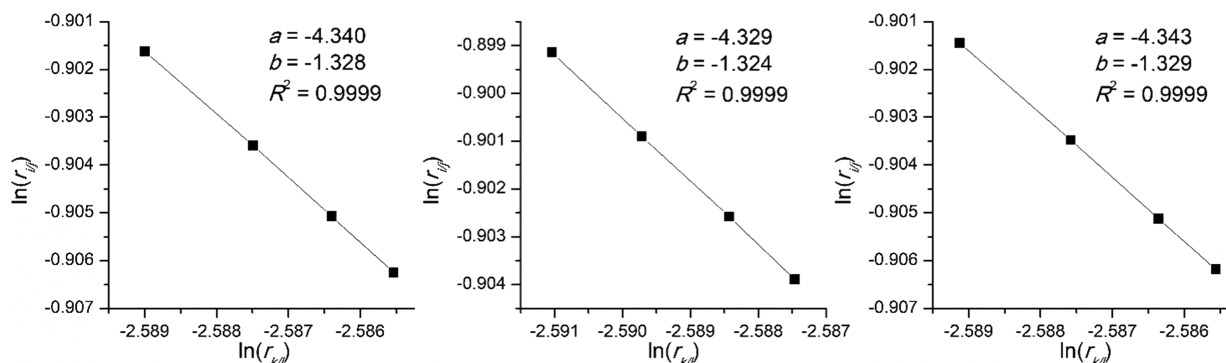


Figure 2. Regression plots of NIST SRM 3149 selenium in the solution obtained after thiol resin treatment (sample, middle chart) against NIST SRM 987 strontium (brackets, the first and the last charts).

regression model produced the best results in artificial seawater samples with the mean delta value closest to the expected one and low standard deviation, proving its applicability and ability to eliminate the matrix effect.

Isotope Measurements of Selenium in Selenomethionine Samples and CRM SELM-1. After proving the validity of the proposed method of Se isotope ratio determination in standard and model solutions, it was applied for the determination of $\delta^{82/78}\text{Se}$ values in SELM-1, selenomethionine samples, and self-prepared Se-enriched yeast produced by fermenting *Saccharomyces cerevisiae* in a selenium-rich medium (Se-yeast in Table 5). As shown in Table 5, the δ values of all samples after the correction using both IS–SSB and ORM–SSB models agree well within reported 2SD in all cases. Nevertheless, either IS–SSB or ORM–SSB could be recommended for a precise analysis of Se fractionation in samples with matrices similar to those presented in this study, albeit we expect that when the matrix is much heavier, then IS–SSB will show poorer performance to that of ORM–SSB. In consistency, the application of SSB mass bias correction model led to very high SD and significantly different δ values than those provided by ORM–SSB and IS–SSB.

The accuracy of developed methods for Se isotope ratio determination was verified by measuring the $\delta^{82/78}\text{Se}$ value in

selenium-enriched yeast-certified reference material SELM-1 and comparing it with the literature data,¹⁹ which was obtained by hydride generation for matrix separation and MC-ICP-MS detection. The preliminary measurements of SELM-1 sample composition using quadrupole ICP-MS have shown that there is a considerable content of Rb in the prepared solution (Table 3) that corresponds to approximately 2% of the amount of spiked Sr. In this case, ^{87}Rb isotopes would surely interfere the registered signal for ^{87}Sr .⁵¹ For this reason, the second configuration of detectors was used that allowed to measure the $^{84}\text{Sr}/^{86}\text{Sr}$ isotope ratio instead of $^{84}\text{Sr}/^{87}\text{Sr}$. Despite the sample matrix, the measured $\delta^{82/78}\text{Se}$ in SELM-1 using the proposed method is in excellent agreement with the literature data¹⁹ confirming the accuracy of the proposed method.

The data in Table 3 also confirm that the matrix of the SELM-1 sample is much more complicated than in Se-methionine samples as concentrations of nearly every component are much higher. Besides, due to the lower Se concentration in the SELM-1, dilution of the sample to reduce the matrix effect is impossible. Nevertheless, the application of IS–SSB and ORM–SSB correction models resulted in $\delta^{82/78}\text{Se}$ values with a low standard deviation (Table 5). Once again, the correction of isotope ratios using the SSB technique alone led to inaccurate and imprecise results. After the application of the ORM–SSB correction model, a very close result to the

previously reported value¹⁹ was achieved. On the other hand, the $\delta^{82/78}\text{Se}$ value obtained using the IS–SSB correction differed from the expected one. This could be caused by insufficient matching of Se concentration and matrix between standard and sample solutions, which is necessary for this correction model.

During the ORM experiment on different samples, it was observed that P_{max} and P_0 values usually slightly differ for standard and sample, causing the deviation from linearity of regression curves. To minimize this interfering effect, the instrument was usually optimized at slightly higher RF power (usually 1320 W), albeit the working range was kept the same (1300–1345 W). Such methodological modification improved regression curves resulting in R^2 values higher than 0.9999.

The other two elements (Rb and Br) with atomic masses close to Se were also checked as possible internal standards for Se isotope ratio determination. As to bromine, its application was complicated as the regression curves during the mass bias correction using ORM were usually nonlinear. This may indicate that Se and Br exhibit different fractionation behavior under the same plasma conditions. On the other hand, the application of rubidium with its two naturally occurring isotopes ^{85}Rb and ^{87}Rb resulted in linear regression curves and precise Se isotope ratio values, as in the case of Sr. However, as strontium has the first ionization potential value closer to the respective value of selenium, it was selected as an internal standard in all further investigations to minimize any possible experimental deviations coming from this difference of ionization potentials.

CONCLUSIONS

A novel and simple method using ORM–SSB for mass bias correction for the accurate and precise determination of Se isotope ratio in matrix samples without separation of selenium from sample matrices was developed. ORM–SSB performance was compared to IS–SSB for robustness and the possibility of the elimination of matrix influences. It was shown that ORM–SSB enables precise and accurate measurements of the Se isotope ratio in moderately heavy matrix samples. This newly developed method enables, among other, direct measurements of Se isotopic fractionation in samples of selenium yeast or isolated amino acids, which opens a new opportunity in the field of application of isotope research to study processes in living organisms. ORM–SSB is an encouraging tool for the investigation of Se isotope ratios after off-line column separation of selenium. In addition, ORM–SSB produces accurate Se isotope ratios in artificial seawater, opening its application in samples of geological origins (selenium ores, selenium-rich waters). To the best of our knowledge, this is the first application of ORM for isotope ratio measurement using the Nu Instrument spectrometer, and we believe it can serve as a complete guide on how to perform this type of measurements on Plasma II instruments.

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Notes

The authors declare no competing financial interest.

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