Interference-free selenium isotope abundance ratio measurements using the Sapphire Collision/Reaction Cell

Highlights

- Efficient Ar dimer elimination using a He-N_2 gas mixture in the Sapphire Collision/Reaction Cell for simultaneous detection of all Se isotopes
- Fully mass-dependent Se isotope fractionation and deviations between different Se standard solutions
- 2σ SD short-term repeatability < 35 ppm and internal precision < 25 ppm for ^{80}Se/^{78}Se
- Robustness against concentration mismatching of up to 20 % between bracketing standard and sample

Introduction

Selenium has six major isotopes and is an element with main applications in low-temperature geochemistry and biochemistry. Although Se is an important micronutrient, and as such is a critical tracer of metabolic processes, it becomes toxic at high concentrations. Understanding its biological cycling could therefore help in preventing or finding treatments for infectious diseases, cancer, or diabetes because of its anti-inflammatory or antioxidant properties. Due to its various oxidation states, it is also used as a redox tracer to reconstruct the evolution of Earth's atmosphere and marine environments.

Selenium isotope analysis by MC-ICP-MS is challenging for two reasons: (i) Due to the high ionisation potential of Se the sensitivity is usually low. Cold-vapour hydride generation can overcome this limitation, however stable operation of such systems is difficult. (ii) Plasma-based interferences from $ArAr^+$, $ArArH^+$, and Kr^+ affect all Se isotopes, in addition to potential sample-matrix-based interferences from Ge^+, AsH^+, or BrH^+. The use of a Collision/Reaction Cell offers great potential to facilitate Se isotope abundance ratio measurements by eliminating or minimising such isobaric interferences. Here we investigate the use of He-H_2 and He-N_2 collision/reaction gas mixtures to remove polyatomic and isobaric interferences, enabling the simultaneous quantification of the isotopic abundances of all Se isotopes.

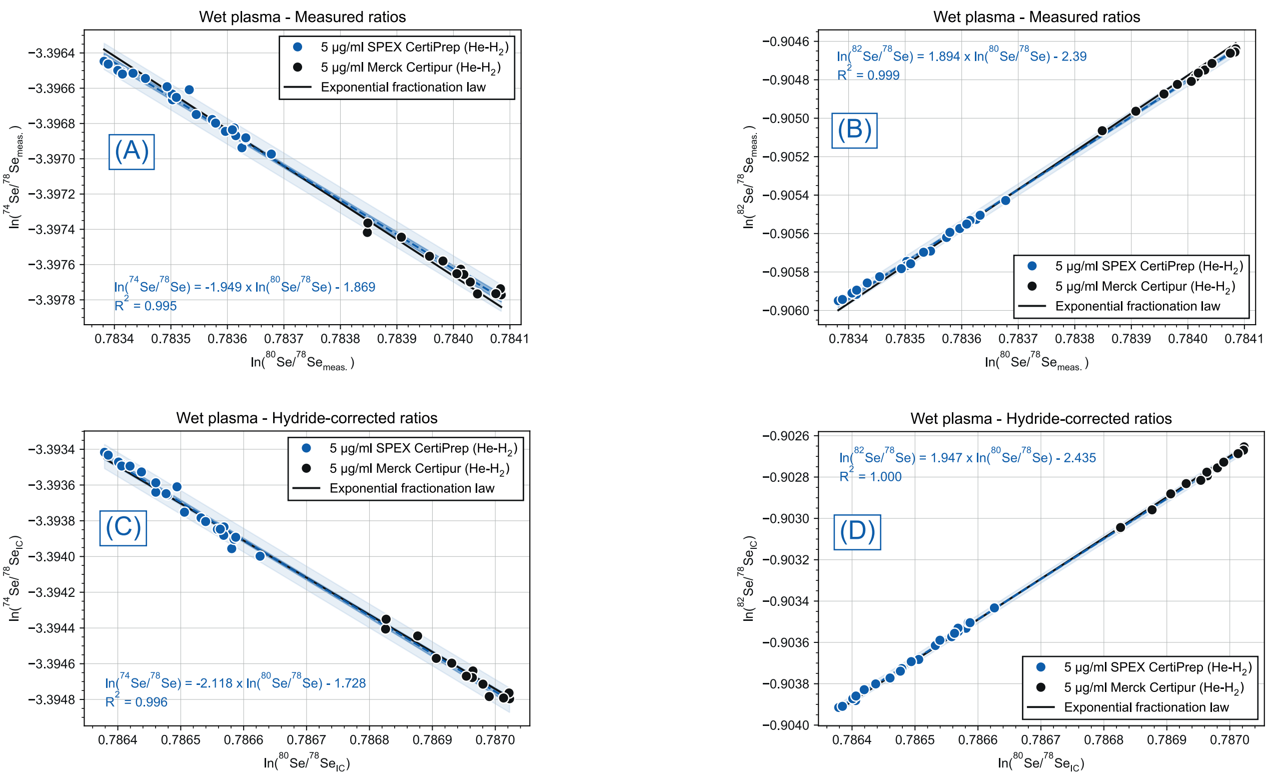

Fig. 1 Selenium isotope abundance ratio fractionation with a He-H_2 CRC gas mixture for measured (meas.) $^{74}Se/^{78}Se_{meas.}$ vs. $^{80}Se/^{78}Se_{meas.}$ (**A**) and $^{82}Se/^{78}Se_{meas.}$ vs. $^{80}Se/^{78}Se_{meas.}$ (**B**) isotope abundance ratios, and hydride interference-corrected (IC) $^{74}Se/^{78}Se_{IC}$ vs. $^{80}Se/^{78}Se_{IC}$ (**C**) and $^{82}Se/^{78}Se_{IC}$ vs. $^{80}Se/^{78}Se_{IC}$ (**D**) isotope abundance ratios. The black reference line indicates the theoretical fractionation line for mass-dependent isotope fractionation according to Russell's exponential law.

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Methodology

Argon dimer interferences can be eliminated or minimised via charge transfer with H_2 or by ligand exchange reaction with N_2 (Olesik and Gray, 2014). Besides these main interferents, minor isobaric interferences from $^{74}Ge^+$ on $^{74}Se^+$ and $^{76}Ge^+$ on $^{76}Se^+$, as well as $^{78}Kr^+$ on $^{78}Se^+$, $^{80}Kr^+$ on $^{80}Se^+$, and $^{82}Kr^+$ on $^{82}Se^+$ must be considered, the latter of which can be minimised via the Collision/Reaction Cell as well. Selenium isotopes may further form SeH, especially when using H_2 as reaction gas, which will interfere on $^{77}Se^+$ for $^{76}Se^1H^+$ and $^{78}Se^+$ for $^{77}Se^1H^+$. These interferences therefore all need to be accounted and, if necessary, corrected for. Potential SeH contributions are corrected for using $^{78}SeH^+$ (m/z = 79), assuming no $^{79}Br^+$ is present and that $^{38}Ar^{40}Ar^1H^+$ formation is insignificant. As measurements were conducted using pure Se standard solutions, no Ge interference correction was performed, and Kr interferences are quantified using $^{83}Kr^+$.

Measurements were conducted in wet plasma mode with standard wet cones and a plasma shield, and 5 µg/ml Se standard solutions were introduced using a self-aspirating 100 µl/min glass nebulizer, corresponding to a measurand uptake rate of 8.3 ng/s and sensitivities of 10 V/ppm were achieved for He-H_2 and He-N_2 gas mixtures. Data were acquired on Faraday cups equipped with 10^{11} Ω resistor pre-amplifiers for an integration time (IT) of 5 s in 1 block of 40 acquisition cycles, equivalent to 200 s of data acquisition and consumption of 1.66 µg of Se per measurement.

To evaluate the nature of instrumental mass bias (mass-dependent or mass-independent isotope fractionation), instrument stability, and short-term repeatability, two 5 µg/ml Se concentration standard solutions (SPEX CertiPrep and Merck Certipur) were measured against each other repeatedly over the course of nine hours. The susceptibility to concentration mismatching was evaluated using 4 µg/ml, 5 µg/ml , and 6 µg/ml SPEX CertiPrep Se standard solutions prepared from the same standard batch. During both experiments, the 5 µg/ml Se SPEX CertiPrep standard was used as the bracketing standard and results are reported in δ-notation. On-peak acid blanks (2 % HNO_3) were acquired for 100 s before each standard run, and each run was proceeded by a 30 s rinse and a 180 s wash in 2 % HNO_3.

Results and Discussion

Efficient Ar-based interference removal using a He-H_2 gas mixture (He = 2 ml/min and H_2 = 5 ml/min) in the Sapphire CRC has been successfully demonstrated for several isotopic systems such as K, Ca, Fe, or Cu. However, He-H_2 will form Ar_2H and SeH as evidenced by ca. 100 mV signal on m/z = 79 ($^{78}SeH^+$) and slightly non-mass-dependent Se isotope abundance ratio fractionation (**Fig. 1A** and **1B**). After SeH correction based on the measured $^{78}SeH^+/^{78}Se^+$, and assuming no $^{79}Br^+$ is detected, fractionation slopes are mass-dependent (**Fig. 1C** and **1D**). Although this indicates that hydride correction is largely

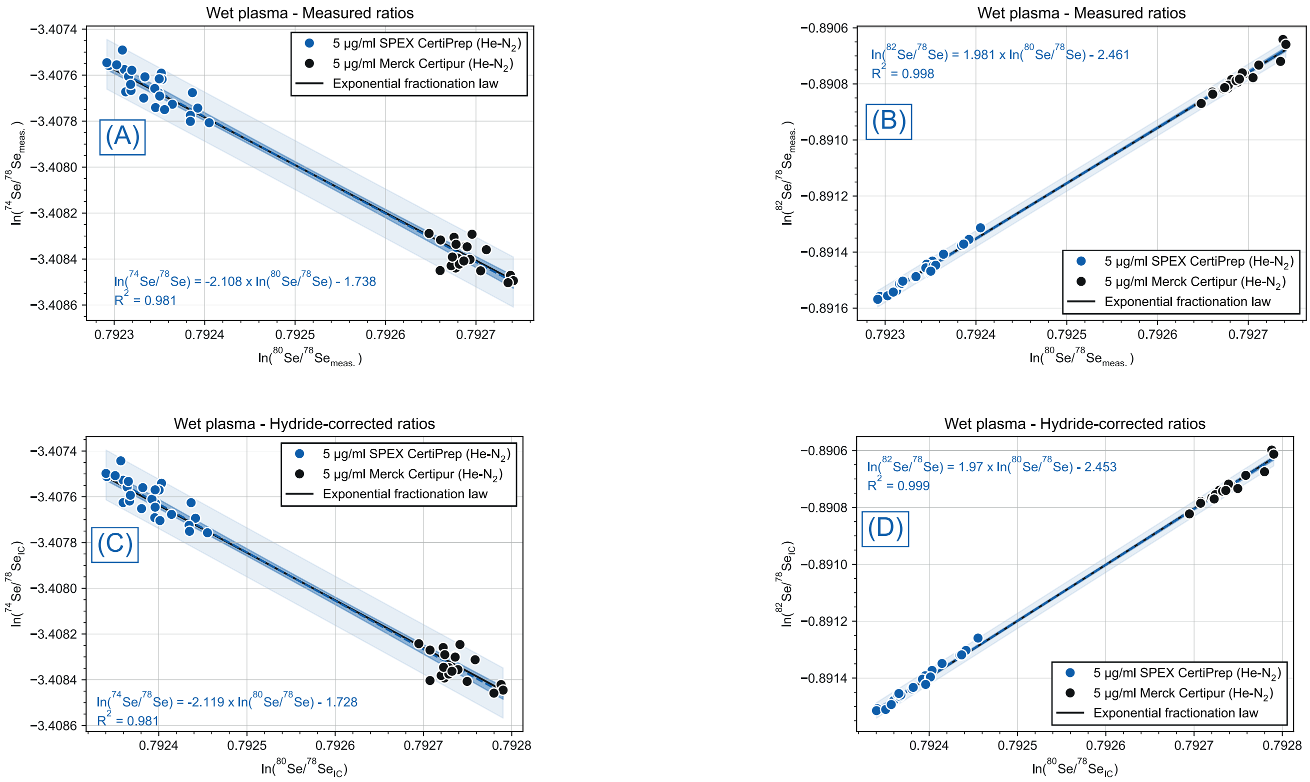

Fig. 2 Selenium isotope abundance ratio fractionation using a He-N_2 CRC gas mixture for measured (meas.) $^{74}Se/^{78}Se_{meas.}$ vs. $^{80}Se/^{78}Se_{meas.}$ (**A**) and $^{82}Se/^{78}Se_{meas.}$ vs. $^{80}Se/^{78}Se_{meas.}$ (**B**) isotope abundance ratios, and hydride interference-corrected (IC) $^{74}Se/^{78}Se_{IC}$ vs. $^{80}Se/^{78}Se_{IC}$ (**C**) and $^{82}Se/^{78}Se_{IC}$ vs. $^{80}Se/^{78}Se_{IC}$ (**D**) isotope abundance ratios. The black reference line indicates the theoretical fractionation line for mass-dependent isotope fractionation according to Russell's exponential law.

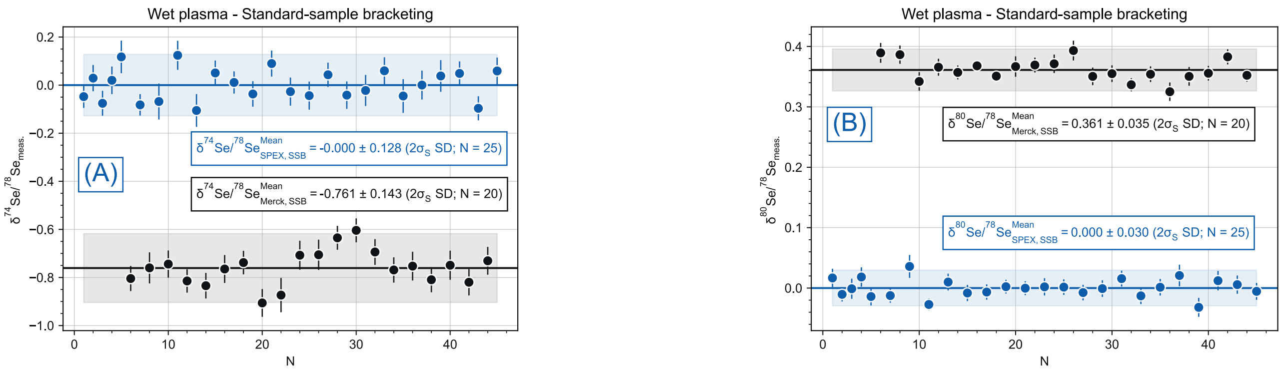

Fig. 3 Selenium isotope abundance ratio deviations (in δ-notation) determined in two 5 µg/ml Se concentration standard solutions with SPEX CertiPrep as bracketing standard and Merck Certipur as unknown shown as (**A**) $\delta^{74}Se/^{78}Se_{meas.}$ and (**B**) $\delta^{80}Se/^{78}Se_{meas.}$. Solid lines and shaded areas indicate sample mean ± 2σ SD, and error bars on the data points indicate 2σ SE of the individual measurement.

accurate, this correction step may introduce susceptibility to matrix effects and concentration mismatching considering hydride formation rates between blank, standard and samples may be affected by matrix components and differ.

As an alternative to charge transfer with H_2, ligand exchange transfer using N_2 has been shown to be an efficient method to remove Ar dimers for Se isotope measurements (Olesik and Gray, 2014). Here, a cell gas mixture of He = 1 ml/min and N_2 = 1.5 ml/min fully removes all Ar-based interferences and cell-based hydride formation is minimised as evident by $^{78}SeH/^{78}Se_{meas.}$ < 0.00016. Measured isotope abundance ratios are fractionated following Russell's exponential law (**Fig. 2A** and **2B**), with no significant difference between measured and interference-corrected ratios (**Fig. 2A-D**). Nitrogen-based interference removal therefore is the optimal choice for isotope abundance ratio measurements of all Se isotopes.

The short-term repeatability and measurement precision of the method were evaluated using two 5 µg/ml Se concentration standard solutions, with SPEX CertiPrep (N = 25) being the bracketing standard and Merck Certipur (N = 20) being the unknown. Deviations in δ-notation are fully mass-dependent with ca. 0.18 ‰/amu for each isotope abundance ratio and the 2σ SD short-term repeatability is < 143 ppm for $\delta^{74}Se/^{78}Se$, < 33 ppm for $\delta^{76}Se/^{78}Se$, < 24 ppm for

Tab. 1 Mean ± 2σ SD standard-bracketed δ-values for 5 µg/ml solutions of SPEX CertiPrep (bracketing standard) and Merck Certipur Se concentration standards using He-N_2 in the Sapphire Collision/Reaction Cell.

Standard		$\delta^{74}Se/^{78}Se$	$\delta^{76}Se/^{78}Se$	$\delta^{77}Se/^{78}Se$	$\delta^{80}Se/^{78}Se$	$\delta^{82}Se/^{78}Se$	N
SPEX CertiPrep	Mean	0.000	0.000	0.000	0.000	0.000	25
	2σ SD	0.128	0.030	0.023	0.030	0.062	
Merck Certipur	Mean	-0.761	-0.370	-0.182	0.361	0.717	20
	2σ SD	0.143	0.033	0.024	0.035	0.075	

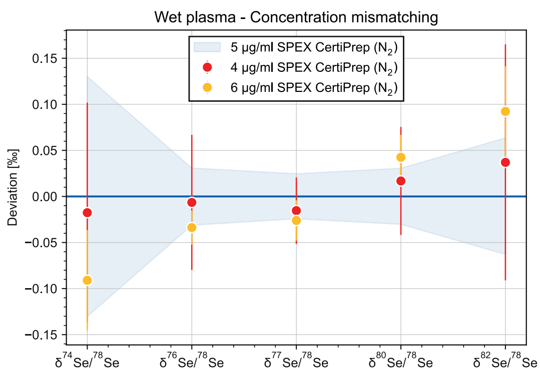

Fig. 4 Selenium isotope abundance ratio deviations (in δ-notation) determined for concentration mismatched 4 µg/ml and 6 µg/ml SPEX CertiPrep Se standard solutions measured against a 5 µg/ml SPEX CertiPrep Se standard solution as bracketing standard. The solid line and shaded area indicate sample mean ± 2σ SD of the bracketing standard (N = 25), and error bars on the data points indicate 2σ SD of six individual measurements each.

$\delta^{77}Se/^{78}Se$, < 35 ppm for $\delta^{80}Se/^{78}Se$, and < 75 ppm for $\delta^{82}Se/^{78}Se$ over the course of 9 hours (**Fig. 3**; **Tab. 1**). The individual measurement precision (2σ SE) is < 25 ppm for $^{76}Se/^{78}Se$, $^{77}Se/^{78}Se$, and $^{80}Se/^{78}Se$, < 75 ppm for $^{74}Se/^{78}Se$, and < 36 ppm for $^{82}Se/^{78}Se$.

Measurements of concentration mismatched standards and samples can introduce measurements biases due to unequal isotope fractionation and resulting inadequate fractionation correction by, e.g., standard-sample bracketing. To evaluate the susceptibility of the method to concentration mismatching, a trio of 4 µg/ml, 5 µg/ml, and 6 µg/ml SPEX CertiPrep Se standard solutions was prepared from the same standard batch. The 5 µg/ml Se SPEX CertiPrep standard was then used as bracketing standard whereas the 4 µg/ml and 6 µg/ml standard solutions were analysed as unknowns. The results are reported in δ-notation (**Fig. 4**) and demonstrate that a concentration mismatch of up to 20 % between bracketing standard and sample can be robustly accommodated by the CRC approach.

Conclusions

In conclusion, N_2-based interference removal using the Sapphire Collision/Reaction Cell is an efficient and precise method for isotope abundance ratio measurements of all Se isotopes. The approach is robust against concentration mismatching of up to 20 % between bracketing standard and samples and achieves a 2σ SD short-term repeatability < 35 ppm for $^{80}Se/^{78}Se$.

References

Olesik & Gray (2014). Advantages of N_2 and Ar as reaction gases for measurement of multiple Se isotopes using inductively coupled plasma-mass spectrometry with a collision/reaction cell. Spectrochimica Acta Part B: Atomic Spectroscopy, 100, 197-210.