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Sapphire Note **SP05**

Uranium isotope abundance ratio determination as UO_2 species via mass shifting with O_2 in a Sapphire Collision/Reaction Cell

Highlights

- 99.9 % of UO_2 formation when using O_2 as cell gas with sensitivity > 1500 V/ppm or > 900 V per ng/s
- High fractionation stability over several hours
- Short-term repeatability of 70-100 ppm ($2\sigma_S$ SD) with a measurement precision $2\sigma_S$ SE of 50-70 ppm for $^{235}U/^{238}U$ using 13 ng U and a mass-scaled measurement precision of $2\sigma_s^m$ SE = 180-252 ppm^m per measurement,
- Robustness against concentration mismatching up to at least 25 %
- Excellent measurement trueness even when measuring samples with highly different degrees of ^{235}U enrichment, with $^{235}U/^{238}U_{NBS\text{-}U030}$ = 0.031426 ± 0.000003 ($2\sigma_S$ SD; N = 6) and $^{235}U/^{238}U_{NBS\text{-}U050}$ = 0.052777 ± 0.000005 ($2\sigma_S$ SD; N = 6)

Uranium is the heaviest of the naturally occurring elements and comprises two long-lived radioactive isotopes (^{235}U with $t_{1/2}$ = 0.704 Ga and ^{238}U with $t_{1/2}$ = 4.47 Ga) and one short-lived radioactive isotope (^{234}U with $t_{1/2}$ = 246 ka; naturally abundant through continuous decay of ^{238}U; Andresen et al., 2017). The U series decay chains end with stable Pb isotopes. As such, U has found wide-spread application in geochronology, from dating of ancient geological and cosmological processes via U-Pb dating (e.g., Allegre et al., 1995; Amelin et al., 2010; Chang et al., 2006; Chew et al., 2011) to dating of very recent processes (< 1 Ma) such as carbonate formation through the U-series disequilibrium series including ^{234}U (Ivanovich, 1994). Uranium is also widely used as nuclear fuel with artificially enriched $^{235}U/^{238}U$, and more recently U isotope abundance ratios have been used to trace geochemical processes such as fluid-rock interactions and/or redox processes (Kendall et al., 2013; Lu et al., 2020). For many of these numerous applications, the high accuracy and precision determination of U isotope abundance ratios is vital.

In the more specific case of U samples from the nuclear industry, ^{238}U might interfere with ^{238}Pu. However, U can be mass shifted from Pu using O_2 as U readily forms UO_2 species whereas Pu does not. This study exemplarily uses the U + O_2 = UO_2 reaction to demonstrate the mass shifting capabilities of the Sapphire Collision/Reaction Cell (CRC) by determining $^{235}U/^{238}U$ ratios as UO_2^+ species.

Uranium dioxide generation in the CRC will result in the formation of various UO_2 species with different and interfering masses as both elements comprise three main isotopes each, as well as nucleosynthetic U isotopes such as ^{236}U. For example, $^{235}U^{16}O^{17}O^+$ and $^{236}U^{16}O_2^+$ will interfere as both have *m/z* = 268, and $^{235}U^{17}O^{18}O^+$, $^{236}U^{17}O_2^+$, $^{236}U^{16}O^{18}O^+$, and $^{238}U^{16}O_2^+$ will interfere as all four have *m/z* = 270. For U isotope abundance ratio determination in natural samples, oxygen-based interferences are negligible due to the low abundances of ^{17}O and ^{18}O. For U isotope abundance ratios analyses including ^{236}U, a full oxygen interference correction model needs to be applied to determine accurate U isotope abundance ratios using ion counters. Such O interference correction models are well established for TIMS analysis of, e.g., W as WO_3 (e.g., Trinquier et al., 2017; Archer et al., 2017) or Os as OsO_4 (e.g., Luguet et al., 2008), and in-run $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios for UO_2 can be determined by simultaneously measuring $^{238}U^{16}O_2^+$, (*m/z* = 270), $^{238}U^{16}O^{17}O+$ (*m/z* = 271), and $^{238}U^{16}O^{18}O^+$ (*m/z* = 272).

Measurements were conducted in dry plasma with standard dry Ni cones and 20 ng/ml U standard solutions were introduced using an Apex Omega desolvator with a 100 µl/min PFA nebulizer, i.e. the measurand uptake rate was 0.033 ng/s. Data were acquired on Faraday cups equipped with 10^{11} Ω pre-amplifiers ($^{235}U^{16}O_2^+$ on L4, $^{238}U^{16}O_2^+$ on L2, $^{238}U^{16}O^{17}O^+$ on L1, and $^{238}U^{16}O^{18}O^+$ on Ax) for an integration time (IT) of 4 s in 3 blocks of 10 acquisition cycles, equivalent to 120 s of data acquisition and consumption of 13 ng of U per measurement. 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 180 s wash in 2 % HNO_3.

To optimise UO_2 formation in the Sapphire Collision/Reaction Cell, cell gas flows were varied over a range of 0.5-2 sccm for O_2 and 0.5-7 sccm for He while keeping all other cell and beam path parameters constant during the respective tests. The maximum sensitivity is observed for an O_2 cell gas flow of 0.7 sccm (**Fig. 1a**), while isotope abundance ratio fractionation starts to plateau around an O_2 cell gas flow of 1.0 sccm (**Fig. 1b**). As a compromise between sensitivity and minimising fractionation, and thereby potentially minimising concentration mismatching effects, subsequent runs were conducted with an O_2 cell gas flow of 1.0 sccm.

The addition of He to the CRC decreased the sensitivity and further fractionates U isotopes. Helium therefore does not appear to be needed as make-up gas for thermalising the U + O_2 reaction, and only a cell gas flow of O_2 = 1 sccm is used. The $^{238}U^+$ and $^{238}U^{16}O^+$ signals are < 1 mV for these conditions and combined with the fractionation plateau of the measured $^{235}U/^{238}U$ ratio indicate that effectively all U is transformed into UO_2 species. The maximum sensitivity achieved during subsequent runs was 1692 V/ppm or 975 V per ng/s.

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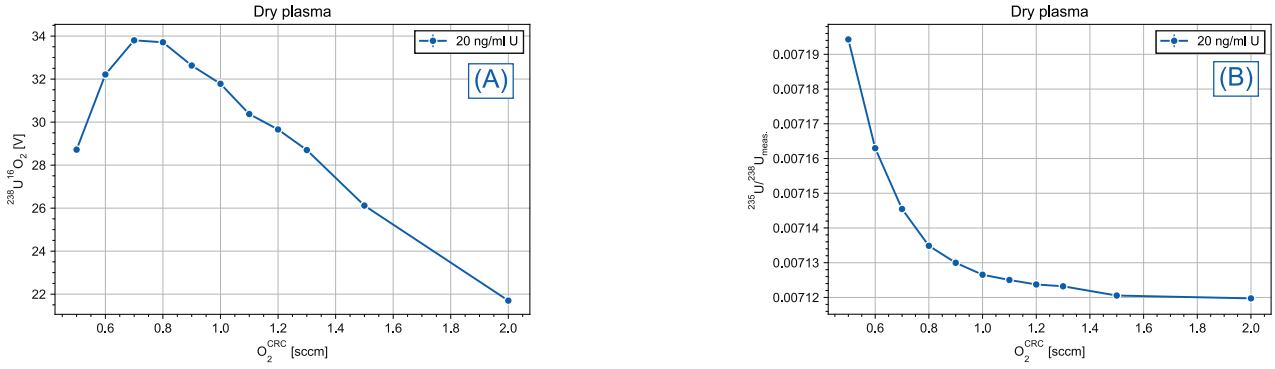

Fig. 1 Collision/Reaction Cell (CRC) sensitivity and fractionation tests conducted for mass shifting of U with O_2 as function of O_2^{CRC} gas flow in (**A**) as measured voltage at *m/z* = 270 ($^{238}U^{16}O_2$+), and (**B**) as $^{235}U/^{238}U_{meas.}$.

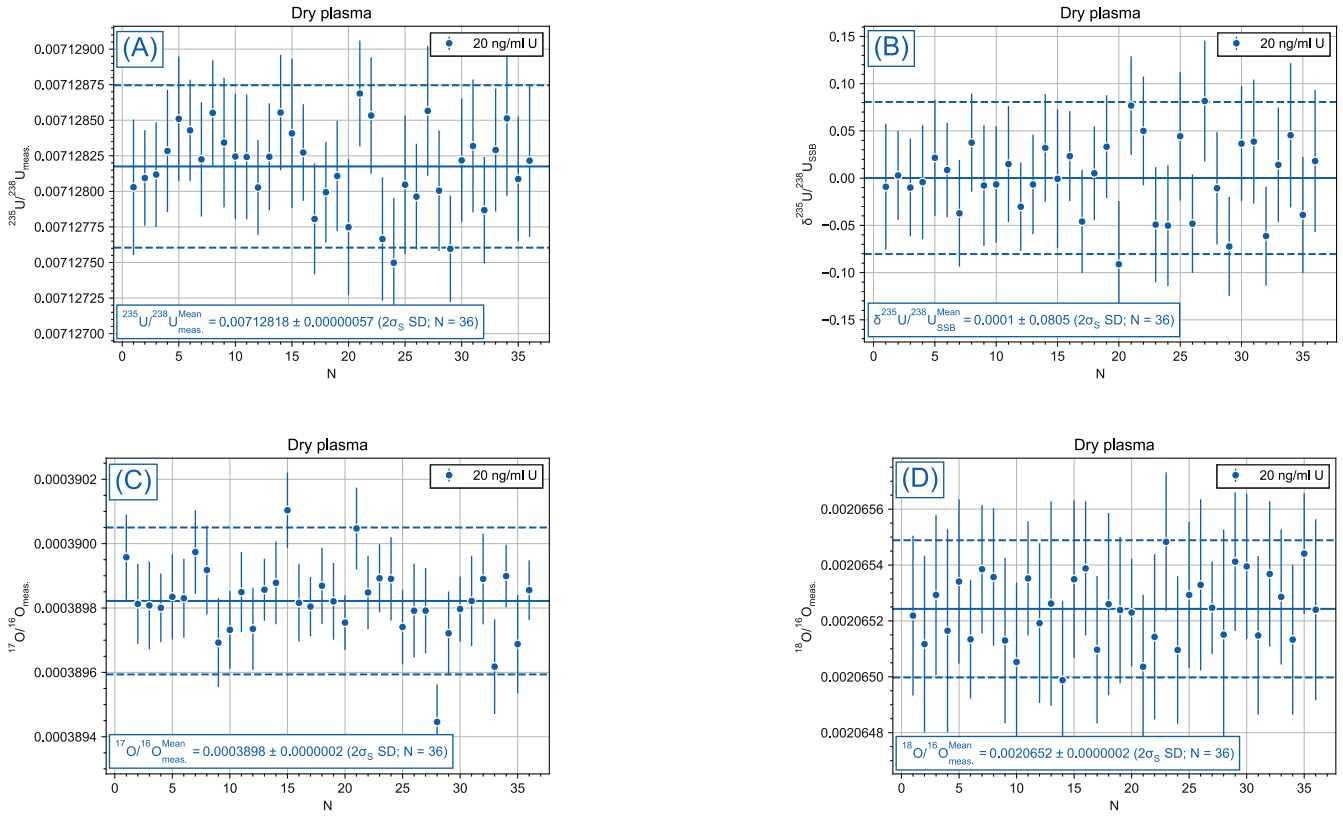

Fig. 2 Short-term repeatability of simultaneous U and O isotope abundance ratio measurements on a 20 ng/ml natural U standard as (**A**) measured (meas.) $^{235}U/^{238}U_{meas.}$, (**B**) sample-standard bracketed $\delta^{235}U/^{238}U_{meas.}$, (C) $^{17}O/^{16}O_{meas.}$, and (D) $^{18}O/^{16}O_{meas.}$. Solid and dashed lines indicate sample (S) mean ± $2\sigma_S$ SD, and error bars on the data points indicate the $2\sigma_S$ SE measurement precision of the individual measurement.

The short-term repeatability of the method was evaluated with repeated measurements of a 20 ml natural U standard over the course of approximately 3 hours. The mean measured (meas.) $^{235}U/^{238}U_{meas.}$ = 0.00712818 ± 0.00000057 ($2\sigma_S$ SD; n = 36) of the session demonstrates a high isotope fractionation stability and measurement repeatability (**Fig. 2a**). In sample-standard bracketed (SSB) δ-notation, $\delta^{235}U/^{238}U_{SSB}$ (**Fig. 2b**) are well-reproducible within 81 ppm ($2\sigma_S$ SD; n = 36). The $2\sigma_S$ SE measurement precision of individual measurements using 13 ng of U are 50-70 ppm for $^{235}U/^{238}U$, corresponding to a mass-scaled measurement precision (see **Glossary**) $2\sigma_S$ SE of 180-252 ppm^m. The in-run determined O isotopic compositions of $^{17}O/^{16}O_{meas.}$ = 0.0003898 ± 0.0000002 ($2\sigma_S$ SD; N = 36; **Fig. 2c**) and $^{18}O/^{16}O_{meas.}$ = 0.0020652 ± 0.0000002 ($2\sigma_S$ SD; N = 36; **Fig. 2d**) are well reproducible and in agreement with the natural (nat.) O isotopic composition of $^{17}O/^{16}O_{nat.}$ = 0.000381 ± 0.000010 and $^{18}O/^{16}O_{meas.}$ = 0.002055 ± 0.00014 (Berglund and Wieser, 2009). The accurate and reproducible determination of the O isotopic compositions thereby reveals the lack of significant U hydride formation (i.e., from the acid matrix). Thus, in-run determined O isotope abundance ratios can be used for accurate UO_2 interference correction.

The robustness of the method against concentration mismatching of the analyte in samples and bracketing standards was tested using 20 ng/ml natural U standard as bracketing standard measured against a 22 ng/ml U and a 25 ng/ml natural U standard from the same U standard batch. Measured $^{235}U/^{238}U_{meas.}$ ratios (**Fig. 3a**) and sample-standard bracketed $\delta^{235}U/^{238}U_{SSB}$ (**Fig. 3b**) for all three standards are in excellent agreement with $\delta^{235}U/^{238}U_{SSB,\ 20ng} = 0.000 \pm 0.071$ ($2\sigma_S$ SD; N = 61), $\delta^{235}U/^{238}U_{SSB,\ 22ng/ml} = -0.038 \pm 0.103$ ($2\sigma_S$ SD; N = 20), and $\delta^{235}U/^{238}U_{SSB,\ 25ng/ml} = 0.016 \pm 0.094$ ($2\sigma_S$ SD; N = 20). Combined with a high repeatability for the three standards, this demonstrates the robustness of the method against concentration mismatching of at least up to 25 %.

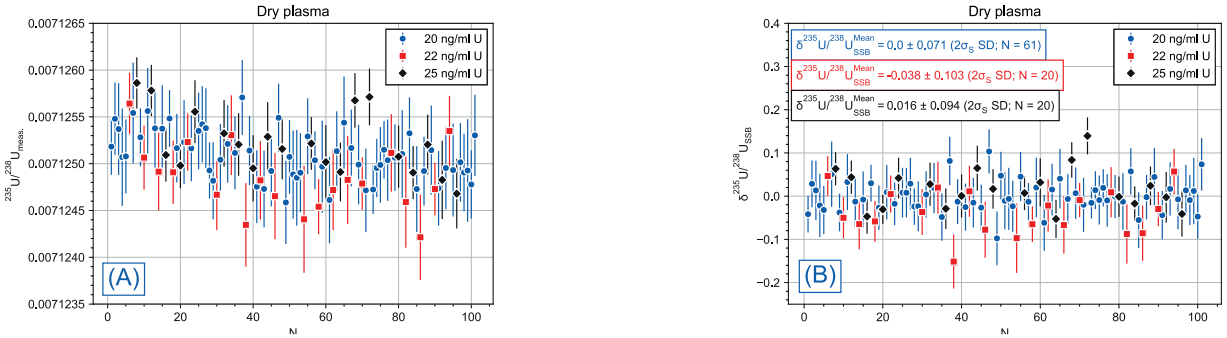

Fig. 3 Concentration-mismatched U isotope abundance ratio measurements using natural U standard solutions with 20 ng/ml (bracketing standard), 22 ng/ml, and 25 mg/ml of U shown as (**A**) measured (meas.) $^{235}U/^{238}U_{meas.}$, and (**B**) sample-standard bracketed (SSB) $\delta^{235}U/^{238}U_{SSB}$. Error bars on the data points indicate the $2\sigma_S$ SE measurement precision of the individual measurement.

An evaluation of the measurement trueness of the method was conducted using the enriched U standard reference materials U010, U030, and U050 from the National Bureau of Standards (NBS; New Brunswick, USA), which contain 1 %, 3 %, and 5 % of ^{235}U, respectively.
In a first run, the $^{235}U/^{238}U$ ratio of the NBS U030 standard was determined by standard bracketing with the NBS U010 standard. The measurements were mass bias corrected (MBC) by internally normalising the bracketing standard NBS U010 to a certified reference value of $^{235}U/^{238}U_{U010,Reference} = 0.010140$ using Russell's law, and applying the obtained mean mass bias factor to the NBS U030 standard. A second run determined the $^{235}U/^{238}U$ ratio of the NBS U050 reference material using NBS U030 as bracketing standard and internal normalisation to $^{235}U/^{238}U_{U030,Reference} = 0.031430$. Considering the large differences in $^{235}U/^{238}U$ ratios between the standards, two 30 s rinses followed by two 180 s wash sequences were performed to minimise memory effects and cross-contamination when switching between standards. Data are not corrected for minute $^{235}U^{17}O^{18}O^+$ interferences on $^{238}U^{16}O_2^+$.

For the NBS U030 standard the mean $^{235}U/^{238}U_{MBC} = 0.031426 \pm 0.000003$ ($2\sigma_S$ SD; N = 6) and for the NBS U050 standard the mean $^{235}U/^{238}U_{MBC} = 0.052777 \pm 0.000005$ ($2\sigma_S$ SD; N = 6), which are well in agreement with the certified reference values of $^{235}U/^{238}U_{030,Reference} = 0.031430 \pm 0.000031$ (**Fig. 4a**) and $^{235}U/^{238}U_{050,Reference} = 0.052784 \pm 0.000053$ (**Fig. 4b**), respectively. Uranium isotope abundance ratios can thus be determined with excellent accuracy and precision when mass shifting with O_2. The high measurement trueness after mass bias correction using internal normalisation in bracketing standards following Russell's law further demonstrate fully mass-dependent isotope fractionation throughout the Sapphire MC-ICP-MS.

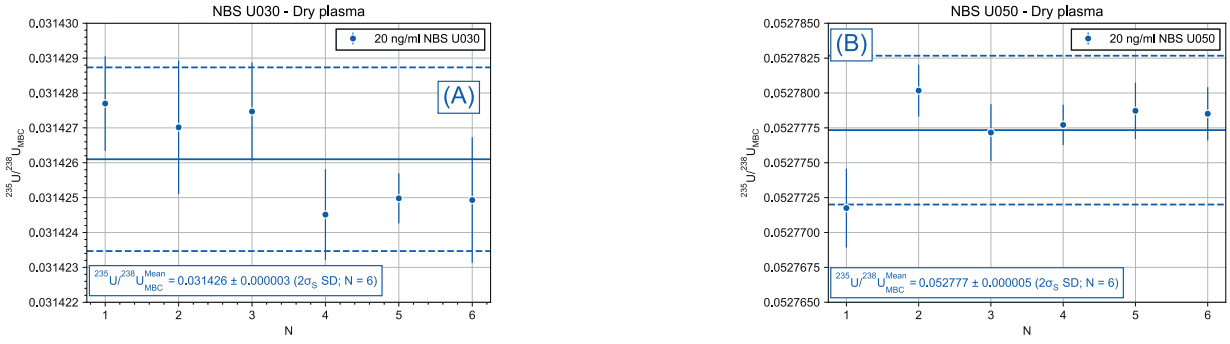

Fig. 4 Uranium isotope abundance ratios determined in two certified enriched U standards from Nation Bureau of Standards (NBS) as 20 ng/ml solutions showing (**A**) the mass bias corrected (MBC) $^{235}U/^{238}U_{MBC}$ in determined in NBS U030 using NBS U010 as bracketing standard for mass bias correction by normalisation to $^{235}U/^{238}U_{U010,Reference} = 0.010140$, and (**B**) $^{235}U/^{238}U_{MBC}$ in determined in NBS U050 using NBS U030 as bracketing standard for mass bias correction by normalisation to $^{235}U/^{238}U_{U030,Reference} = 0.031430$. Solid and dashed lines indicate sample (S) mean ± $2\sigma_S$ SD, and error bars on the data points indicate the $2\sigma_S$ SE measurement precision of the individual measurement.

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The generation of UO_2 species using O_2 in the Sapphire Collision/Reaction Cell to determine U isotope abundance ratios is highly effective (> 99.9 % of UO_2 formation) and yields a sensitivity > 1500 V/ppm. The instrument thereby displays a high isotope fractionation stability, and measured $^{235}U/^{238}U$ isotope abundance ratios are repeatable within 70-100 ppm ($2\sigma_S$ SD) with internal $2\sigma_S$ SE of 50-70 ppm of $^{235}U/^{238}U$. Concentration mismatching tests reveal robustness for concentration mismatching of at least up to 25 % and the measurement trueness is excellent for certified U standards, even when measuring samples with highly different degrees of ^{235}U enrichment.

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