Uranium oxide interference determination by direct measurement of natural U

Measurement of the uranium isotopic composition of double-spiked ($^{233}$U-$^{235}$U or $^{233}$U-$^{236}$U) samples as UO$_2^+$ species requires the subtraction of the isobaric interference of $^{18}$O-bearing $^{233}$UO$_2$ on the predominant target $^{235}$U$^{16}$O$_2$ peak at mass 267 (Schmitz, 2004), or the isobaric interference of $^{18}$O-bearing $^{236}$UO$_2$ on the predominant target $^{238}$U$^{16}$O$_2$ peak at mass 270. This requires an estimate of the isotopic composition of oxygen contributing to dioxide ion generation.

This issue has been encountered in other high-precision isotopic determination where the isotopes were measured as oxide, most notably Wasserburg et al [Wasserburg et al., 1981] on TIMS NdO measurements and recently associated with negative-ion TIMS Os analyses [Luguet et al., 2008]. Wasserburg et al [Wasserburg et al., 1981] documented direct measurement of the NdO$^+$ $R_{18}$ inside the mass spectrometer (in their instrument and others) and made two observations: (1) intra-lab variation in $R_{18}$ with values ranging from 0.00210 to 0.00216 and (2) within run variation in $R_{18}$ with values changing from 0.00208 (early in run) to 0.00213 (late in run). Luguet et al [Luguet et al., 2008] documented significant run to run variation with $R_{18}$ ranging form 0.00202 to 0.00205, and less significant intra-run variation.

Nier (1950) gave percentage abundances corresponding to $^{18}$O/$^{16}$O = 0.0020439 and $^{17}$O/$^{16}$O 0.0003749. IUPAC 2000 (De Laeter et al., 2003) present $^{18}$O molar fraction of 0.002 05 (molar fraction $^{16}$O = 0.99757) and $R_{18} = 0.002055$. However, the studies outlined above (and others) indicate inter- and intra-laboratory variation in $R_{18}$ and $R_{17}$ is potentially significant. Presented here is an adaptation of the Wasserburg et al. (1981) NdO$^+$ approach for the direct determination of $R_{18}$ and $R_{17}$ modified for UO$_2^+$.

For $R_{18}$ ($=^{18}$O/$^{16}$O):

\[
\frac{272}{270}_{\text{meas}} = \frac{^{238}U^{18}O^{16}O + ^{238}U^{16}O^{18}O}{^{238}U^{16}O^{16}O} \tag{1}
\]

\[
\frac{272}{270}_{\text{meas}} = \frac{^{238}U^{16}O^{16}O \left(^{18}O^{16}O \right) + ^{238}U^{16}O^{16}O \left(^{18}O^{16}O \right)}{^{238}U^{16}O^{16}O} \tag{2}
\]
\[
\frac{272}{270}_{\text{meas}} = \frac{^{238}U^{16}O^{16}O \left[ \frac{18}{16}O + \frac{18}{16}O \right]}{^{238}U^{16}O^{16}O}
\] (3)

\[
\frac{272}{270}_{\text{meas}} = \left[ \frac{18}{16}O + \frac{18}{16}O \right]
\] (4)

The other potential interferences (\(^{236}U^{18}O^{18}O\) and \(^{236}U^{17}O^{17}O\) and on the 272 peak and \(^{236}U^{17}O^{17}O\), \(^{236}U^{16}O^{16}O\), \(^{236}U^{18}O^{16}O\) and \(^{234}U^{18}O^{18}O\) on the 270 peak) are considered minor/zero for unspiked natural Uranium and are ignored for this purpose.

**For R\(_{17}\) (= \(^{17}O/^{16}O\)):**

\[
\frac{271}{270}_{\text{meas}} = \frac{^{238}U^{17}O^{16}O + ^{238}U^{16}O^{17}O}{^{238}U^{16}O^{16}O}
\] (5)

\[
\frac{271}{270}_{\text{meas}} = \frac{^{238}U^{16}O^{16}O \left( \frac{17}{16}O \right) + ^{238}U^{16}O^{16}O \left( \frac{17}{16}O \right)}{^{238}U^{16}O^{16}O}
\] (6)

\[
\frac{271}{270}_{\text{meas}} = \frac{^{238}U^{16}O^{16}O \left[ \frac{17}{16}O + \frac{17}{16}O \right]}{^{238}U^{16}O^{16}O}
\] (7)

\[
\frac{271}{270}_{\text{meas}} = \left[ \frac{17}{16}O + \frac{17}{16}O \right]
\] (8)

The other potential interferences (\(^{235}U^{18}O^{18}O\) on the 271 peak and \(^{236}U^{17}O^{17}O\), \(^{236}U^{16}O^{16}O\), \(^{236}U^{18}O^{16}O\) and \(^{234}U^{18}O^{18}O\) on the 270 peak) are considered minor/zero for unspiked natural Uranium and are ignored for this purpose.

Thus it is possible to determine both R\(_{17}\) and R\(_{18}\) by direct measurement of any U reference material enriched in \(^{238}U\) (e.g., CRM 112a, CRM U500):

\[
R_{17} = \left[ \frac{271}{270}_{\text{meas}} \right] / 2
\] (9)
\[ R_{18} = \sqrt{\left( \frac{272}{270} \right)_{\text{meas}}} / 2 \] (10)

References


