

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 $^{233}\text{UO}_2$ on the predominant target $^{235}\text{U}^{16}\text{O}_2$ peak at mass 267 (Schmitz, 2004), or the isobaric interference of ^{18}O -bearing $^{236}\text{UO}_2$ on the predominant target $^{238}\text{U}^{16}\text{O}_2$ 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 from 0.00202 to 0.00205, and less significant intra-run variation.

Nier (1950) gave percentage abundances corresponding to $^{18}\text{O}/^{16}\text{O} = 0.0020439$ and $^{17}\text{O}/^{16}\text{O} = 0.0003749$. IUPAC 2000 (De Laeter et al., 2003) present ^{18}O molar fraction of 0.002 05 (molar fraction $^{16}\text{O} = 0.99757$) 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} ($= ^{18}\text{O}/^{16}\text{O}$):

$$\left(\frac{272}{270}\right)_{\text{meas}} = \frac{{}^{238}\text{U}^{18}\text{O}^{16}\text{O} + {}^{238}\text{U}^{16}\text{O}^{18}\text{O}}{{}^{238}\text{U}^{16}\text{O}^{16}\text{O}} \quad (1)$$

$$\left(\frac{272}{270}\right)_{\text{meas}} = \frac{{}^{238}\text{U}^{16}\text{O}^{16}\text{O} \left(\frac{{}^{18}\text{O}}{{}^{16}\text{O}}\right) + {}^{238}\text{U}^{16}\text{O}^{16}\text{O} \left(\frac{{}^{18}\text{O}}{{}^{16}\text{O}}\right)}{{}^{238}\text{U}^{16}\text{O}^{16}\text{O}} \quad (2)$$

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

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

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

For R_{17} ($= {}^{17}\text{O}/{}^{16}\text{O}$):

$$\left(\frac{271}{270}\right)_{meas} = \frac{{}^{238}\text{U}^{17}\text{O}^{16}\text{O} + {}^{238}\text{U}^{16}\text{O}^{17}\text{O}}{{}^{238}\text{U}^{16}\text{O}^{16}\text{O}} \quad (5)$$

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

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

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

The other potential interferences (${}^{235}\text{U}^{18}\text{O}^{18}\text{O}$ on the 271 peak and ${}^{236}\text{U}^{17}\text{O}^{17}\text{O}$, ${}^{236}\text{U}^{16}\text{O}^{18}\text{O}$, ${}^{236}\text{U}^{18}\text{O}^{16}\text{O}$ and ${}^{234}\text{U}^{18}\text{O}^{18}\text{O}$ 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 ${}^{238}\text{U}$ (e.g., CRM 112a, CRM U500):

$$R_{17} = \left[\left(\frac{271}{270}\right)_{meas} \right] / 2 \quad (9)$$

$$R_{18} = \left[\left(\frac{272}{270} \right)_{meas} \right] / 2 \quad (10)$$

References

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