## Part I. Uranium oxide interference correction algorithms

Measurement of the uranium isotopic composition of double-spiked (233U-235U) samples as UO2+ species requires the subtraction of the isobaric interference of 18O-bearing 233UO2 on the predominant target 235U16O2 peak at mass 267. The probability of forming a double 17O-bearing uranium dioxide molecule is so low as to make a 233U17O2 interference of negligible importance for this measurement. The probability of an 18O dioxide substitution is estimated by the relative abundance of 18O, also safely approximated by 18O/16O, which may be assigned a value of 0.002055 (De Laeter et al., 2003) or directly measured from loads of natural U (see Part II). Both possible 18O substitutions into the dioxide molecule must be considered. The maths for the correction of the two measured U isotope ratios are given below.

For correcting the 235U/233U (or 233U/235U) ratio:

 (1)

 (2)

 (3)

 (4)

 (5)

 (6)

 (7)

 From IUPAC 2000, but see pg. 3 for direct measurement. (8)

 (9)

 (10)

 (11)

The final form of eqn. 11 accommodates those accustomed to both measuring and then entering the 233U/235U ratio into data reduction software.

For correcting the 238U/235U ratio:

 (12)

 (13)

Combining with eqn. 11…

 (14)

For those used to measuring the 238U/235U and 233U/235U ratios…

 (15)

 (16)

This last form accommodates those accustomed to both measuring and entering the 238U/235U and 233U/235U ratios into data reduction software. These corrections (eqns. 11 and 16) can be simply added as functions in the user maths of the mass spectrometer method files, or they can be done off-line (for example as a group of cells within the UPbR data reduction workbook).

These algorithms, including the assumed 18O abundance have been confirmed empirically by splitting large spiked sample U loads and running as both metal and oxide. When combined with the sample Pb isotope abundances, there is excellent agreement (better than 0.1%) in calculated Pb/U ratios between the metal and corrected oxide uranium isotope measurements.

## Part II. Oxygen isotope composition determination by direct measurement of natural U

Measurement of the uranium isotopic composition of double-spiked (233U-235U or 233U-236U) samples as UO2+ species requires the subtraction of the isobaric interference of 18O-bearing 233UO2 on the predominant target 235U16O peak at mass 267 (Schmitz, 2004), or the isobaric interference of 18O-bearing 236UO2 on the predominant target 238U16O2 peak at mass 270. This requires an estimate of the isotopic composition of oxygen contributing to dioxide ion generation (see Part I).

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 18O/16O = 0.0020439 and 17O/16O 0.0003749. IUPAC 2000 (De Laeter et al., 2003) present 18O molar fraction of 0.002 05 (molar fraction 16O = 0.99757) and R = 0.002055. However, the studies outlined above (and others) indicate inter- and intra-laboratory variation in R18 and R17 is potentially significant. Presented here is an adaptation of the Wasserburg et al. (1981) NdO+ approach for the direct determination of R18 and R17 modified for UO2+.

18

**For R18 (= 18O/16O):**

 (1)

 (2)

 (3)

 (4)

The other potential interferences (236U18O18O and 236U17O17O and on the 272 peak and 236U17O17O, 236U16O18O, 236U18O16O and 234U18O18O on the 270 peak) are considered minor/zero for unspiked natural uranium and are ignored for this purpose.

**For R17 (= 17O/16O):**

 (5)

 (6)

 (7)

 (8)

The other potential interferences (235U18O18O on the 271 peak and 236U17O17O, 236U16O18O, 236U18O16O and 234U18O18O 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 R17 and R18 by direct measurement of any U reference material enriched in 238U (e.g., CRM 112a, CRM U500):

 (9)

 (10)

## References

De Laeter, J.R., Böhlke, J.K., De Bièvre, P., Hidaka, H., Peiser, H.S., Rosman, K.J.R, and Taylor, P.D.P., 2003. Atomic weights of the elements: Review 2000. Pure Appl. Chem, vol 75, pp. 683-800.

Luguet, A., et al. (2008), 184Os/188Os and 186Os/188Os measurements by Negative Thermal Ionisation Mass Spectrometry (N-TIMS): Effects of interfering element and mass fractionation corrections on data accuracy and precision, *Chem Geol*, *248*(3-4), 342-362.

Nier, A.O., (1950) A redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon, and potassium: *Physics Review*, v. 77, p. 789-793.

Wasserburg, G.J., Jacobsen, S.B., DePaolo, D.J., McCulloch, M.T., and Wen, T., (1981) Precise determination of Sm/Nd ratios, Sm and Nd isotopic abundances in standard solutions: *Geochimica et Cosmochimica Acta*, v. 45, p. 2311-2323.