APPLICATION OF THE OXIDE FRACTIONATION FOR CORRECTION OF URANIUM FRACTIONATION IN THERMAL IONIZATION MASS SPECTROMETRY

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Abstract
A methodology for correcting the fractionation of uranium isotopes during thermal ionization mass spectrometric analysis is evaluated. Using UO\(^+\) ions for analysis, the fractionation of the oxygen isotopes is correlated to the fractionation in U data using different certified isotopic standards of uranium for analysis. It has been found that more than 99.9% fractionation in the uranium analysis can be accounted for in this method. The reproducibility of the methodology was evaluated using the principal component analysis of the experimental data performed over a wide period of time.

Introduction
Thermal Ionization Mass Spectrometry (TIMS) is widely employed for the isotopic analysis of a variety of elements. The main limitation of the technique is the time dependent, variable isotopic fractionation. Precise and accurate uranium isotopic data is of interest in geochronology as well as in nuclear technology.

Earlier, we had reported an internal correction methodology to account for fractionation in U isotopic analysis using UO\(^+\) ions and the oxygen isotope ratio\(^1\). The method of oxygen ratio is attractive in case of uranium, since uranyl ions are completely solvated in the nitric acid medium and most probably, the oxygen ratio in UO\(_2\)\(^+\) is expected to be more closer to that of the acid used for the dissolution of uranium sample.

It was of interest to check the robustness of this methodology and also to verify whether there is any variation in the observed correlation due to the changes in the oxygen environment at different periods of analysis. This has been observed in the method reported recently where the oxygen isotope for fractionation correction in B was much different than that is obtained using ReO\(_4\)\(^-\) ions\(^2\) and hence there was a systematic bias in the determination of boron isotope ratio in the sample.

In order to ascertain the application of the oxygen fractionation correction, fresh analysis of samples were performed over a period of time, in order to account for the differences in the oxygen ratios expected on the Rhenium filament as well as the conditions of analysis (e.g. vacuum in the ion source etc) which may vary significantly over a period of time. Analyses were performed over a period of one year using different certified isotopic standards of uranium

Experimental
The different certified standards of uranium analyzed were NIST SRMs U-005, U-050, U-200 & U-500 which cover a wide range of isotopic composition of uranium. The analyses were performed using tantalum filament as evaporation filament and rhenium as the ionization filament as in our previous study, since these provided...
more stable and increased yield of UO$^+$ ions [1]. The analyses of U as UO$^+$ ions were performed at lower ionization filament temperatures. The data were acquired using static mode of multicolonction. The data were recorded to obtain the ion current ratios of 251/254, 251/256 & 254/256, corresponding to the UO$^+$ ions of the isotopes of U ($^{235}$U & $^{238}$U) and those of oxygen ($^{18}$O & $^{16}$O).

### Results and discussions

Fig. 1 shows the correlation obtained for the observed ion intensity ratios for m/q 256/254 corresponding to the $^{18}$O/$^{16}$O oxygen isotope ratio in the sample with that of 256/251 which corresponds to $^{18}$O.$^{235}$U/$^{16}$O.$^{238}$U ratio for the certified standard U-050. In the figure, the observed oxygen ratio data is also plotted with the expected slope of certified U isotope ratio. It can be seen that the two lines are almost coinciding and the slope of the observed data closely coincides with the expected ratio and accounts for more than 99.99% of the fractionation (around -0.3 mil is the residual fractionation). Similar curves were also obtained for the other certified standards of uranium.

Table 1 shows the observed slope for similar plots obtained for the other standards. It can be seen that there is significant difference for the slopes for U-005 and U-500 from that of the expected slope, while it is similar in case of other standards (−0.3 milli). This can be due to the fact that in case of U-005 and U-500, due to the small intensity of ion current at m/q of 251 and 256 respectively, which results in the heating conditions that may be significantly different during the different analyses, which results in a different fractionation pattern in comparison to the other standards. It can also be seen that all the slopes are lesser than that expected for all the certified ratios. Further studies are needed to ascertain this source of bias in the oxygen ratio, by using a certified Oxygen ratio standard for the HNO$_3$ solution and checking the observed ratio obtained during TIMS analysis.

In order to confirm that the analysis conditions remained similar over this long period of time, a principal component analysis (PCA) of the observed ratios was performed. Fig. 2 shows the plot of PCA scores for the different standards. It can be seen that except for U-005,
all the other analysis are very similar and hence it can be ascertained that there is no abnormality in the data that is collected over a period of time for the analysis. The observed difference in the NIST-SRM-U-005 may be due to the fact that since the $^{235}$U content is too less in this standard, there can be some difficulty in exactly reproducing the analysis conditions during the different analyses.

**Conclusions**

From this study, it can be seen that over a period of time, the methodology of oxygen fractionation to correct for uranium fractionation is valid, and hence provides a viable option for correcting the fractionation of uranium during TIMS analysis. The negative bias observed needs further investigation using a different source of $^{18}$O which will provide an insight into identifying the source of oxygen during the analysis.

**References**
