STUDIES ON THE APPLICATION OF INTERNAL NORMALIZATION IN THE DETERMINATION OF URANIUM ISOTOPIC RATIO USING OXYGEN ISOTOPIC RATIO

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Introduction

Thermal Ionization Mass Spectrometry is an internationally recognized mass spectrometric technique, for the determination of isotopic composition and concentration of various elements in a variety of matrices. It is a highly preferred technique, due to its ability to provide data with high precision and accuracy. But it has some limitations due to the inherent time-dependent isotope fractionation, in the ion source. A variety of methodologies have been developed and employed, to account for this isotope fractionation. These are (i) external normalization (ii) internal normalization and (iii) total evaporation and ion current integration. Each of the methods has its inherent advantages as well as limitations.

In this paper, we describe a new methodology of internal normalization, to correct for the isotopic fractionation of U, using UO$^+$ ions for obtaining isotopic analysis data for U. The methodology is promising for application to U isotopic analysis by TIMS. The suitable conditions for application of this method are also discussed in this paper.

Experimental

Certified reference materials of U namely NIST CRM-005, CRM-010, CRM-050, CRM-200 and CRM-500 were used in this work. About 1 mL of the solutions containing U in the range of 1 to 2 mg was loaded on to high purity tantalum filament, employed as the evaporation filament in the double filament assembly. High purity rhenium was used as the ionization filament. The samples were analyzed in a thermal ionization mass spectrometer, equipped with multiple Faraday cup detection system, under static mode of multi-collection. Instead of the conventionally employed U$^+$ ions, UO$^+$ ions were employed for acquiring the isotopic composition data of U.

Results and Discussion

The filament heating conditions for obtaining a stable signal of UO$^+$ ions, were initially obtained by studying the variation in the ion current, as a function of both evaporation filament current at constant ionization filament current, as well as with that of ionization filament current at constant evaporation filament current. This data is shown in Figs. 1 and 2 respectively. As can be seen, significant signal of UO$^+$ is obtained at lower ionization filament currents and higher vaporization currents respectively. It should also be noted, that this type of behaviour was only observed when Ta was used as the evaporation filament and not observed in case of rhenium filament. This may be due to the fact, that as the samples are loaded in atmosphere and treated under red hot conditions,
significant amount of Ta is also converted as oxide, which provides a stable supply of oxygen for the formation of UO\(^+\) ions during analysis.

Based on these studies, the conditions for analysis of U as UO\(^+\) ions were optimized and employed for the further analysis of all the certified standards of U. U isotopic ratio in the sample \(^{235}U/^{238}U\) was obtained, using m/q of 251 and 254 respectively, while that of Oxygen (i.e \(^{18}O/^{16}O\)) was obtained, using data of m/q 256 and 254 respectively.

The fractionation in U, O was calculated, using the certified ratios for \(^{235}U/^{238}U\) and the oxygen isotopic ratio of 0.002096, determined previously in our laboratory. A plot between Oxygen fractionation \([256/254]_{\text{obs}}/\text{(18O/16O)T}\] with respect to the product of U fractionation and Oxygen fractionation \([\text{(256/251)}_{\text{obs}}/\text{((238U/235U)}_{\text{cert}}\text{(18O/16O)T})]\] is shown in Fig. 3. As can be seen, the correlation between O K-Factor with the product of K-factors for U & O is linear for the conditions of analysis applied in this study. Knowing the K-factor for oxygen in the sample (obtained from m/q ratio 256/254), one can obtain the combined fractionation of both U & O which can then be applied for correcting the K-factor for U (in the ratio 256/251).

Another correlation with respect to O fractionation/mass unit (i.e. 2) vs. UO fractionation per mass unit (i.e 5) was also tried, using this data. This is shown in Fig. 4. This also gave a linear relation and can also be applied for correcting the isotope fractionation in U. Knowing the K-factor/mass unit for oxygen in the sample (obtained from m/q ratio 256/254), one can obtain the K-factor for UO which can then be applied for correcting the K-factor for UO (in the ratio 254/251). The precision in U isotopic analysis obtained from 256/251 ratio would be poorer, since \(^{18}O\) is the less abundant isotope, while the second correlation would give a better precision on the isotopic ratio of
U in addition to correcting for isotope fractionation. These correlations were then applied for a number of independent U analyses (of certified standards). Both the correlations were found to correct for fractionation of U in the analysis significantly. In some of the analyses, it was found that this method was not applicable. In these analyses, it was also found that the O ratio measured from 256/254 was not stable or was decreasing from one block to another. It was also observed, that the fractionation correction by this internal normalization improved the results whenever the oxygen isotopic ratio between individual blocks was stable or showed an increasing trend and yielded poorer results, whenever the oxygen isotopic ratio measured between individual blocks was not constant and showed decreasing trend. This can be interpreted as while there was increasing trend, significant amount of oxygen compound between Ta and U was present on the filament for analysis, which provided a positive fractionation, while in the other case, the fractionation trend is negative for oxygen indicating the non-availability of oxygen supply from the intermetallic (U-Ta) Oxide compound, formed on the surface of the filament. This variation is possible since the loading of the sample is done manually and slight variations from loading (ie heating conditions employed for drying the sample) is probable.

While the results of this study are interesting, for regular application in case of analysis of actual samples, the conditions of analysis may tend to vary which would reduce the confidence in the application of this methodology. The intermetallic oxide compound formed on the filament has to be characterized by suitable means, for obtaining a suitable condition for loading can be optimized, for increasing the confidence on application of this methodology on a regular basis.

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