ION SOURCE CHEMISTRY DURING SIMULTANEOUS ANALYSIS OF THORIUM AND URANIUM BY THERMAL IONISATION MASS SPECTROMETRY (TIMS)

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Introduction

Thermal ionisation mass spectrometry (TIMS) is conventionally a single element analysis technique and requires the element to be present in the purest chemical form to achieve the ultimate in terms of precision and accuracy in isotope ratios determination. However, in many practical situations, such a condition cannot be satisfied. For example, when Th is irradiated in a nuclear reactor, $^{233}$U is produced along with other isotopes of U viz. $^{232}$U, $^{234}$U, $^{235}$U, $^{236}$U and $^{238}$U. Inspite of the separation and purification of this U from bulk of Th, there would always be small amounts of Th associated with purified fraction of U. Depending upon the separation efficiency, U/Th amount ratio in the purified U fraction would vary and this would alter the ion source chemistry occurring in the thermal ionisation source of the mass spectrometer compared to when the pure forms of U or Th are analysed by TIMS. Hence, it was of interest to study the ion source chemistry of Th and U during their simultaneous mass spectrometric analysis by TIMS.

Experimental

Different synthetic mixtures were prepared by mixing solutions of thorium nitrate and uranyl nitrate (both natural). The samples were loaded onto the sample filament of a high purity double rhenium filament assembly from the dilute HNO$_3$ medium and were subjected to TIMS analysis.

The temperature (heating current) of the ionisation filament was fixed (about 6A) by monitoring the $^{187}$Re$^+$ signal and was maintained constant throughout the analysis. The vaporisation filament was heated manually in steps upto about 5A. The various ions monitored at different temperatures of the vaporization (sample) filament were U$^+$, UO$^+$, UO$_2$$^+$, Th$^+$, ThO$^+$ and ThO$_2$.$^+$ and the corresponding m/z values were 238, 254, 270, 232, 248 and 264, respectively.

Results and Discussion

Figs. 1, 2 and 3 present the results obtained on ion source chemistry of U and Th when present together on the sample filament of a double rhenium filament assembly. It may be noted that the intensity ratios plotted in these Figures are normalized w.r.t. the amount ratio of U/Th in the
mixture. Among the various ions monitored, only U\(^+\), UO\(^+\), ThO\(^+\) were observed to have sufficient intensity and hence these were only used to compare the ion source chemistry.

Fig. 1 shows the change in U\(^+\)/ThO\(^+\) intensity ratio as a function of vaporization filament heating current. It is obvious that the intensity of U\(^+\) ion current is significantly higher than that of ThO\(^+\) in all the synthetic mixtures up to the vaporization filament heating current of about 3.5 A. Further, it is seen that when the amount of Th in the mixture increases, the intensity of U\(^+\) decreases significantly (curve C). This means that in the presence of Th, one will have to load relatively large amount of U on the filament to get sufficient ion current of U\(^+\) for precise and accurate analysis.

Fig. 2 presents the change in UO\(^+\)/ThO\(^+\) intensity ratio as a function of vaporization filament heating current. In above cases, there is a decrease in the UO\(^+\)/ThO\(^+\) intensity ratio with increasing vaporization filament heating current. Further, it is observed that UO\(^+\) intensity is quite appreciable even at vaporization filament heating current up to about 3.5 A. This suggests that the presence of Th along with U on the filament enhances the stability of UO\(^+\) compared to when pure uranium sample is used for TIMS analysis.

Fig. 3 shows the U\(^+\)/UO\(^+\) intensity ratio as a function of vaporization filament heating current. In all the cases studied, the intensities of U\(^+\) and UO\(^+\) are comparable which again shows that the presence of Th on the filament leads to stabilization of UO\(^+\) ion.

These studies indicate that the presence of large amount of Th (Th/U > 10) on the filament will degrade the precision of U isotopic analysis by monitoring U\(^+\) ions due to their poor yield. Further for Th isotopic analysis, ThO\(^+\) should be preferred to Th\(^+\) ion due to higher intensity of the oxide species. Also during the determination of \(^{232}\)U in \(^{233}\)U by TIMS, it would be interesting
to carry out the analysis using \( \text{U}^+ \) as well as \( \text{UO}^+ \) ions and this would be helpful to verify the presence/absence of isobaric interference of \( ^{232}\text{Th} \) at \( ^{232}\text{U} \).

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