SIMULTANEOUS ANALYSIS OF URANIUM AND PLUTONIUM USING THERMAL IONIZATION MASS SPECTROMETRY

K. L. RAMAKUMAR, S. JEYAKUMAR, R. M. RAO, L. GNANAYYAN, H. C. JAIN

Fuel Chemistry Division, Bhabha Atomic Research Centre,
Trombay, Bombay 400 085 (India)

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Simultaneous isotopic analysis of uranium and plutonium using thermal ionization mass spectrometer coupled to a multi-collector detection assembly with 9 Faraday cups has been reported earlier. Subsequently investigations have been carried out (1) to understand the applicability of correction methodologies available to account for the contribution of $^{238}$Pu at $^{238}$U and (2) to evaluate the effectiveness of these methodologies on the accuracy of $^{235}$U/$^{238}$U atom ratio being determined, particularly when samples containing different U/Pu atom ratios. Isotopic fractionation for both U and Pu in the simultaneous isotopic analysis has been compared with the results of the individual analysis of these elements. The different isotopic fractionation factors observed for U were attributed to different conditions of analysis. There was no significant difference in the isotopic fractionation patterns for Pu. The consideration to extend this method to actual samples from our observations on synthetic samples with different U/Pu atom ratios containing U and Pu isotopic reference standards is described.

A knowledge of isotopic composition of elements is needed for a number of reasons. In nuclear technology for example, the fissile and fertile isotopic content in nuclear fuel materials such as uranium and plutonium and the isotopic composition of neutron absorbing elements such as boron, cadmium etc. are required. In geochemistry and cosmochemistry, the knowledge of isotopic composition of elements present in terrestrial and non-terrestrial samples could throw light on their formation. Geological age determination of the rocks is possible only when the isotopic composition of certain "geological clock" elements is known accurately. In chemistry, accurate analytical methods are based on the use of enriched isotopes of elements in isotope dilution analysis. Thermal ionization mass spectrometry (TIMS) has been and continues to be the main workhorse for precise and accurate isotopic analysis. The attractive features of TIMS have been well documented. The main limitation of TIMS is its applicability to single elemental analysis only. The simultaneous analysis of two or more elements particularly after the advent of commercial instruments with multi-collection detector facilities having as many as 9 detectors has the following advantages: (1) requirement of separating the elements becomes redundant, ((2) separate filament loadings for individual elements are avoided, (3) time required for mass spectrometric analysis is reduced, and (4) overall cost benefit is realised. However, a necessary requirement for
such an oligo-elemental analysis by TIMS is that the elements should have similar m/z range and somewhat similar evaporation and ionization behavior. Efforts have been made in literature to analyse two elements such as uranium and plutonium sequentially from an anion exchange resin bead loaded on a single filament\textsuperscript{4-6} using a custom built two stage tandem mass spectrometer with pulse counting detection system.

A method for the simultaneous isotopic analysis of uranium and plutonium using a commercially available TIMS instrument has been developed in our laboratory\textsuperscript{7} with a precision and accuracy better than 0.2\%. Subsequently more investigations on the simultaneous isotopic analysis have been carried out with the following objectives: (1) to understand the applicability of different correction methodologies available to account for the contribution of $^{238}$Pu at $^{238}$U, (2) to evaluate the effectiveness of these methodologies on the accuracy of the determination $^{235}$U/$^{238}$U ratio, particularly when samples contain different U/Pu atom ratios, (3) to compare the isotopic fractionation behavior of uranium and plutonium isotopes during the simultaneous and individual analysis, and (4) to consider the extension of this method to actual samples from synthetic samples with different U/Pu ratios containing U and Pu isotopic reference standards. Furthermore, simultaneous analysis of U and Pu could provide an opportunity to evaluate and compare their vaporization and ionization behavior under thermal ionization conditions.

**Experimental**

*Samples and reagents:* Isotopic reference materials SRM--010--U ($= 1$ atom\% $^{235}$U) and SRM--947--Pu ($= 77$ atom\% of $^{239}$Pu) available from National Institute of Standards and Technology (NIST, USA) were used in the preliminary investigations. An in-house plutonium working standard and uranium chemical assay standard SRM--950a--U available from NIST were used in subsequent studies.

DOWEX 1X4 anion exchange resin, 200--400 mesh (Dow Chemical Company, USA) was used to purify Pu solutions.

AnalaR grade nitric acid and acid leached glassware were used throughout the investigations.

Double rhenium filament assembly was used for loading the samples.

*Instrument:* A Finnigan MAT--261 TIMS instrument upgraded with a multi-collector Faraday cup detector system was used. The mass calibration of the instrument was normally carried out by establishing a 6th degree polynomial relation between the reference magnetic fields corresponding to 6 known m/z values covering the atomic mass range of 20 to 240. The performance of the instrument is checked at least once every day by analyzing isotopic reference materials of uranium and plutonium. Further details of the instrument, Faraday cup selection for the uranium and plutonium isotopes,