REDOX DETERMINATION OF URANIUM IN PRESENCE OF PLUTONIUM IN LOW PHOSPHORIC ACID MEDIUM AND THE RECOVERY OF PLUTONIUM

SOME NEW OBSERVATIONS

G. R. RELAN,* A. R. JOSHI,** R. H. IYER*

*Nuclear Materials Accounting Cell,
**Radiochemistry Division, Bhabha Atomic Research Centre,
Trombay, Bombay-400 085 (India)

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Quantitative determination of uranium in (U, Pu)O₂ fuels is usually done by the DAVIES-GRAY method. High concentrations of phosphoric acid in the analytical waste generated by this method make the recovery of plutonium rather complex. Studies on the recovery of plutonium from nitric acid medium containing different concentrations of H₃PO₄ by conventional anion-exchange procedure reveal that more than 90% of the plutonium can be easily recovered when the phosphoric acid concentration is less than 0.5 M in the solution. A method was developed for the determination of uranium in the presence of plutonium, which involves the reduction of U(VI) to U(IV) by Fe(II) in a medium of 3.5M H₃PO₄ + 4.5M H₂SO₄ instead of 10-11M H₃PO₄ so as to have the H₃PO₄ concentration ~0.6M in the waste. A number of determinations of uranium in UO₂(NO₃)₂ working standard solutions and (U, Pu) synthetic solutions with uranium at the 3-7 mg level were carried out by this method. The precision obtained was better than ±0.2% and the accuracy was also within the precision limits. The resulting analytical waste generated was directly subjected to anion exchange separation for the recovery of plutonium which was found to be more than 90%.

Introduction

The determination of uranium at various stages of the nuclear fuel cycle with a high degree of precision and accuracy is one of the essential requirements in nuclear materials accounting and chemical quality control of fuel materials. Some of the important aspects to be considered while judiciously selecting the method for the determination of uranium and/or plutonium in (U, Pu)O₂ and reprocessing streams are: (1) the method should be simple, rapid and capable of giving good precision and accuracy; (2) the sample size required for the analysis should be small to reduce difficulties in handling radioactivity and (3) the analytical waste generated should be small in volume and should be amenable to easy recovery of plutonium.
The redox method most widely used for the determination of uranium in \((\text{U, Pu})\) fuels is based on the one reported by DAVIES and GRAY\(^1\). It involves the reduction of \(\text{U(VI)}\) to \(\text{U(IV)}\) in concentrated \(\text{H}_3\text{PO}_4\) by excess \(\text{Fe(II)}\) followed by selective oxidation of unused \(\text{Fe(II)}\) by \(\text{HNO}_3\) catalyzed by molybdate ions and subsequent titration of \(\text{U(IV)}\) with standard \(\text{K}_2\text{Cr}_2\text{O}_7\) to visual end point. However, several modifications\(^2-^8\) have been introduced when the method was intended for the analysis of uranium in \((\text{U, Pu})\) fuels or process solutions. The sensitivity of the end point detection was improved by the addition of \(\text{V(IV)}\) after the oxidation step, where the \(\text{H}_3\text{PO}_4\) is 3M as suggested by EBERIE et al.\(^2\) or by further bringing down the concentration of \(\text{H}_3\text{PO}_4\) to 1M as reported by CHITNIS et al.\(^8\). A bi-amperometric method\(^3\) based on the pertinent reactions of DAVIES and GRAY\(^1\) has also been reported.

The recovery of plutonium from the analytical waste becomes necessary from the economic, strategic, health and safety points of view. Though the above methods are quite precise, accurate, fast and routinely employed for the determination of uranium in uranium – plutonium-based fuels, they suffer from the disadvantage that the waste solution so generated contains high concentrations of phosphoric acid (1–3M), thereby making the recovery of plutonium difficult. A method was therefore developed for the determination of uranium such that the final solution after the titration contains the minimum possible phosphate ion concentration at the same time maintaining the total volume small. The method has been checked rigorously for the precision and accuracy attainable and the results are reported here. The results of investigations on the recovery of plutonium from the waste generated by the present method are also presented in this paper.

**Experimental**

**Apparatus**

For the potentiometric titration, digital voltmeter was used with a saturated calomel reference electrode and a Pt indicator electrode.

For amperometric titrations, a pair of identical Pt-wires was used in conjunction with an amperometer made in this Division.

For ion-exchange studies, a column of 1.2 cm dia and 12 cm height and a few microcolumns packed with Dowex 1 \(\times\) 4, \(\text{NO}_3\) form, 50–100 mesh were used.

To study the ion-exchange behaviour, plutonium in aqueous solution was assayed radiometrically by counting the alpha activity of small known volumes.