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Optimization of Analytical Method for the Simultaneous Determination of Uranous and Total Uranium in the Process Samples of Nuclear Fuel Reprocessing Plant

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ABSTRACT
Optimization of redox titrimetric method for the simultaneous determination of uranous and total uranium in the process samples of nuclear fuel reprocessing is described in the present paper. The objective of this study was to reduce the waste volume as well as the sulfate ion concentration in the waste solution. Precision and accuracy obtained in this method are comparable with the conventional method.

Key words: *Total uranium, Uranous, Single aliquot.*

1. INTRODUCTION

India had successfully demonstrated the technology of reprocessing of mixed carbide (70% Pu, 30% U) spent fuel discharged from the fast breeder test reactor in the facility called compact reprocessing of advanced fuels in lead shielded facility at Kalpakkam. This facility had carried out several batches of reprocessing of spent fuels with a burn up of 155 GWd/Te and a cooling time of around 2 years.

Spent fuel discharged from nuclear reactor is worldwide reprocessed using plutonium uranium redox extraction (PUREX) process [1,2]. This flow sheet consists of the chop-leach process in the head end step, co-extraction cycle for removal of fission products and partitioning cycle for separation of uranium and plutonium by the solvent extraction step, followed by further purification of the uranium and plutonium products before converting them to their respective products. Concurrent R and D activities have been conducted in modifying the flowsheet to improve recovery of Pu and U, overall DF from FP with reduced number of mass transfer equipments and ultimately to reduce the waste volumes.

Partitioning of uranium and plutonium is accomplished by the addition of uranous to selectively reduce the valency of Pu(IV) to Pu(III), which is in extractable. It is therefore, essential to know the concentration of Uranous U(IV) and U(VI) during the partitioning cycle of the PUREX process. Uranos present in the solution can be determined by spectrophotometry [3,4] redox titrimetry as well as complexometric titration [5] methods. Uranyl concentration in the sample is determined by subtracting uranous concentration from total uranium concentration in the sample.

Total uranium concentration in spent nuclear fuel reprocessing plant streams are determined by mass spectrometry [6,7] K-edge densitometry [8] energy dispersive X-ray florescence [9], electro-analytical methods [10] and [11,12]. The methods mentioned mainly focused on the determination of total uranium in diverse matrix. In view of possibility of presence of uranyl and uranous along with hydrazine (>0.5 M) in the aqueous streams of partitioning process, the reported methods may not be suitable for the determination of uranyl and uranous together. Conventionally uranous in the electrolyzer sample is analyzed by redox titrimetric method employing Ferroin indicator in >2.5 M sulfuric acid as titrating medium [13]. Total uranium is analyzed [14,15] by taking a different aliquot following modified Davis Grey method after evaporation of the sample with $HClO_4$ to remove interference of hydrazine. This method generates a waste solution bearing 0.7-1 M sulfuric acid as the medium. Sahoo et al. [16], reported the determination of total uranium and uranous in the elctrolyzer (for the generation of uranous) samples and indicated that the hydrazine did not interfere in the

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total uranium analysis if its concentration is <0.2 M. In general, elctrolyzer samples are having hydrazine concentration >0.2 M. Hence, this method may not be suitable for these samples. A new method is optimized for the determination of uranous and total uranium in aqueous solution (nitric acid medium) having hydrazine concentration >0.2 M without performing perchloric acid evaporation in-order to remove the interference of hydrazine. The overall objective of this study was to reduce the waste volume generation during the chemical analysis. The results of this study is presented in this paper.

2. EXPERIMENTAL

Uranyl nitrate solution was prepared by dissolving U_3O_8 powder in nitric acid. A stock solution of uranous in nitric acid medium along with 0.5 M hydrazine was prepared by electrolyzing uranyl nitrate solution. The reagents used in these experiments are of analytical reagent grade, and the Millie-Q water was used for all reagent preparation and the experiments. Uranous and total uranium were analyzed.

2.1. Determination of Uranous by Standard Method

Aliquot in the range of 2-25 mg was taken in a beaker. 15 mL of water was added to it followed by the addition of 9 mL of 9 M sulfuric acid and 0.5 mL of Ferroin indicator. The mixed solution was then titrated with a standard $K_2Cr_2O_7$ solution, till the end point is reached. The uranous concentration was determined from the titer value.

2.2. Determination of Uranous by the Present Method

Aliquot in the range of 2-25 mg was taken in a beaker. 5 mL of water was added to it followed by addition of 0.5 mL 9 M H_2SO_4 and 1 mL of barium diphenylamine sulfonate (BDAS) and then it was titrated against standard $K_2Cr_2O_7$ solution, till the appearance of violet color. The uranous concentration was determined from the volume of $K_2Cr_2O_7$ solution consumed.

2.3. Determination of Total Uranium by Standard Method

Suitable aliquot in the range of 3-10 mg is taken in a beaker. Prior to addition of other reagents, the sample is treated with $HClO_4$ acid to destroy hydrazine. 0.5 mL of 1.5 M sulfamic acid, 5 mL H_3PO_4 acid and 0.5 mL 1 M ferrous ammonium sulphate (FAS) were added to this content and then swirled for 2 min for complete reduction of U(VI) to U(IV). After that 0.5 mL of 10 M HNO_3, 0.5 mL of 1.5 M sulfamic acid and 0.2 mL ammonium molybdate were added in the resulting solution and waited for 5 min. In this mixture 6 mL of 9 M H_2SO_4, 7 mL water and 0.5 mL of 0.04% of BDAS were added and titrated with standard $K_2Cr_2O_7$ solution. Total uranium concentration was determined from titer value.

2.4. Determination of Total Uranium by the Present Method

After uranous analysis, the solution is taken for total uranium determination by adding reagents in the following order: 0.2 mL of 3 M $NaNO_2$ was added into the content and swirled for 2 min. Then, 1 mL of 1.5 M of sulfamic acid and 10 mL of concentrated ortho H_3PO_4, 0.5 mL 1 M (FAS in 1M sulfuric acid) were added and swirled for 2 min for the conversion of uranyl to uranous. After ensuring the complete, other reagents such as 0.5 mL of 1.5 M sulfamic acid, 0.5 mL of 10 M nitric acid and 0.2 mL of 0.2% ammonium molybdate were added for the destruction of excess ferrous and waited for 5 min to get clear color the added 6 mL of 9 M H_2SO_4 followed by 25 mL of water and BDAS indicator. This solution was titrated with standard $K_2Cr_2O_7$ till the appearance of violet color. The total uranium concentration was calculated from the titer value obtained.

3. RESULTS AND DISCUSSION

3.1. Effect of Sulphuric Acid on Uranous Determination

Uranous determination in the conventional method is carried out by the addition of sulfuric acid. A large excess of sulfuric acid i.e., >2.5 M is present in the titrating medium than usual concentration of around 1 M of sulfuric acid for such titrations. Hence, a detailed study of the effect of sulfuric acid on the uranous determination is carried out in the current study, by varying the concentration of sulfuric acid and results are shown in Figure 1. It is observed from the figure that determined uranous concentration remains same in the range of sulfuric acid concentration in the titrating medium. Hence, 0.3 M of sulfuric acid was found to be adequate in the titrating medium.

3.2. Effect of Sodium Nitrite on Total Uranium Determination

The solution obtained after determination of uranous consists of hydrazine along with uranium. In the conventional method (Davies Gray) total uranium is determined after hydrazine is destroyed by perchloric

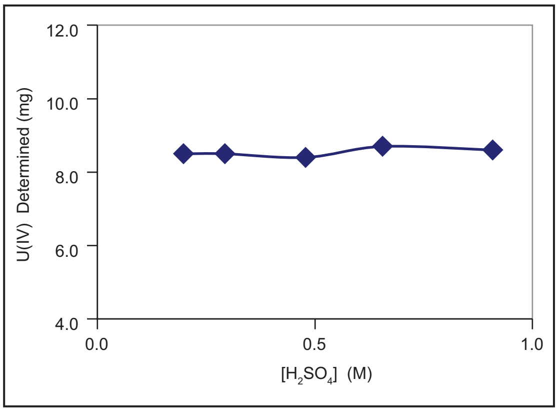

Figure 1: Effect of sulphuric acid concentration.

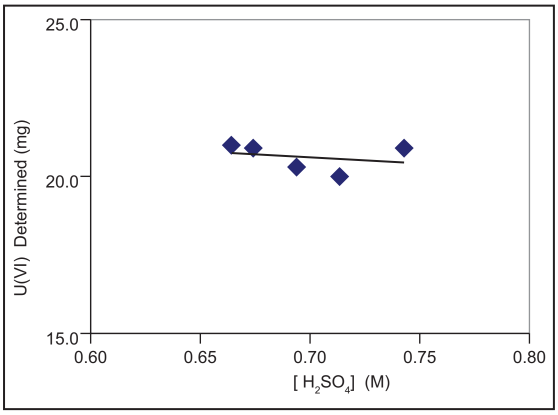

Figure 2: Effect of sulphuric acid concentration in titrating medium.

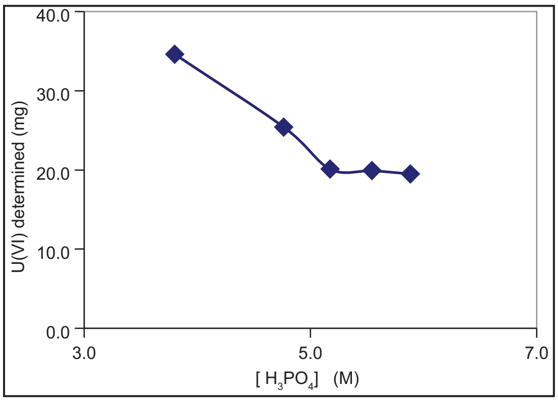

Figure 3: Effect of phosphoric acid concentration.

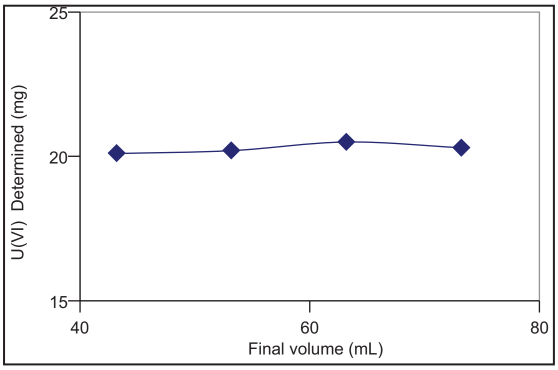

Figure 4: Effect of dilution.

acid treatment. Hydrazine can also be destroyed by sodium nitrite in order to avoid perchloric acid treatment [17]. Therefore, effect of sodium nitrite solution on total uranium determination was studied and the results of these studies are given in Table 1. It is observed that when 0.1 mL of 3 M sodium nitrite is added, total uranium concentration determined was found to be lower as compared to 0.2 mL or 0.3 mL of 3 M sodium nitrite. The reason for lower value of total uranium concentration with 0.1 mL of sodium nitrite is due to interference of undestroyed hydrazine. Whereas, addition of more than 0.1 mL of 3 M sodium nitrite, hydrazine is destroyed completely thereby eliminating the interference of hydrazine. Therefore, 0.3 mL of 3 M sodium nitrite was found to be optimum.

3.3. Effect of Sulphuric Acid on Total Uranium Determination

In the conventional method the final acidity of sulfuric acid for the total uranium determination is maintained around 1 M sulfuric acid. In order to reduce the concentration of sulfuric acid a detailed studies were carried and the results are presented in the Figure 2. It observed from the figure that the determined total uranium concentration was found to be same for all the sulfuric acid concentration range studied. Hence, a titrating solution acidity of 0.7 M in titrating medium was found to be optimum.

3.4. Effect of Ortho-phosphoric Acid Concentration on the Total Uranium Determination

The other parameter that can affect the determination of total uranium is the concentration of ortho-phosphoric acid in the titrating medium. Therefore, studies were carried out at a fixed dilution and the results are shown in the Figure 3. It can be seen from this figure that total uranium concentration determined in the sample is higher than the uranium taken for the analysis. This is because, the concentration of ortho-phosphoric acid before dilution was <5.2 M, which results in sluggish conversion of U(VI) to U(IV) ions or vice versa. On the other hand when ortho phosphoric acid concentration in the titrating medium is >5.2 M total uranium concentration determined is found to be same as taken in aliquot. Hence, during the analysis the concentration of ortho-phosphoric acid in the titrating the medium more than 5.2 M was optimum.

3.5. Effect of Dilution on the Total Uranium Determination

The effect of dilution on the determination of total uranium is studied, and the results are given in Figure 4. The result of this study indicates that the total uranium concentration determined is nearly constant for the final volume of 43-73 mL. Hence, 25 mL of water was found to be optimum for the analysis of total uranium concentration.

The parameters thus optimized are used for the simultaneous determination of uranous and the total uranium. Experiments were carried out by following the developed procedures, and the results are given in Table 2. The data given in the table shows that uranous and total uranium analyzed in a single aliquot is nearly comparable to conventional methods. The precision obtained is <1%.

The waste volume generated during analyses of uranous and total uranium by conventional method is 25-27 mL of 3 M sulfuric acids in the uranous determination and 87-90 mL of 0.7-1 M sulfuric acid in the total uranium estimation. Hence, a total volume

Table 1: Effect volume of sodium nitrite solution on determination of total uranium.

Volume of 3 M $NaNO_2$ (mL)	Amount of total uranium found (mg)
0.1	19
0.2	20.1
0.3	20.3

*Total [U] taken: 20.5 mg

Table 2: Comparative results of standard method and present method.

S. no	U (IV) (gpl)		U (VI) (gpl)	
	Ferroin method	This method	Davies-Gray	This method
1.	90.6	92.0	203.6	197.2
2.	90.4	91.4	203.8	197.8
3.	90.7	91.6	204.1	197.6
4.	90.5	91.9	203.3	197.5
5.	90.3	91.8	203.9	197.8
6.	90.7	91.5	203.5	197.5
Average	90.5 (0.7)*	91.7 (0.4)*	203.7 (0.5)*	197.6 (0.9)*

*Relative standard deviation values for both the analysis

of about 110-112 mL of 1-1.1 M sulfuric acid bearing waste is generated per sample analysis. The waste volume generated in the current method is around 44-47 mL of 1-1.1 M sulfuric acid per sample analysis. Hence by following the present method the waste volume is reduced by nearly 2.0-2.3 times with a same concentration of sulfuric acid.

4. CONCLUSIONS

Uranous and total uranium can be analyzed in a single aliquot, and the precision and accuracy of analyses is comparable with the conventional methods. In the new method, the total waste volume generated is about 45 mL as compared to a volume of around 120 mL of waste solution in the conventional method. Hence, this method can be followed for the samples obtained from the partition step and uranium reconversion process during reprocessing of fast reactor fuels.

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****Bibliographical Sketch***

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