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Minimum Analytical Waste Generation based Analytical Procedures for Studies on the In-situ Electrochemical Partitioning of the PUREX Process

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Abstract:*In-situ* electrochemical partitioning is a suitable option for the separation of uranium and plutonium from each other for high plutonium content fuels such as FBR fuels. Hence, experimental studies were carried out in a 20-stage electrolytic mixer-settler with uranium solution to evaluate the performance of electrodes and mixer settlers. In the present paper, minimum analytical waste generation based analytical procedures were developed for the determination of the of U(IV), U(VI), nitric acid, hydrazine. A spectrophotometer equipped with a fiber optic probe is used for monitoring of oxidation states and concentration of uranium in both organic and aqueous medium. Acidity and hydrazine concentrations were estimated simultaneously by pH metric method. During the *in-situ* electrochemical reduction of uranium in the stages of mixer-settler process samples are validated with proper time interval using the procedures as mentioned above. Several experimental runs were carried out with different flow sheet conditions. The obtained results are in good agreement with predicted values. A potentiometric method is used for the determination of higher concentrations of U(VI) and U(IV) in the aqueous and organicphases.

Keywords: In-situ electrochemical partitioning, PUREX process, Electrolytic mixer settler, Nitric acid, Uranium, Hydrazine, pH metry, Potentiometry, Spectrophotometry.

1 Introduction

In the reprocessing of the spent nuclear fuels, uranium and plutonium first separated from the bulk of the fission products. Plutonium is then separated from uranium, purified and further refined depending on the specific requirement of fuel-solvent extraction based method PUREX (Plutonium Uranium Extraction) process used for this purpose [1]. Partitioning of uranium and plutonium is a critical step in the reprocessing of spent nuclear fuel. In the partitioning step, the separation between uranium and plutonium is accomplished by selectively reducing the oxidation state of Pu(IV) to Pu(III), which has low distribution ratio [2]. As a result, it is in-extractable in the organic phase. Various partitioning methods were reported in the literature for the separation of uranium and plutonium using reducing agents. A mixture of sulphuric/nitric acid [3], acetohydroxamic acid [4], ferrous sulphamate [5], hydroxylamine nitrate [6-7], hydrazine stabilized uranium (IV) [8], and electrolytic partitioning [9] are employed for reducing step. Each method has its advantages and disadvantages. Sulphuric acid is highly corrosive, hence cannot be used in the plant. HAN/hydrazine required low acidity and plutonium may undergo polymerization. Ferrous sulphamate generates highly destructive solid waste, and 20 times the stoichiometric ratio of plutonium is needed. The application of uranous also requires 5–10 times the stoichiometric ratio of plutonium and hence increases the plant load. The *in-situ* electrochemical reduction is the most suitable options for high plutonium bearing fuels like FBR fuels. Generally, in the case of thermal reactor fuel reprocessing on the outside generated U(IV) is used as a reducing agent for plutonium reduction in the contemporary salt-free flowsheet. Usually, significant excess (6-10 times of technical requirement) of U(IV) is necessary for adequate separation between uranium and plutonium. In Pressured Heavy Water Reactor (PHWR) fuel plutonium content is about 0.3% whereas plutonium contentment in FBR fuel is between 21–28 %. Using U(IV) as a reducing agent in the case of Fast Breeder Reactor (FBR) fuel is not a feasible option because it will require

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recycling of a large amount of uranium and also lead to the size limitation of the equipment. The alternate option is to employ electrochemical *in-situ* reduction process in the partitioning step of the fast reactor reprocessing plant to achieve separation between uranium and plutonium [9]. *In-situ* reduction process has several advantages over other methods. The process is simple to operate, easy to control remotely, highly efficient and waste management cost is low as there is no external chemical addition for reduction purpose. In this present paper, modification of analytical methods based on the zero or minimizes the waste generation and remote analysis to avoid man-rem exposure is reported. Use this methodology for the estimation of experimental concentration profile like nitric acid, hydrazine, U(IV), U(VI) and DBP. For this, a 20 stage laboratory-scale electrolytic mixer-settler partitioning is carried out. Several experimental runs are carried out with different flowsheet conditions. The obtained results are compared with predicted values and found to be in good agreement..

2 Experimental

2.1 Reagents

All reagents are analytical grade. All chemicals (99%, S D Fine chemicals, Mumbai) are used. Double distilled water is used for all reagents preparation and titrations. Nitric acid (Ranbaxy Chemicals, AR grade) is used. The following reagent preparation methods are recommended.

1. *Sulphamic acid (1.5M)*:15 g of sulphamic acid was dissolved in 100 ml standard measuring flask with distilled water
2. *Treated Phosphoric acid (85%)*: 2.5 ml of 0.05N $K_2Cr_2O_7$ solution was added to 500 ml of phosphoric acid and shook well.
3. *Ferrous sulphate (1M)*: 28 g of $FeSO_4.7H_2O$ was weighed and transferred into a 100 ml volumetric flask, it was dissolved in 10 ml concentrated sulphuric acid and then diluted to mark with distilled water. Do not use the solution after one week.
4. *Nitric acid - 8M, sulphamic acid - 0.15M, ammonium molybdate - 0.4% (Acid Mixture)*: 0.4 g of ammonium molybdate was dissolved in 40 ml of warm water and then transferred to a mixture of 50 ml of concentrated nitric acid and 10 ml of 1.5M sulphamic acid. Do not use the solution after two weeks.
5. *Diluents*: Dissolved 100 mg of vanadylsulphate is dissolved in 100 ml of 1M sulphuric acid. Use the solution on the same day.
6. *Standard Potassium dichromate solutions*: Analar grade potassium dichromate obtained from BDH chemicals Ltd was used. Weighed three clean and dry 50 ml volumetric flasks with stoppers. Approximately 0.5 g of AR potassium dichromate was transferred from a pre-weighed weighing bottle into one of the flasks through a clean and dry funnel by carefully and gently topping the weighing bottle. Weigh the bottle again. Dissolved the dichromate by adding distilled water and made up to the mark. From this solution, prepared solution I (~ 0.04 m.eq/g) and solution II (~ 0.001m.eq/g) with suitable dilution.
7. *Sodium Carbonate (0.05M) solution:* Weighed quantity of AnalaR grade BDH sodium carbonate, was dissolved in distilled water in a standard measuring flask [10].
8. *Formaldehyde solution:* 37-40% W/V obtained from M/s Sarabhai M Chemicals Baroda, India
9. *Uranyl Nitrate solution*: Nuclear grade U_3O_8 was dissolved in 1:1 HNO_3,and uranium concentration was determined by potentiometric redox titration using modified Davies and Gray method [11-12].
10. *Uranous Nitrate solution*: U (VI) was electrolytically reduced to U (IV). 20 g/l uranyl nitrate solution in 1 - 1.5M HNO_3 containing 0.5M hydrazine was reduced at the fresh surface of Ti cathode (with a Pt as an anode) at a current density of ~ 15 mA/cm^2 to obtain ~ 70% conversion to U (IV). For the standardization of U (IV) stock solution, aliquots were taken in 9 ml of 9M H_2SO_4. 15 ml of water was added and titrated with standard $K_2Cr_2O_7$ using ferroin as an indicator [13].

2.2 Instrumentation

A constant temperature water bath MIC-66A (±0.10^{o}C) (Modern Scientific Instrument Company, Mumbai) used for the temperature-controlled studies. The microbalance supplied by Sartorius Model CP 225D, maximum capacity 160 g and ten microgram sensitivity, readability and precision for all weighing operations. DC power supply unit Model IEPS 3010 by ITEK Engineers is used for electrolytic destruction experiments. Indigenously made fiber optic aided spectrophotometer technique with one cm path length dip-type probe is used to measure the absorbance. All titration was performed on titration system model E526manufactured by Metrohm, Switzerland. pH adjustments were carried out using Chemlabs, digital pH-meter model Micro-07, Bangalore.

Electrochemical *in-situ* reduction process setup is shown in Fig.1. A prototype 20 stage electrolytic ejector mixer-settler unit made in polypropylene materials. The experimental uranium solution having a concentration of uranium about 67 g/L and free acid is 4M in the presence of hydrazine (0.25*M*) with Platinum mesh as anode and cathode made of Titanium. The flow rates of organic (30%TBP), aqueous (uranyl nitrate) and strip solution are maintained at 7mL/min, 7 mL/min and 4mL/min respectively and current density of about 5 mA/cm^2 is applied during the electrolysis.

2.3 Experimental Procedures

A semi-automatic potentiometric method is used for the determination of U(VI) in the aqueous [14] and organic phases. A spectrophotometer equipped with a fiber optic dip-type probe was used to determine U(IV), whereas acidity and hydrazine concentrations were estimated simultaneously by pH metric method [15-16].

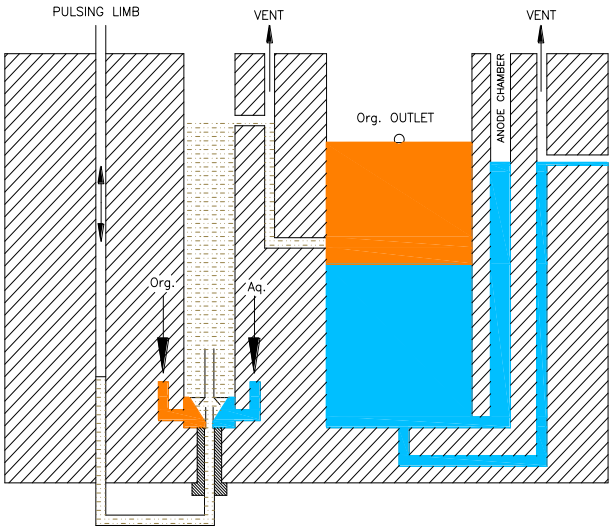

Fig.1: Schematic of one stage of mixer-settler bank.

2.3.1 Determination of Uranium (VI)

Determination of uranium by redox titration using modified Davies Gray method [12] needs strict kinetic control. Sequential addition of reagents, mixing of reagents and time during for each addition should be strictly followed to get better accuracy. Hence, though Davies Gray method is a very well-known technique, with the systematic procedure is mentioned here to carry out miniaturized titration to obtain accurate and precise results. The chemical conditioning involving the addition of reagents used in the present work is described below.

Accurately measured aliquot containing 2 to 20 mg of uranium was transferred into a 50 ml Berzelius beaker. To this 0.7 ml of 1.5M sulphamic acid was added followed by addition of 5.0 ml of treated phosphoric acid and the mixture was subjected to uniform stirring for one minute, to ensure no phase separation of the viscous phosphoric acid layer. 0.7 ml of ferrous sulphate solution was added. The solution was stirred well for 30 seconds. In the next step, 1.5 ml of nitric acid–sulphamic acid molybdate mixture were added and thoroughly mixed till the dark brown colour produced has disappeared. Allow the solution to stand for three minutes. Subsequently, 15 ml of the diluent was poured and continuously stirred by using magnetic stirred. Electrode assembly was then lowered into the solution and titrated immediately with standard dichromate solutions. A sharp jump in potential was obtained around 589-800 mV by using pre-weighed polythene weight burette and calculates the concentration of uranium in the aliquot.

2.3.1 Determination of U(IV)

U(IV) was generated by electrolytic method and samples were taken periodically with proper time interval. The concentration of U(IV) in samples was estimated by potentiometry using Metrohm auto titroprocesser-670. 9 mL of 9 M sulphuric acid in 15 mL of water was taken in a beaker. 0.1 mL of the aliquot and lowered the electrode in this solution. The titration was completed by titrating this solution against standard potassium dichromate and the end point was detected by potential variation. The titration was repeated at least five times to find the very precisely the consumption of standard dichromate solution.

2.3.2 Determination of U(IV), Free acidity and Hydrazine

Analytical techniques along with the experimental parameters for sequential determination of U(IV), free acidity and hydrazine from a single aliquot. In this technique involved the determination of U(IV) using fiber-optic UV-Vis spectrophotometry. The determination of free acidity by non-complexing medium and titration with sodium carbonate to pH 3.0, adding formaldehyde to liberate the acid equivalent to hydrazine and continuing titration with same sodium carbonate have been well documented by Ganesh et al. [15].

2.3.3 Determination of Traces Amount of Hydrazine by Spectrophotometry

Simple, accurate and easy spectrophotometric method is used for analysis of hydrazine in trace amount. Para-dimethylaminobenzaldehyde produces a specific yellow reaction product with hydrazine in dilute nitric acid [25]. The intensity of the yellow colour follows Beer's law over the range 0.045 – 0.125 µg/mL at 454 nm.

2.3.4 Stability of U(V)

The stability of Uranous nitrate solution in room temperature was carried out with different concentrations of U(IV), free acidity and hydrazine such as [U(IV)] = 67.1, 40, 18.12 and 4.1 g/L, free acidity [H^+] = 0.95, 0.39, 0.39 and 0.8 M, and [$N_2H_5^+$] = 0.87, 0.76, 0.76 and 0.7M. The concentration of U(IV), free acidity and hydrazine were analyzed periodically with a function of time. Increased stability is achieved with higher acid concentrations and with minimum exposure to air.

2.3.5 Direct Determination of DBP

To take the fixed concentration of uranyl nitrate solution into 10 mL volumetric flask and made up to mark with 3M nitric acid and measured the absorbance at three different wavelengths like 426, 414 and 404 nm

respectively. To add a suitable aliquot of DBP from the stock solution of in the range of 100-1000 ppm to the same 10 mL volumetric flask and again measured the absorbance changes of the solution using fiber optic aided spectrophotometry. Blank also was run with the 3M nitric acid solution.

3 Results and Discussion

The basic principle of determination of uranium by modified Davies Gray method involves, uranium(VI) is reduced to uranium(IV) in a strong phosphoric acid medium (≥10M) by the excess of Fe(II) in sulfamic acid medium. This excess Fe(II) is selectively oxidized by nitric acid in the presence of Mo(VI) and sulfamic acid. Then U(IV) is titrated with a standard solution of potassium dichromate solution after diluting the solution to 3*M* phosphoric acid concentration with 1*M*sulphuric acid containing a small amount of V(IV) to get sharp endpoint. In this method, it is essential to avoid any reoxidation of U(IV) before the titration. Thus, all the reactions times must be rigorously controlled. It is known that conditional potential of Fe(III)/Fe(II) couple is lower in phosphoric acid medium, but the potential for the U(VI)/U(IV) and V(IV)/V(III) couples are increased. This method is versatile in the sense that plutonium, if present, along with uranium, does not interfere.

An automatic titrating system has been employed to locate the equivalence points. Hence, human errors associated with the detection of the endpoint affect the precision of the technique. For the determination of uranium in a variety of samples, the method suggested by Davies and Gray [12] and modified by Eberle *et al.*[17] is widely used. This method is essentially based on the following chemical reactions.

U(VI) is reduced to U(IV) by Fe (II) ion is not possible in H_2SO_4, HNO_3 or HCl medium, whereas in H_3PO_4 medium of 10.5M concentration,

$$UO_2^{2+} + 2Fe^{2+} + 4H^+ \xrightarrow{NH_2SO_3H} U^{4+} + 2Fe^{3+} + 2H_2O$$

Excess Fe(II) is selectively oxidized by nitric acid (HNO_3) in the presence of molybdenum (VI) catalyst, without oxidizing tetravalent uranium ions.

$$Fe^{2+} + HNO_3 \xrightarrow{\text{Mo (VI) Catalyst}/NH_2SO_3H} Fe^{3+} + NO_X + N_2\uparrow$$
$$3Fe^{2+} + NO_3^- + 4H^+ \xrightarrow{Mo(VI)} 3Fe^{3+} + NO + 2H_2O$$
$$Fe^{2+} + NO_3^- + 2H^+ \xrightarrow{Mo(VI)} Fe^{3+} + NO_2^- + H_2O$$
$$Fe^{2+} + Mo^{6+} \rightarrow Mo^{5+} + Fe^{3+}$$
$$2Mo^{5+} + NO_3^- + 2H^+ \rightarrow 2Mo^{6+} + NO_2^- + H_2O$$

The nitrogen oxides (NO, NO_2) formed during reduction of Fe (II) is neutralized by sulfamic acid. This is necessary since they are reducing agents, and thus, they are reducing agents, and therefore they interfere with the analysis.

$$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O \qquad E^o = +0.94v$$
$$HNO_2 + H^+ + e^- \rightarrow NO + H_2O \qquad E^o = +0.98v$$
$$NO + NO_3^- + 2H^+ + e^- \rightarrow 2HNO_2 \qquad E^o = +0.517v$$
$$HNO_3 + 2NO + H_2O \rightarrow 3HNO_2$$
$$HNO_2 + NH_2SO_3H \rightarrow H_2SO_4 + N_2\uparrow + H_2O$$

In a diluted phosphoric acid solution, the following reactions take place. Therefore, the phosphoric acid solution must be highly concentrated.

$$U^{4+} + 2Fe^{3+} + 2H_2O \rightarrow UO_2^{2+} + 2Fe^{2+} + 4H^+$$
$$Fe^{2+} + VO^{2+} + 2H^+ \rightarrow V^{3+} + Fe^{3+} + H_2O$$

The role of vanadyl ion in sharpening the endpoint appears to be due either to the simultaneous consumption of both Fe(II) and V(III) species, thus accelerating the rate of main reaction and causing a quick rise in the conditional potential or to the dominance of electrode response by the V(IV)/V(III) couple [18-19]. Systematic errors can arise if part of the VO^{2+} is oxidized by air to V^{5+}. To prevent this, the vanadyl solution should be prepared in an acid medium and frequently checked for V^{5+}. The use of sulphamic acid to remove nitrous acid is a well-established analytical procedure. In the case where the addition of the reagent is essential to prevent nitrite catalyzing nitric acid oxidation of Fe^{2+} and U^{4+}

$$HNO_2 + NH_2SO_3H \rightarrow H_2SO_4 + N_2\uparrow + H_2O$$

After the addition of a vanadium (IV) solution, uranium (IV) reacts with it leading to vanadium (III).

$$U^{4+} + 2VO^{2+} \rightarrow UO_2^{2+} + 2V^{3+}$$

Vanadium (III) is titrated with chromium (VI) since the direct titration of U(IV) is very slow.

$$Cr_2O_7^{2-} + 6V^{3+} + 2H^+ \rightarrow 2Cr^{3+} + 6VO^{2+} + H_2O$$

This reaction is equivalent to

$$Cr_2O_7^{2-} + 3U^{4+} + 2H^+ \rightarrow 2Cr^{3+} + 3UO_2^{2+} + H_2O$$

Therefore, 1 mole $Cr_2O_7^{2-}$ corresponds to 3 moles $U^{4+}$and z = 3 for potassium dichromate. The results obtained by this procedure are reasonably accurate and precise but are accompanied by two difficulties. First, the manual addition and location of equivalence point make it a slow process, and again the location of equivalence point is a matter of personal judgment of analyst. To overcome these difficulties a microprocessor-based automatic titrating system was brought into the operation and a procedure has been developed for the rapid and accurate determination of uranium. Results obtained by above mentioned method has been presented in this communication.

Determination of U(IV)

The effect of sulphuric acid on the uranous concentration was estimated by varying concentration of sulphuric acid. The results are shown in fig.2.From this, above 9M sulphuric acid concentration, constant potential obtained

during the end point by potentiometry.

Stability of U(IV)

U(IV) is very unstable due to HNO_2, which is always present in the extraction system and oxidize both U(IV) and Pu(III). To avoid the oxidation of Pu(III) and U(IV) in nitrate solution, it is essential to eliminate nitrous acid. Hydrazine is most commonly used as stabilizer along with U(IV).Hydrazine reacts with nitrous acid faster than Pu(III) and very effective for the destruction of HNO_2 when compared with sulphamic acid, urea and formaldehyde are well documented[2].In absence of stabilizer, the oxidation of U(IV) by HNO_2 is autocatalytic reaction. This reaction is forms faster as the concentration of HNO_2 increase. Slade 1961 [20] reported that the oxidation of U(IV) by oxygen and nitrous acid in both organic and aqueous phases. In nitrate solutions, U(IV) is unstable toward HNO_2oxidation by HNO_3.

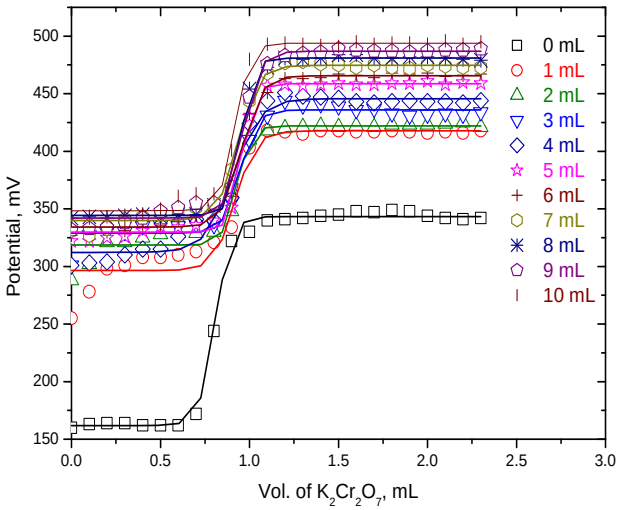

Fig.2: Effect of sulphuric acid in U(IV) estimation. Conditions: [U(IV)]= 19.07 g/L, $[H^+]$ = 0.99M, $[N_2H_4]$ =0.87 M

The reactions are.

$U^{4+} + 2HNO_2 \rightarrow UO_2^{2+} + 2NO + 2H^+$ (fast)
$U^{4+} + NO_3^- + H_2O \rightarrow UO_2^{2+} + HNO_2 + H^+$ (slow)
$2NO + HNO_3 + H_2O \rightarrow 3HNO_2$ (at low acidity)

The net reaction for oxidation is important as a means of producing NO_2. Once sufficient HNO_2 is produced, U(IV) is oxidized via following equations. Oxidation of U(IV) in nitric acid can be decreased to a very low rate by adding hydrazine as stabilizing agent. The U(IV) oxidation was about 0.5% per day when the solution contained 0.5-1M nitric acid and 0.2M hydrazine. The decrease in hydrazine concentration was about 0.5M per month. So longer time storage of U(IV) nitrate solution required periodic addition of hydrazine to stabilizer. Better U(IV) solution stored in amber bottle to avoid the photochemical oxidation. The stability of U(IV) is necessary required. Electrochemical reduction of uranyl nitrate solutions in different

concentration of metal ion, nitric acid and hydrazine in laboratory scale prepared and find the stability of U(IV) in nitric acid was carried out. The composition of uranyl stock solution was prepared based on the process and plant conditions. The concentration of U(IV), acidity and hydrazine were analyzed periodically and the concentration profile of U(IV) determined as a function of time is shown in figure. 3. The stability of U(IV) in nitric acid solution increases with increasing acidity. This is due to the suppression of reaction is represented follows.

$NO + 2HNO_3 \rightarrow 3NO_2 + H_2O$ (at acidity above 3.5M)

The concentration of U(IV) is more stable in higher nitric acid concentration. If less than 0.5M nitric acid, U(IV) is more rapidly oxidized to U(IV) in 0.8M hydrazine stable due to an oxygen-spared solution with only diffusion to transfer oxygen through solution.

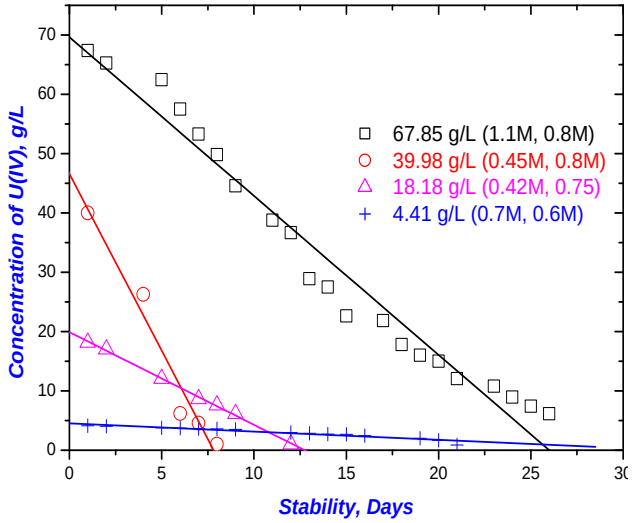

Fig.3: Stability of U(IV) in nitric acid medium in open conditions with different concentration of U(IV), acidity and hydrazine

□ [U(IV)]=67.85 g/L, $[H^+]$ =1.1M, $[N_2H_4]$ = 0.87M
○ [U(IV)]=40.0 g/L, $[H^+]$ =0.45M, $[N_2H_4]$ = 0.76M
Δ [U(IV)]=18.2 g/L, $[H^+]$ =0.42M, $[N_2H_4]$ = 0.76M
\+ [U(IV)]=4.41 g/L, $[H^+]$ =0.7M, $[N_2H_4]$ = 0.68M

Direct determination of DBP

The complex formation of uranium with DBP has been thoroughly studied and hence, no significant changes were done to adapt the experimental conditions for the determination of DBP. The absorbance was plotted against the concentration of DBP in Fig. 4, which describe the typical calibration graph for standard uranium solutions at different wavelengths in 3M nitric acid medium. The system obeyed Lambert-Beer's law at three different wavelengths in the concentration range of 100-1000 µg/mL of DBP. Fig. 5 shows that typical absorption spectrum of

different DBP concentration with correlation coefficient of 0.999 and RSD 2% at different wavelengths with uranium. All the measurements were carried out in triplicate. The data comparison between present technique and conventional spectrophotometric method has provided along with precision and accuracy in table 1. These values were within the error band of ±2%. The obtained results are found to be a good agreement. This method is suitable for process control samples within the error limit.

Table 1: Comparison of estimated values of DBP by present and standard spectrophotometry.

S. No	Determination of DBP (ppm)	
	Spectrophotometry	Present method
1	468.7±1.04	469.2±0.96
2	171.5±0.89	170.7±0.31
3	622.9±1.16	624.2±0.91
4	513.1±1.04	512.2±0.77

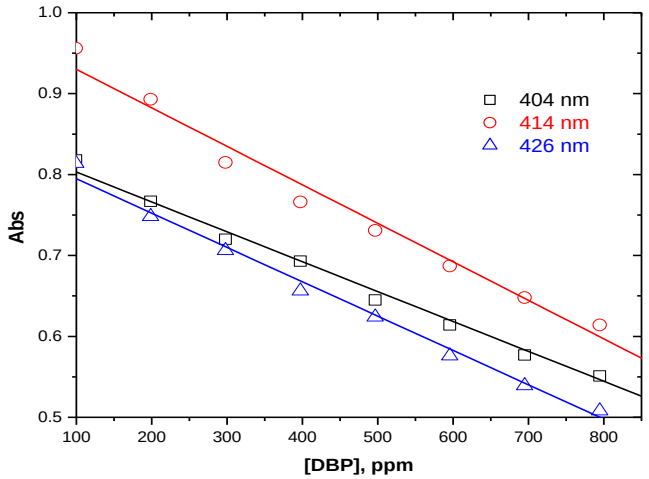

Fig.4: Typical calibration graph for U-DBP complex in 3M nitric acid medium at 404, 414 and 426 nm.

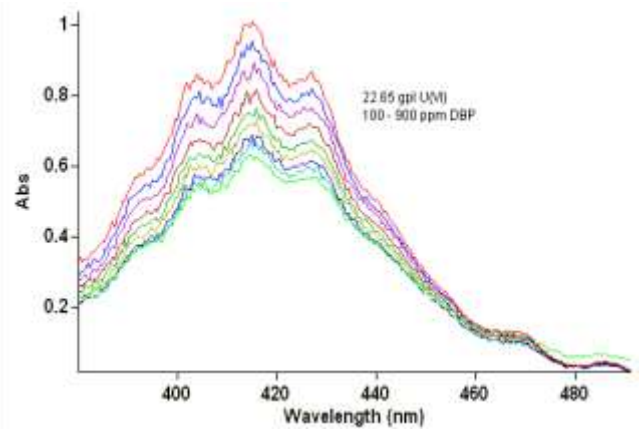

Fig.5: Typical absorption spectrum of U-DBP complex at 3M nitric acid medium.

Determination of hydrazine

The direct, simple and sensitive spectrophotometric method for analysis of hydrazine with para-dimethyl-aminobenzaldehyde. The yellow colour complex follows Beer's law over the range 0.045 – 0.125 µg/mL at 454 nm. Using this method to estimate the trace amount of hydrazine in samples [25].

Experimental flow sheet conditions are described in Fig.6. Each stage of experimental, samples is generated during the electrochemical generation of U(IV) for in-situ partitioning studies. Typical results obtained by using this proposed methodology and instrumentation for the determination of U(VI), U (IV), free acidity and hydrazine in samples mentioned above experimental studies are reported in Fig. 7. The typical absorption spectrum of sequential determination of U(VI) and U(IV) in some stage profile samples are represented in Fig.8.This confirms the ease of operation and utility of the developed procedure.

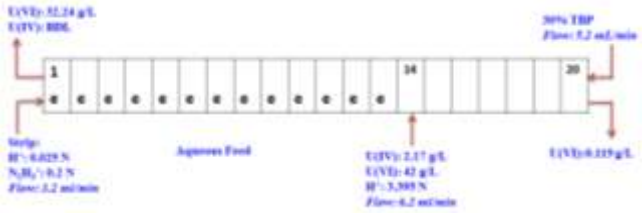

Fig.6: Experimental flow sheet conditions.

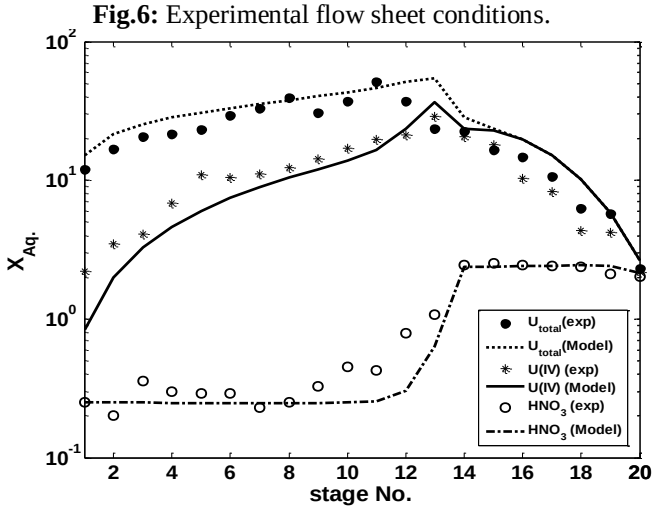

Fig..7: Stage profile of total Uranium, U(IV) and free acid.

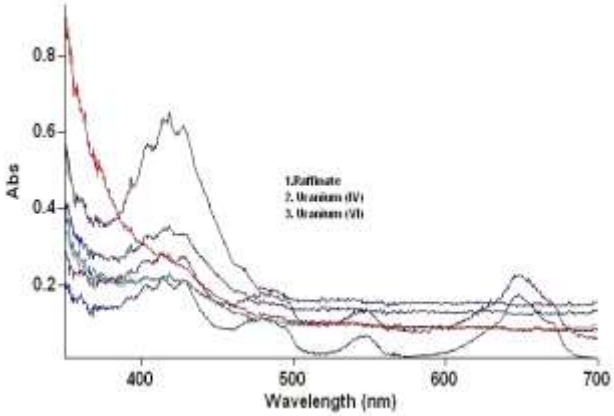

Fig.8: Typical absorption spectrums of some stage profile of raffinate, U(VI) and U(IV) samples.

3 Conclusion

In situ electrochemical reduction of uranium and plutonium was carried out using mixer settler. This technique gives a satisfactory partitioning of uranium and plutonium and no external chemical addition for reduction purpose. A new computer simulation code PUSEP (Plutonium Uranium Solvent Extraction Programme) has been developed and has been used to calculated concentration profiles in partitioning co decontamination contactors of PUREX process involving in-situ electrochemical reduction of uranium and plutonium. The model equation development includes countercurrent multi mixer settler contactors, and it is restricted to mass transfer equilibrium. At presents, the solutes /components consider in the model equation are U(VI), U(IV), Pu(IV), Pu(III) nitric acid and hydrazine. Computer code provides transient behaviour of mixer settler contractor from some initial condition to steady-state condition calculated profiles of Uranium [total uranium i.e. U(IV)+(VI),U(IV) and acid are in reasonably good agreement with the published experimental results. The deviations observed in the plutonium profile in the low concentration zone may probably are uncertainty in the estimation of distribution coefficient in the low concentration region. The comparison between the experimental results and the model and algorithm results demonstrated that the model and algorithm presented here might be a useful tool for design, optimization and evolution problem in a solvent extraction system. Further studies are in progress to incorporate auto-oxidation of Pu(III) byHNO_2 in portioning contractors. This process is simple to operate, accessible to remote and waste management cost is low. The developed method for sequential determination of U(IV), free acid and hydrazine in the presence of hydrolysable metal ions is simple, sensitive and applicable to all ranges of nitric acid and heavy metal ion concentration relevant to PUREX process used for nuclear fuel reprocessing. The result obtained by the developed procedure for U (IV), free acid and hydrazine in samples were compared with those obtained from redox titrimetry [24], oxalate and sulphate methods [20-21]. The results are found to be in good agreement. The overall recovery of nitric acid is 98% with 3% relative standard deviation. The method described here for the determination of U (IV), free nitric acid and hydrazine concentrations in processing/reprocessing solutions of nuclear fuels does not generate corrosive analytical waste, provides accurate and precise results and saves man-rem exposure.

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