

Determination of Lanthanides, Thorium, Uranium and Plutonium in Irradiated (Th, Pu)O₂ by Liquid Chromatography Using α -Hydroxyisobutyric Acid (α -HIBA)

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ABSTRACT

An HPLC method is presented for the separation and determination of lanthanides (Lns), thorium (Th), uranium (U) and plutonium (Pu) from irradiated (Th, Pu)O₂. Individual separation of Lns, Th, U and Pu is a challenging task because of 1) lanthanides having similar physical and chemical properties, 2) presence of complex matrix like irradiated fuel and 3) the co-existence of multiple oxidation states of Pu. Different procedures were developed for separation of individual lanthanides and actinides. The individual lanthanides were separated on a dynamically modified reversed phase (RP) column using n-octane sulfonic acid as an ion interaction reagent and employing dual gradient (pH and concentration) of α -hydroxyisobutyric acid (HIBA). In order to improve the precision on the determination of Lns, terbium (Tb) was used as an internal standard. The method was validated employing simulated high level liquid waste. Concentrations of lanthanides viz. lanthanum (La) and neodymium (Nd) in the dissolver solution were determined based on their peak areas. Th, U and Pu were separated on a RP column using mobile phase containing HIBA and methanol. Since Pu is prone to exist in multiple oxidation states, all the oxidation states were converted into Pu (IV) using H₂O₂ in 3 M HNO₃. Under the optimized conditions, Pu(IV) eluted first followed by Th and U. The concentrations of Th, U and Pu were determined by standard addition method and were found to be 1.10 ± 0.02 mg/g, 5.3 ± 0.3 μ g/g and 27 ± 1 μ g/g, respectively, in the dissolver solution of irradiated fuel. These values were in good agreement with the concentration of Th determined by biamprometry and those of U and Pu by isotope dilution thermal ionization mass spectrometry.

Keywords: HPLC; Lanthanides; Th; U; Pu; α -HIBA; Irradiated (Th, Pu)O₂

1. Introduction

The Indian nuclear program envisages the effective utilization of thorium (Th) as a fertile material for the sustained production of electricity in the country [1]. Unlike the natural uranium (U) based fuel which contains ²³⁵U as the fissile material, thorium based fuel initially requires the addition of fissile materials like ²³³U, ²³⁵U and ²³⁹Pu from outside. Mixture of (Th, ²³³U) O₂ and (Th, ²³⁹Pu) O₂ was proposed as fuel for advanced heavy water reactor (AHWR) to make system self-sustaining in ²³³U [2,3]. In order to assess the performance of (Th, Pu) O₂ MOX fuel, prior to its introduction in commercial reactors, (Th, 4%

Pu)O₂ fuel clusters were irradiated in the Pressurized Water Loop (PWL) of CIRUS reactor, BARC. The implementation of mixed oxide based fuel cycle requires development of methodologies for evaluating the performance of the fuel in the reactor. Burn-up is an important parameter for nuclear fuel development, fuel management and fuel performance analysis [4,5]. Burn-up is defined as the atom percent fission of heavy element (mass ≥ 225) during its life time in the reactor. Radiochemical and chemical analysis methods are generally used for burn-up determination of irradiated nuclear fuels [6]. The destructive method involved dissolution of fuels followed by individual separation and determination of

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fission products and heavy elements. Isotope dilution-thermal ionization mass spectrometry (ID-TIMS) is an established method for the determination of burn-up [5,7,8].

Development of new methodologies for the separation and determination of Lns, Th, U and Pu is essential for burn-up determination of thorium based nuclear fuel [9]. Different methods based on solvent extraction, ion exchange, precipitation, liquid chromatography, etc. have been reported for the separation of Lns, Th, U and Pu in various matrices [10,11]. Among these methods, high performance liquid chromatography (HPLC) is a fast and highly efficient technique and has been applied for the separation of lanthanides and actinides in nuclear fuel samples and geological samples [12-16]. Due to the fast separation and less amount of the sample handling in HPLC, it minimizes the exposure to highly radioactive samples and is, therefore, attractive for the separation of fission products. Cassidy *et al.* studied the separation of lanthanides fission products using a dynamic ion exchange column from different fuel samples like UO_2 and $(\text{Th}, \text{U})\text{O}_2$ fuels [17,18]. However, in presence of bulk of actinides, the individual separation of lanthanides was not reported. Lanthanides were separated in a group by conventional ion exchange method and subsequently injected into HPLC after removal of Th and U. This off-line separation requires multiple monitoring elements and there are chances of loss of analytes. The reported method gave good reproducibility among different runs for the same aliquot but results were inconsistent for different aliquots of same fuel. Sivaraman *et al.* carried out extensive studies on the separation of lanthanide fission products for fast breeder test reactor fuels [19-21]. They determined the stability constant of actinide-HIBA complexes under different chromatographic conditions. However, $(\text{Th}, \text{Pu})\text{O}_2$ is a unique fuel tested for AHWR reactor and liquid chromatographic method for separation of Lns from this matrix is not reported in literature. Various RP based methods have been reported for the separation of Th, U and Pu using hydroxyl carboxylic acid like HIBA and mandelic acid [22-24]. In most of the reported method, the lanthanides, U and Th are present in comparable amounts. Studies were carried out previously in our laboratory using ion interaction reagent (IIR) on the reversed phase (RP) column for the separation of lanthanides from Th and U [25]. Under the optimized chromatographic conditions using dual gradient of pH and concentration of mobile phase, lanthanides were separated out from bulk of Th and U from simulated irradiated thorium sample. However, the separation and determination of Lns, Th, U and Pu from irradiated $(\text{Th}, \text{Pu})\text{O}_2$ fuel employing HPLC have not been reported so far.

Present paper deals with the individual separation of Lns, Th, U and Pu in an irradiated $(\text{Th}, \text{Pu})\text{O}_2$ fuel. Handling of $(\text{Th}, \text{Pu})\text{O}_2$ fuel samples is more challenging

because of the radiation dose associated with the dissolver solution, presence of large amount of Th which is vulnerable to hydrolysis and multiple oxidation states of Pu under the chromatographic conditions [26]. Since the chromatographic behavior of lanthanides is different than tetravalent and hexavalent actinides, two different separation procedures are developed. The challenges of the present studies are: 1) individual separation of lanthanide fission products in presence bulk of Th and interference of trivalent actinides in Lns separation, 2) difficulties in the quantification of Pu because of its multiple oxidation states, and 3) individual separation of Th(IV), Pu(IV) and U(VI).

2. Experimental

2.1. Instrumentation

The HPLC system consisted of an L-2130 (Elite LaChrom, Hitachi) low-pressure quaternary gradient pump and an L-2450 (Elite LaChrom) diode array detector. C_{18} monolith RP column (100 mm \times 4.6 mm, Chromolith, Merck) and C_{18} particulate RP column (150 mm \times 4.6 mm, 5 μm , Supelcosil) were used as the stationary phases. Solutions were injected into the column using a Rheodyne injector (Model 9725i) with a 100 μL loop. The eluted species were monitored after post-column reaction with a metallochromic reagent, which was added using a reciprocating pump (Eldex Laboratories Inc.) into a low dead volume-mixing tee (Valco). The signal from the detector was processed by EZChrom software package.

2.2. Reagents

All solutions were prepared using deionised water from Milli-Q system (Millipore) and were filtered through a 0.45 μm membrane filter (Millipore) prior to using. α -HIBA (Lancaster) was used as an eluent. Sodium n-octane sulphonate monohydrate (Fluka) and tetrabutylammonium iodide (Sigma-Aldrich) were used as the ion interaction reagents (IIR). ICP-standards of the lanthanides, U and Th (Inorganic Venture) were used after appropriate dilutions with Milli-Q water and mobile phase. HNO_3 and NH_4OH (Merck) were used for adjusting the pH of the mobile phase. H_2O_2 (Merck) in combination with HNO_3 was used as a redox reagent to bring Pu into the IV oxidation state. For ion exchange separation, Dowex 1 \times 8, 200 - 400 mesh size (Sigma-Aldrich) and Bio-Rad AG 1 \times 2, 200 - 400 mesh size (Bio-Rad) were used as stationary phases. Arsenazo (III) (Fluka) was used as the post-column metallochromic reagent (PCR). The arsenazo complexes of Lns, Th, U and Pu were monitored at 653 nm. Irradiated $(\text{Th}, \text{Pu})\text{O}_2$ sample received from Post-Irradiated Examination Division (PIED), BARC was used for the method development. NIST-

SRM-950a U_3O_8 , $K_4Pu(SO_4)_4$ and enriched isotope of ^{142}Nd were used as spikes for ID-TIMS analysis of U, Pu and Nd, respectively.

2.3. Procedure

Appropriate quantities of α -HIBA and sodium n-octane sulfonate were dissolved in water and made to solutions with concentrations 0.5 M and 0.1 M, respectively. α -HIBA was adjusted to the desired pH using high-purity NH_4OH and HNO_3 . Mobile phase flow-rate of 1.0 mL min^{-1} was used. The PCR solution [1.5×10^{-4} M Arsenazo (III) and 0.01 M urea in 0.1 M HNO_3] was delivered at a flow rate of 0.3 mL min^{-1} . The lanthanides, Th, U and Pu solution of appropriate concentrations were prepared after dilution with mobile phase. Concentration of Pu was determined by biamperometry titration [27]. Dissolution of irradiated fuel sample was carried out in a facility housed in a shielded glove box. Aliquots from the irradiated fuel dissolver solution were transferred to a shielded fume-hood for further experiments.

For the determination of Lns, about 0.5 g of dissolved sample solution was taken and 2.5 ppm of Tb was added as an internal standard. This solution was directly injected into HPLC through 100 μ L injection port. The mobile phase containing α -HIBA of pH 6.5 was changed from 0.05 M to 0.15 M in 30 min; whereas α -HIBA of pH 3.5 was changed from 0.15 M to 0.3 M in a time interval of 30 to 40 min. A C_{18} RP column (250 mm \times 4.6 mm) was used for the individual separation of Lns. For validation of method using ID-TIMS, all the aliquots were subjected to necessary chemical treatments to ensure depolymerisation and proper isotopic homogenization. The spiked and unspiked aliquots were used for separation by anion exchange using Dowex 1 \times 8, 200 - 400 mesh resin in 9 M HCl medium [8]. The effluent containing Th and fission product fraction was collected. Pu and U fractions were sequentially eluted from the column using 0.1 M hydroxylamine hydrochloride in 5M HCl and 0.5 M HNO_3 , respectively. The fraction containing Th and fission products was subjected to a second stage anion-exchange separation using Dowex 1 \times 8200 - 400 mesh resin in 7 M HNO_3 medium. The non-retained fission product fraction was collected and subjected to a third stage separation using Bio-Rad AG 1 \times 2200 - 400 in a mixture containing HNO_3 and MeOH to separate Nd fraction [8].

3. Results and Discussion

3.1. Separation and Determination of Lns from Irradiated (Th, Pu) O_2

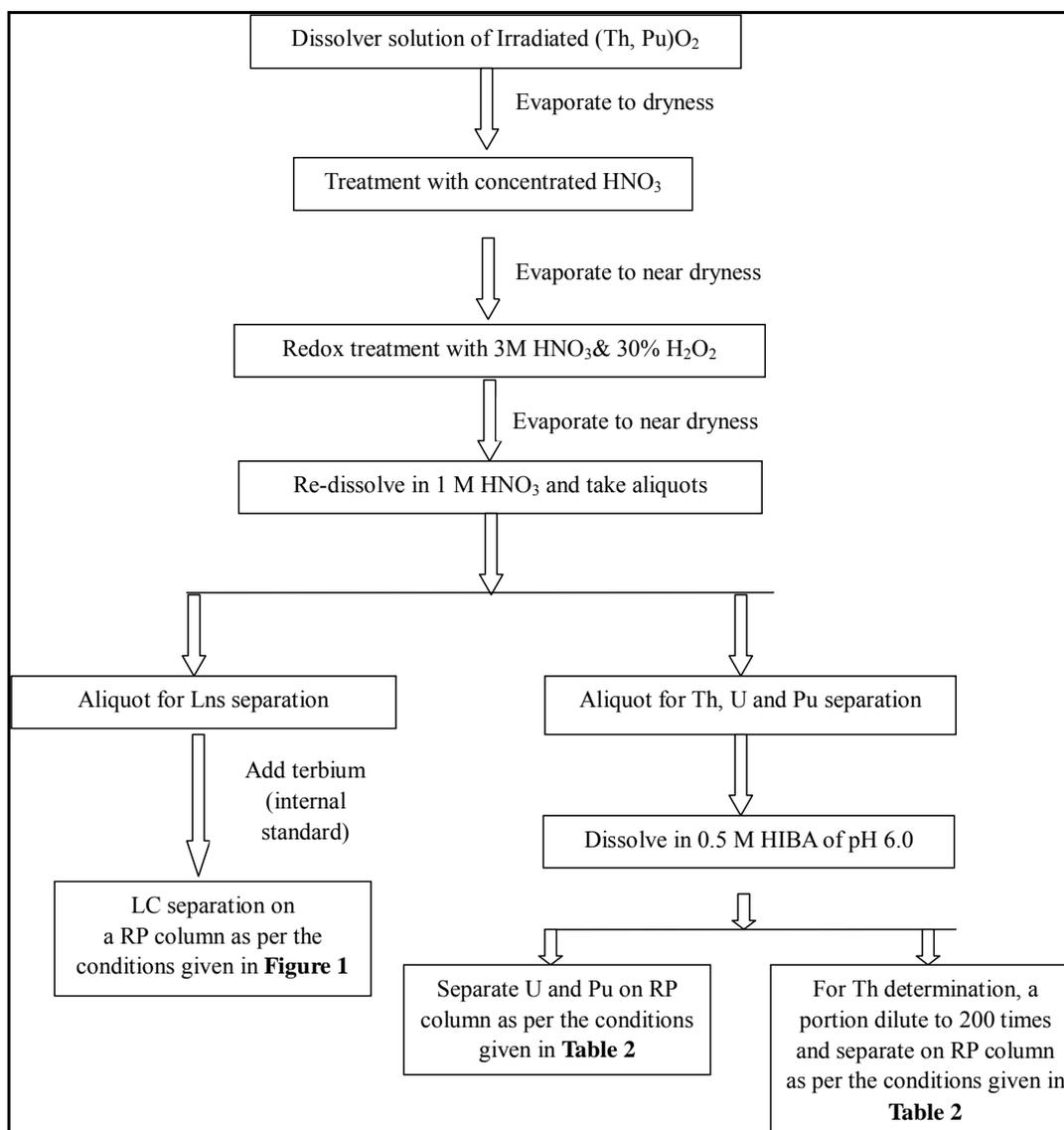
3.1.1. Chromatographic Behavior of Lanthanides, Th, U and Pu

In solution, under the chromatographic conditions, lan-

thanides exist in III oxidation state whereas Th and U exist in IV and VI states, respectively. The situation in the cases of Pu is different. In view of the closeness of redox potential values, Pu can exist in different oxidation state viz. III, IV and VI simultaneously. Retention behaviors of Lns and Pu(III) is different from Th(IV), U (VI), Pu(VI) and Pu(IV) when α -HIBA was used as an eluent on RP column [21]. With α -HIBA, Lns and Pu(III) form mainly cationic complexes which are different from those formed by Th, U, Pu(VI) and Pu(IV) [25]. Thus Lns-HIBA complexes can be separated on dynamically modified RP column using an IIR which is sorbed onto the column converting hydrophobic surface into the charged surface, for ion exchange separation of lanthanides [28]. However, Th, U and Pu(IV) get sorbed onto the RP column by hydrophobic interaction, when α -HIBA is used as a complexing reagent. In presence of large amounts of IIR, the actinides were found to elute in between the lanthanides which makes lanthanides determination difficult. Hence, at a given concentration of IIR, the surface of RP column remains partly ionic and hydrophobic in nature. The separation of lanthanides from Th, U and Pu was performed using dual gradient (pH and Concentration) of α -HIBA. At higher pH, tetravalent and hexavalent actinides are retained better than lanthanides on dynamically modified reversed phase column leading to the elution and separation of lanthanides prior to actinides. Due to the complex nature of irradiated (Th, Pu) O_2 fuel matrix, two different separation procedures were developed as presented in **Scheme 1**. In the first stage, Lns were separated and determined on dynamically modified column whereas the separation and determination of Th, U and Pu was achieved using RP column.

3.1.2. Determination of Lanthanides in Irradiated (Th, Pu) O_2 Sample by HPLC

A C_{18} reversed-phase column, dynamically modified with n-octane sulphonate, was used as the stationary phase for separation of lanthanides from irradiated (Th, Pu) O_2 fuel. It was reported that with increase in the concentration of IIR, the retention of Lns increases whereas the retention of Th and U decreases [28]. Th being the matrix element in the present case, the concentration of IIR selected was 5 mM to separate Lns without affecting the Th holding capacity. Effect of pH showed that at lower pH, higher fraction of HIBA remains in the unionized form, resulting in faster elution of U and Th whereas, at $pH \geq 5.0$, Th and U showed stronger retention than lanthanides and eluted after Lns. With the increase in concentration of HIBA at pH 4.0, Lns, Th and U showed decrease in retention. Dual gradient (pH and concentration) of HIBA was used for the separation of Lns, Th, U and Pu. Pu was found to elute as multiple peaks in chromatographic run due to the presence of its



Scheme 1. Flow chart for liquid chromatographic separation of Lns, Th, U and Pu from irradiated (Th, Pu) O_2 fuel.

multiple oxidation states. Hence, dissolver solution was evaporated to near dryness and treated with H_2O_2 in 3M HNO_3 to convert all the Pu into (IV), and Pu was re-dissolved in 0.1 M HNO_3 to maintain in single oxidation state. Lns were separated by using the gradient condition. Initially, HIBA of pH 6.5 was used for the separation of lanthanides followed by elution of actinides with HIBA of pH 3.0. Under these chromatographic conditions, Pu(IV) elutes along with Th and U and hence does not cause any interference to the lanthanide peaks. Henceforth Th, U and Pu are in the oxidation states, Th(IV), UO_2^{2+} and Pu(IV), respectively. The response of the Lns with post-column reagent was found to vary with the mobile phase concentration and pH. Therefore, terbium was used as an internal standard. The advantages of internal standard approach are: 1) calibration plot for a wide

concentration range is not required. Single injection of the sample is sufficient, and 2) matrix effects do not influence the results since the standard is introduced into the sample. Relative response factors (RRF) for the individual Lns pairs were calculated using the simulated samples. For a pair of Tb and La, the RRF can be calculated as

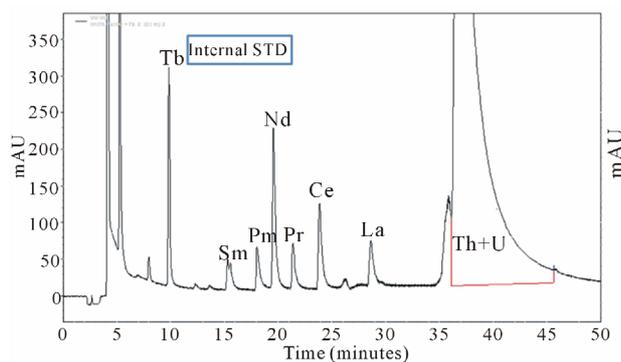
$$RRF = C_{Tb} / C_{La} * A_{La} / A_{Tb}$$

where, C and A represent concentration and absorbance (peak area) of the lanthanides, respectively.

The RRFs of the different pair of La/Tb, Pr/Tb, Nd/Tb and Sm/Tb were found to be constant and are presented in **Table 1**. Validation of lanthanides determination was carried out by employing a simulated high level liquid waste solution. Concentrations of lanthanide fission

Table 1. Relative response factors (RRF) for the lanthanides pairs.

Lanthanide pair	RRF
La/Tb	0.94
Ce/Tb	1.03
Pr/Tb	0.77
Nd/Tb	0.92
Sm/Tb	0.89

**Figure 1. Direct injection of dissolver solution of irradiated (Th, Pu)O₂ fuel. Conditions: α -HIBA of pH 6.5 changed from 0.05 M to 0.15 M in 30 min; α -HIBA of pH 3.5 changed 0.15 M to 0.3 M from 30 min to 40 min; Column: C₁₈ RP (250 mm \times 4.6 mm).**

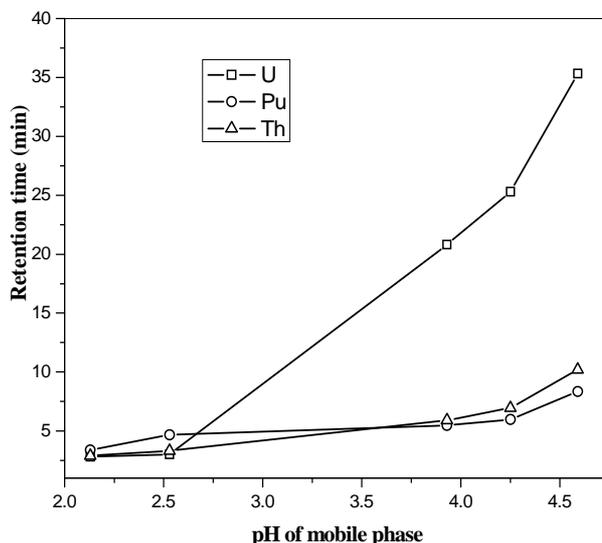
products (La, Ce, Pr, Nd and Sm) were determined based on their peak area employing terbium as an internal standard. **Figure 1** shows the chromatogram of the separated lanthanides from the irradiated sample. Concentrations of La, Pr, Nd and Sm in the dissolver solution of irradiated (Th,Pu)O₂ sample were determined based on the internal standard approach and were found to be $0.6 \pm 0.05 \mu\text{g/g}$; $0.4 \pm 0.01 \mu\text{g/g}$; $1.8 \pm 0.1 \mu\text{g/g}$ and $0.5 \pm 0.02 \mu\text{g/g}$, respectively.

3.2. Optimization of Chromatographic Conditions for the Separation of Th, U and Pu

U forms $[\text{UO}_2(\text{IBA})]^+$, $[\text{UO}_2(\text{IBA})_2]$ and $[\text{UO}_2(\text{IBA})_3]^-$ whereas Th and Pu form $[\text{M}(\text{IBA})]^{3+}$, $[\text{M}(\text{IBA})_2]^{2+}$, $[\text{M}(\text{IBA})_3]^+$ and $[\text{M}(\text{IBA})_4]$ (M = Th or Pu) types of complexes with HIBA [21,29]. Dominance of one species over the other depends upon the pH and concentration of HIBA which is responsible for the relative difference in the retention times of Th, U and Pu. Hence the effects of chromatographic conditions such as pH of the mobile phase, concentration of HIBA on the retention of Th, U and Pu was studied.

3.2.1. pH of Mobile Phase

Figure 2 shows the effect of pH of the mobile phase on the retention behavior of Th, U and Pu. At $\text{pH} \leq 2.5$, Pu

**Figure 2. Effect of pH of the mobile phase on the retention of Th, U and Pu. Chromatographic conditions: 0.1 M of HIBA and Column: C₁₈ RP (100 mm \times 4.6 mm, Chromolith).**

showed strong retention compared to Th which in turn showed stronger retention than U. This is due to the fact that at lower pH, Pu and Th form predominantly $\text{M}(\text{IBA})_4$ type of species whereas U exists as cationic species. However, at $\text{pH} \geq 3.5$, retention of U drastically increases compared to marginal increase in the retention of Th and Pu. This is because at higher pH, Th and Pu undergo hydrolysis and must be forming $[\text{Th}(\text{IBA})_4(\text{OH})_n]^{n-}$ and $[\text{Pu}(\text{IBA})_4(\text{OH})_n]^{n-}$ (where $n = 1$ or 2) species, respectively. Being the anionic species, Th and Pu complexes show relatively poor retention on the RP column. In the case of U, the dominating species at higher pH are $[\text{UO}_2(\text{IBA})_2]$ and $[\text{UO}_2(\text{IBA})_3]^-$, which are sufficiently hydrophobic in nature and exhibit strong retention on RP column. With further increase in $\text{pH} \geq 5.0$, U was not eluted till 60.0 mins whereas the retention time of Th and Pu was 13.3 and 9.9 mins, respectively. Finally, pH 4.3 of the mobile phase was chosen for studying the effect of concentration of HIBA.

3.2.2. Effect of Concentration of HIBA

Retention behavior of Th, U and Pu was studied as a function of concentration of α -HIBA at pH 4.3. As it is seen in **Figure 3**, the retention of Th, U and Pu were decreasing with the increase in concentration of HIBA. The decrease in the retention times of the actinides with increase in concentration of HIBA is attributed to the competition between the undissociated HIBA molecules and actinide-HIBA complex for the C₁₈ stationary phase. With the increase in concentration of HIBA used as an eluent, the number of undissociated HIBA molecules in the mobile phase increases and this results in faster dis-

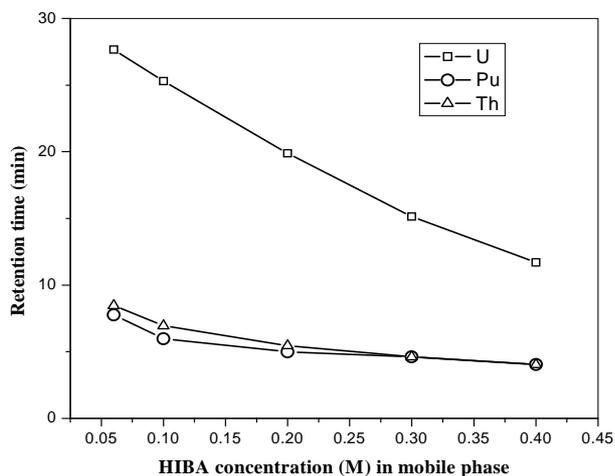


Figure 3. Effect of concentration of α -HIBA in the mobile phase on the retention of Th, U and Pu. Chromatographic conditions: pH of mobile phase, 4.3 and other conditions are same as in Figure 2.

placement of actinide-HIBA complexes from the stationary phase. However, retention of U decreased drastically indicating the hydrophobic nature of U-HIBA complex. 0.1 M of HIBA was chosen for separation studies.

3.3. Mechanism of Retention of Th, U and Pu

To study the mechanism of retention of Th, U and Pu on the RP column, n-octane sulphonic acid (IIR) was introduced in the mobile phase with the varying concentration. **Figure 4** shows the change in retention of Th, U and Pu as a function of concentration of n-octanesulphonate (n-OSA). The sorption of n-octanesulphonate on the stationary phase results into the formation of cation exchange sites. Dominance of cationic species $[M(\text{IBA})]^{3+}$, $[M(\text{IBA})_2]^{2+}$, $[M(\text{IBA})_3]^{+}$ of Th and Pu would be indicated by an increase in the retention time with increase in the concentration of IIR. As seen from the Figure, the retention times of Th, U and Pu decrease with increase in the concentration of n-octanesulphonate. This shows that the retention of Th, U and Pu on RP column is by hydrophobic mechanism and there is competition from the hydrophobic n-octanesulphonate. The studies on the influence of n-octane sulphonate clearly indicate that the hydrophobic character of U-HIBA is much higher than those of Th-HIBA and Pu-HIBA. The sorption of the IIR molecules onto the stationary phase is also occurring based on the hydrophobic interaction. U-HIBA complex shows a pronounced fall in retention time with the increasing concentration of IIR, owing to its highest hydrophobic character.

3.4. Effect of Composition of MeOH on the Retention of Th, U and Pu

Figure 5 shows the retention behavior of Th, U and Pu

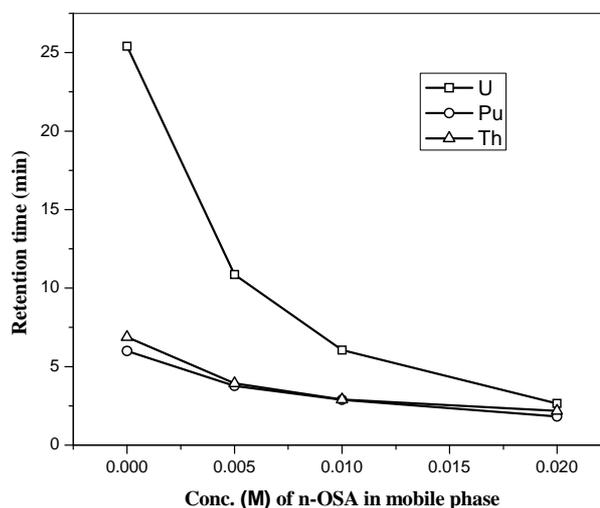


Figure 4. Effect of n-octane sulphonate on the retention of Th, U and Pu. Chromatographic conditions: Concentration of HIBA, 0.1 M and pH 4.3, Column: C_{18} RP (100 mm \times 4.6 mm, Chromolith).

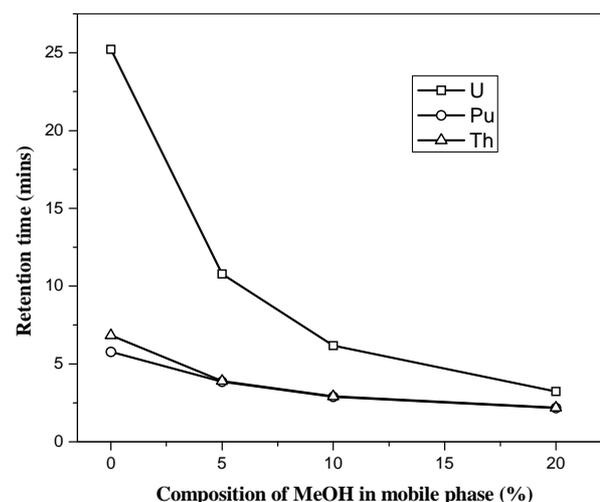


Figure 5. Effect of composition of MeOH in mobile phase on the retention of Th, U and Pu. Chromatographic conditions: same as Figure 4.

with change in percentage of MeOH in the mobile phase. The retention of U decreases drastically compared to that of Th and Pu which indicates relatively more hydrophobic nature of U-HIBA complex. The presence of MeOH also resulted in improving the peak shape and shortening the retention time. Since Th and Pu separation was getting affected at higher percentage of MeOH, it was proposed to use MeOH as a gradient for the separation of Th, U and Pu from the actual dissolver sample.

3.5. Separation and Determination of Th, U and Pu from Irradiated (Th, Pu) O_2 by RP-HPLC

The above optimized chromatographic conditions were

Table 2. Gradient condition for separation of Th, U and Pu.

Time (mins)	HIBA (pH = 6.5) (M)	HIBA (pH=2.0) (M)	% MeOH (v/v)
0.00	0.125	0.005	7
10.00	0.125	0.05	7
20.00	0.125	0.05	30
30.00	0.125	0.05	30

used for the sequential elution of Pu, Th and U. In order to improve the resolution between Th and Pu, gradient condition, as given in **Table 2** was employed. To improve the resolution as well as Th holding capacity, a larger stationary phase of dimension 250 mm × 4.6 mm was used. Aliquots of irradiated sample were evaporated to near dryness and were taken in the mobile phases containing pH 6.5 of 0.13 M α -HIBA, and were injected through 100 μ L injection port. As shown in **Figure 6**, lanthanides and other trivalent species are eluted at the solvent front. Th, U and Pu are retained on the column because of the formation of hydrophobic species using α -HIBA as an eluent. Under the optimized conditions, the elution pattern was Pu (IV) followed by Th and U. This is due to the fact that at higher pH for Th and Pu(IV), $M(\text{HIBA})_4$ type of species are most dominating whereas for U, $[\text{UO}_2(\text{IBA})_3]^-$ is the major species. However, the lower retention time of Pu and Th compared to U can be explained on the basis of strong hydrolysis nature of Th and Pu (IV) in the chromatographic conditions resulting in the formation of $[M(\text{IBA})_4(\text{OH})_2]^{2-}$. The concentrations of Pu, Th and U were determined by standard addition method and were found to be 27 ± 1 $\mu\text{g/g}$, 1.10 ± 0.02 mg/g , and 5.3 ± 0.3 $\mu\text{g/g}$, respectively, in the dissolver fuel solution.

3.6. Validation of HPLC Method

Isotope dilution-thermal ionization mass spectrometric (ID-TIMS) methodology was employed for the concentration determination of U, Pu and Nd in the dissolver fuel samples. Chemical separation of U, Pu and Nd fractions in the dissolver solution was carried out to eliminate the potential isobaric interferences during the mass spectrometric analysis as well as to get good ion yield in TIMS. Nd, U and Pu fractions obtained from unspiked and spiked aliquots were used to determine isotopic composition and concentration by ID-TIMS, respectively. Concentrations of U, Pu and Nd in the sample were found to be 5.3 ± 0.3 % $\mu\text{g/g}$, $26.8 \pm 0.2\%$ $\mu\text{g/g}$ and $1.8 \pm 0.2\%$ $\mu\text{g/g}$, respectively. Concentration of Th in the dissolver solution, determined biamperometrically using EDTA as a titrant, was found to be $1.03 \pm 0.2\%$ mg/g [30]. The concentrations of Nd, Th, U and Pu obtained were in good agreement with the concentrations determined by HPLC.

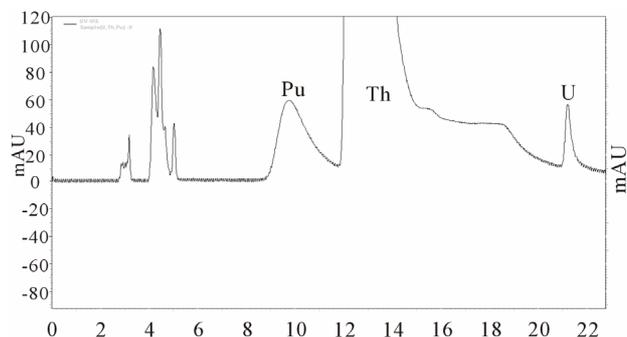


Figure 6. Direct injection of dissolver solution of irradiated (Th, Pu)O₂ fuel. Conditions: α -HIBA of pH 6.5, 0.125 M; α -HIBA of pH 2.0 from 0.005 M to 0.05 M in 10.0 mins; MeOH 7.0% till 10 mins, then 7% to 30% till 20 mins; Column: C₁₈ RP (250 mm × 4.6 mm).

4. Conclusion

An HPLC method employing α -HIBA was developed for the separation of Lns, Th, U and Pu in the irradiated fuel samples. Dynamically modified RP column was used for the separation of Lns employing dual gradient condition. The method was successfully applied for determining the concentrations of Lns. Determination of Th, U and Pu was carried out on RP column. Pu was maintained in single oxidation state using redox treatment with H₂O₂ and HNO₃. Under the optimized conditions, the concentration of Pu was also determined which was in good agreement with the concentration obtained by ID-TIMS.

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