

Separation Behavior of U(VI) and Th(IV) on a Mixed Ion Exchange Column Using 2,6-Pyridine Dicarboxylic Acid as a Complexing Agent and Determination of Trace Level Thorium in Uranium Matrix Employing High Performance Ion Chromatography

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ABSTRACT

Retention behavior of U(VI) and Th(IV) as their 2,6-pyridine dicarboxylic acid (PDCA) complexes on reversed phase and ion exchange (cation, anion and mixed ion exchange) columns was studied and based on the results, a simple ion chromatography method for the determination of trace level thorium in uranium oxide using 0.075 mM 2,6-pyridine dicarboxylic acid (PDCA) and 1 M KNO₃ in 1.2 M HNO₃ as eluent (flow rate 1 mL/min) was proposed. The advantage of the developed method is that the separation of uranium matrix is not required prior to the ion chromatographic determination of trace Th. Separation was carried out on a mixed ion exchange stationary phase and a 10⁻⁴ M arsenazo (III) solution was used as post column reagent for detecting the separated metal ions. The separation of Th from uranium using PDCA in the present investigation is attributed through cation exchange mechanism. A calibration plot was constructed by following the standard addition method over the concentration range of 0.25 to 10 ppm of Th in the presence of uranium matrix, which resulted in a linear regression coefficient of 0.9978. The precision of the method was better than 5% and the LOD for Th was found to be 0.1 ppm (S/N = 3). The method has been validated by comparing the results with the results obtained from ICP-MS analysis where the Th is separated from the uranium matrix. The proposed method is simple, rapid, accurate and cost effective compared to techniques like ICP-MS or ICP-AES and is suitable for the routine kind of analysis.

Keywords: Ion Chromatography; Uranium; Thorium; 2,6-Pyridine Dicarboxylic Acid

1. Introduction

The development of fast breeder reactors in India is inevitable as India has limited resources of uranium and the vast thorium resources require breeder cycle for exploitation [1,2]. The Proto Type Fast Breeder Reactor (PFBR), a first commercial fast breeder reactor of India, is under construction and it will use a mixed uranium-plutonium oxide (MOX) as fuel. Thorium is a trace impurity associated with all uranium based fuels [3]. Thorium, on irra-

diation with a neutron produces ²³³U, is a useful fissile isotope. Small amounts of ²³²U isotope are also produced along with ²³³U. ²³²U is an undesirable isotope as its radioactive decay chain produces short-lived and gamma emitting radionuclides ²¹²Bi and ²⁰⁸Tl, leading to high radiation exposure [4]. Hence, the uranium based fuels that are used in the fast reactors has stringent specification for Th and in India, the limit is fixed as 200 ppm_w [5]. Hence, determination of trace Th in uranium is indispensable in the chemical quality control of fast reactor fuels.

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Although different analytical techniques are available for the determination of Th at trace levels [6-8], they require quantitative separation of Th from uranium matrix which is a prerequisite for analytical determination. An ICP-MS method [9] was earlier reported from our laboratory for the determination of Th in uranium matrix, which employed a two-stage separation sequence involving an initial solvent extraction for the removal of uranium matrix followed by an ion exchange purification to get the required quality of sample solutions suitable for ICP-MS analysis. The conventional separations followed by instrumental analysis employing ICP-MS or AES are time consuming and expensive. To adopt on routine basis, a reliable, cost effective and rapid analytical method is desirable.

Ion chromatography (IC) and High performance liquid chromatography (HPLC) are promising techniques for the separation of polyvalent metal cations by adding suitable complexing agents in the mobile phase [10-13]. Many chromatographic studies have been reported on the selective separation of Th and U in variety of samples using reversed phase surfaces with weak organic acids as chelating agents [14,15]. In these separations, the extent of separation depended on the nature of the metal complexes formed and their conditional stability constants [16]. Interestingly, it is reported that the elution order of U and Th on a reversed phase surface could be altered by selecting a suitable complexing agent. For example, an elution order of Th followed by U was observed in a RP surface when α -hydroxy isobutyric acid (α -HIBA) was used as a complexing agent [17,18]. However, this elution order got reversed when mandelic acid (MA) was used in place of α -HIBA [19]. The change in elution order may be explained on the basis of differences in the complexing abilities of the ligands with respect to individual metal cation, effective charge, thermodynamic and kinetic stabilities and hydrophobicities of the metal complexes formed.

Although α -HIBA and MA are widely used as complexing agents in the separation of U and Th, 2,6-pyridine dicarboxylic acid (PDCA), a non-hydroxy dicarboxylic acid, has been identified as a promising ligand for the separation of heavy metal ions [20-23]. The reversed phase surfaces dynamically modified with PDCA [22,24] showed stronger retention for U(VI) than Th(IV) due to the high affinity exhibited by the UO_2^{2+} ion for PDCA [20]. A study reports [22] that dynamic modification of a small PRP column with 0.1 mM PDCA in 1 M KNO_3 and 0.5 M HNO_3 could separate some of the acid hydrolysable heavy metal ions like U, Th, Zr, etc. It also states that the lanthanides and other transition metal cations have no retention on the column and get excluded at the solvent front.

Other than RP columns, ion exchange columns were also used for the separation of U and Th. The ion chro-

matographic separation of U and Th using pure ion exchange separation is difficult due to the large differences in their distribution ratios. This is because the UO_2^{2+} and Th^{4+} ions have considerable differences in their ion exchange affinity. Separation of U(VI) as UO_2^{2+} on a low capacity strong cation exchanger has been reported [25]. Even though few studies reported the separation of U and Th from water and geological samples using a pure cation exchange column with gradient elution of a mobile phase consisted of HCl and Na_2SO_4 [26,27], use of hydrochloric acid as eluent was not recommended for routine analysis due to its corrosiveness, which demanded utmost care on the instrument maintenance. Earlier in our laboratory, we have separated uranium and thorium using a short length cation exchange column using a mobile phase consisting of 0.08 mM PDCA in 0.24 M KNO_3 and 0.22 M HNO_3 (pH \sim 0.6) [23]. This method was found suitable for the rapid separation of both U and Th at trace level concentrations; however, it would not be possible to extend the procedure when one of the metal ions was at higher concentrations.

The studies that reported the basis of RP-surface modifications and ion exchange separations were capable of providing good separation between U and Th, provided their concentrations were comparable. However, the separation of U and Th is a difficult task when one of these metal ions presents in large amount. When determining one metal ion at trace level in the presence of large excess of other, the system loses its capacity, resulting in poor resolution between the analytes [21]. The most practicable way is to remove matrix element by means of conventional methods like solvent extraction, column chromatography and ion exchange prior to the IC or HPLC. Such sample preparation procedures are not only time consuming and laborious but also susceptible to cause inconsistency in the recoveries of the analyte of interest. Moreover, methods that follow pre-separation followed by instrumental analysis demand the use of certified reference materials to assess the recoveries.

Since the objective of this study is to separate trace thorium from the dissolved uranium oxide samples by direct sample injection, one of the desired conditions to realize the objective is to have an elution order of Th(IV) followed by U(VI) so as to get the elution of Th first and then the matrix U. This elution order can be obtained by separating them on a reversed phase column (modified and unmodified) using α -HIBA as eluent [11]. But, the separation of Th in presence of bulk U could not be realized by following the reported procedures. A good separation of lanthanides, Th and U at relatively large concentrations was reported [17] where the C-18 RP column was coated with bis-2-ethylhexyl succinamic acid (BE-HSA). However, the same study showed that it could not separate Th from U when the uranium concentration in the sample was more than 5 mg/mL. Mandelic acid, an-

other complexing agent frequently used in the separation of U and Th, could not be used as it brings reversed order of elution *i.e.* U followed by Th and both uranium and thorium mandelate complexes interact hydrophobically with the reversed phase surface and exhibit significant retentions. A similar elution order was reported in the case of cation exchange chromatography as uranium forms weaker cationic species with the frequently used eluents like hydrochloric and nitric acids [28]. This elution order may be useful in the present case only when U(VI) has no or least interaction with stationary phase so that it can get eluted at the solvent front. The realization of this condition obviously depends on the selection of an appropriate stationary phase and a suitable complexing agent. Ion exchange separation of metal ions can be affected by adding weak organic acids in the mobile phase, which reduces or alters the effective charge of the metal ions by forming either cation, neutral or anion complexes and the nature and stability of the metal complexes would decide the method of ion exchange (anion or cation) separation. Nowadays, stationary phases having both cation and anion exchange capacities are found to be more useful in separating heavy and transition metal ions [29] because the separation is controlled by the concentrations of free metal ions and the various insitu metal complexes formed, which are in an equilibrium with each other [30]. One such mixed ion exchanger namely Ion Pac CS5A has been widely used for the separation of lanthanides and transition metal cations in several matrices [31-33].

Hence it is decided to examine Ion Pac CS5A mixed ion exchanger column in the present investigation for the separation of traces of Th from bulk of U as it 1) contains both strong anion and cation exchangers (anion exchange capacity: 40 $\mu\text{eq}/\text{column}$ and cation exchange capacity: 20 $\mu\text{eq}/\text{column}$), and 2) displays anion and cation exchange properties while separating the metal cations by choosing an appropriate complexing agent [34]. In the present investigation, PDCA has been chosen as complexing agent as it has high affinity for complex formation with polyvalent metal cations. The main advantages in using PDCA as a complexing agent are: 1) it can be used with low pH or high acid concentration and 2) the concentration of PDCA required in the mobile phase to facilitate the separation is very low ($\sim 10^{-5}$ M) compared to the concentrations of the hydroxy carboxylic acids ($\sim 10^{-1}$ M) required. Since the nuclear fuel samples (mg amounts) are often dissolved in mineral acids and subsequently aliquots are made out of this solution for wet analyses, it is desirable to use PDCA as complexing agent, which would enable the direct injection of the samples into the system.

The aim of this investigation was to develop a rapid

and reliable method for the separation and determination of trace level thorium in uranium oxide using a mixed ion exchanger column and PDCA as a complexing agent.

2. Experimental

2.1. Instrumentation

The IC system used in the present study was DX500 (Dionex CA, USA). It consisted of a solvent delivery pump (GP-50) and an absorption detector (AD20). A pneumatic post column reagent addition facility consisting of a 1000 mL reservoir bottle, gas pressure gauge to control the flow rate of the gas, a T-junction and a 75 μL capacity reaction coil was placed between the separator column and the detector. The samples were injected through a 50 μL loop fitted to a Rheodyne six port injector. The separator columns used were 1) Ionpac CS5A (4.6 \times 250 mm) with CG5A guard column (4.6 \times 50 mm) (Dionex CA, USA), 2) Ionpac AS11 HC (4.6 \times 250 mm) with AG11 guard column (4.6 \times 50 mm) (Dionex CA, USA) and 3) IC Pak Cation, 4.6 \times 50 mm (Waters, USA). The pH measurements were made on a CL-5 pH meter (Toshniwal, India).

2.2. Reagents

All the reagents were of analytical grade (AR). Standard stock solution of uranium was prepared by dissolving nuclear grade U_3O_8 and its concentration was determined by biampometry method [35]. Standard stock solution of Th (97.8 mg ml^{-1}) was prepared by dissolving nuclear grade $\text{Th}(\text{NO}_3)_4$ (IRE, India) in 3 M HNO_3 and the Th concentration was determined by complexometric titration with EDTA using xylenol orange as indicator. 2,6-pyridine dicarboxylic acid (PDCA) (99%, Aldrich Chemical corporation Inc.) was used as such. 0.01 M PDCA solution was prepared in water and appropriate volume of this solution was used in the preparation of mobile phase. Nitric acid was of suprapure grade (Merck, India). All solutions were prepared using high purity deionised water (18.2 M Ω) obtained from a Milli Q water system (Millipore, USA). The eluents were filtered through nylon 6,6, membrane filters (0.45 μm) prior to their use. A post column reagent of 4.5×10^{-5} M Arsenazo-III in 0.1N HNO_3 was added through a PEEK make T-junction with a flow rate of 0.8 ml min^{-1} for the detection of the separated metal ions at 655nm.

3. Results and Discussion

3.1. Preliminary Investigation

Earlier we reported the separation of U and Th as their PDCA complexes using cation exchange column with a mobile phase of 0.08 mM PDCA in 0.24 M KNO_3 and

0.22 M HNO₃ (pH ~ 0.6) [23]. A study that dealt with the chelation ion chromatography (CIC) separation could successfully separate Th(IV) and U(VI) on a neutral polystyrene resin column dynamically modified with PDCA [14]. Based on the reported studies, to start with, an eluent composition of 0.1 mM PDCA in 1M KNO₃ and 0.5 M HNO₃ (pH ~ 0.3) was arbitrarily used with the mixed ion exchanger column viz. Ionpac CS5A. With this eluent, there can be three possible mechanisms in which the metal complexes can interact with the stationary phase and they are: 1) cation-exchange 2) anion-exchange provided the metal ions form anionic complexes with PDCA and 3) chelation ion chromatography. Interestingly, unlike the modified RP column, the mixed ion exchange column exhibited strong retention for Th (IV) whereas U(VI) got eluted immediately after the solvent front. Hence, the elution order observed in the present case is U(VI) followed by Th (IV), which is similar to that of the elution order obtained with strong cation exchange stationary phase [23,26,27]. This indicates that in the case of mixed ion exchanger, the chelation exchange mechanism responsible for retaining U (VI) and Th (IV) on the RP substrate is insignificant, probably the mixed ion exchanger column was not sufficiently modified with PDCA to get the elution order similar to that of the RP column. Since the observed elution order is similar to that of the order obtained with cation exchange separation, it is necessary to study the role of anion exchanger in the column, if any.

3.2. Effect of Concentration of PDCA

In order to understand the effect of PDCA concentration on the retention of both U(VI) and Th(IV), concentration of PDCA in the mobile phase was varied from 0.04 to 0.2 mM by keeping the concentrations of other two components namely KNO₃ (1 M) and HNO₃ (0.5 M)

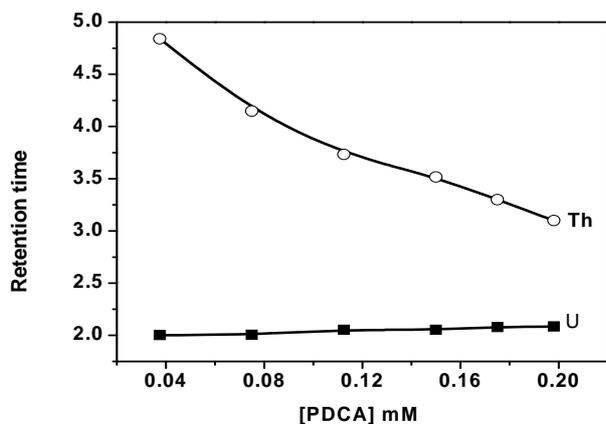


Figure 1. Effect of concentration of PDCA on the retention of U and Th separated on a mixed ion exchanger column. The concentrations of KNO₃ and HNO₃ in the eluents were kept as 1 M and 0.5 M respectively.

constant. The variation in pH of the eluent was insignificant while varying the PDCA concentration because the concentration of HNO₃ in the eluent was large compared to the concentration of PDCA. The retention trend obtained is shown in **Figure 1**. Increasing PDCA concentration in the mobile phase had virtually no effect on the retention of U(VI) whereas the retention of Th(IV) was drastically reduced.

The PDCA concentration was not increased beyond 0.2 mM because 1) the resolution between the two peaks was poor and 2) the detection sensitivity of the Th(IV)-arsenazo-III complex reduced significantly beyond 0.15 mM PDCA. The observed retention behavior of U(VI) shows that it has least retention on the column and this can occur only when U(VI) forms a stable neutral complex with PDCA. This is because the formation of either a cation or an anion complex of U(VI)-PDCA would have exhibited significant retention since the column has both cation and anion exchange sites. The equilibrium distribution of PDCA (uncomplexed) species differs with pH. PDCA is a dicarboxylic acid having $pK_1 = 2.10$ and $pK_2 = 4.68$ for an ionic strength of 0.1 M [36]. It has been reported that PDCA (H₂L) predominantly exists as HL⁻ form when the eluent pH ≤ 1 whereas at higher (alkaline) pH, it can be transformed into L²⁻ form [34]. Since the eluent pH < 1, the existence of HL⁻ form is predominant than that of L²⁻ form of the ligand. Hence, U(VI) may be forming probably a 1:2 with HL⁻ or 1:1 complex with L²⁻ form of PDCA. Though we cannot offer any evidence for the formation of the neutral complex(es), the strong retention of U(VI)-PDCA complex on a reversed phase surface [14] supports this assumption. Theoretically, though a neutral complex in equilibrium with either its pure metal ions or other kind of complex cations can have feeble interaction on cation exchange sites provided the complex formed is kinetically labile. In the present case, the complex formed has no interaction with both anion and cation exchangers and this may be due to high stability of the U-PDCA neutral complex formed. Since there was no significant change in the retention of U(VI) while increasing PDCA concentration in the eluent, the formation of weak anionic complex of U-PDCA was not appreciable in the present case.

In the case of Th(IV), it exhibited significant retention on the mixed ion exchanger column. Elution with increasing PDCA concentration in the mobile phase decreased the retention of Th(IV). The proposed cation exchange models in literature [37] report that increasing the concentration of complexing agent decreases the retention time of metal ions due to their formation as neutral or weak anionic complexes. Whereas in anion exchange model reports that only strong anion metal-ligand complexes can interact with the anion exchange sites and hence, increasing the concentration of complexing agent

in the eluent would increase in the retention time. In order to conclude about the probable nature of the metal complexes and their interaction with ion exchange sites, it is necessary to study the retention of U or Th with the components of eluent individually.

Initially, separations were carried out by varying the concentration of PDCA between 0.02 mM to 0.4 mM in 0.2 M HNO₃ (necessary to avoid hydrolysis of U and Th) without taking KNO₃ in the mobile phase. It was observed that with 0.02 mM PDCA, U appeared at 4.0 minutes whereas the same appeared at 2.7 minutes when the PDCA concentration was increased to 0.1 mM and subsequent increase of PDCA up to 0.4 mM did not change the retention time significantly. In contrast, Th(IV) peak did not appear at all. A similar observation was made when pure HNO₃ (0.5 to 2 M) or pure KNO₃ (0.2 to 1.8 M) was used as eluent. Eluents with mixture of HNO₃ and KNO₃ of varying concentrations were also used and there was no difference in the retention of U(VI) compared to that of the pure HNO₃/KNO₃. However, interestingly it was observed that Th(IV) appeared when the pH of the mixed eluent was less than 1. Further, it was seen that the elution of thorium was so slow that it resulted in a broad peak. Therefore, it may be concluded that in the absence of PDCA in the eluent, the thorium elution with KNO₃+HNO₃ may be due to the formation of its nitrate complex and the formation of such nitrate complex is pH dependent.

Therefore, it is seen from the experiments carried out with PDCA, KNO₃ and HNO₃ individually as well as with various combinations that for the separation of Th(IV), for the purpose of analytical determination, a mobile phase with the combination of all three components is required. The observations showed that at this low concentration of PDCA, the elution of Th(IV) occurred only when a KNO₃ is added along with minimum 0.1 M HNO₃ concentration. It has been observed that eluents with PDCA concentration above 0.08 mM were not found suitable for separating trace Th in the presence of large excess of uranium. Therefore, the PDCA concentration has been fixed at 0.075 mM. This concentration would reduce the interactions between UO₂²⁺-PDCA complex with the stationary phase, which is desirable to realize the elution of U peak immediately after or at the excluded peak.

3.3. Effect of Concentration of KNO₃

The retention trends of U(VI) and Th(IV) shown in **Figure 1** suggest that U(VI) predominantly forms a neutral complex and gets eluted immediately after the excluded peak and Th(IV) forms weak neutral or anionic complex and most probably, the mechanism responsible for the retention of Th(IV) on the column is due to cation exchange. However, addition of relatively high concentra-

tion of KNO₃ may suppress the ion exchange process due to the presence of large concentration of K⁺ ions (acts as competing cation). It was observed that the retention time of U(VI) was unaltered whereas the retention time of Th(IV) decreased when the concentration of KNO₃ (0.2 to 1.8 M) was increased in the mobile phase and by keeping the PDCA and HNO₃ concentrations as 0.075 mM and 0.2 M, respectively.

The retention time of Th(IV) decreases drastically in the concentration range of 0.2 to 1.2 M and subsequently there was a little decrease up to 1.8 M. The drastic reduction in retention time may be attributed due to two reasons: 1) increasing [KNO₃] increases the ionic strength of the eluent. While using cation-exchange column with complexing eluent, the affinity of metal ions for ion-exchange resins decreases as ionic strength increases and therefore, the retention time decreases and 2) NO₃⁻ from KNO₃ may be competing with PDCA in complex formation. To identify the role of KNO₃, separations were carried out with PDCA and HNO₃ combinations where the nitrate was supplied in the form of HNO₃. For instance, instead of 0.5 M HNO₃ + 0.5 M KNO₃ + 0.075 mM PDCA (pH 0.3) an eluent of 0.075 mM PDCA in 1 M HNO₃ was prepared and pH was adjusted by adding LiOH. It was seen that with the latter mobile phase composition, Th could not be eluted from the column. This suggests that K⁺ is acting as competing ion which reduces the bare metal ions (U and Th) interactions with ion exchange sites.

Equation for cation (complex ion) exchange is expressed as

$$\log D_m = \log K_{MA} - \log a_{M(L)} + n \log C - n \log [A^+]$$

where D_m is the distribution coefficient of the metal in presence of complexing agent, K_{MA} is the selectivity coefficient between the metal and competing cation, a_{M(L)} is complex formation coefficient, C is the capacity of the ion exchanger and [A⁺] is the concentration of the competing cation.

The distribution coefficient (D_m) of the metal is a function of the concentration of the competing cation (A⁺) and that of the complexing agent in the mobile phase. Since in the present case the competing cations in the mobile phase are K⁺ and H⁺, the elution mainly depends on the concentration of K⁺ ions as it has high selectivity over H⁺. On increasing the KNO₃ concentration in the eluent decreased the retention times of only Th(IV) whereas the retention times of U(VI) was unaffected throughout the concentration range (**Figure 2(a)**). Th(IV) retention times decreased steadily as the KNO₃ concentration was raised up to 1.2 M and subsequent increment of rise in KNO₃ concentration did not reduce the retention times appreciably. As this trend is expected in the case of cation exchange of Th(IV), a plot of log k (reten-

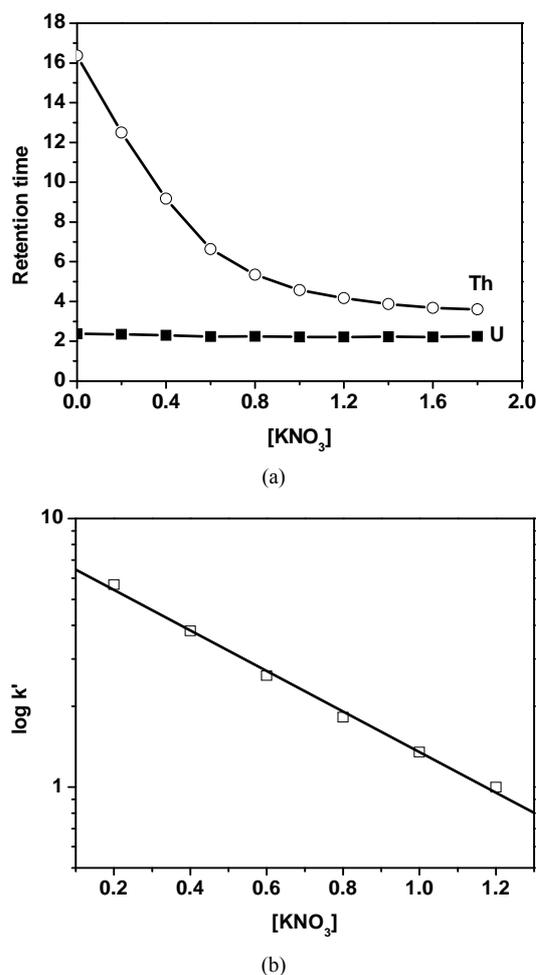


Figure 2. (a) Effect of concentration of KNO_3 on the retention of U and Th separated on a mixed ion exchanger column (the concentrations of PDCA and HNO_3 in the eluents were 0.075 mM and 0.5 M respectively) and (b) plot of $\log k$ (retention factor) of Th against $[KNO_3]$.

tion factor) against KNO_3 concentration over the range of 0 - 1.2 M brought a straight line with negative slope (**Figure 2(b)**) indicating the separation is predominantly by cation exchange mechanism. The optimum KNO_3 concentration was fixed as 1.0 M as this provided the desired separation between U(VI) and Th(IV).

3.4. Effect of Concentration of HNO_3

Addition of HNO_3 and its concentration plays an important role in controlling the effective ligand concentration in the mobile phase, which decides the nature of metal-complex. In addition, HNO_3 prevents the hydrolysis of metal cations as these heavy metal ions belong to acid hydrolysable group. Moreover, the H^+ ions from the nitric acid also act as the competing ion during the elution of metal cations or cation complexes. To investigate the influence of HNO_3 concentration on the elution, two sets of experiments were conducted. In the first set, HNO_3

concentration was varied over a range between 0.5 and 1.5 M.

It was expected that increasing acid concentration would reduce the effective concentration of ligand, which would affect the complexation of U(VI) leaving more metal cations and in such case, the retention times for both Th(IV) and U(VI) are expected to be increased. However, there was no appreciable change in the retention times observed. Interestingly, there was a steady improvement in the symmetry of Th(IV) peak was observed. In the second set, the pH of the mobile phase was varied from 0.3 to 4.0. For preparing the eluents, dilute nitric acid of appropriate concentration was used and final pH adjustment was done with dilute LiOH solution. Increasing eluent pH caused the retention times of Th(IV) to decrease and of U(VI) to increase. In addition, the order of elution reversed from pH 2 onwards (**Figure 3**). There are two ways in which this can be explained. First, increase of eluent pH leads to increase in the effective ligand (HL^-) concentration and therefore, U(VI) tends to form anion complex, which interacts with anion exchanger resulting increasing trend in the retention. On the other hand, it has not resulted in change in the complex forming behavior of Th(IV) significantly and hence, retention time decreased. There could also be a possibility of column modification due to the hydrophobic interactions between the phenyl group of PDCA and the polystyrene-divinyl benzene skeleton of the resin. On increasing pH of the eluent, the dissociation of acid groups on the immobilized chelating ligand produces an increase in the conditional stability constants of the surface metal complexes and it causes the retention times of the metal ions to increase [15]. Between Th(IV) and U(VI), it has been reported that the U(VI)-PDCA (1:1) complex has high stability constant ($\log K_1 = 4.72$) [38] and hence, it is more retained than Th(VI). The existence of this mechanism would have been confirmed only by carrying out separations at higher pH levels. However, such studies are not affordable in this case as the hydrolysis of heavy metal ions cannot be prevented.

From the analytical point of view, considering the desired order of elution, separation factor and other chromatographic parameters, it is desirable to have higher concentration of HNO_3 and accordingly the HNO_3 concentration was fixed as 1.2 M in the mobile phase.

3.5. Elution with a Pure Cation Exchange Column

Preceding investigations suggest that the elution behavior of Th(IV) was mainly due to the cation exchange mechanism. On the other hand U(VI) was eluted as its neutral complex, which gets eluted immediately after the excluded peak indicating that it has least interaction with both cation and anion exchangers. It has been seen that a

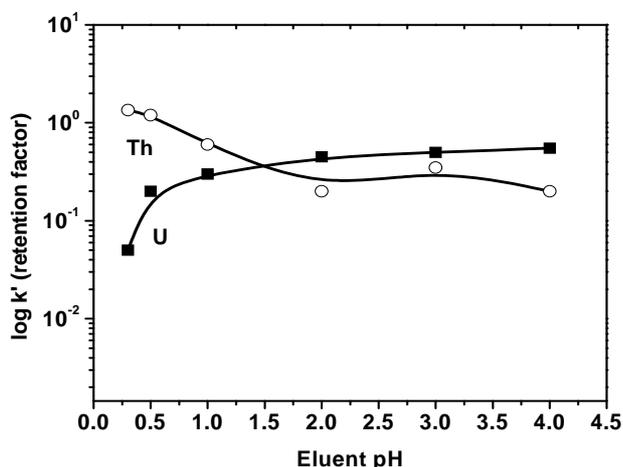


Figure 3. Effect of eluent pH on the retention of U and Th on a mixed ion exchanger column. The [PDCA] and [KNO₃] were 0.075 mM and 1.0 M respectively.

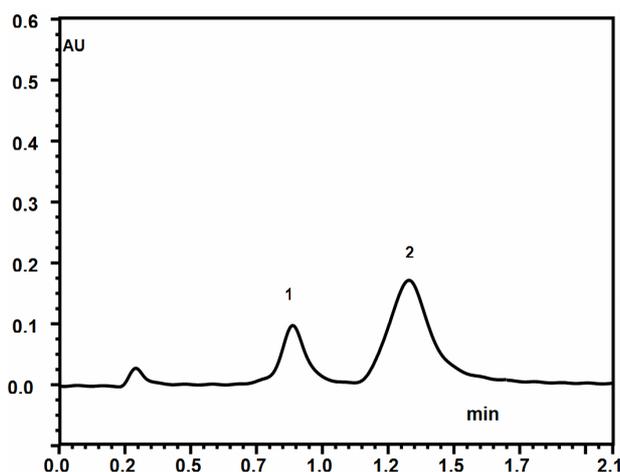


Figure 4. Typical chromatogram obtained for a standard solution of U(VI) and Th(IV) using cation exchanger column. Peaks (1) U(VI) – 3 ppm and (2) Th(IV) 3 ppm. Column: IC Pak Cation (4.6 × 50 mm). Eluent: 0.1 mM PDCA and 0.12 M KNO₃ in 0.1 M HNO₃; Flow rate: 1 ml/min. Detection: Post column addition of 4.5 × 10⁻⁵ M arsenazo-III and detection at 656 nm.

mobile phase of 0.1 mM PDCA and 0.12 M KNO₃ in 0.1 M HNO₃ brought good separation between U(VI) and Th(IV) and **Figure 4** shows a typical chromatogram obtained. The order of elution was as same as that of the one obtained with the mixed ion exchanger column. Effects of concentrations of PDCA and KNO₃ on the retention of Th(IV) showed similar trend in both mixed ion exchange and cation exchange columns. This suggests that the separation of Th(IV) is mainly due to cation exchange. In order to understand the separation with mixed ion exchange column and the role of anion exchange, it is necessary to carry out separations with pure anion exchange column too.

3.6. Separation with Pure Anion Exchange Column

When similar investigations were carried out with a pure anion exchange column (IonPac AS11 HC column), the elution order was reversed where Th peak appeared immediately after the excluded peak followed by U. while increasing the PDCA concentration (from 0.08 - 0.5 mM) in the mobile phase it was observed that there were no significant changes in the retention time of both U and Th. This indicates that up to 0.5 mM PDCA both U and Th are not forming stable anionic complexes. This observation suggests that Th may be forming weak anionic and neutral complexes with PDCA. In the present case, the appreciable retention of U cannot be explained on the basis of formation of anionic complex because the retention time did not increase while increasing the PDCA concentration. Probably the neutral U-PDCA complex may be interacting on the surface of the column hydrophobically as it showed in the case of reverse phase surface. Therefore, it may be concluded that the cation exchange sites of the mixed ion exchange column play predominant role in the separation of U and Th. However, the anion exchange sites present in the mixed ion exchange column may be reducing the hydrophobic interaction of U-PDCA neutral complex, though we cannot offer any evidence.

3.7. Effect of Other Metal Ions

Since the uranium oxide fuel samples are expected to have other metallic impurities like Fe, Cd, Cu, Ca, Mg, Ni, Cr, Mn, Mo, rare earth elements etc. (within the specification limits), separations were carried out in the presence of these metal ions to observe the interference effects, if any, during the separation of Th. For this purpose, two synthetic sample solutions were prepared and used. The first solution was a mixture of thorium with transition metals (Ca and Mg were also added) and the second one consisted thorium and mixture of all lanthanides. The individual metal ion to Th concentration ratio was kept ten in both the solutions. It has been observed that the first solution did not give any peak whereas the second solution containing mixture of lanthanides showed a small triplet peak after the uranium peak with very poor detection sensitivity. Therefore, the formulated eluent composition was found to be suitable for the interference free determination of Th. A typical chromatogram obtained for a standard solution containing U and Th is shown **Figure 5**.

3.8. Effect of Matrix ion on the Separation of Th

Under the optimized separation conditions, the uranyl ion eluted very close to the excluded peak and the retention capacity factor (k') for uranium was 0.2. Hence, separa-

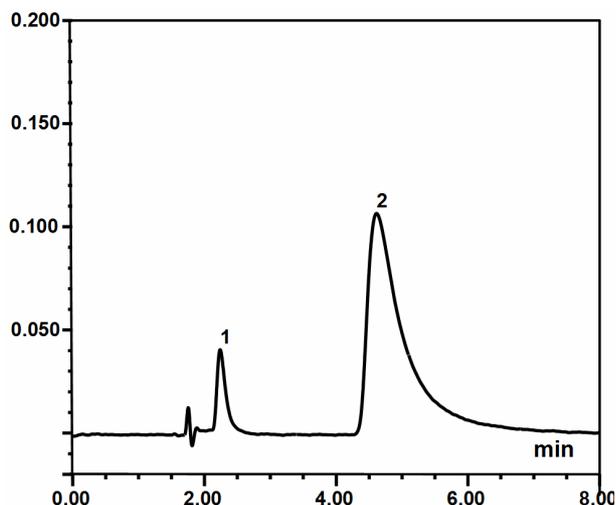


Figure 5. Chromatogram obtained for a standard mixture solution containing U and Th. Peaks (1) U(VI) 1 ppm and (2) Th(IV) 2.5 ppm. Column: IonPac CSSA (4 × 250 mm). Eluent: 0.075 mM PDCA and 1M KNO₃ in 1.2 M HNO₃. Flow rate: 1 mL/min. Detection: Post column addition with 4.5×10^{-5} M Arsenazo-III in 0.1 N HNO₃ at 656 nm; flow rate: 0.8 mL/min.

ration of trace Th from bulk uranium may be feasible because most of the uranium may get excluded along with solvent front, which can reduce the possibility of column swamping. Several synthetic samples in duplicates having U/Th ratios 1, 2, 20, 200, 400 and 1.8×10^4 were prepared and injected for Th separation. The observed recoveries for Th in each case have been listed in **Table 1** and the recoveries of Th were found to be more than 90%, which showed that the method has high tolerance for uranium and hence, the direct separation of Th from the dissolved uranium samples is feasible.

3.9. Calibration and Method Validation

Since the success of an analytical method is critically dependent upon how accurately the concentrations of the analytes are known and how closely the matrix of the standards match with that of the samples to be analyzed, construction of a calibration plot in presence of matrix is desirable as the instrumental response is read in an almost identical chemical environment for both samples and calibration standards. This will compensate the matrix effect on the measurements. Therefore, high purity UO₂ was dissolved in nitric acid and the solution was made up to a known volume. Several aliquots were prepared and varying volumes of a standard Th solution were spiked except for one aliquot. The spiked aliquots were made up to a known volume keeping a final concentration of U in all aliquots at 87 mg/mL. A calibration plot was constructed between the peak areas and their respective Th concentrations in the presence of matrix uranium (87 mg of U/mL of the standard solution), which

showed a linear relation with a regression coefficient of 0.9975 and the plot obtained is shown in **Figure 6**.

The Th content of the uranium blank solution was calculated from the intercept of the plot. The limit of detection (LOD) was calculated as 0.1 ppm of Th using S/N = 3 formula. The method was validated by analyzing a U₃O₈ reference material (ILCE-IV) employing both the present method and ICP-MS (a well established procedure [9,39] for the separation of trace Th from the uranium matrix prior to the ICP-MS analysis was followed). Accurately weighed quantities (~0.4 g) of this U₃O₈ reference material were dissolved in Conc.HNO₃ and heated to dryness. Further they were re-dissolved in 5 mL of 0.5 M HNO₃ and injected into the IC for separation. Another set of dissolved samples were subjected to solvent extraction for the removal of matrix U using aliquat-336 [40] and the final separated fractions were taken in 0.5 M HNO₃. The values obtained are listed in **Table 2** and they are in good agreement with the mean value reported by the ICP-MS method. The chromatograms obtained for a direct injection is shown **Figure 7**.

3.10. Procedure and Sample Analysis

A sample size of 0.4 - 0.5 g was dissolved in Conc.HNO₃

Table 1. Effect of concentration of U (matrix) on the separation of Th.

Sample Code	[UO ₂ ²⁺] μg/mL	[Th ⁴⁺] μg/mL	U/Th ratio	Observed [Th] μg/mL	Recovery Th%
S-1	5	5	1	4.9	98.0
S-2	10	5	2	4.78	95.6
S-3	100	5	20	4.81	96.2
S-4	1000	5	200	4.85	97.0
S-5	2000	5	400	4.65	93.0
S-6	88,000	5	1.8 E ⁴	4.73	94.6

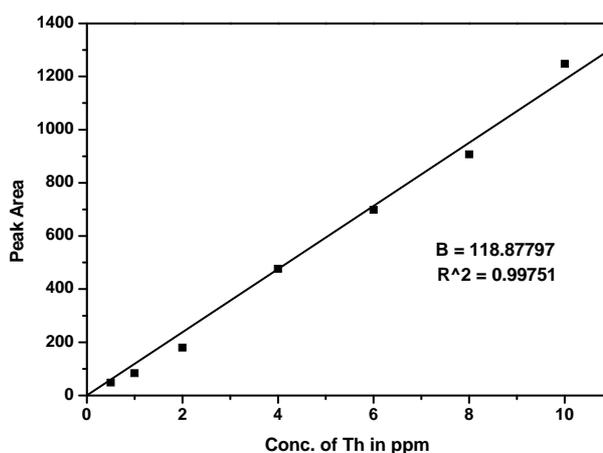


Figure 6. Calibration plot obtained for Th over a concentration range of 0.25 - 10 ppm in the presence of 87 mg of U/mL of the standard solutions.

Table 2. Results obtained for a U₃O₈-reference material.

Sample Analysis	Sample Code	[Th ⁴⁺] by IC (ppm _w) ^b	Mean	Mean reported by ICP-MS
Direct Analysis ^a	D-1	75.5	74.0 ± 1.6	72.5 ± 2.2
	D-2	72.7		
	D-3	74.6		
	D-4	71.8		
	D-5	75.2		
After Solvent Extraction ^c	S-1	72.3	71.4 ± 1.3	
	S-2	69.8		
	S-3	72.7		
	S-4	70.9		

^a0.5 g of sample dissolved and made up to ~20 g by 0.1N HNO₃ and 50 µL of this solution was injected into IC. ^beach value quoted is a mean obtained from three replicate injections. ^c0.5 g of sample was dissolved in HCl and U was separated by aliquat-336 [40] in 6 M HCl.

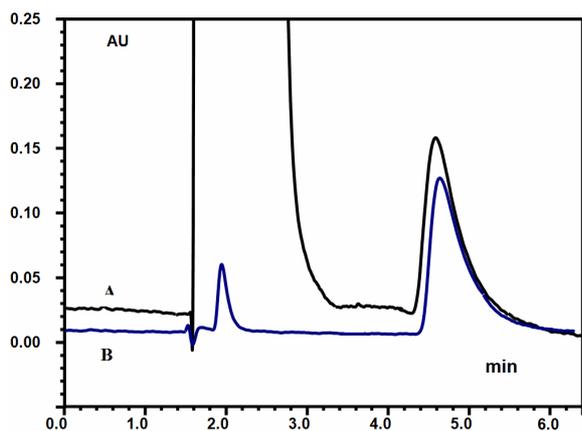


Figure 7. Typical chromatograms obtained for a U₃O₈-Reference material sample (A) direct injection of dissolved uranium solution (B) sample injected after removal of uranium (matrix) by solvent extraction.

and evaporated to dryness. Further, it was re-dissolved in 0.5 M HNO₃ to have a final volume of 5 mL and 50 µL of this solution was injected into IC for separation. A mobile phase of 0.075 mM PDCA and 1M KNO₃ in 1.2M HNO₃ was used at a flow rate of 1 mL/min for separation. The separated fraction of metals are detected and measured by post column addition of 4.5 × 10⁻⁴ M arsenazo-III at a flow rate of 0.8 mL/min. The results obtained for typical samples are listed in **Table 3**.

4. Conclusion

The proposed method was successfully used for the determination of trace levels of Th in uranium matrix without employing prior separation of matrix. The method is simple, rapid, accurate and promising for its adaptation in the routine quality control analysis of uranium based

Table 3. Results obtained for uranium samples.

Sample	Conc. of Th (ppm _w) ^a
UO ₂ – SG	18.3 ± 1.3
U ₃ O ₈ – NFC-1	15.7 ± 1.4
U ₃ O ₈ – NFC-2	23.6 ± 1.7

^amean of three analyses.

fuels.

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