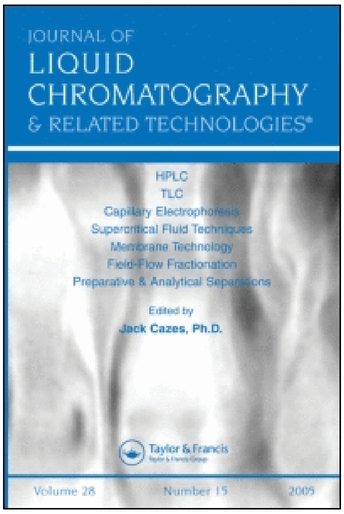

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Retention Behaviour of Uranium and Thorium and Their Determination on an Amide-Coated Reverse Phase Column by HPLC

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ABSTRACT

The retention behaviour of uranium and thorium was investigated using a reverse phase column modified with *N*,*N*-dialkyl amides, such as dihexyl hexanamide (DHHA), dibutyl hexanamide (DBHA), diisooctyl butanamide (DiOBA), or dioctyl hexanamide (DOHA). α-Hydroxy isobutyric acid (HIBA) is employed as the mobile phase. The retention behaviour was compared with that observed on the uncoated C_{18} support. The retention was also investigated on C_{18} modified with another neutral

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extractant, trihexyl phosphate (THP), uncoated C_8 support, and amide-coated C_8 support, to understand the retention mechanism. Uranium and thorium can be separated from each other with good peak profiles and baseline resolution. Rapid separations could be achieved by proper choice of column coating. On the basis of these studies, a HPLC technique has been developed for the separation and determination of uranium in the presence of large amounts of thorium, i.e., uranium can be estimated accurately in the presence of about 1000 times of thorium.

Key Words: Uranium; Thorium; Amide-coated support; Reverse phase column.

INTRODUCTION

The determination of uranium and thorium is of particular interest with respect to the nuclear industry.[1] Accurate determination of uranium, often in low concentration levels, is important to evaluate the performance of various nuclear processes. For example, some process samples generated during the recovery of ^{233}U from irradiated thorium contain trace quantities of uranium in the presence of large amounts of thorium. Analysis of actinides, including uranium, in environmental samples is also required as a part of safety procedures. HPLC based separation methods have been developed and reported for the separation of uranium from thorium.[2–8] Barkley et al.[1] studied the separation of uranium, thorium, and rare earths on a C_{18} column, using dynamic ion exchange methods employing *n*-octane sulphonate and α-HIBA. They also reported the separation of uranium and thorium on a reverse phase column, employing α-HIBA with 10% methanol as the mobile phase. This method was employed for the determination of rare earths and thorium in uranium ore refining processes. Haddad and co-workers[4] reported the retention behaviour of thorium(IV) and uranyl ion as α-HIBA complexes on a reverse phase column. They employed a mobile phase containing 0.4 M HIBA with 10% methanol and the separation was complete in about 14 min. Calibration plots for uranium and thorium were reported in the 0–10 ppm range. Haddad and co-workers[5] also studied the retention behaviour of uranium and thorium using glycolic and mandelic acid as eluents. They reported the influence of methanol content in the mobile phase in typical reverse phase conditions. Elchuk et al.[6] reported reverse phase separation of lanthanides, actinides, and transition metals by employing mandelic acid as eluents. The uranium–thorium separation was completed in about 20 min. Harrold et al.[7] investigated the ion-chromatographic separation of uranium and thorium present in natural waters and geological materials.

Sutton et al.[8] compared the retention behaviour of uranium and thorium on high-efficiency resin substrates impregnated or dynamically coated with metal chelating compounds. They separated uranium and thorium on a calmagite impregnated polystyrene column using a mixture of KNO_3, nitric acid and oxalic acid. They also studied the separation on a PAR column with nitric acid as eluent. They found that the column dynamically coated with dipicolinic acid gave the best results for the separation of uranium and thorium. Sivaraman et al.[9,10] have developed an extraction chromatographic technique for the separation of uranium from lanthanides, and other fission products. Suresh et al.[11] had developed a spectrophotometric method for the determination of trace levels of uranium in the presence of thorium. The method involves the use of Br-PADAP chromogenic reagent using cyclohexane tetra acetic acid (CyDTA) as masking agent, and the detection was carried out at 577 ± 1 nm. This method involves the modification of solution composition depending upon the thorium concentration.

It is to be noted that in all the separations reported in the literature, uranium and thorium were present in the sample at comparable levels. However, the thorium fuel cycle demands the quantification of micro levels of uranium in the presence of bulk thorium. The separation and accurate determination of uranium in the presence of a large excess of thorium is challenging, and there is no report in the literature of a simple liquid chromatographic technique to meet this requirement.

In recent years, *N*,*N*-dialkyl amides have been shown to be promising candidates for actinide recovery.[12,13] They are particularly selective in extracting the actinides in the tetravalent and hexavalent states. Since their solubility in aqueous phase is reported to be very low, it can be expected that they would be attractive candidates for actinide separations employing extraction chromatography. Various *N*,*N*-dialkyl amides have been synthesized and their extraction behaviour has been studied in our laboratory.[14] In the present study, we have attempted to study the retention behaviour of uranium and thorium and their determination, by HPLC using columns coated with four different amides viz., dihexyl hexanamide (DHHA), dibutyl hexanamide (DBHA), diisooctyl butanamide (DiOBA), and dioctyl hexanamide (DOHA). The amide concentration in the coating solution was varied over a wide range. A similar study was conducted to understand the retention mechanism of uranium and thorium, using a column coated with trihexyl phosphate (THP), another neutral extractant. The influence of mobile phase concentration and its pH on the separation was also investigated. This paper also reports the results of the quantitative determination of micro levels of uranium in thorium matrix.

EXPERIMENTAL

Instrumentation

The liquid chromatographic system consisted of a solvent delivery pump (Jasco PU-1580), UV-VIS spectrophotometric detector (Jasco UV-1570), reverse phase C_{18} column (250 × 4.6 mm, 5 μ, Hypersil), and a post-column delivery system (Jasco PU-1580). Uranium and thorium solutions were injected into the column through a 20 μL sample loop injector (Rheodyne 7725). The post-column reagent was delivered at a flow rate of 1.5 mL/min. The effluent from the HPLC column was mixed with the post-column reagent using a T connector before it reached the detector. The U/Th–arsenazo(III) complexes were monitored at 655 nm. The following columns were also employed: C_{18} column (250 × 4 mm, 5 μ, Merck), C_8 (250 × 4.6 mm, 5 μ, HiQ sil C_8), and C_{18} (100 × 4.6 mm, 5 μ Spherisorb).

Reagents and Procedures

The stock solutions and eluents were prepared in water, which was distilled and purified in a Milli-Q deionizing unit. α-Hydroxy isobutyric acid (Sigma) was used as the eluent. Appropriate amounts of HIBA were dissolved in water and the pH of the solution was adjusted with dilute ammonia. The post-column reagent, Arsenazo(III) (Tokyo-Kasei) was prepared in water (1.5×10^{-4} M) and used as such, throughout the course of this study.

Thorium and uranium stock solutions were prepared from thorium(IV) nitrate and uranyl nitrate, respectively. The solutions of thorium and uranium were standardized by complexometric titration with DTPA and gravimetry (as U_3O_8), respectively.

Synthesis and Characterization of Amides

The amides, DBHA (molecular weight 227), DHHA (283), DiOBA (311), and DOHA (311) were synthesized by reacting corresponding secondary amine with acyl chloride in the presence of triethyl amine in 1 : 1 : 1 molar ratio in dry ether medium at 0°C.[15] The reaction mixture was stirred for 2 hr. The crude reaction mixture was washed by alkali and acid, and was dried over anhydrous sodium sulphate. The product was purified by vacuum distillation and characterised by elemental analysis, IR, ^{1}H NMR, and HPLC. The purity of the amide was determined by non-aqueous potentiometric titration[16] and found to be more than 99%.

Column Preparation

The amides of appropriate concentration were dissolved in methanol–water mixture, in the ratio 60 : 40 or 70 : 30, depending on the amide concentration. For e.g., the solution of 2×10^{-2} M DHHA was prepared in 70 : 30 methanol/water mixture, whereas the solution of 2×10^{-3} M DHHA was prepared in 60 : 40 mixture. It was found, that a clear solution of 2×10^{-2} M DHHA could be prepared only when the methanol content was kept as high as 70% v/v. The THP solutions of 0.5×10^{-3}, 1×10^{-3}, and 2×10^{-3} M concentrations were prepared in methanol–water mixtures (60 : 40 v/v). The solutions used for coating the 250 mm length column were prepared in 500 mL quantity. The coating solutions, mobile phase, and post column reagent solutions were degassed and filtered through 0.5 μm filter prior to use. The coating was carried out at a flow rate of 0.5 mL/min. The 250 mm length columns were pre-equilibrated with about 50 mL of the mobile phase prior to sample injection.

A 100 mm length C_{18} column was packed using reverse phase 5 μ particles. Amides were coated on this column by passing solutions (100 mL) of appropriate concentration at a flow rate of 0.25 mL/min. The column was pre-equilibrated with about 25 mL of the mobile phase prior to sample injection.

All experiments were carried out at room temperature. Each data reported in this paper was obtained, at least, in triplicate.

Estimation of Amide Present in Coated Column

The actual quantity of amides that were coated on to the column was determined in the following manner. The column loaded with the amide was washed with water and the sorbed amide in the column was removed using methanol (60 mL) and an aliquot of the solution was injected into the HPLC system (C_{18} with methanol as mobile phase). The amide was detected and measured at 214 nm. The amide content was determined from a calibration plot, which was obtained by injecting aliquots of standard solutions of amide in methanol.

RESULTS AND DISCUSSION

Reproducibility of the Coated Columns

The reproducible retention behaviour for U and Th on coated columns was confirmed by injecting solutions of U and Th over a period of mobile phase passage. For e.g., capacity factors for thorium and uranium did not vary even after passing several litres of mobile phase through the coated column. The reproducibility of the coating with DHHA (0.02 M) was also confirmed by washing the amide completely from the coated column with methanol, recoating the surface with amide solution, and measuring the retention time. Three independent amide coating/washing runs were performed to confirm the reproducibility of the coating. Reproducible values of capacity factor were obtained for both thorium and uranium.

Influence of Various Amides on the Separation

Figure 1 shows the separation of uranium from thorium using amide-coated columns. Though a solution of about 2×10^{-3} M was used for coating the column, the actual amount sorbed on to the reverse phase support for DOHA, DiOBA, DHHA, was found to be 0.873, 1, and 1.03 mmol, respectively. However, in the case of DBHA, which has a lower hydrophobicity, a 4×10^{-3} M feed solution was used instead to obtain 0.98 mmol sorption. A solution of 0.2 M HIBA (pH 4.25) was used as the mobile phase in these studies. The results in Fig. 1 (A–D) indicate excellent baseline separation for uranium from thorium. The retention for thorium and uranium on these coated columns is similar, even though DHHA coated columns exhibits marginally higher retention for uranium. Since these amide-coated columns exhibited retention behaviour for uranium and thorium with little difference, a complete investigation was carried out only typically with DHHA and DiOBA coated columns.

It is to be noted that all these separations were carried out on the same column, i.e., after the experiments, the amide-coated column was washed with water, amide removed with methanol, and column re-coated with another amide.

Influence of Mobile Phase pH and Concentration on the Retention of Th(IV) and U(VI)

The influence of mobile phase pH and concentration on the retention behaviour of U(VI) and Th(IV) was investigated on the DHHA (0.029 M) coated column. The pH of the HIBA solution (0.2 M) was varied from 2.5 to 4.25 and its concentration was varied from 0.05 to 0.2 M (pH 4). The capacity factors for both Th(IV) and U(VI) were found to increase with increase in pH. For e.g., the capacity factor for thorium increased from 0.22 to 0.53, whereas for uranium it increased from 1.05 to 3.64. The separation

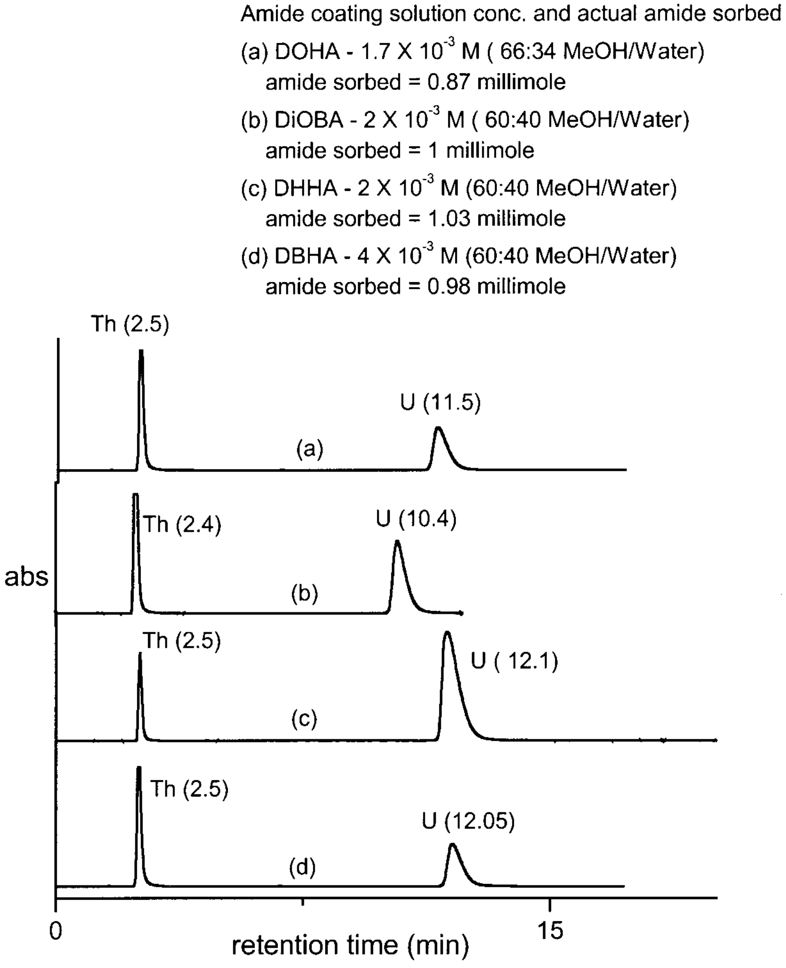

Figure 1. Retention of Th(IV) and U(VI) on amide-coated columns. Column: C_{18} (250 × 4.6 mm, 5 μ, Hypersil). Mobile phase: HIBA (0.2 M, pH 4.25); flow rate: 2 mL/min. Post-column detection: arsenazo(III), 1.5 mL/min, detection: 655 nm.

factor for U/Th (ratio of capacity factors) was found to increase with mobile phase pH. It increased from 4.8 at pH 2.5 to 6.9 at pH 4.25. It would normally be expected that increase of pH would result in a reduction in retention time, because of the enhanced dissociation of complexing reagent leading to a higher extent of complexing of metal ion. The increase in retention with increase in pH is, therefore, surprising. It is to be noted that the retention exhibited by uranium and thorium may not be due to any ion-exchange type of interaction, since lanthanides did not exhibit any retention under similar conditions. When HIBA concentration was varied from 0.05 to 0.2 M, the capacity factor for uranium remained almost constant (3 ± 0.05), and it decreased in the case of thorium (0.61–0.48).

Species Formed During the Complexation of Uranium and Thorium with HIBA

Uranium Species

Uranyl and thorium ions interact with HIBA and form the following complexes:

$$UO_2^{2+} + HIBA \longrightarrow [UO_2(IBA)]^+, [UO_2(IBA)_2], \text{ and } [UO_2(IBA)_3]^-$$

$$Th^{+4} + HIBA \longrightarrow [Th(IBA)]^{+3}, [Th(IBA)_2]^{+2}, [Th(IBA)_3]^+, \text{ and } [Th(IBA)_4]$$

It was reported[4]that complexation of uranyl ion by α-HIBA would result in the species $[UO_2(IBA)]^+$, $[UO_2(IBA)_2]$, and $[UO_2(IBA)_3]^-$ with 15%, 40%, and 45%, respectively, for 0.05 M HIBA at $pH = 4.0$, whereas it is 5%, 30%, and 65% for 0.1 M and <1%, 20%, and 80% for 0.2 M HIBA. In the present study, the capacity factor for uranyl ion was found to increase with the pH of the mobile phase. The species, $[UO_2(IBA)_2]$ also would exist in solution, along with the anionic complex, $[UO_2(IBA)_3]^-$ at pH 2.5. However, the capacity factors obtained under these conditions are lower compared to the one at pH 4.25, where $[UO_2(IBA)_3]^-$ H^+ (or NH_4^+) would be the most predominant species. $[UO_2(IBA)_3]^-$ is always the predominant species, even at low HIBA concentrations, and the same is the case for all the HIBA concentrations (0.05–0.2 M) used in this study. The constant capacity factor obtained under these conditions, indicates that the sorption of the anionic complex is a predominant mechanism. The high affinity exhibited by $[UO_2(IBA)_3]^-$ complex on reverse phase, as well as amide-coated reverse phase support, could be attributed to its high degree of hydrophobicity.

However, the above argument does not preclude the preferential extraction of the species, $UO_2(IBA)_2$ onto the amide-coated support from a mixture of $[UO_2(IBA)]^+$, $[UO_2(IBA)_2]$, and $[UO_2(IBA)_3]^-$. This may affect the equilibrium to result in the generation of more of the neutral complex and its subsequent transfer to the stationary phase. However, further studies are necessary to confirm the nature of species being extracted into the stationary phase.

Thorium Species

The content of the species, $Th(IBA)_4$ is expected to increase when the pH of HIBA solution is varied from 2.5 to 4.25. Increased retention of thorium with mobile phase pH only implies that the complex $Th(IBA)_4$ is the predominantly sorbed species on to the coated support. The species $[Th(IBA)]^{+3}$, $[Th(IBA)_2]^{+2}$, and $[Th(IBA)_3]^{+}$ would be predominant only when HIBA concentrations is below <10 mM, and their relative concentration would be less than 5% for 0.2 M HIBA, whereas $[Th(HIBA)_4]$ is more than 95%.[4]

Early Elution of Thorium with Respect to Uranium

The capacity factors of thorium(IV) are lower compared to U(VI) and thorium elutes prior to uranium from the coated supports. If the sorption mechanism is controlled only by the hydrophobic nature of the complexes, this behaviour is surprising, since $Th(IBA)_4$ and $[UO_2(IBA)_3]^-$ are the dominant Th– and U–HIBA complexes, respectively. The complex $Th(IBA)_4$ is expected to be equally or more hydrophobic than uranium–HIBA complex, $[UO_2(IBA)_3]^-$, and should exhibit affinity similar to that of uranium complex onto the stationary phase. Thus, the hydrophobicity of the complexes is not perhaps the only factor influencing the retention behaviour. In fact, there was a significant increase in retention for both uranium and thorium when the bare support column C_{18} was changed from Hypersil to Merck make (Fig. 2). Similarly, there was a considerable increase in retention for both uranium and thorium on the C_8 support compared to C_{18} support (Fig. 2). If hydrophobicity of the complexes alone decides their retention, there would not be a significant change in their retention on these supports.

Role of Amide Coating: Reduction in C_{18} Surface

During the studies on the effect of amide concentration in coating solution on retention of uranium and thorium, we observed that coating with higher quantities of amide resulted in shorter retention times for both uranium and thorium. The separation of uranium and thorium was initially studied on a column coated with DHHA (0.002 M). α-HIBA (0.2 M, pH = 4.25) was used as the eluent. The separation was completed in about 13 min (Fig. 3). Subsequently, a column coated using 0.02 M DHHA and another coated using 0.029 M DHHA were studied for separation behaviour. U and Th could be separated from each other within 8 min using 0.02 M coated column, and the separation time was about 5 min with 0.029 M coated

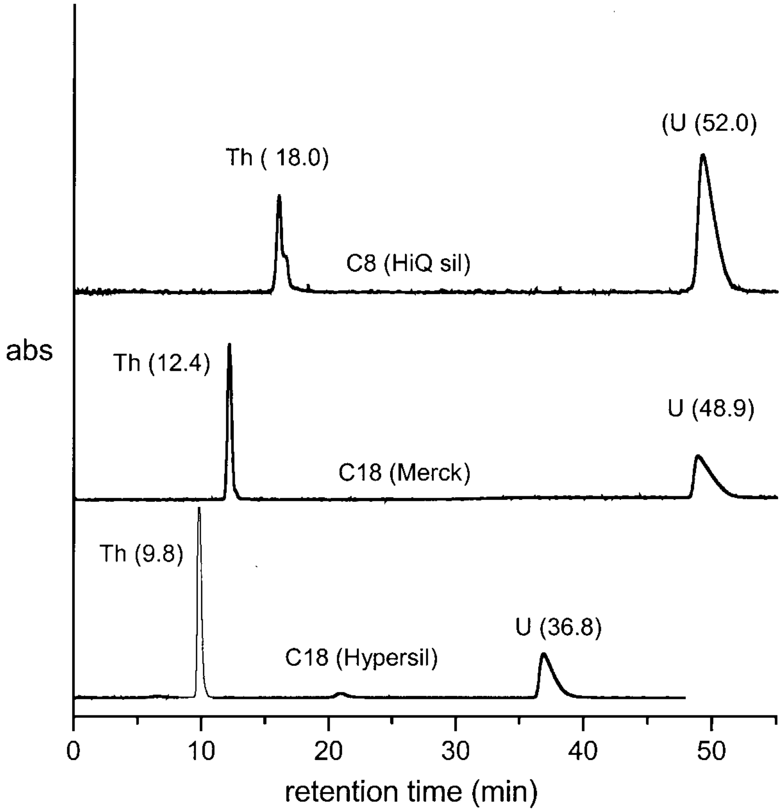

Figure 2. Comparison of U(VI) and Th(IV) retention on reverse phase supports. Mobile phase: HIBA (0.2 M, pH 4.25); flow rate: 2 mL/min. Column: (a) C_{18} (250 × 4.6 mm, 5 μ, Hypersil), (b) C_{18} (250 × 4 mm, 5 μ, Merck), (c) C_8 (250 × 4.6 mm, 5 μ particle, HiQ sil).

column. This is a surprising observation, since it would be normally expected that increasing the amide content on the "inert" support would lead to increased extraction of the metal ion resulting in higher retention times. A decrease in retention times for both thorium and uranium on the amide coated column compared to the bare C_{18} surface, can be explained only if it is assumed that the column support is not actually "inert", and in fact, plays a predominant role in the extraction. It can then be explained that with decrease in the "uncovered" surface area of the support due to the coating of the amide, the retention time decreases with increase in extent of coating. It can be argued, that if the role of the extractant was only to cover

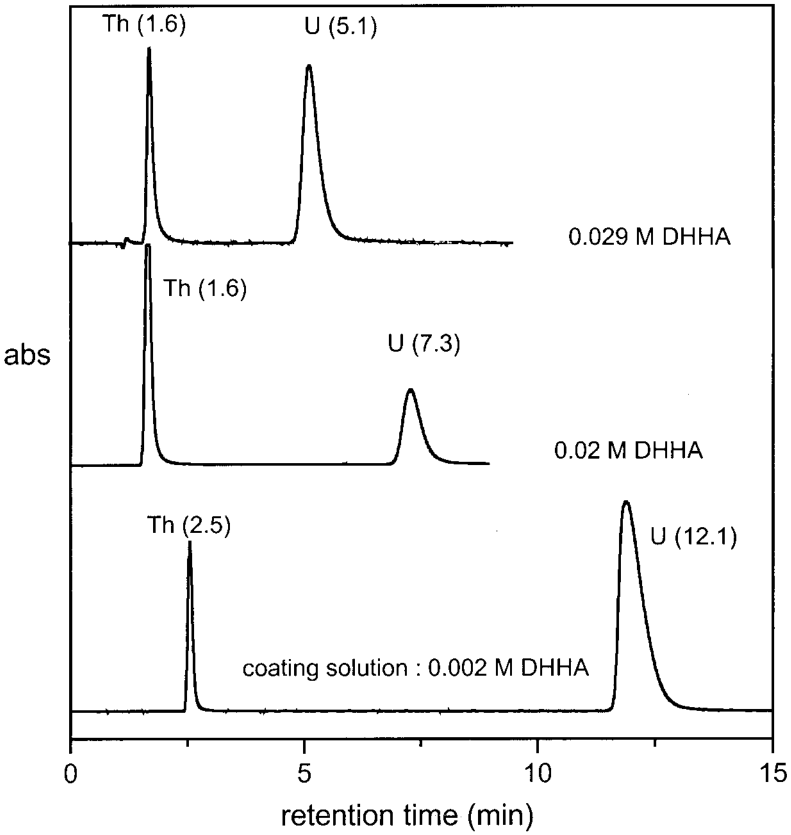

Figure 3. Variation in retention of Th(IV) and U(VI) as a function of DHHA concentration. Column: C_{18} (250 × 4.6 mm, 5 μ, Hypersil) coated with DHHA. Mobile phase: HIBA (0.2 M, pH 4.25), flow rate: 2 mL/min.

the C_{18} surface, other neutral extractants coated on C_{18} also should exhibit similar behaviour. To test this hypothesis, the separation was investigated on a C_{18} surface coated with a different neutral ligand, THP.

Studies with THP Coated Column

Figure 4 demonstrates the separation of uranium from thorium, from the THP coated support. The separation could be completed in about 13 min for the 0.5×10^{-3} M THP column, whereas it was about 10 and 7 min for

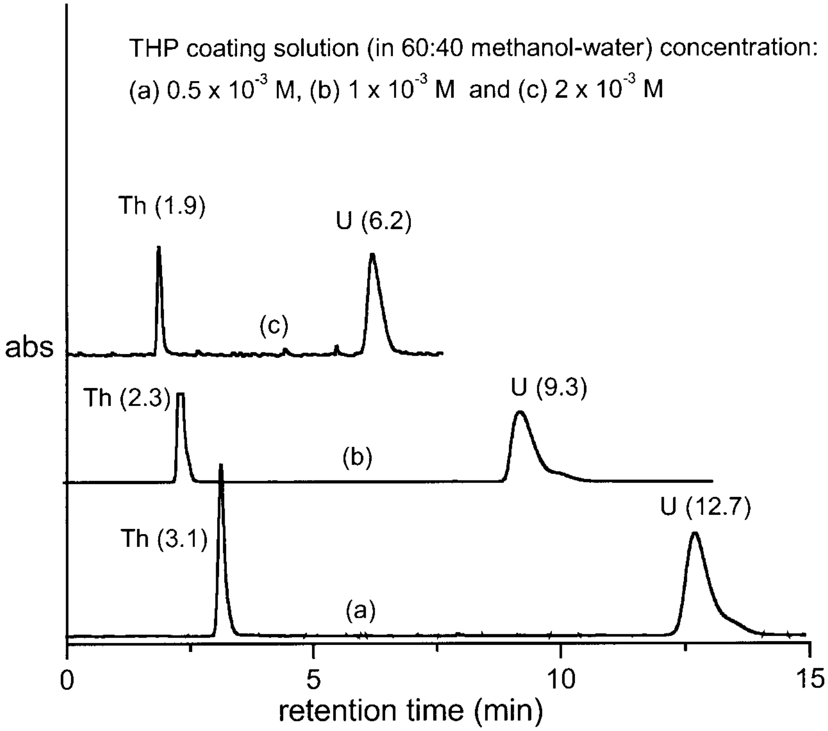

Figure 4. Retention behaviour of U(VI) and Th(IV) on THP coated reverse phase column. Column: C_{18} (250 × 4.6 mm, 5 μ Hypersil). Mobile phase: HIBA (0.2 M, pH = 3.75); flow rate: 2 mL/min. Column coated with (a) 0.5×10^{-3} M, (b) 1×10^{-3} M, and (c) 2×10^{-3} M THP solutions (THP solution in methanol–water, 60 : 40).

the 1×10^{-3} and 2×10^{-3} M coated columns, respectively. Higher amounts of THP coated on to the column leads to reduced retention times for uranium as well as thorium, a trend similar to that observed with amide-coated surfaces.

Separation on Amide-Coated C_8 Support

The retention for U(VI) and Th(IV) on the C_8 column was higher than that of C_{18} when HIBA (0.2 M, pH 4.25) was used as the eluent (Fig. 2). The retentions for both U and Th were found to increase when the pH of HIBA was varied from 3 to 4.5. Subsequently, DiOBA (2×10^{-3} M) was coated on the C_8 column and examined for its retention of U and Th (Fig. 5). There was a reduction in retention times for both species compared to the uncoated support. The retention for U and Th gradually decreased with increased amide coating on the coated column. The separation and retention behaviour was similar to the one obtained with the C_{18} support.

The above experimental results suggest that the role of the neutral extractant, in the range of coating conditions used, is mainly the reduction of C_{18} surface available for adsorption. A higher retention time for uranium and thorium on the amide-coated column compared to the bare support, can be expected only when the coated amide plays some role on the separation, other than merely covering the C_{18} surface. This can be experimented by coating with larger quantities of amide to eliminate the retention contribution from C_{18}. To confirm this hypothesis, the retention of uranium and thorium

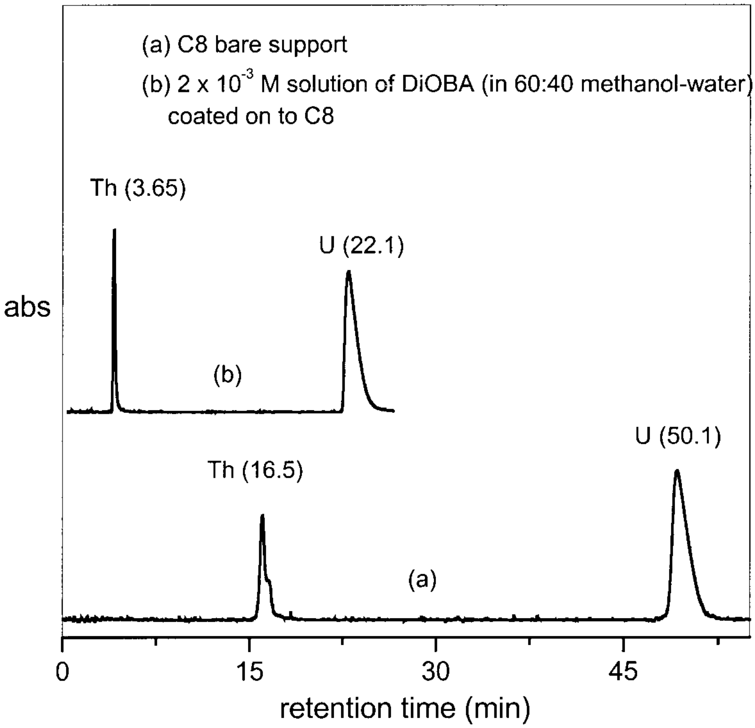

Figure 5. Retention of Th(IV) and U(VI) on (a) C_8 (250 × 4.6 mm, 5 μ) and (b) DiOBA coated on to C_8 (0.002 M in methanol–water 60 : 40). Mobile phase: HIBA (0.2 M, pH 4.25); flow rate: 2 mL/min.

were investigated by coating larger quantities of amide. This could be carried out easily on a shorter column length. Hence the retention behaviour of uranium and thorium at high amide loadings was investigated using 100 mm length column coated with amide.

Studies with DiOBA Coated 10 cm Column

Solutions of DiOBA with concentrations ranging from 8×10^{-4} to 1.29×10^{-2} M were passed and coated onto the 10 cm column. Figure 6 demonstrates the influence of amide on the retention of Th and U. The retention for both U and Th on the coated columns (Fig. 6a and b) were less compared to the uncoated column, a trend similar to one observed with 250 mm column. However, when the amide concentration in the coating solution was raised to 3.2×10^{-3} M, the retention time for U was comparable to that of uncoated column (Fig. 6c). When the coating solution concentration was further raised to 6.4×10^{-3} M, the retention time for uranium increased to 15.2 min compared to 9.8 min with the uncoated column (Fig. 6d). At a coating solution concentration of as high as 12.9×10^{-3} M, the retention for uranium was about 3.75 times higher compared to that of plain support (Fig. 6e).

Another interesting feature of the above chromatograms, is the retention behaviour of thorium. For e.g., the retention time for uranium is higher than that obtained with uncoated column, but that of thorium is still less compared to that of uncoated column (Fig. 6d). This clearly implies that under these experimental conditions amide extracts uranium preferentially over thorium. The trend continued when the coating solution concentration was raised to 12.9×10^{-3} M, i.e., retention for thorium was only about 1.5 times compared to that of uncoated column, whereas it was about 3.75 times for the uranium. The relative retentions of uranium and thorium species are also graphically represented in Fig. 7.

Comparison with Literature Data

Barkley et al.[1] earlier reported separation of U from Th on a C_{18} and PRP column employing HIBA as the eluent. They reported that the addition of organic solvent to HIBA decreased retention times of U(VI) and Th(IV). They also reported that increase in HIBA concentration had only a moderate effect on the retention of uranium and thorium; however, decrease in pH caused large reduction in retention time. The results obtained from the present studies on amide-coated columns also showed a similar trend in retention behaviour, i.e., fall in capacity factor for both U and Th when pH

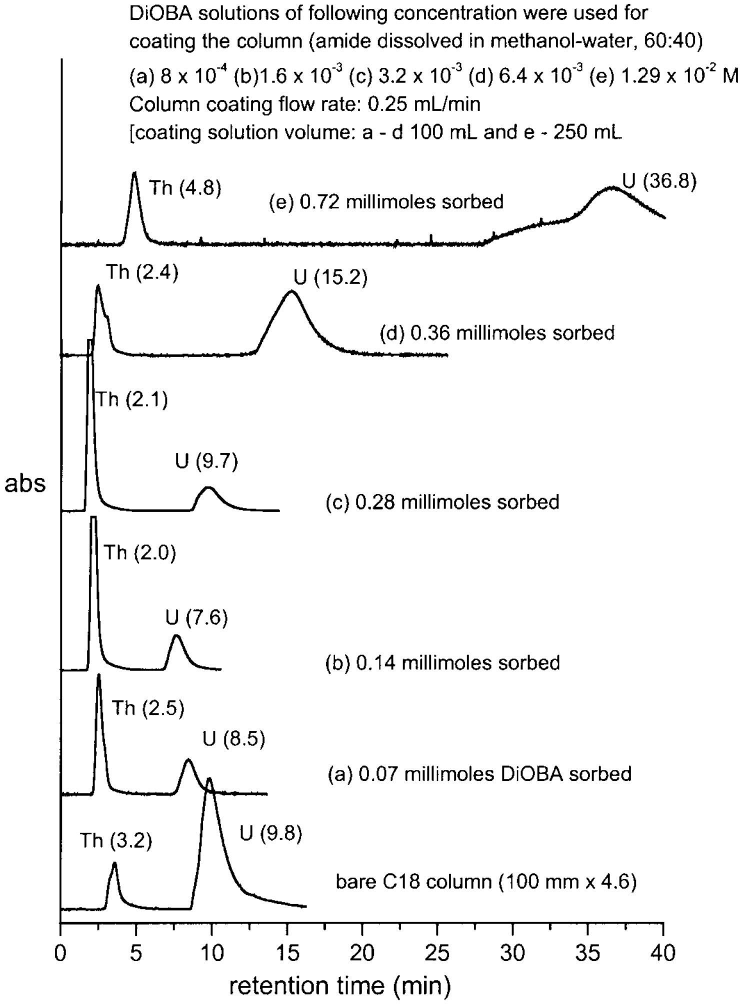

Figure 6. Elution behaviour of U(VI) and Th(IV) on DiOBA coated reverse phase column (100 × 4.6 mm dia, 5 μ). Mobile phase: HIBA (0.2 M, pH 3.50); flow rate: 2 mL/min.

was changed from 4.25 to 2.5. Similarly, the concentration of HIBA did not significantly influence the retention of uranium.

Fuping et al.[4] examined in detail the retention behaviour of uranium and thorium on C_{18} using HIBA. It was found that when the percentage of methanol in the mobile phase was varied, both thorium(IV) and uranyl complexes

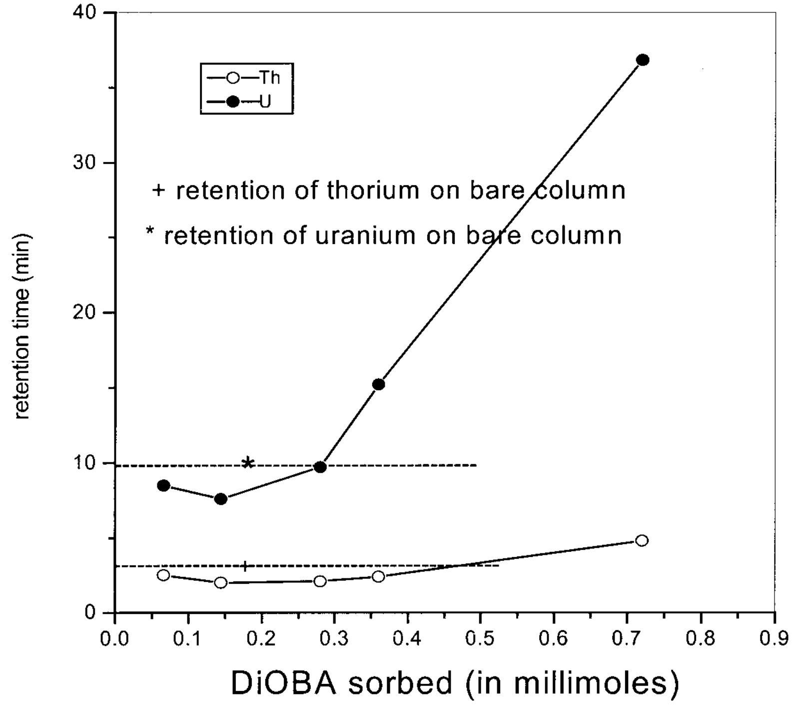

Figure 7. Relative retention of Th(IV) and U(VI) on DiOBA coated column. Experimental conditions as in Fig. 6.

exhibited reversed-phase behaviour. They reported that the U– and Th–HIBA complexes were retained on the reverse phase column predominantly by a hydrophobic adsorption mechanism, despite the complexes being anionic under most conditions studied.

Quantitative Determination

A column coated using 2.87×10^{-2} M DHHA with α-HIBA (0.2 M, pH 2.5) was used for the rapid separation of uranium and thorium. The separation could be completed in less than 3 min (Fig. 8) and resulted in good baseline separation with excellent peak profiles. This system can be employed for separation and determination of uranium and thorium when they are in comparable levels.

However, for the separation and quantitative analysis of uranium in the presence of large quantities of thorium, a reverse phase column coated with

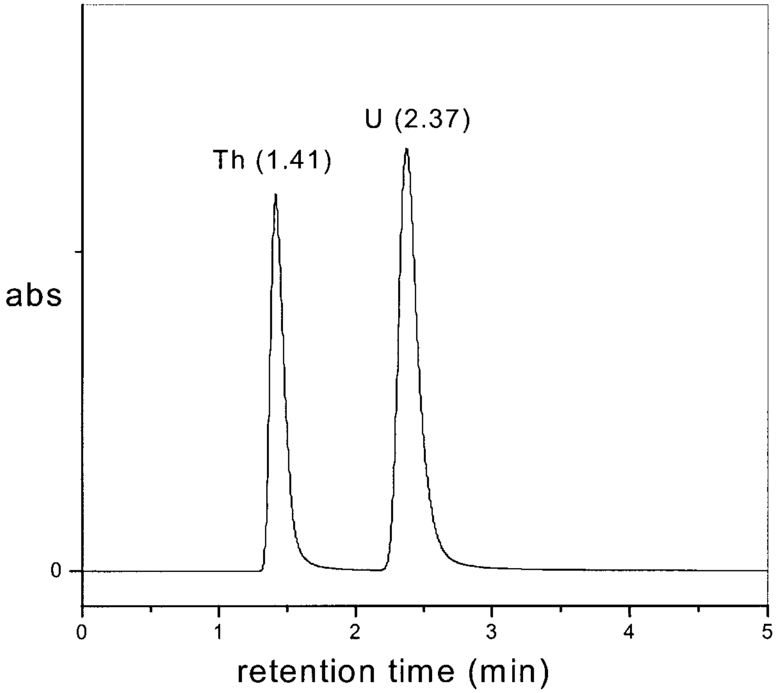

Figure 8. Rapid separation of Th(IV) and U(VI) using DHHA coated column. Column: C_{18} (250 × 4.6 mm, 5 μ Hypersil) coated with 0.0287 M DHHA. Mobile phase: HIBA (0.2 M, pH 2.5), flow rate: 2 mL/min, PCR: arsenazo(III), 1.5 mL/min, detection: 655 nm. Sample:U(VI), 85 μg/mL and Th(IV), 50 μg/mL, 20 μL sample injected.

0.02 M DHHA was used with α-HIBA (0.2 M, pH = 4.25) as the mobile phase. Though the separation time was higher, i.e., about 7.5 min (Fig. 3), compared to the one obtained in Fig. 8, this experimental condition was chosen to provide well resolved uranium peaks from thorium when large quantities of the latter would be injected into the HPLC system, i.e., when U/Th ratios are more than 1 : 100.

Individual Calibration

Initially, uranium (10–1000 μg/mL) and thorium (10–1000 μg/mL) samples were separately injected for preparing the calibration plots. A linear calibration plot was obtained for uranium ($r^2 = 0.999$) (Fig. 9). A uranium solution with a concentration of 5 μg/mL also gave a detectable

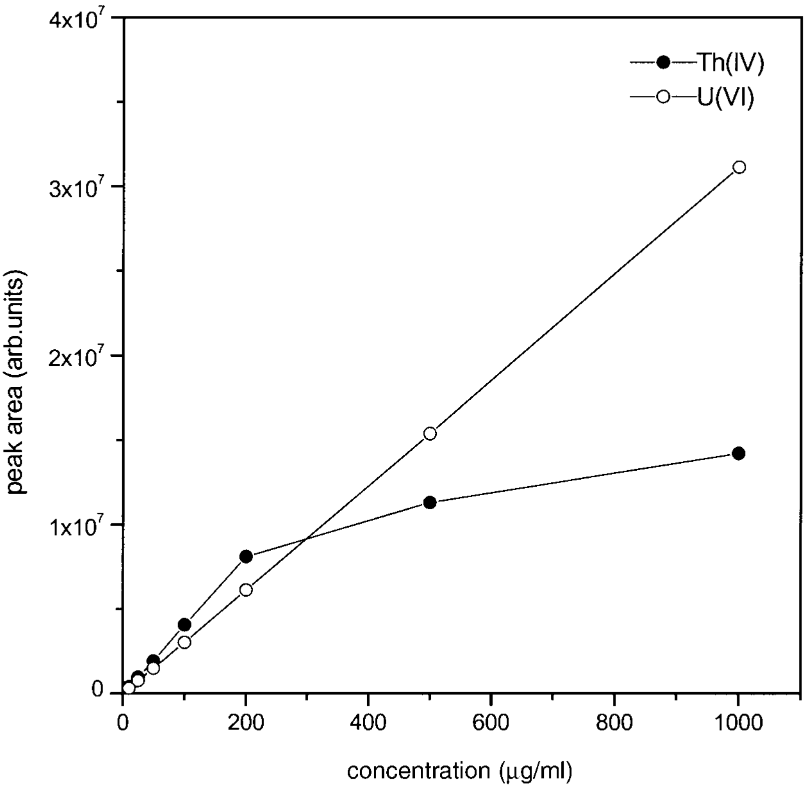

Figure 9. Calibration plots for Th(IV) [10–1000 μg/mL] and U(VI) [10–1000 μg/mL]. Column: C_{18} (250 × 4.6 mm, 5 μ Hypersil) coated with 0.02 M DHHA. Mobile phase: HIBA (0.2 M, pH 4.25); flow rate 2 mL/min, PCR detection: arsenazo(III), 1.5 mL/min, 655 nm. Sample volume injected: 20 μL.

peak, though this peak could not be used for calibration. In the case of thorium, linearity was observed only up to 200 μg/mL ($r^2 = 0.999$, for the range 10–200 μg/mL) (Fig. 9). The concentration of the post-column complexing reagent, arsenazo-III was subsequently increased from 1.5×10^{-4} to 3×10^{-4} and further to 6×10^{-4} M to provide excess post-column reagent to ensure complete complexation of the metal ion. Even under these conditions, linearity for thorium was observed in the range of 10–200 μg/mL as earlier, and deviation was observed beyond this range. This deviation, perhaps is due to a change in the stoichiometry of the Th(IV)–Arsenazo complex at high thorium concentrations.

Determination of Trace Levels of Uranium in the Presence of Bulk Thorium

In this study, the concentration of uranium was varied from 10 to 1000 μg/mL and thorium concentration was kept constant at 10 mg/mL. Smaller quantities of uranium (10 μg/mL) can be determined in the presence of thorium (10 mg/mL), i.e., 1000 times by this method ($r^2 = 0.999$). Studies were also carried out to prepare a calibration curve for uranium (10–1000 μg/mL) in the presence of higher thorium content (20 mg/mL). The correlation coefficient r^2 value was, however, found to be only 0.980 deviation from linearity observed when uranium concentration exceeds beyond 200 μg/mL.

Experiments were also carried out to study the peak profiles of uranium in the presence of large concentrations of thorium (100 mg/mL) (Fig. 10). It is clearly evident from the figure that the quantification of uranium was not

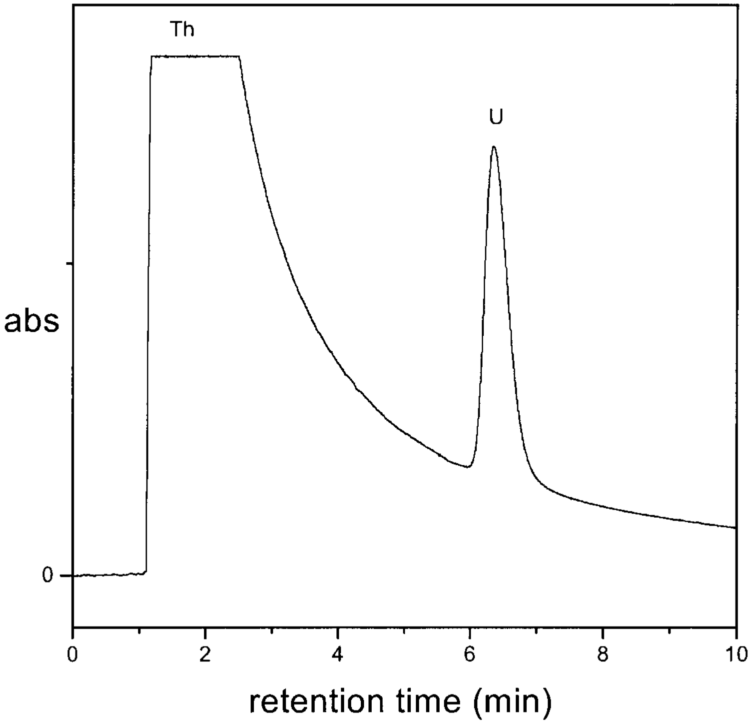

Figure 10. Separation of U(VI) (500 μg/mL) from Th(IV) (100 mg/mL). Column: C_{18} (250 × 4.6 mm, 5 μ Hypersil) coated with DHHA (0.02 M). Mobile Phase: HIBA (0.2 M, pH 4.25); flow rate: 2 mL/min. Sample volume injected: 20 μL.

directly possible due to thorium tailing into the uranium peak. However, the uranium fraction can be re-injected for isolation (recovery) and quantification purpose.

Application to Real Samples

An attempt was made to validate this technique by analysing uranium in thorium. For this study, standard samples of uranium in thorium were prepared in which uranium content was determined by Br-PADAP based spectrophotometric method,[11] and thorium by complexometric titration with DTPA. The results are given Table. 1. The uranium content measured by both techniques agreed within 1–2%. These results show that this method can be used for the analysis of samples containing uranium and thorium with a ratio of up to 1 : 1000.

Determination of Uranium in the Presence of Rare Earths and Thorium in Simulated Monazite Leach Liquor

Since the DHHA coated column offered high-resolution separations for uranium from thorium, an attempt was also made to determine uranium in a solution, simulating the composition of monazite leach liquor. A DHHA coated column was used for the separation. A solution containing lanthanides (total, 18 mg/mL), thorium (2.7 mg/mL), and uranium (87 μg/mL) was prepared and injected into the HPLC system. The separation is shown in Fig. 11. Uranium concentration could be determined within ±2%.

Table 1. Determination of uranium.

Sample number	Uranium taken (μg/mL)[a]	Thorium content (mg/mL)	Uranium found by HPLC (μg/mL)[b]
1	10.0	10	10.1
2	25.0	10	25.3
3	87.0	10	88.0
4	250.0	10	247.0
5	25	20	25.6
6	240.0	20	229.0

[a] Analysed by Br-PADAP method.

[b] Experimental condition as in Fig. 10; values given are average of three independent injections.

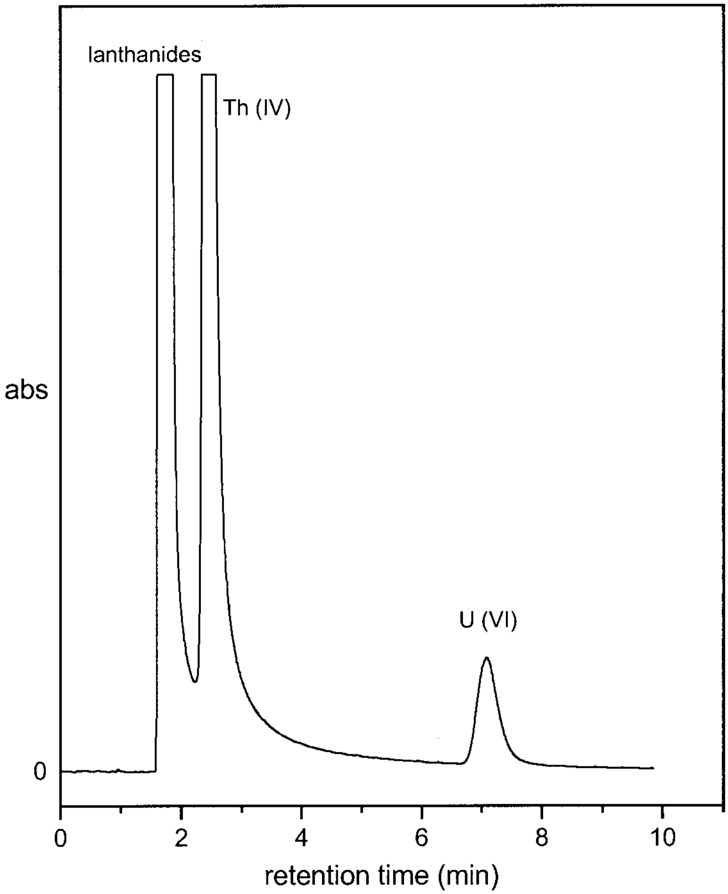

Figure 11. Separation and determination of uranium in the presence of lanthanides and thorium. Column: C_{18} (250 × 4.6 mm, Hypersil) coated with 2×10^{-2} M DHHA. Mobile phase: HIBA (0.1M, pH 3.50); flow rate: 1.5 mL/min. Sample: uranium (87 μg/mL), thorium (2.7 mg/mL), and lanthanides (18 mg/mL), volume injected: 20 μL.

CONCLUSIONS

Uranium and thorium can be separated from each other by using reverse phase columns modified with *N*,*N*-dialkyl amides. The coated columns gave excellent baseline separation for uranium from thorium. The separation on shorter columns with larger amide coating showed interesting retention behaviour, amide (DiOBA) exhibiting stronger retention for uranium over thorium. Uranium could be accurately estimated in the presence of about 1000 times of thorium. The amide content on the coated column can be varied and the analysis period can be modified conveniently as per the requirement, e.g., when both uranium and thorium are present in comparable levels, a column coated with 0.03 M DHHA could be used with HIBA (0.2M, pH 2.5), since the separation and determination of uranium could be completed well within 3 min. However, when thorium is present in large quantities, i.e., when Th/U ratios exceeds above 100, a column coated with 0.02 M DHHA can be employed. Typically, milligram quantities of amide are required to modify the column and the coated columns are stable for long periods, e.g., several hundreds of samples were injected in a single coated column. The coated support exhibits potential to recover uranium from large quantities of thorium. The variation of the retention for uranium and thorium with loading of amide on the C_{18} surface presents interesting behaviour, with a scope for further investigation.

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