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Studies on the retention behaviour of α -hydroxyisobutyric acid complexes of thorium(IV) and uranyl ion in reversed-phase high-performance liquid chromatography

Hao Fuping and Paul R. Haddad*

Department of Chemistry, University of Tasmania, G.P.O. Box 252C, Hobart, Tasmania 7001 (Australia)

Peter E. Jackson and Joe Carnevale

Millipore Australia, Waters Chromatography Division, Private Bag 18, Lane Cove, N.S.W. 2066 (Australia)

ABSTRACT

The retention behaviour of complexes of thorium(IV) and uranyl ion with α -hydroxyisobutyric acid (HIBA) on a C_{18} reversed-phase column is investigated. Using a mobile phase comprising 400 mM HIBA at pH 4.0 in 10:90 (v/v) methanol–water, the thorium(IV) peak was eluted before the uranyl peak, despite the fact that calculations based on formation constants suggested that the thorium(IV) was present as the neutral tetra(HIBA) complex, whilst uranyl was present as the anionic tris(HIBA) complex. Hydrolysis of the thorium(IV) complex (with subsequent inclusion of hydroxyl in the coordination sphere of the metal ion and formation of an overall negative charge) is proposed as a likely explanation for the early elution of this complex. When the percentage of methanol in the mobile phase was varied, both thorium(IV) and uranyl complexes exhibited reversed-phase behaviour. The retention times of both complexes decreased when the concentration of HIBA in the mobile phase was increased over the range 50–600 mM, despite the fact that increased complexation should be favoured. This effect was attributed to competition for the adsorption sites on the stationary phase by neutral, protonated HIBA in the mobile phase. A retention mechanism based on hydrophobic adsorption (rather than cation-exchange) is suggested.

INTRODUCTION

Ion-interaction chromatography using dynamically coated columns has been applied widely to the separation of lanthanides [1–3]. In this method, a C_{18} column is generally used and is coated with sodium *n*-octanesulphonate (OSA) as the ion-interaction reagent (IIR) to convert it into a dynamically coated cation-exchange column. A suitable ligand, usually α -hydroxyisobutyric acid (HIBA), is added to the mobile phase and serves the purpose of reducing the effective charge on the injected metal ions and so enabling them to be eluted within a reasonable time. Detection has generally been per-

formed by spectrophotometry after post-column reaction with a suitable dye, usually 3,6-bis[(*o*-arsenophenyl)azo]-4,5-dihydroxy-2,7-naphthalenedisulfonic acid (Arsenazo III) or 4-(2-pyridylazo)resorcinol (PAR). The advantage of ion-interaction chromatography is the ease with which the column ion-exchange capacity and selectivity can be altered. Several studies have confirmed that the lanthanide ions are separated predominantly by a cation-exchange mechanism with retention being moderated by the complexing effects of the eluent ligand. Gradient elution may be effected in these systems by progressively increasing the concentration of HIBA in the mobile phase [1].

In the course of these studies it has been noted that thorium(IV) and uranium(VI) (as uranyl ion) were eluted in the early part of the chromatogram

* Corresponding author.

and showed similar retention times to some of the lanthanides. However, when eluent parameters were varied, the behaviour of thorium(IV) and uranyl showed some differences to that of the lanthanides, suggesting that a different retention mechanism could be operating. Thorium(IV) and uranyl could either be eluted amongst the lanthanides or after them by varying the OSA concentration in the mobile phase. Retention of thorium(IV) and uranyl as HIBA complexes on a C_{18} column was then demonstrated without the presence of an anionic IIR (such as OSA) in the mobile phase and this effect was used subsequently as a means to preconcentrate these species [4,5]. When the eluent ligand was changed to mandelic acid, thorium(IV) and uranyl showed greater retention than the lanthanides and again could be retained without the use of an anionic IIR in the mobile phase [6].

Whilst some of the factors influencing retention of HIBA complexes of thorium(IV) and uranyl have been reported, the mechanism of their retention on a reversed-phase column remains unclear. In the present study we have examined in detail the factors which affect retention and have related the trends observed to the nature of the complexes which exist under the chromatographic conditions used. A coherent retention mechanism is then described and used to derive chromatographic conditions suitable for the determination of thorium(IV) and uranyl using a solid-phase preconcentration procedure.

EXPERIMENTAL

Instrumentation

The HPLC system consisted of a Millipore–Waters (Milford, MA, USA) Model 590 programmable pump, a Model U6K injector and a Model 481 UV–Vis spectrophotometric detector coupled to a Waters 820 chromatography data station. The detector was operated at 658 nm. The analytical column was a Waters μ Bondapak C_{18} reversed-phase column (300×3.9 mm I.D.), fitted with a C_{18} guard column housed in a Waters Guard-Pak pre-column module. The post-column reagent solution was delivered with a Waters reagent delivery module.

Reagents and procedures

The mobile phase was prepared using HIBA (Sigma, St. Louis, MO, USA), HPLC-grade methanol (Millipore–Waters) and water treated with a Millipore (Bedford, MA, USA) Milli-Q water purification system. The most commonly used mobile phase comprised 400 mM HIBA and 10% methanol, adjusted to pH 4.0 with sodium hydroxide. The post-column reagent solution contained 0.13 mM Arsenazo III (BDH Laboratory Chemical Division, UK), 10 mM urea (May & Baker, Dagenham, UK) and 62 mM acetic acid in Milli-Q water. Both the mobile phase and the post-column reagent solution were filtered through a Millipore 0.45- μ m membrane and degassed in a ultrasonic bath prior to use.

Thorium and uranium standards were prepared from thorium(IV) nitrate (May & Baker) and uranyl nitrate (Ajax Chemicals, Sydney, Australia), respectively. Stock solutions of 1000 mg/l were prepared initially and were further diluted as required.

The column was re-equilibrated with each new mobile phase for at least 20 min prior to injections being made. All experiments were carried out at room temperature, except in the studies on the effect of temperature on retention, in which case a Waters temperature control module was used. Each data point throughout this research was obtained at least in duplicate.

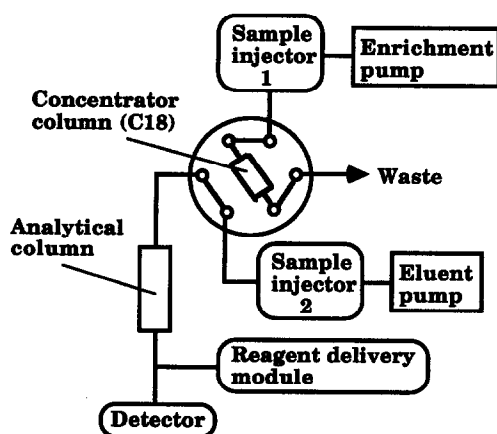


Fig 1. Schematic representation of the preconcentration system used. Note that two injectors were used so that samples could be applied either by direct injection (injector 2) or using preconcentration (injector 1).

Preconcentration studies

For the preconcentration procedure the apparatus was configured as shown in Fig. 1, in which a six-port high-pressure switching valve was added between the injector and the analytical column. The sample was prepared in 20 mM HIBA solution at pH 4.0 and a 1.0-ml portion was loaded into injector 1 (which was fitted with a 2-ml loop) and pumped through a Waters μ Bondapak C_{18} guard column, using 40 mM acetic acid (pH 4.0) as the driving solvent, using the enrichment pump. The valve was then rotated and the adsorbed complexes back-flushed onto the analytical column using the normal eluent. The switching sequence used to control the valves was performed through the Waters 820 chromatography data station. Direct injection of samples was possible using sample injector 2 in Fig. 1.

RESULTS AND DISCUSSION

Selection of eluent ligand

Polyvalent cations, such as UO_2^{2+} and Th^{4+} , are not suited to direct cation-exchange methods because the magnitude of the electrostatic interaction of these species with the functional groups on the ion exchanger is such that these cations are very strongly retained. They are best separated chromatographically as complexes with a suitable ligand and these complexes can be formed either prior to the separation step or *in situ* by adding the ligand to the mobile phase. In general, the latter approach is the more convenient and was pursued in this work.

Thorium(IV) and uranyl are known to form complexes with a wide range of ligands, with the most stable complexes being with hydroxycarboxylic

TABLE I

OVERALL FORMATION CONSTANTS FOR THORIUM-(IV) AND URANYL COMPLEXES WITH HIBA IN AQUEOUS SOLUTION

Measured in 1 M $NaClO_4$ at 20°C. Data from refs. 7 and 8.

Species	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
Thorium(IV)	4.43	8.15	11.06	13.60
Uranyl	3.18	5.13	6.67	—

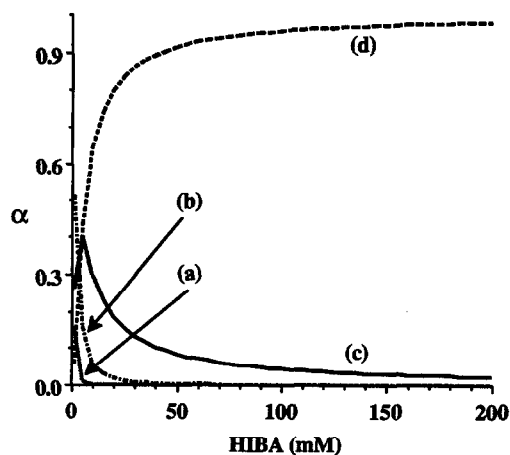


Fig. 2. Fraction (α) of each thorium(IV)-HIBA complex present at various concentrations of HIBA at pH 4.0. (a) $Th(HIBA)^{3+}$; (b) $Th(HIBA)_2^{2+}$; (c) $Th(HIBA)_3^+$; (d) $Th(HIBA)_4$. Calculated using the formation constants given in Table I.

acids, such as glycolic, mandelic, lactic and hydroxybutyric acids [7]. The overall formation constants observed for HIBA are amongst the highest and are given in Table I. The distribution of the various complexes of HIBA with thorium(IV) and uranyl as a function of HIBA concentration in the range 0–200 mM is given in Figs. 2 and 3, respectively. These distributions were calculated using a pH of 4.0, at which point the HIBA ($pK_a = 3.77$) is 63% ionised.

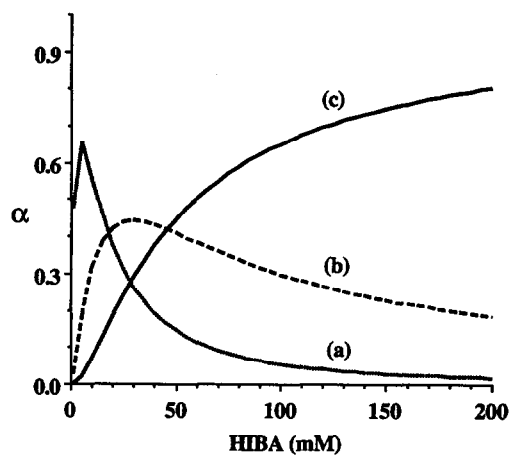


Fig. 3. Fraction (α) of each uranyl-HIBA complex present at various concentrations of HIBA at pH 4.0. (a) $UO_2(HIBA)^+$; (b) $UO_2(HIBA)_2^-$; (c) $UO_2(HIBA)_3^-$. Calculated using the formation constants given in Table I.

This pH was chosen because it is near to that of the maximum buffer capacity for HIBA. These figures may be used to select experimental conditions under which only one type of complex with each metal ion is present in solution so that the resultant chromatography can be simplified. Fig. 2 shows that the tetra(HIBA) complex of thorium(IV) dominates at most HIBA concentrations. This species does not become the sole complex present until the HIBA concentration reaches at least 400 mM (not shown in Fig. 2). On the other hand Fig. 3 shows that the distribution of HIBA complexes with uranyl varies markedly with HIBA concentration. Even at 400 mM HIBA, the uranyl ion is distributed chiefly as the tris(HIBA) complex (89.4%) and the bis(HIBA) complex (10.1%). If thorium(IV) and uranyl were injected into a 400 mM HIBA solution buffered at pH 4.0, it would therefore be expected that the thorium would be present solely as the tetra(HIBA) complex, whilst the uranyl would be present predominantly as the tris(HIBA) complex. Since HIBA can be expected to be present in its deprotonated form in metal complexes, the thorium complex should be neutral, whilst the uranyl complex should be anionic.

Selection of a suitable chromatographic method can be based on these predictions, and reversed-phase chromatography should be appropriate for thorium and anion-exchange chromatography (or ion-interaction chromatography using a cationic IIR) for uranyl. When reversed-phase chromatography was examined using a C₁₈ column with a mobile phase comprising 10% methanol and 400 mM HIBA at pH 4, the chromatogram shown in Fig. 4 resulted. The observed elution order was opposite to that expected from Figs. 2 and 3 in that the uranyl complex [presumed to be anionic and containing fewer ligand molecules than the thorium(IV) complex] was the more strongly retained. Further studies were therefore undertaken to determine the factors affecting retention and to elucidate the retention mechanism.

Factors affecting retention

The influence of the percentage of organic modifier in the mobile phase is shown in Fig. 5, using methanol as the modifier. Retention changes were measured over the range 0–20% methanol at 400 mM HIBA for both thorium(IV) and uranyl, and at

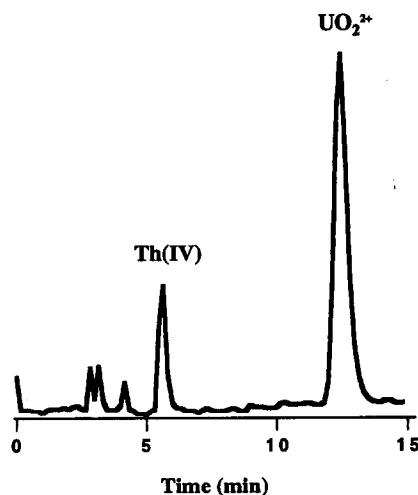


Fig. 4. Chromatogram of thorium(IV) (1.0 ppm) and uranyl (4.0 mg/l). Conditions: Waters μ Bondapak C₁₈ column, mobile phase of 400 mM HIBA at pH 4.0 in 10:90 (v/v) methanol–water at a flow-rate of 1 ml/min. Detection by absorbance at 658 nm after post-column reaction with Arsenazo III.

20 mM HIBA for thorium(IV). For comparison, the retention of a neutral reference compound (in this case, phenol) was also measured and is included in Fig. 5. In all cases, linear plots of $\log k'$ versus the percentage of methanol were obtained, indicating that these solutes were being retained by a reversed-phase mechanism. It will be noted that this conclusion applies for the thorium(IV) complex even when

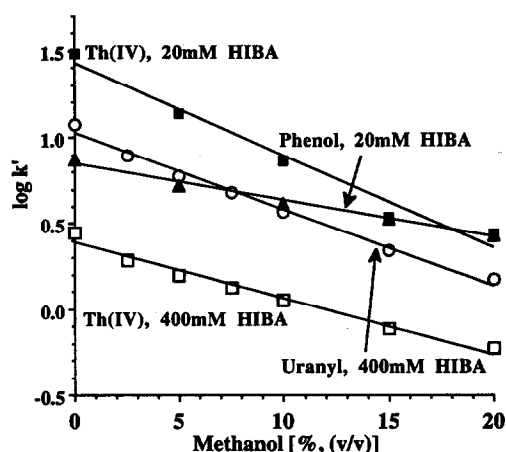


Fig. 5. Effect on retention of varying percentages of methanol in the mobile phase. With the exception of the methanol concentration, chromatographic conditions were as for Fig. 4.

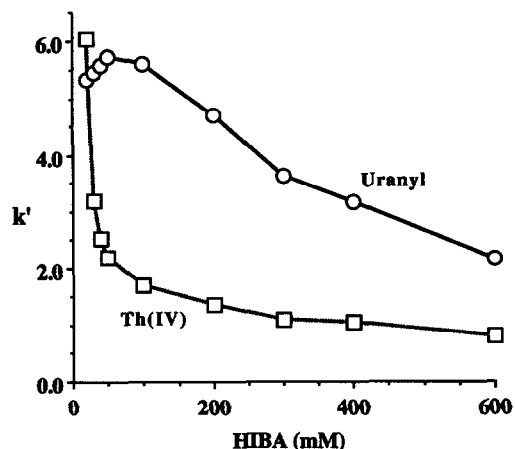


Fig. 6. Dependence of capacity factors for thorium(IV) and uranyl on the concentration of HIBA in the mobile phase. With the exception of the HIBA concentration, chromatographic conditions were as for Fig. 4.

the HIBA concentration is as low as 20 mM. Results similar to those shown for methanol were also obtained using acetonitrile (over the range 0–15%) as the organic modifier.

The effect of the concentration of HIBA on retention is shown in Fig. 6, which indicates that the capacity factors for both thorium(IV) and uranyl decreased overall with increasing HIBA concentration, with the most rapid changes being observed for thorium(IV) at HIBA concentrations of less than 50 mM. It should be possible to compare these

TABLE II
EFFECTS OF MOBILE PHASE pH ON RETENTION

The mobile phase comprised 50 mM HIBA (pH 4.0) and 20% methanol. The retention time of phenol was unaltered over the pH range studied.

pH	Retention time (min)	
	Thorium(IV)	Uranyl
2.5	4.5	4.1
3.0	4.9	5.3
3.5	5.2	6.7
4.0	5.9	9.5
4.5	8.8	16.0

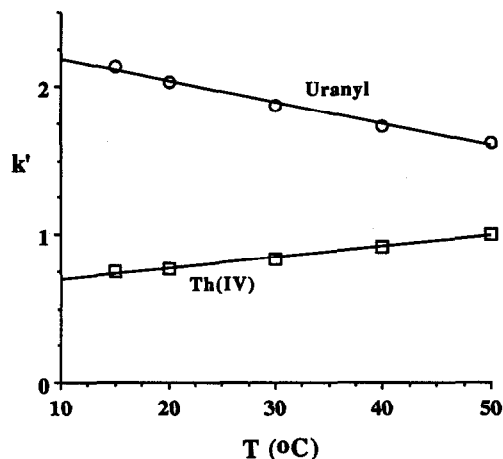


Fig. 7. Effect of temperature on capacity factors of thorium(IV) and uranyl. With the exception of the temperature, chromatographic conditions were as for Fig. 3.

observations with the predicted forms of the metals complexes shown in Figs. 2 and 3, however, contradictions emerge. In the range 0–50 mM HIBA, Fig. 2 suggests that there is an increasing proportion of the neutral thorium(IV) tetra(HIBA) complex present, so that one would expect retention to increase progressively as the HIBA concentration is raised. The opposite trend occurs in Fig. 5. Similarly, the proportion of the uranyl tris(HIBA) complex rises progressively over the range 100–200 mM HIBA, but retention decreases.

The mobile phase pH was varied over the range 2.5–4.5 and the retention times of both thorium(IV) and uranyl were found to increase, as shown in Table II. The effect of variation of the temperature of the mobile phase on capacity factor was also studied and the results are shown in Fig. 7. The progressive decrease in capacity factor for uranyl with increasing temperature is in accordance with typical reversed-phase behaviour [9], but anomalous effects were observed for thorium(IV), which showed an increase in capacity factor with temperature. Similar effects for thorium(IV) and uranyl have been reported for eluents containing mandelic acid [6].

Studies were undertaken in which both cationic and anionic IIRs were added to the mobile phase as a means of determining whether the eluted metal ions were present as anionic, neutral or cationic spe-

TABLE III
EFFECTS OF ANIONIC AND CATIONIC ION-INTERACTION REAGENTS ON RETENTION

Mobile phase ^a	Retention time (min)			Relative retention time	
	Phenol	Thorium(IV)	Uranyl	Thorium(IV)	Uranyl
80 mM HIBA, 5 mM TBA ⁺	11.0	4.6	8.2	0.42	0.74
400 mM HIBA, 5 mM TBA ⁺	9.7	3.7	7.4	0.38	0.76
80 mM HIBA	11.0	5.3	8.1	0.48	0.74
400 mM HIBA	9.3	4.3	6.1	0.46	0.66
80 mM HIBA, 5 mM OSA ⁻	11.0	4.2	5.1	0.38	0.46
400 mM HIBA, 5 mM OSA ⁻	9.5	3.5	4.0	0.37	0.42

^a TBA⁺ = Tetrabutylammonium; OSA⁻ = octanesulfate.

cies. In each case, the column was equilibrated with the desired mobile phase, thorium(IV), uranyl and phenol (as a neutral marker compound) were injected and the relative retention time (comparative to that of phenol) of each metal was calculated. The results are given in Table III, which shows that at the higher HIBA concentrations, the only significant change observed was a reduction in the relative retention time for uranyl in the presence of octanesulfonate as the IIR. This suggests that the uranyl complex may be anionic under these conditions, but the observed increase in relative retention time in the presence of tetrabutylammonium as the IIR was only slight. The conclusions reached from these studies are two-fold. First, any charge present on the complexes is sufficiently diffuse that it does not exert a great effect on retention. Second, there is a consistent trend for all solutes, including the neutral marker, for retention time to decrease as the concentration of HIBA is increased. This suggests that HIBA itself is adsorbed onto the stationary phase and at the high concentrations used, probably precludes any appreciable adsorption of the IIR (which is present at much lower concentrations than HIBA), thereby preventing the IIR from significantly influencing retention. Decreases in relative retention times for thorium(IV) in the presence of octanesulfonate also suggest an anionic complex, but corresponding increases in retention when tetrabutylammonium was added to the mobile phase were not observed.

Mechanism of retention

Evaluation of the above factors affecting reten-

tion of the HIBA complexes of thorium(IV) and uranyl on a reversed-phase column was undertaken in order to suggest a retention mechanism which explains all of the observed trends. The behaviour of the uranyl complex is perhaps the more straightforward. The effect of increasing the percentage of organic modifier (Fig. 5) and the temperature effect (Fig. 7) are consistent with reversed-phase adsorption. Despite the fact that complete complexation leads to the formation of the anionic tris(HIBA) complex, the resultant charge distribution must be sufficiently diffuse that the complex exhibits a degree of hydrophobicity that permits reversed-phase adsorption. The decreased retention noted when the concentration of HIBA in the mobile phase is increased above 80 mM can be considered to result from increasing competition for the stationary phase adsorption sites by the considerable amount of unionized HIBA in the mobile phase. This effect has been suggested previously to explain a similar retention trend for mandelic acid complexes of uranyl on a reversed-phase column. Evidence in support of this hypothesis can be seen from the retention behaviour of phenol at the two different HIBA concentrations given in Table III. Here, a decrease in the retention time of phenol was noted with increasing HIBA concentration. This factor will contribute to the behaviour shown in Fig. 5 in addition to the effect that increased formation of the anionic tris(HIBA) complex of uranyl would be expected to favour decreased retention. The retention maximum observed for uranyl at about 50 mM HIBA in Fig. 6 corresponds closely to the point where maximum formation of the neutral bis(HIBA) uranyl

complex occurs (Fig. 3). Finally, the increased retention observed with increasing pH (Table II) can be attributed to increased complexation of uranyl and a concomitant decrease in the concentration of neutral HIBA in the mobile phase.

The retention behaviour of the thorium(IV) complex is somewhat anomalous in that under most of the conditions examined, it is eluted prior to the uranyl complex, despite the fact that it is expected to be a neutral complex with four ligand molecules, compared to a maximum of three for uranyl. Fig. 5 confirms that reversed-phase retention applies even at low concentrations of HIBA, but the temperature effect shown in Fig. 7 is the opposite to that normally encountered in reversed-phase chromatography. Further anomalies are evident in Fig. 6, where the retention of the thorium(IV) complex is seen to decrease rapidly as the HIBA concentration is increased from 15 to 50 mM and to then show a modest decrease with higher concentrations of HIBA. Fig. 2 would suggest the opposite trends of a rapid increase in retention followed by a plateau region as formation of the neutral tetra(HIBA) complex dominates. Allowing for competition for the stationary phase adsorption sites by unreacted HIBA in the mobile phase could result in decreased retention at high HIBA concentrations, so that a maximum might be expected in the plot for thorium(IV) in Fig. 6. The effect of pH on retention of thorium(IV) is similar to that observed for uranyl and can again be attributed to increased complex formation and reduced levels of neutral HIBA in the mobile phase.

One possible explanation for these results lies by considering the known propensity for thorium(IV) to hydrolyse in aqueous solution, even at acidic pH values [10], in juxtaposition with the fact that thorium(IV) often exhibits very high coordination numbers when complexed [11]. It is therefore likely that one or more hydroxyl ligands are incorporated into the coordination sphere of the thorium(IV), thereby reducing the overall charge on the complex. This would lead to the bis- or tris(HIBA) complexes being neutral, whilst the tetra(HIBA) complex would be anionic. Comparison of the retention times of the thorium(IV) and uranyl complexes in a mobile phase containing 400 mM HIBA and considering the higher stoichiometry of the former complex suggests that the negative charge on the thorium(IV)

complex should be greater than that for the uranyl complex. This indicates the presence of at least two hydroxyls in the thorium(IV) complex. Some evidence for this is the rapid decline in retention observed for thorium(IV) in Fig. 6 over the HIBA concentration range in which there is conversion of the bis(HIBA) complex (presumably neutral if two hydroxyls are present) into the tris(HIBA) complex (presumably anionic). Decreasing stability of the mixed ligand species at higher temperatures may account for the anomalous increase in retention observed with increasing temperature.

Calibration data and preconcentration studies

Linear calibration plots (correlation coefficient > 0.99) were obtained for both thorium(IV) and uranyl over the concentration range 0–10 mg/l, however, it is likely that linearity extends beyond these upper concentration limits. Detection limits for a 100- μ l injection volume were 22 μ g/l for thorium(IV) and 53 μ g/l for uranyl.

The behaviour of the HIBA complexes of thorium(IV) and uranyl suggests that sample preconcentration techniques could be applied to these solutes. A sample comprising thorium(IV) and uranyl in the presence of 20 mM HIBA at pH 4.0 should permit preconcentration of both species on a C₁₈ concentrator column, with subsequent elution and separation using 400 mM HIBA in 10% methanol. A somewhat similar approach has been used by Kerr *et al.* [4], except that 110 mM HIBA at pH 5.5 was used for enrichment and a mobile phase comprising 220 mM HIBA at pH 3.5 and 25 mM pentanesulfonate was employed for analysis. Our results suggest that these conditions are not optimal. A preconcentration system was configured according to the schematic diagram shown in Fig. 1 and was shown to be applicable to the preconcentration of sample volumes up to 1 ml. Fig. 8 shows a chromatogram of a preconcentrated sample. Under these conditions linear calibration plots over the range 0–300 μ g/l of both thorium(IV) and uranyl were constructed, giving detection limits of 2.2 and 5.8 μ g/l, respectively, for a 1.0-ml sample volume. Recovery studies showed that adsorption of the complexes on the concentrator column was very close to quantitative.

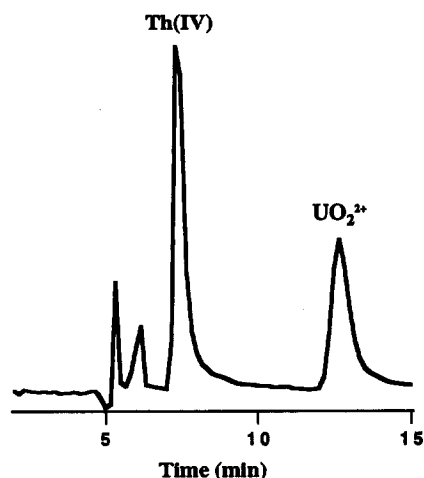


Fig. 8. Preconcentrated sample (1 ml) containing 300 $\mu\text{g/l}$ of both thorium(IV) and uranyl in 20 mM HIBA at pH 4.0. The separation conditions were as for Fig. 4.

CONCLUSIONS

The elution characteristics of HIBA complexes of thorium(IV) and uranyl are dependent on the particular complexes existing in solution under the chromatographic conditions used. In the case of uranyl, the anionic tris(HIBA) complex dominates at 400 mM HIBA (pH 4.0) and is retained on a reversed-phase column by hydrophobic adsorption, despite its anionic nature. On the other hand, thorium(IV) forms a neutral tetra(HIBA) complex, which hydrolyses readily to produce an anionic complex probably containing at least two coordinated hydroxyl ions. This complex is also retained by hydrophobic adsorption, but to a lesser extent than the uranyl complex. The behaviour of

thorium(IV) and uranyl in mobile phases containing HIBA is quite different to that exhibited by lanthanide ions, which are retained by a cation-exchange mechanism. This difference can be explained by the smaller formation constants and lower ligand/metal ratios of these species in comparison to thorium(IV) and uranyl.

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REFERENCES

- 1 C. H. Knight, R. M. Cassidy, B. M. Recoskie and L. W. Green, *Anal. Chem.*, 56 (1984) 474.
- 2 D. J. Barkley, M. Blanchette, R. M. Cassidy and S. Elchuk, *Anal. Chem.*, 58 (1986) 2222.
- 3 R. M. Cassidy, S. Elchuk, N. L. Elliot, L. W. Green, C. H. Knight and B. M. Recoskie, *Anal. Chem.*, 58 (1986) 1181.
- 4 A. Kerr, W. Kupferschmidt and M. Attas, *Anal. Chem.*, 60 (1988) 2729.
- 5 R. M. Cassidy, S. Elchuk, L. W. Green, C. H. Knight, F. C. Miller and B. M. Recoskie, *J. Radioanal. Nucl. Chem.*, 139 (1990) 55.
- 6 S. Elchuk, K. I. Burns, R. M. Cassidy and C. A. Lucy, *J. Chromatogr.*, 558 (1991) 197.
- 7 L. Magon, A. Bismondo, L. Maresca, G. Tomat and R. Portanova, *J. Inorg. Nucl. Chem.*, 35 (1973) 4237.
- 8 L. Magon, G. Tomat, A. Bismondo, R. Portanova and U. Croatto, *Gazz. Chim. Ital.*, 104 (1974) 967.
- 9 P. J. Schoenmakers, *Optimization of Chromatographic Selectivity*, Elsevier, Amsterdam, 1986, p. 67.
- 10 S. Hietanen and L. G. Sillen, *Acta Chem. Scand.*, 22 (1968) 265.
- 11 F. A. Cotton and G. W. Wilkinson, *Advanced Inorganic Chemistry*, Wiley Interscience, New York, 2nd ed., 1967, p. 1090.