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Determination of trace levels of thorium(IV) and uranyl by reversed-phase chromatography with on-line preconcentration and ligand exchange

Fuping Hao, Brett Paull, Paul R. Haddad*

Department of Chemistry, University of Tasmania, GPO Box 252C,, Hobart, Tasmania 7001, Australia

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Abstract

A method for the preconcentration of thorium(IV) and uranyl ions has been developed using pre-column complexation and loading of the complexes onto a short C_{18} concentrator column. It was found that the most important factor contributing to the preconcentration of thorium(IV) and uranyl on a hydrophobic stationary phase was the nature of the ligand added to the sample. Of the ligands investigated, mandelic acid gave the highest recoveries and maximum retention (highest breakthrough volume) of the analytes was achieved using sample solutions containing 42 m*M* mandelate. Following the preconcentration step, analysis of the sample was performed using a μ-Bondapak C_{18} column with an eluent comprising 200 m*M* α-hydroxyisobutyric acid and 10% methanol, adjusted to pH 4.0. The higher formation constants of the solutes with α-hydroxyisobutyric acid (HIBA) resulted in a quantitative ligand-exchange reaction so that the solutes were separated as their HIBA complexes. A linear relationship between the peak area and both the sample concentration and sample loading volume (up to 50 ml) for thorium(IV) and uranyl was obtained with detection limits in the sub-μg/l range. Most common anions did not affect the preconcentration when present at concentrations of up to 1.0 *M*, with the exception of sulfate and acetate. The lanthanides and some transition metals which also formed complexes with mandelic acid were also trapped on the concentrator column and the resulting peaks partially overlapped the thorium(IV) peak in the final analysis. This problem was overcome by using a longer concentrator column. The technique has been applied successfully to the determination of μg/l levels of thorium(IV) and uranyl spiked in sea water.

Keywords: Preconcentration; Thorium; Uranyl

1. Introduction

Most inorganic ions can be determined directly using ion-chromatography. However, for quantitative analysis analyte ions are generally required to be present in the sample at mg/l concentrations. For an analyte below this level, quantification usually requires the injection of a relatively large volume of sample solution or the use of various preconcentration procedures [1,2], the most widely applied of them involving the use of a concentrator column. This column technique is generally convenient to apply and can offer high analyte enrichment factors. With an on-line preconcentration method, a short concentrator column is mounted in front of the analytical column. A measured volume of sample solution is pumped through the concentrator column, onto which the analytes are bound quantitatively.

*Corresponding author.

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Subsequently, the enriched components are transferred onto the analytical column where they are separated and quantified as in conventional chromatographic analysis.

The success of the preconcentration process is dependent on the quantitative binding of the analytes on the concentrator column during the sample loading step and complete transferral of the trapped components onto the analytical column in the subsequent stripping step. There are many parameters that affect preconcentration efficiency, such as the capacity of the concentrator column, sample loading speed and the nature of the sample matrix. In addition, routine analysis requires that the binding of analytes on the concentrator column and their subsequent stripping be reproducible; therefore, the concentrator column should be well equilibrated with an appropriate eluent prior to loading each sample. In the preconcentration process it is also necessary to separate the analytes from the sample matrix. In most cases, a preconcentration system is selected in which the analytes are trapped on the concentrator column and interfering matrix species are washed out during the loading step. Occasionally, a separate washing step is also required after loading the sample.

On-line preconcentration requires the use of one or more six-port high-pressure switching valves to insert or withdraw the concentrator column from the eluent flow-path. An additional HPLC pump is often required for loading the sample. Many articles (e.g. [3–6]) have reported using on-line preconcentration techniques for the determination of trace levels of anions.

In a recent report [7], trace levels of thorium and uranium in mineral sands were determined using reversed-phase chromatography combined with a manual preconcentration procedure, wherein a short cation-exchange column was used as the concentrator. The digested sample solutions were prepared in diluted nitric acid and loaded on the concentrator column using a HPLC pump. The bound analytes were subsequently stripped from the concentrator column with a concentrated α-hydroxyisobutyric acid (HIBA) solution for chromatographic analysis. The chromatographic results showed good agreement with those obtained using X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS).

In earlier studies [8], we showed that thorium(IV) and uranyl HIBA complexes were retained on reversed-phase columns based on a conventional hydrophobic absorption mechanism. This mechanism was different to that of the lanthanides, which were retained in the presence of an anionic ion-interaction reagent through an ion-exchange mechanism. Further investigation [9] revealed that replacing HIBA in the mobile phase with other α-hydroxycarboxylic acid ligands, such as hydroxyacetic (glycolic) acid and phenylhydroxyacetic (mandelic) acid resulted in varying retention times for thorium(IV) and uranyl complexes. It was observed that thorium(IV)- and uranyl mandelate complexes were retained longer than HIBA- and glycolate complexes under the same conditions, due to the presence of a phenyl group on the mandelic acid molecule, which greatly increased the hydrophobicity of the complexes. It is, therefore, expected that thorium(IV) and uranyl preconcentration would be improved if the sample was prepared in a mandelate solution and preconcentrated on a short reversed-phase column.

The work reported here concerns an on-line preconcentration system combined with a ligand-exchange step and reversed-phase chromatography, which is applied to determine μg/l levels of thorium(IV) and uranyl. The cation-exchange concentrator used in the above-mentioned off-line preconcentration study [7] was replaced with a short C_{18} column and the thorium(IV) and uranyl samples were prepared in mandelate solutions. The effects of concentrator column size and ligand concentration were investigated. The sample loading parameters and the effect of extraneous anions and cations in the sample matrix on the efficiency of the preconcentration system were also examined. Finally, the on-line preconcentration method was applied to the determination of thorium(IV) and uranyl spiked into seawater.

2. Experimental

2.1. Instrumentation

In this study a single-valve preconcentration system was used, which consisted of a Model 590 programmable pump, a C_{18} Guard-Pak insert concentrator housed in a Guard-Pak Pre-column Mod-

ule, and a six-port automated switching valve. This preconcentration system was coupled to the direct injection chromatographic system described in previous studies [7,8]. A μ-Bondapak C_{18} reversed-phase column (300×3.9 mm I.D.) was used as the analytical column. The post-column reaction (PCR) solution was delivered by a Reagent Delivery Model (RDM). All instrumentation was supplied by Waters (Milford, MA, USA).

2.2. Reagents

All water used in this study was purified by passage through a Millipore (Bedford, MA, USA) Milli-Q water purification system. Most of the analytical mobile phases employed contained 100 m*M* HIBA (Sigma, St. Louis, MO, USA) and 10% HPLC-grade methanol (Waters), adjusted to pH 4.0. The PCR solution consisted of 0.13 m*M* Arsenazo III, buffered in 10 m*M* urea (May and Baker, Dagenham, UK) and 62 m*M* acetic acid (BDH, Victoria, Australia). Both the mobile phase and the PCR solution were filtered through a 0.45-μm filter membrane and degassed in an ultrasonic bath prior to use.

Thorium and uranium standards were prepared from thorium(IV) nitrate (May and Baker) and uranyl nitrate (Ajax Chemicals, Sydney, Australia). Stock solutions of 1000 mg/l were prepared and then further diluted in 30 m*M* mandelic acid (Koch-light Laboratories, Colnbrook, UK). Standards were adjusted to pH 4.0 for the purpose of preconcentration and also contained 1% methanol in order to wet the surface of the reversed-phase concentrator. All solutions were filtered and degassed by a vacuum method prior to loading on the concentrator. Other metal solutions were prepared from their nitrate salts (analytical grade) or from oxides dissolved in nitric acids. No further purification was used for reagents employed in the study of interference effects. Solution of anions were obtained by dilution of concentrated acids in Milli-Q water and neutralised using sodium hydroxide.

2.3. Preconcentration procedures

The single-valve preconcentration system was operated in a sequence of four steps. Firstly, the chromatographic eluent was pumped through both the concentrator and the analytical columns for equilibration, whilst the sample solution was flushed through the connecting tubes prior to the valve and thence to the waste. In the next step the valve was rotated to insert the concentrator column into the sample flow-path. After a measured volume of sample solution was loaded onto the concentrator, the valve was rotated back and the trapped solutes were back-flushed onto the analytical column by the analytical HIBA eluent. Finally, the concentrator column was withdrawn from the flow-path and the eluent was pumped directly into the analytical column where the analytes were separated and quantified in the conventional manner. Thorium(IV) and uranyl standards were injected directly onto the analytical column in equivalent amounts to those preconcentrated in order to calculate recoveries. Thorium(IV), uranyl, lanthanides and transition metals were all detected at 658 nm after PCR reaction with Arsenazo III. All experiments were carried out at room temperature.

3. Results and discussion

3.1. Preliminary investigations

At the commencement of this study, an on-line preconcentration system was constructed based on the cation-exchange manual preconcentration system described previously [7]. By adding a six-port switching valve, the concentrator column could be automatically switched into and out of the chromatographic eluent flow-path. The cation-exchange concentrator (Waters Ion-Exclusion Guard-Pak insert, sulphonic acid functionalised, 0.2 g of 5 mequiv/g resin) was conditioned with 7.5 *M* nitric acid and then washed with 10 ml of deionised water. Some adjustments were made to the above procedure in order for it to be suitable for on-line preconcentration, such as reducing the sample size from 20 to 1.0 ml, and stripping the analytes with the analytical mobile phase, which consisted of 400 m*M* HIBA in 10% methanol at pH 4.0. However, poor recoveries were obtained for 0.5 mg/l standards: 46% for thorium(IV) and 62% for uranyl relative to an equivalent amount (50 μl of 10 mg/l standards) injected directly onto the analytical column. In addition, when the concentrator column was inserted

into the analytical eluent flow-path, the trapped cations were eluted as a single broad peak, indicating that the analytical mobile phase was not strong enough to elute these cations in a small volume. A stronger eluent (2.0 *M* HIBA) was tried; however, this led to excessive band broadening on the analytical column. Alternatively, when the nitric acid concentration used to condition the concentrator column was reduced, the cations showed less affinity for the exchanger and could be eluted quantitatively using the 400 m*M* HIBA eluent. Unfortunately, these conditions did not allow quantitative binding of the analytes during the loading step. It was therefore concluded that this system was not suitable for on-line preconcentration and that an alternative means of performing the preconcentration step was required.

3.2. Concentrator columns

Although there are many factors which affect preconcentration efficiency, perhaps the most important is the nature of the concentrator column. The requirements of the concentrator column are two-fold. Firstly, its capacity should be large enough to quantitatively bind all the analytes during the sample loading step. For "real" samples, not only the analytes but some matrix components in the sample are also trapped on the concentrator column which requires that the concentrator capacity be even larger. Secondly, the affinity of the analytes for the concentrator stationary phase should be weak enough to allow the analytes to be eluted with the analytical mobile phase during the stripping step. This process is governed by the eluotropic strength of the concentrator and the stripping eluent, which in this study was fixed since the analytical mobile phase was used as the stripping eluent. Therefore, various types of concentrator column were investigated.

In a previous study, Elchuk and Cassidy [10] developed a preconcentration method to determine trace levels of uranium in ground water, using a C_{18} Guard-Pak insert as the concentrator column. The sample was prepared in dilute HIBA (0.11 *M*) and 2 ml were loaded on the concentrator. Finally, the enriched uranyl was stripped with the analytical mobile phase. In order to determine the differences between the C_{18} (μ-Bondapak) and the cation-exchange (Ion-exclusion) Guard-Pak inserts, a direct injection system was constructed using these cartridges as the analytical column. Fig. 1 shows the chromatograms obtained using this system with a mobile phase comprising 100 m*M* HIBA in 10% methanol (pH 4.0), delivered at 1.0 ml/min. With the C_{18} guard column, both thorium(IV) and uranyl were completely eluted within 1.5 min. However, with the cation-exchange guard column, thorium(IV) and uranyl were bound more strongly and became difficult to elute rapidly using the 100 m*M* HIBA eluent. If the cation-exchange guard column was used as the concentrator column, a large volume of eluent would be required to transfer the bound analytes to the analytical column, resulting in peak broadening. Sodium and manganese were added to the mobile phase to increase the eluent strength, but

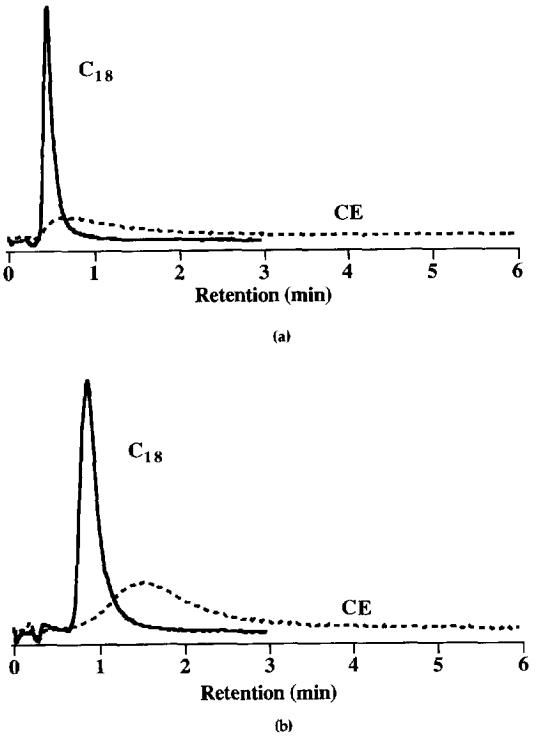


Fig. 1. Chromatograms obtained for thorium(IV) (a) and uranyl (b) using short columns. A cation-exchange (CE) and a C_{18} Guard-Pak cartridge were used with 100 m*M* HIBA in 10% methanol at pH 4.0 as the eluent. Detection at 658 nm after PCR reaction with Arsenazo III. A 50-μl volume of 10 mg/l thorium(IV) and uranyl standards was injected.

the chromatogram showed no change. For all subsequent experiments the C_{18} column was chosen as the concentrator.

Prior to the on-line preconcentration study, the breakthrough volume for the C_{18} guard column was examined in order to determine the maximum sample loading volume. Previous studies [9] have found that the thorium(IV)- and uranyl mandelate complexes were retained longer than certain other ligand complexes on a C_{18} reversed-phase column. For this reason, breakthrough volumes were calculated using thorium(IV) and uranyl standards prepared in mandelate solutions at pH 4.0.

Table 1 lists the breakthrough volumes of the C_{18} Guard-Pak insert concentrator column in relation to various metal and ligand concentrations. When the mandelate concentration was increased from 10 to 50 m*M*, a maximum breakthrough volume for uranyl was observed at 42 m*M* mandelate. This was in accordance with theoretical calculations based on the overall formation constants, which predicted that the distribution of the neutral uranyl bis-mandelate complex reached a maximum at this ligand concentration. However, the thorium(IV) breakthrough volume decreased as the mandelate concentration increased, but it was still much larger than that of the uranyl complex at any mandelate concentration over this range. When the uranyl concentration was changed from 100 to 400 μg/l, a slight decrease in the breakthrough volume was observed.

Table 1
Breakthrough volumes for uranyl andd thorium(IV) on a C_{18} guard column

Mandelate in sample (m*M*)	Breakthrough volume (ml)			
	Uranyl		Thorium(IV)	
	100 μg/l	200 μg/l	400 μg/l	200 μg/l
10	15.8	12.9	–	–
30	57.5	45.9	48.8	354
42	–	61.5	–	245
50	31.7	29.7	30.0	110

Uranyl and thorium(IV) standards were prepared individually in various mandelate solutions containing 1% methanol at pH 4.0. The samples were pumped directly through a μ-Bondapak C_{18} Guard-Pak cartridge and monitored at the column outlet at 658 nm after PCR reaction with Arsenazo III.

3.3. The nature of the ligand

Having selected a suitable concentrator column, the on-line preconcentration system was reconstructed using the C_{18} Guard-Pak insert. Various ligands, such as HIBA, glycolate and mandelate, were added to the sample solution in order to select the most suitable for thorium(IV) and uranyl preconcentration. A total of 10 ml of 100 μg/l thorium(IV) and uranyl mixed standard, prepared in 1% methanol at pH 4.0 together with 30 m*M* mandelate, HIBA or glycolate was loaded. Fig. 2 shows the recoveries obtained with the C_{18} guard

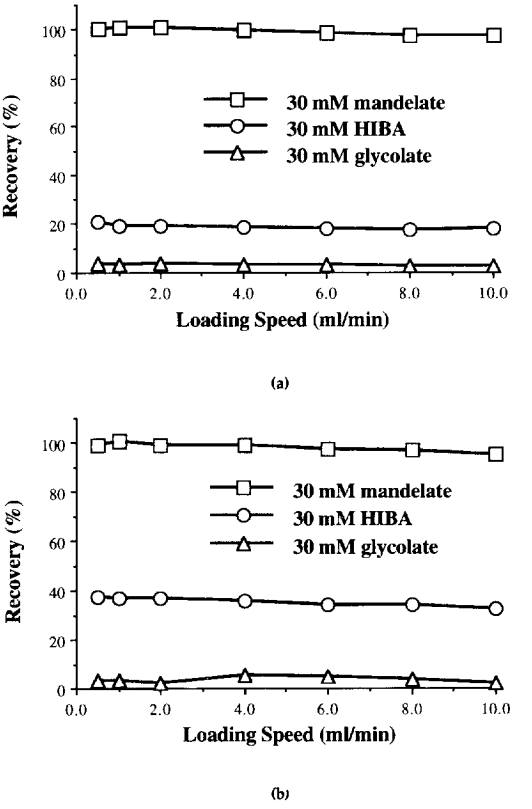


Fig. 2. Effect of different ligands on thorium(IV) and uranyl preconcentration. Standards (100 μg/l) were prepared in 30 m*M* HIBA, glycolate or mandelate (1% methanol, pH 4.0). A 10-ml volume of (a) thorium(IV) and (b) uranyl was loaded onto a C_{18} guard column concentrator. A μ-Bondapak C_{18} column (300×3.9 mm I.D.) was used with 100 m*M* HIBA in 10% methanol (pH 4.0) as the mobile phase. Detection was at 658 nm after PCR with Arsenazo III.

column concentrator, calculated by comparing the peak area in the preconcentration chromatogram with that obtained by direct injection of the equivalent amount of analytes. In the mandelate solution, both thorium(IV) and uranyl recoveries were approximately 100%. However, the recoveries were only 20% for thorium(IV) and 40% for uranyl in the HIBA solution, whilst both recoveries were less than 10% in the glycolate solution. Theoretical calculations using equilibrium constants predicted that the distribution of thorium(IV) and uranyl complexes was very similar for the three ligands. A likely explanation for the observed recoveries is the hydrophobicity differences among the three ligands. For the less hydrophobic ligands (HIBA and glycolate) the complexes could not be quantitatively bound on the C_{18} column during the sample loading step, so the recoveries for these complexes were very low. All samples were subsequently prepared in mandelate for further study of the preconcentration system. However, our previous studies had shown that mandelic acid was not a suitable ligand for the chromatographic separation of thorium(IV) and uranyl because of the very poor chromatographic efficiency which resulted. Therefore, the approach adopted in this work was to use mandelic acid as the ligand for the preconcentration step and HIBA as the ligand for the separation step. This approach is possible due to the higher thermodynamic stabilities of the HIBA complexes and the rapid kinetics of the ligand-exchange process.

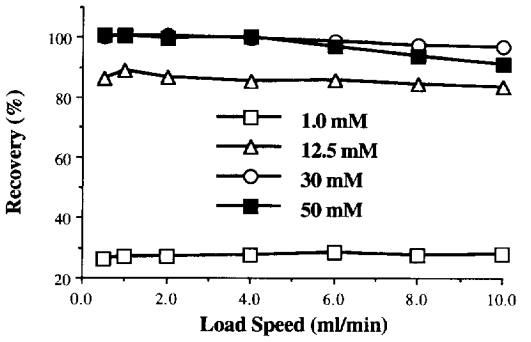
To examine the effect of mandelate concentration in the sample on thorium(IV) and uranyl preconcentration, thorium(IV) and uranyl mixed standards (100 μg/l) were prepared in various concentrations of mandelate and 1% methanol (pH 4.0). Fig. 5 shows the recoveries obtained by loading 10 ml of these mixed standards. In 1.0 m*M* mandelate both thorium(IV) and uranyl recoveries were less than 50%. However, the recoveries increased as the mandelate concentration increased. In 30 m*M* mandelate both thorium(IV) and uranyl recoveries reached approximately 100%. According to theoretical calculations, in 1.0 m*M* mandelic acid at pH 4.0, most of the uranyl exists as the free ion (75%) and the neutral uranyl bis(mandelate) complex accounts for only 0.72% of the total, whilst the neutral thorium(IV) tetra(mandelate) complex accounts for 3.2% of the total. Therefore they cannot be bound quantitatively to the hydrophobic surface of the C_{18} column under these conditions. At higher concentrations, more multi-ligand complexes are formed. These hydrophobic species are retained on the C_{18} column, leading to higher recoveries. These results were in accordance with those observed in the breakthrough volume study.

3.4. Sample loading speed

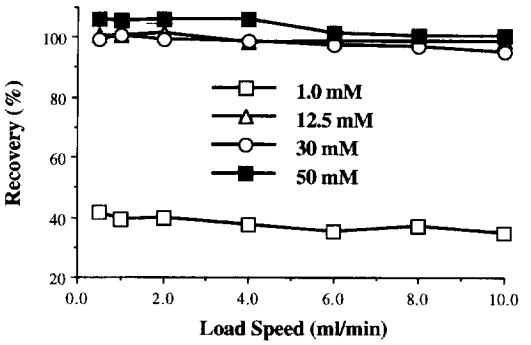
During the above study on the effect of ligand type and concentration on recovery, the significance of the speed of sample loading was also investigated. For each of the standard solutions, loading onto the concentrator was carried out at various flow-rates in the range of 0.5–10 ml/min, whilst keeping the total volume loaded (10 ml) constant. The total volume was far less than the breakthrough volume, so the concentrator capacity was not an important factor in the interpretation of the results. With each of the standard solutions, estimates of the recoveries at various flow-rates were obtained by comparing peak areas from the preconcentration runs to those obtained using direct injection. The results are also plotted in Fig. 2 for each ligand investigated and in Fig. 3 at various mandelate concentrations. These figures show that the sample loading speed had little effect on thorium(IV) and uranyl preconcentration up to a flow-rate of 5.0 ml/min. A slight decrease was observed when the flow-rate was higher than 6.0 ml/min. In subsequent studies, the sample loading speed was kept less than 5.0 ml/min.

3.5. Linearity

The effect of sample loading volume on thorium(IV) and uranyl peak areas was examined over the range of 5–120 ml. A mixed standard containing 100 μg/l each of thorium(IV) and uranyl was prepared in 30 m*M* mandelate and 1% methanol (pH 4.0), and loaded at a flow-rate of 4.0 ml/min. A linear relationship between the peak area for both analytes and the loading volume was observed up to 50 ml, with regression coefficients of $r=0.998$ for thorium(IV) and $r=1.000$ for uranyl, However, when the loading volume exceeded 50 ml, a non-linear response was observed, especially for the



(a)



(b)

Fig. 3. Effect of mandelate concentration in the sample on thorium(IV) and uranyl preconcentration. A C_{18} guard column was used as the concentrator. The sample was prepared in various concentrations of mandelate and 1% methanol (pH 4.0). A 10-ml volume of 100 μg/l (a) thorium(IV) and (b) uranyl was concentrated. Other conditions were the same as in Fig. 2.

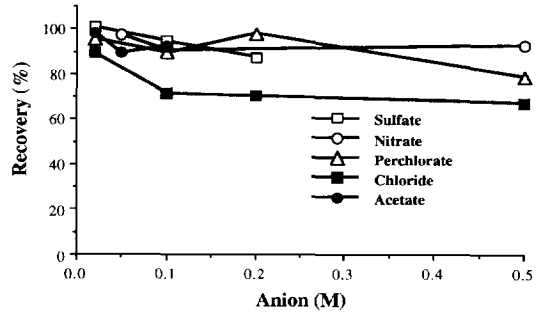
uranyl. Similar results were obtained when thorium(IV) and uranyl concentrations were reduced to 10 or 1 μg/l. These results were in accordance with those observed in the breakthrough volume study (Section 3.2). When the surface of the stationary phase was fully equilibrated with the metal complexes, continued loading caused self-elution. These results suggested that the critical volume for the C_{18} guard column was approximately 50 ml under the conditions used. Compared to uranyl, the thorium(IV) mandelate complex was retained more strongly on the reversed-phase concentrator; therefore, its linear calibration range extended up to 100 ml for the 10 μg/l thorium(IV) standard.

The effect of sample concentration on the peak areas of thorium(IV) and uranyl was also studied. Thorium(IV) and uranyl standards over the range of 1–200 μg/l ($n=8$) were prepared in 30 m*M* mandelate and 1% methanol (pH 4.0). A total of 50 ml of each standard solution was loaded on the C_{18} guard column concentrator at a flow-rate of 4.0 ml/min. A linear relationship between the peak area and the sample concentration was observed for both thorium(IV) and uranyl over this range. Regression coefficients of $r=0.999$ for thorium(IV) and $r=0.997$ for uranyl were obtained.

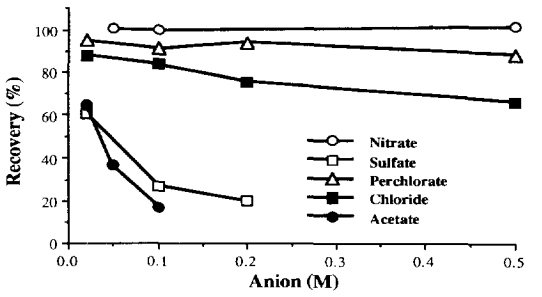
3.6. Interference effects of anions and cations in the sample solution

Fig. 4 shows the effect of common anions present in the sample on thorium(IV) and uranyl preconcentration. Nitric, perchloric, hydrochloric, sulfuric and acetic acid were added separately into 10 μg/l thorium(IV) and uranyl standards, then adjusted to pH 4.0 with dilute sodium hydroxide. The final standard solution also contained 30 m*M* mandelate and 1% methanol. The observed interference effects were dependent on the nature of the anion used. No significant effect on recovery was observed by adding 0.025–0.50 *M* nitrate to the sample, whilst a slight decrease in recovery with 0.50 *M* perchlorate or chloride was noted. Sulfate and acetate strongly affected uranium preconcentration, such that, in 0.1 *M* sulfate or acetate, about 70–80% of the uranyl present was lost during the preconcentration procedure. It was likely that the sulfate and acetate ions were incorporated into the uranyl-mandelate coordination sphere, causing uranyl to self-elute during the loading step. This was also noted in a previous investigation [7], where uranyl was reported to elute at the solvent front when samples were prepared in sulfuric acid.

The effect of cations present in the sample solution was also examined. Various concentrations of metals were added into the 10 μg/l thorium(IV) and uranyl standard solutions. A total of 50 ml of these standards was loaded onto the C_{18} guard column concentrator. Once again, interference effects were dependent on the nature of the cation used. No significant interferences were observed for Na(I), Mn(II), Co(II), Ni(II) and Zn(II), even when they were present in the standard solutions at concen-



(a)



(b)

Fig. 4. Effect of anions on (a) thorium(IV) and (b) uranyl preconcentration. Various concentrations of anions were prepared in 10 μg/l thorium(IV) and uranyl standards containing 30 m*M* mandelate and 1% methanol at pH 4.0. A total of 50 ml of these samples was concentrated. Other conditions were the same as in Fig. 2.

trations that were 2500 times higher than those of thorium(IV) and uranyl. In fact, the C_{18} concentrator breakthrough volume increased when these metals were present, perhaps due to a salting-out effect. However, when lanthanides and Fe(III) and Cu(II) were added to the standard solutions, they also formed complexes with mandelate and were trapped on the C_{18} guard column concentrator. In the final analysis step, these complexes were eluted as a matrix peak which partially masked the thorium(IV) peak, especially when the interferences were present at higher concentrations than those of thorium(IV) and uranyl.

3.7. Precision of the method

The precision of the on-line preconcentration technique was determined at different sample concentration levels. Thorium(IV) and uranyl standards (5, 20 and 100 μg/l) were prepared in 30 m*M* mandelate and 1% methanol, adjusted to pH 4.0. Repeated (n=6) loading of these standards on the C_{18} guard column concentrator was performed and the observed precision is listed in Table 2. In all cases, adequate precision was obtained.

3.8. Determination of trace levels of thorium(IV) and uranyl spiked into seawater

Having optimised the on-line preconcentration conditions, the technique was applied to the determination of trace levels of thorium(IV) and uranyl spiked into seawater. The seawater matrix was selected for two reasons. Firstly, it is not uncommon for nuclear waste samples to be in the form of brine solutions. Secondly, seawater represents a challenging matrix in terms of interferences and an analytical method developed for this matrix is likely to be applicable to a wide range of less complex sample types. Thorium(IV) and uranyl (10 μg/l) were spiked into seawater, to which 30 m*M* mandelate and 1% methanol had previously been added and the pH had been adjusted 4.0. A total of 50 ml of this sample was loaded onto the C_{18} Guard-Pak column

Table 2
Precision of thorium and uranium preconcentration

Concentration	5 μg/l		20 μg/l		100 μg/l	
Metal	Thorium(IV)	Uranyl	Thorium(IV)	Uranyl	Thorium(IV)	Uranyl
R.S.D.(%)	1.008	0.446	3.906	0.992	1.316	0.119

Note: n=6.
Various concentrations of thorium(IV) and uranyl were prepared in 30 m*M* mandelate and 1% methanol (pH 4.0). A total of 50 ml of these solutions was loaded onto a C_{18} guard column concentrator. Other conditions were as described in the text.

concentrator and analysed as described above. The initial chromatogram showed that thorium(IV) and uranyl could be preconcentrated under these conditions. However, a large matrix peak was also observed which partially overlapped the thorium(IV) peak. This indicated that the on-line preconcentration system needed some modification for use in seawater analysis.

Seawater in the open ocean contains about 3.5% total salts [11], mainly sodium chloride. Despite transition metals being present at low concentrations in seawater, significant amounts of these species were accumulated on the concentrator column when a large volume of seawater was loaded. Variation of either the amount of HIBA or methanol in the analytical mobile phase did not result in any significant improvement in the resolution obtained in the final chromatogram. Attempts were therefore made to improve the separation using longer C_{18} reversed-phase concentrator columns. It was expected that thorium(IV) and uranyl would be quantitatively bound on a longer concentrator, whilst at the same time being at least partially separated from the interfering metals during the sample loading step. Fig. 5 shows the chromatograms obtained using three sizes of concentrator column, combined with a Waters C_{18} Nova-Pak cartridge (150×3.9 mm I.D.) as the analytical column. Using either a 50- or a 100-mm concentrator column, thorium(IV) could be completely separated from the matrix peak, and both thorium(IV) and uranyl recoveries reached 100%. However, the use of a 100-mm concentrator was not practical because the total chromatographic time was too long and the back pressure was too high when it was inserted into the analytical eluent flow-path. All the seawater analyses were therefore carried out using the Nova-Pak C_{18} (50×3.9 mm I.D.) cartridge as the concentrator column.

After optimising the system for the longer concentrator column, calibration studies were undertaken and showed a linear relationship between peak area and the loading volume (up to 90 ml) for uranyl, and higher for thorium(IV). Regression coefficients of $r=0.997$ for thorium(IV) and $r=0.999$ for uranyl were obtained. Fixing the total volume at 90 ml, various concentrations of thorium(IV) and uranyl spiked into seawater were loaded onto the concentrator, giving linear calibration curves (regression

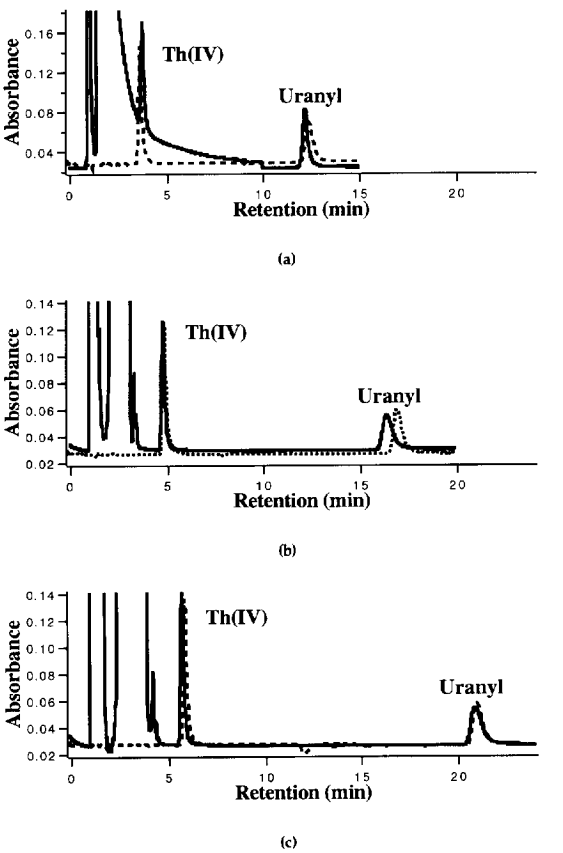


Fig. 5. Chromatograms of thorium(IV) and uranyl obtained using C_{18} concentrator columns of various sizes: (a) Guard-Pak, (b) 50×3.9 mm and (c) 100×3.9 mm. A Nova-Pak C_{18} column (150×3.9 mm I.D.) was used as the analytical column with 200 m*M* HIBA in 5% methanol at pH 4.0 as the eluent. Other conditions were the same as in Fig. 2. The dashed lines show direct injections of equivalent quantities of thorium(IV) and uranyl standards.

coefficients were $r=0.992$ for thorium and $r=0.921$ for uranyl) over the range 10–50 μg/l ($n=5$).

Finally, the use of a single column for both preconcentration and analysis was examined as a possible alternative to the above two column system. The configuration of the new chromatographic system was similar to that used previously, except that the analytical column was removed. The sample was loaded onto the concentrator in one direction and the analytical mobile phase was then pumped through the same column but in the opposite direction. Fig. 6 shows chromatograms obtained using columns of different sizes. The advantage of using a short

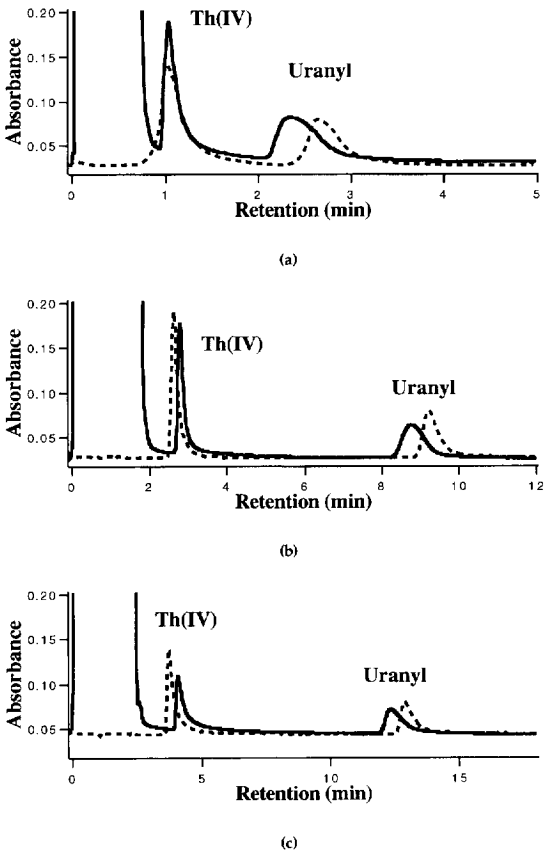


Fig. 6. Chromatograms obtained by preconcentration and separation on a single column. Nova-Pak columns (a) 50×3.9 mm, (b) 100×3.9 mm and (c) 150×3.9 mm were used with 200 m*M* HIBA in 5% methanol at pH 4.0 as the eluent. A 15.0-ml volume of 50 μg/l thorium(IV) and uranyl spiked into seawater was loaded (solid lines) and 75 μl of 10 μg/l concentrated standards were injected directly (dashed lines).

column was that the analysis time was minimised. With the 50 mm column, the analysis could be completed within 4 min. However, the thorium(IV) peak could not be separated completely from the matrix peak under these conditions (Fig. 6a). This problem was solved by using a longer column. The results show that the 100 mm column (Fig. 6b) was the most practical, giving good separation, as well as a relatively short analysis time.

Quantitative recoveries were achieved for uranyl with each column, but the thorium(IV) recovery was only 80% at best. It is possible that some of the thorium(IV) was flushed to waste during the sample loading step because the column had been conditioned with the HIBA eluent prior to the introduction of the sample. In a further experiment, an equilibration step with mandelate was added prior to each preconcentration, which improved the thorium(IV) recovery to 87%. The above single column technique provides a simple alternative to the two column system. However, as the above recovery data illustrates, the two column system is preferable.

4. Conclusions

In the preconcentration of thorium and uranyl using a short C_{18} column as the concentrator, the most important factors were the nature and concentration of the ligand used to prepare the sample solution. The most hydrophobic ligand, mandelic acid, gave better binding of the metal ions than HIBA or glycolic acid and in 30 m*M* or more mandelic acid, both thorium and uranium recoveries reached 100%. However, HIBA gave superior separation of the analytes, so that a ligand-exchange system was devised wherein the analytes were concentrated as mandelic acid complexes and then separated as HIBA complexes.

The flow-rate of the sample loading on the concentrator did not affect the recovery within the range of 0.5–5.0 ml/min. There was a linear relationship between the peak area and the loading volume up to 50 ml, but the bound solutes were self-eluted when the loading volume was greater than 50 ml. Most of the common mineral acids had no effect on thorium(IV) and uranyl enrichment, except for sulfuric and acetic acids, due to their ability to form complexes with the analytes. No significant interferences were observed for Na(I), Mn(II), Co(II), Ni(II) and Zn(II), even when these cations were present at concentrations that were 2500 times greater than those of thorium(IV) and uranyl. It was found that the breakthrough volume of the C_{18} concentrator column increased when these metals were present, probably due to a salting-out effect. However, lanthanides, Fe(II) and Cu(II) also formed complexes with mandelate and were trapped on the C_{18} concentrator. In the final analysis step, these complexes were eluted as a matrix peak that partially overlapped the thorium(IV) peak. However, this

problem was corrected by using a larger concentrator. This on-line preconcentration technique has been applied successfully to the determination of trace levels of thorium(IV) and uranyl in a saline sample (spiked into seawater) after minor modification of the system.

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