

Determination of thorium and uranium in mineral sands by ion chromatography

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Abstract

Thorium and uranium can be determined by ion chromatography using a C₁₈ reversed-phase column and a complexing eluent of hydroxyisobutyric acid followed by post-column derivatization with Arsenazo III and detection at 658 nm. A number of sample dissolution and clean-up procedures were evaluated in order to permit the application of the chromatographic method to the analysis of mineral sands. Dissolution procedures investigated included a variety of acid digestions and alkali fusion with peroxide, borate, carbonate, hydroxide and pyrosulphate fluxes. Sample clean-up protocols were then studied in order to overcome matrix interference effects. The optimal sample preparation procedure involved a tetraborate fusion/nitric acid leach followed by either cation-exchange pretreatment, or simply dilution in concentrated hydroxyisobutyric acid, depending upon the sample type. The results obtained using the chromatographic method showed good agreement with X-ray fluorescence and inductively coupled plasma mass spectrometry for ilmenite, synthetic rutile, zircon and rutile mineral sands with detection limits (in the original mineral sand) in the order of 1.0 µg/ml for the two analytes.

1. Introduction

The determination of thorium and uranium at trace levels in environmental samples is typically carried out using techniques such as radiochemistry [1], atomic absorption spectroscopy [1], neutron activation analysis [2], inductively coupled plasma mass spectrometry (ICP-MS) [3], isotope dilution mass spectrometry [4] and X-ray fluorescence (XRF) [5]. However, these techniques are often not suited to routine analysis, due to interferences from other metals present in the matrix, cost of operation or poor detection limits [6,7]. Ion chromatography (IC) has been widely applied to the separation of

lanthanides and also thorium and uranium [6–10]. These species are typically separated on a C₁₈ reversed-phase column using a mobile phase containing an ion interaction reagent (e.g. *n*-octanesulphonate) and a complexing agent (e.g. hydroxyisobutyric acid, HIBA) followed by post-column derivatization using either Arsenazo III {3,6-bis[(*o*-arsenophenyl)azo]-4,5-dihydroxy-2,7-naphthalene disulfonic acid} or PAR [4-(2-pyridylazo) resorcinol] with visible detection.

Thorium(IV) and uranium(IV), as the uranyl ion, exhibit somewhat different retention behaviour to the lanthanides and it has been shown that their HIBA complexes can be retained on a C₁₈ column without the need for an ion interaction reagent (IIR) in the mobile phase [11,12]. Also, when mandelic acid was used as the complexing ligand, thorium(IV) and the uranyl

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ion could again be retained on a C_{18} column without the need for an anionic IIR in the mobile phase [13], and it has recently been proposed that such complexes are retained by a mechanism of hydrophobic adsorption rather than dynamic cation-exchange [14]. Alternatively, thorium and uranium have also recently been separated by cation-exchange chromatography using a gradient of hydrochloric acid and sodium sulphate prior to post-column reaction detection [6].

Many of the above IC separations have been applied to the determination of thorium and uranium in samples including natural waters [6,11], uranium ore [11], irradiated fuel materials [9,10,12] and geological matrices such as basalt, phosphate rock and river sediments [6,7]. The IC determination of thorium and uranium in mineral sands is a complex problem due to the fact that the sample matrix is very difficult to get into solution. Indeed, IC appears to have been used only once previously for the analysis of metal cations in mineral sands [15].

In this paper, a number of sample preparation procedures were evaluated to enable the determination of thorium and uranium in mineral sands by IC. Dissolution procedures investigated included acid leaching and alkali fusion with peroxide, borate, carbonate, hydroxide and pyrosulphate fluxes. Sample clean-up protocols, including solvent extraction, cation-exchange and selective complexation, were then studied in order to overcome the interference effects of the dissolution matrix upon the chromatographic process. The results obtained using the IC method were compared to those from XRF and ICP-MS for ilmenite, synthetic rutile, zircon and rutile mineral sands.

2. Experimental

2.1. Instrumentation

The liquid chromatograph consisted of a Waters Chromatography Division of Millipore (Millford, MA, USA) Model 590 solvent-delivery system, either a U6K injector or a WISP 712

autoinjector, Model 441 fixed-wavelength UV-Vis detector operated at 658 nm and an 820 Maxima data station. The post-column reagent was delivered (at *ca.* 30 p.s.i.; 1 p.s.i. = 6894.76 Pa) with a Waters pneumatic reagent delivery module (RMD). The analytical column used was a Waters μ Bondapak C_{18} (300×3.9 mm I.D.) reversed-phase column, operated at ambient temperature. Sample digest solutions were loaded through the cation-exchange pretreatment cartridges using a Waters Model 501 solvent-delivery system.

2.2. Reagents

Water purified using a Millipore Milli-Q Water purification system (Bedford, MA, USA) (18 M Ω) was used for all solutions. The mobile phase consisted of 400 mM α -hydroxyisobutyric acid (Sigma, St. Louis, MO, USA) and 10% methanol (HPLC grade obtained from Waters) adjusted to pH 4.0 with sodium hydroxide. The analytical mobile phase was operated at a flow-rate of 1.0 ml/min. The post-column reagent solution contained 0.13 mM Arsenazo III (BDH, Poole, UK), 10.0 mM urea (May & Baker, Dagenham, UK) and 62 mM acetic acid and was delivered through a stainless steel "T" piece at a flow-rate of 1.0 ml/min. All eluents and post-column reagents were prepared daily, filtered and degassed with a Waters solvent-clarification kit. Thorium and uranium standards were prepared from thorium(IV) nitrate and uranyl nitrate (Ajax Chemicals, Sydney, Australia), respectively. Sample pretreatment was carried out using either Alltech (Deerfield, IL, USA) IC H⁺ Maxiclean cartridges (sulphonic acid functionalized, *ca.* 1 g of 5 mequiv./g resin), Waters Accell CM Sep-Pak cartridges (carboxylic acid functionalized, *ca.* 0.4 g of 350 μ equiv./g silica) or Waters ion-exclusion Guard-Pak insert cartridges (sulphonic acid functionalized, *ca.* 0.2 g of 5 mequiv./g resin).

2.3. Sample dissolution procedures

Ilmenite, synthetic rutile, zircon and rutile mineral sand samples were prepared using a

variety of acid leach and fusion procedures, which are detailed below:

Acid leach

Samples (0.5 g) were weighed into 250 ml flasks and 20 ml of concentrated perchloric and nitric acids added. The samples were refluxed for 1 h and boiled to near dryness, cooled and 2.0 g of HIBA were added. The samples were adjusted to pH 4.0 with sodium hydroxide and made up to 100 ml.

Peroxide fusion

Samples (0.5 g) were weighed into a platinum crucible with 4.0 g of sodium peroxide and fused at 1100°C for 15 min. The melt was dissolved with 15 ml of 50% sulphuric acid and 15 ml of 30% hydrogen peroxide; then cooled, diluted, filtered and made up to 100 ml.

Carbonate–tetraborate fusion

Samples (0.5 g) were weighed into a platinum crucible with 1.0 g sodium carbonate and 1.0 g sodium tetraborate and fused at 1100°C for 15 min. The melt was poured into a solution of 20 ml concentrated nitric acid, 5 ml 30% hydrogen peroxide and 25 ml water. The crucible was placed into the above solution and warmed on a hotplate to dissolve the melt. The crucible was then removed, washed with water, the solution cooled and made up to 100 ml.

Tetraborate fusion

Samples (0.5 g) were weighed into a platinum crucible with 2.0 g sodium tetraborate and fused at 1100°C for 15 mins. The melt was poured into a solution of 5 ml concentrated nitric acid and 50 ml water. The crucible was placed into the above solution and warmed on a hotplate to dissolve the melt. The crucible was then removed, washed with water, the solution cooled, filtered and made up to 100 ml.

Pyrosulphate fusion

Samples (0.5 g) were weighed into a vicor quartz 250-ml conical flask with 5.0 g potassium pyrosulphate and fused over a meaker burner at 800–900°C to obtain a clear melt. The melt was

cooled and 10 ml of concentrated sulphuric acid was added. The solution was warmed to dissolve the melt then 5 ml of concentrated hydrochloric acid and 50 ml water were added. The solution was cooled and made up to 100 ml.

Tetraborate–carbonate fusion

Samples (0.5 g) were weighed into a platinum crucible with 2.5 g sodium tetraborate and 1.0 g sodium carbonate and fused at 1100°C. The melt was poured into a solution of 10 ml concentrated sulphuric acid and 40 ml water. The crucible was placed into the above solution and warmed on a hotplate to dissolve the melt. The crucible was removed, washed with water, the solution cooled and made up to 100 ml.

Hydroxide fusion

Samples (0.5 g) were weighed into a zirconium crucible with 4.0 g sodium hydroxide and fused at 1100°C for 15 min. Concentrated nitric acid (15 ml) was added to the crucible and the slurry heated to near dryness on a hotplate. The solution was cooled, filtered and made up to 100 ml.

2.4. Cation-exchange pretreatment procedure

The final cation-exchange sample pretreatment procedure used to evaluate the various fusion/digest approaches consisted of firstly conditioning the ion-exclusion cartridge with 5.0 ml of 7.5 M nitric acid followed by 5.0 ml of water. The sample digest was then loaded onto the cartridge at 2.0 ml/min with an HPLC pump after diluting the sample to ensure that the acid concentration did not exceed 0.2 M in order to allow quantitative binding of thorium and uranium ions. The cartridge was then washed with 1.0 ml water to remove the interstitial sample and flushed with air to remove the water. Finally, the bound thorium and uranium were eluted from the cartridge with 2.0 ml of 2.0 M HIBA into a pre-rinsed 4.0 ml autosampler vial and the cartridge flushed with air to ensure complete collection of the entire 2.0-ml volume.

3. Results and discussion

3.1. Preliminary investigations

In a previous paper, we investigated the retention behaviour of thorium(IV) and uranium (as the uranyl ion) complexes of HIBA on a C_{18} reversed-phase column and proposed that such complexes are retained by a mechanism of hydrophobic adsorption [14]. Optimal conditions were established for the determination of thorium and uranium which utilized a mobile phase of 400 mM HIBA and 10% methanol at pH 4.0 with a μ Bondapak C_{18} column, a post-column reagent of Arsenazo III and detection at 658 nm. In this paper, we investigate the possibility of applying the above chromatographic method to the determination of thorium and uranium in ilmenite, synthetic rutile, zircon and rutile mineral sands. Fig. 1 shows a chromatogram obtained from a 100- μ l injection of a 10 μ g/ml standard of thorium and uranium using the conditions described above. Thorium and uranium exhibit appreciably different retention behaviour to the rare earth elements and are completely resolved from these potentially interfering species using this chromatographic approach. Another advantage of this technique was

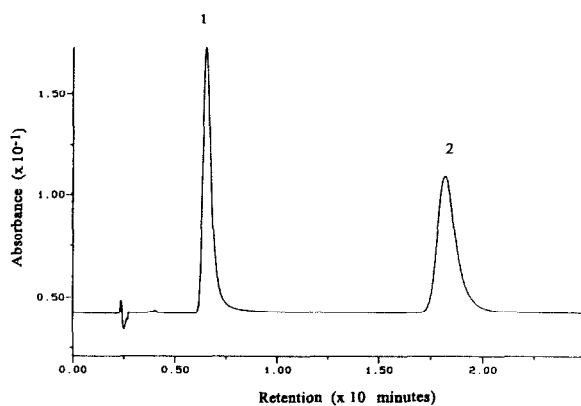


Fig. 1. Separation of thorium and uranium standard. Conditions: column, Waters μ Bondapak C_{18} ; eluent, 400 mM HIBA, 10% methanol at pH 4.0; flow-rate, 1.0 ml/min; injection volume, 100 μ l; post-column reagent, 0.13 mM Arsenazo III, 10.0 mM urea, 62 mM acetic acid delivered at 1.0 ml/min; detection, visible at 658 nm. Solutes: 1 = thorium (10 μ g/ml); 2 = uranium (10 μ g/ml).

that it allowed the injection of large sample volumes before significant peak broadening occurred, resulting in detection limits (at $3\times$ signal-to-noise) of 3.0 and 5.0 ng/ml (using a 1000- μ l injection) for thorium and uranium, respectively. The calibration curves were linear (correlation coefficients >0.9999) from detection limit to approximately 5.0 μ g/ml for the same injection volume. Beyond this sample loading, the analyte response overran the detector. As thorium was typically found in mineral sands at higher concentrations than uranium, calibration curves were routinely prepared for the two analytes using different solute concentrations and injection volumes.

However, despite the excellent linearity and detection limits of the chromatographic method, initial results obtained using direct injection of samples prepared using a peroxide fusion (described in the Experimental) gave very low results (*ca.* 10% recovery) when compared to those obtained with XRF, as detailed in Table 1. The mineral sand samples were then prepared using an alternative dissolution method, a perchloric and nitric acid leach procedure and the results obtained by direct injection of the samples are also shown in Table 1. These results indicated one of two possibilities; that either the sample dissolution procedures did not quantitatively release thorium and uranium from the matrix, or that the dissolution matrix was somehow interfering with the subsequent chromatographic analysis. It has been reported previously [16], for the determination of lanthanides by liquid chromatography, that sulphuric acid levels in the injected solution of >0.09 M reduced the peak heights and retention times of rare earth elements (REEs) when using oxalate as the complexing agent in the mobile phase. The acidity of the sample altered the formation constants of REEs complexes and therefore influenced the degree of complexation of the REEs. In the case of thorium- and uranium-HIBA complexes, it appeared that other (complexing) ions in the sample digest solution were competing with HIBA in the coordination sphere of both thorium and uranium. Consequently, these species were chromatographed as other

Table 1

Thorium and uranium concentrations in original mineral sand samples obtained using direct injection and peroxide fusion or acid leach sample dissolution

Sample	IC		XRF ^a	
	Thorium ($\mu\text{g/g}$)	Uranium ($\mu\text{g/g}$)	Thorium ($\mu\text{g/g}$)	Uranium ($\mu\text{g/g}$)
<i>Ilmenite</i>				
Peroxide fusion	86.4	ND	490	10
Acid leach	426	8.9		
<i>Synthetic rutile</i>				
Peroxide fusion	69.9	ND	430	15
Acid leach	56.2	ND		
<i>Zircon</i>				
Peroxide fusion	ND	48.6	179	217
Acid leach	21.1	ND		
<i>Natural rutile</i>				
Peroxide fusion	8.0	8.0	53	54
Acid leach	29.2	ND		

ND = Not detected.

^a XRF = Results obtained on solid samples.

complexed forms, most of which appeared to elute at the column void volume.

The effect of sample acidity on the chromatographic behaviour of thorium was confirmed by preparing 10 $\mu\text{g/ml}$ thorium standard solutions made up in either 1.0 *M* sulphuric, nitric or hydrochloric acids. The recoveries for the thorium peak were 23, 71 and 87% in sulphuric, nitric and hydrochloric acids, respectively, when compared to a standard prepared in Milli-Q water. Sulphate, nitrate and chloride all form stable complexes with thorium [17] and effectively compete with HIBA in the coordination sphere of the thorium. In fact, the recovery results reflect the degree of stability of the relative complexes, *i.e.* sulphate forms more stable anionic complexes with thorium than does nitric acid, than does hydrochloric acid [17]. Hence, the poor recoveries were obtained as a result of the other (more polar) complexes of thorium eluting at the column void volume. When the 10 $\mu\text{g/ml}$ thorium standard solution was made up in 0.1 *M* sulphuric acid, the recovery for the thorium peak was precisely 100%; however, such an acid concentration was

much too low to effect dissolution of the mineral sand fusion melt. Additionally, when a 10 $\mu\text{g/ml}$ thorium standard solution was made up in 1.0 *M* sulphuric acid and neutralized with sodium hydroxide before injection, the recovery for the thorium peak was only 8%. This result indicated that either the hydroxyl anion could also compete with HIBA in the coordination sphere of thorium, or that the sulphate complex of thorium was more stable under alkaline conditions. The effect of other anions on the uranium recovery was similar to that for thorium, although not as dramatic as uranium formed more stable HIBA complexes than thorium.

Evidently, some form of further sample treatment prior to the chromatographic determination was necessary in order to determine if the sample fusion/acid dissolution procedures were successfully releasing thorium and uranium from the mineral sand matrix. Options would include a very large dilution of the sample digest; the use of an alternative chromatographic approach where the thorium and uranium response were not affected by the presence of other ions in solution; or the removal of thorium and uranium

from the dissolution matrix prior to injection. Unfortunately, thorium and uranium are present in the samples at such low concentrations that a large dilution is impractical and other chromatographic approaches, whether using an ion-exchange, reversed-phase or ion interaction separations, are also likely to be affected by the presence of elevated levels of ions in the sample digest as they all rely on some degree of complexation with the mobile phase to elute the thorium and uranium ions.

3.2. Sample pretreatment

It appeared then that the most appropriate solution to the interference problems was to remove the thorium and uranium from the dissolution matrix prior to the chromatographic step. Two approaches were investigated; solvent extraction and solid-phase (cation-exchange) extraction. It has long been established that thorium and uranium can be extracted from aqueous solutions containing high concentrations of certain metal nitrates using oxygen-containing organic solvents [18]. However, extraction of a 10 $\mu\text{g}/\text{ml}$ thorium and uranium standard solution (containing 1.0 g/ml aluminium nitrate) with ethyl acetate resulted in recoveries of only 30 and 80% for thorium and uranium, respectively. This approach was abandoned after attempts to extract a fusion/digestion sample with ethyl acetate were unsuccessful due to the formation of stable emulsions.

Cassidy [7] has previously used solid-phase (cation-exchange) extraction to concentrate RREs from rock digest matrices prior to chromatographic determination. Alternatively, an iminodiacetate functionalized chelating resin has also been shown to allow preconcentration of uranium and thorium from rock digests prior to gradient cation-exchange separation [6]. Investigation of the binding affinities of thorium and uranium in nitric acid indicated that both thorium and uranium would bind quantitatively to strong cation-exchange resin, provided that the nitric acid concentration of the solution was no greater than 0.1 M [17]. At higher nitric acid concentrations, uranium shows significantly de-

creasing affinity for the cation-exchanger due formation of anionic nitrate complexes. The recoveries of thorium and uranium on several different cation-exchange cartridges were then evaluated using a cation-exchange "pretreatment" protocol based on that of Cassidy [7]. This involved loading an appropriate volume of sample onto a cartridge which had been previously conditioned with 5 ml of 0.1 M nitric acid followed by 1.0 ml of Milli-Q water. The cartridge with the retained sample was washed with 1.0 ml of Milli-Q water, eluted with varying volumes of 7.5 M nitric acid and the effluent collected in a 20-ml beaker. This solution was evaporated to just dryness on a hotplate in the beaker and the sample reconstituted with 2 ml of 400 mM HIBA.

The use of cation-exchange cartridges to quantitatively recover thorium and uranium was initially investigated using a high-capacity IC H^+ Maxiclean cartridge and standard solutions. A 10 $\mu\text{g}/\text{ml}$ thorium and uranium standard solution was loaded onto the Maxiclean cartridge and the effluent collected. Chromatographic analysis of the effluent indicated that both Th and U were quantitatively binding to the cartridge. Eluting the bound metals with 10 ml of 7.5 M nitric acid resulted in recoveries of only 40 and 55% for thorium and uranium, respectively. Evidently, the sample was quantitatively binding to the cartridge and 10 ml of 7.5 M nitric acid was insufficient to quantitatively remove the thorium and uranium from the cartridge. The use of a larger elution volume (30 ml) of 7.5 M nitric acid resulted in improved recoveries of 55 and 90% for thorium and uranium, respectively; however, it appeared that the cartridge capacity was too high to permit quantitative elution within a reasonable volume of nitric acid.

Two lower-capacity cation-exchangers were then investigated for their ability to be used with the cation-exchange pretreatment procedure; an Accell weak acid functionalized cartridge and an ion-exclusion Guard-Pak strong acid functionalized cartridge. Both these cartridges gave quantitative (100%) recoveries for a 10 $\mu\text{g}/\text{ml}$ thorium and uranium standard solution using an elution volume of only 10 ml of 7.5 M nitric acid.

Having established that the two lower-capacity cation cartridges allowed quantitative recoveries for standard solutions, mineral sand samples prepared using an hydroxide fusion were then “pretreated” using the cation-exchange procedure prior to injection. The fusion/digest solutions were diluted a further 10× to reduce the acid concentration to *ca.* 0.1 M in order to ensure quantitative binding of thorium and uranium and 20 ml was loaded using an HPLC pump. The samples were then eluted with 10 ml of 7.5 M nitric acid, evaporated to just dryness and reconstituted in 2.0 ml 400 mM HIBA. The results obtained for ilmenite, synthetic rutile and zircon mineral sands using both the cation-exchange cartridge pretreatment are shown in Table 2.

The use of the ion-exclusion cartridge pretreatment allowed good results to be obtained for the ilmenite sample, however, lower recoveries were obtained using the Accell cartridge. While appropriate for standard solutions, it appeared that the weak acid functionalized Accell cartridge did not have sufficient capacity to quantitatively retain thorium and uranium from dilute acid solutions and no further work was carried out using these cartridges. Fig. 2a shows a chromatogram of a 100- μ l injection of ilmenite prepared by hydroxide fusion directly injected with no pretreatment, while Fig. 2b

Table 2

Thorium and uranium concentrations in original mineral sand samples obtained using hydroxide fusion and cation exchange pretreatment

Sample	Thorium (μ g/g)	Uranium (μ g/g)
<i>Ilmenite</i>		
No pretreatment	195	9.8
Ion-exclusion cartridge	466	13.4
Accell cartridge	438	3.9
<i>Synthetic rutile</i>		
Ion-exclusion cartridge	332	27.3
<i>Zircon</i>		
Ion-exclusion cartridge	21	ND

ND = Not detected.

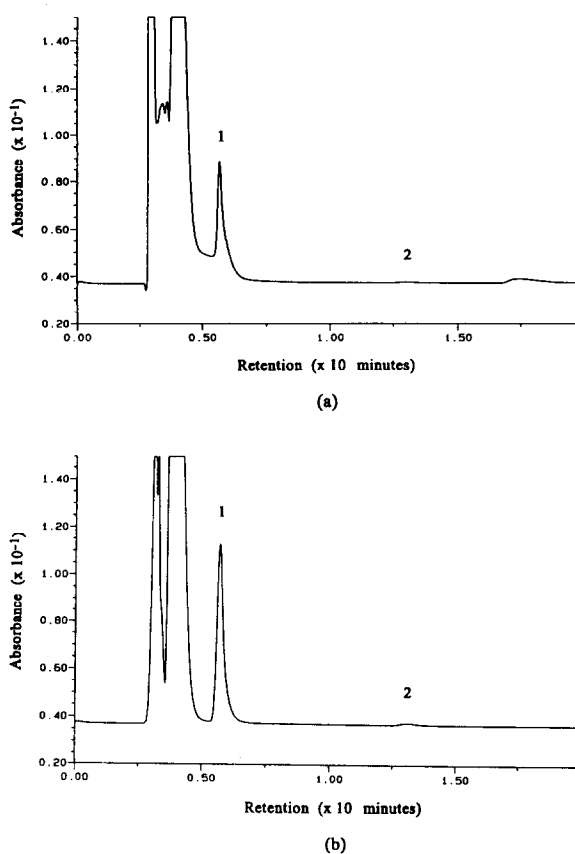


Fig. 2. Chromatogram of ilmenite prepared by hydroxide fusion obtained using (a) direct injection and (b) cation-exchange pretreatment. Conditions as for Fig. 1, except solutes (original concentration): (a) 1 = thorium (465.6 μ g/ml), 2 = uranium (13.4 μ g/ml) and (b) 1 = thorium (238.7 μ g/ml), 2 = uranium (7.4 μ g/ml).

shows a chromatogram of a 100 μ l of the same sample after cation-exchange pretreatment. The chromatograms clearly show that the recovery and peak shape for thorium were significantly improved using the cation-exchange pretreatment for ilmenite samples. However, the results obtained for the synthetic rutile and zircon samples were still poor, perhaps indicating that the hydroxide sample fusion/digestion procedure was inappropriate for these mineral sand types.

Having established the feasibility of using cation-exchange pretreatment to eliminate the dissolution matrix inference problems prior to the chromatographic step, a number of fusion/

digest procedures were then evaluated for use in conjunction with the pretreatment procedure. The cation-exchange pretreatment procedure was modified slightly with 2.0 M HIBA being used to elute the bound thorium and uranium from the ion-exclusion cartridge, instead of 7.5 M nitric acid. This approach gave similar recoveries to the nitric acid elution; however, it avoided the time consuming nitric acid evaporation step and also allowed the possibility for the pretreatment procedure to be automated. The final cation-exchange pretreatment procedure used is detailed under Experimental. The results obtained using a variety of fusion/digestion approaches for ilmenite, synthetic rutile and natural rutile samples prior to cation-exchange pretreatment and chromatographic analysis are detailed in Table 3.

The results indicated that an hydroxide fusion appeared to be appropriate for ilmenite samples, although it was not appropriate for other sample types. A tetraborate fusion procedure appeared to be appropriate for natural rutile, while carbonate–tetraborate, pyrosulphate and tetraborate–carbonate procedures all gave poor recoveries for this sample, particularly for uranium. The most significant differences between the first two procedures and the latter

three was that TiO_2 was insoluble and precipitated from the acid solution to be filtered off with either of the first two approaches; however, it remained in solution when using the other fusion/digestion approaches. It appeared highly probable that the Ti(IV) cation in the digest solution was eluting the more weakly retained uranyl cation from the ion-exclusion cartridge during the sample loading step, resulting in low uranium recoveries. This was confirmed by the fact that ICP-MS analysis of the four natural rutile digests shown in Table 3 all yielded similar results for thorium and uranium, indicating that the solutes were being released into the fusion/digestion solutions, but that the chromatographic recoveries obtained after the pretreatment procedure depended upon the dissolution method used.

The tetraborate fusion/nitric acid digestion procedure appeared to be the most appropriate for all the sample types and was further evaluated for use in conjunction with the cation-exchange procedure. All the mineral sand types were prepared using the tetraborate fusion/nitric acid digestion procedure after which the samples were treated using the cation-exchange pretreatment procedure described under Experimental. The results of the chromatographic analysis, together with the XRF results, are shown in Table 4. The ilmenite sample was fused/digested twice and the natural rutile sample was fused/digested five times, hence the multiple entries in the table for these samples. Fig. 3a–d show chromatograms obtained of the four mineral sand types prepared using the tetraborate fusion/nitric acid digestion and cation exchange pretreatment. The ilmenite and synthetic rutile chromatograms are shown at an injection volume of 200 μl in order to clearly highlight the uranium peak, although the thorium in these two sample types was typically quantitated using a 25–50- μl injection. Considering the differences between the two methods of analysis, the results showed remarkably good agreement. Analysis of the natural rutile digest by ICP-MS gave results for thorium and uranium of 69 and 48 $\mu\text{g/ml}$ respectively, which compared very well to the average results obtained by IC of 60.6 $\mu\text{g/ml}$

Table 3

Thorium and uranium concentrations in the original samples obtained using various fusion/digest procedures and cation-exchange pretreatment prior to chromatographic analysis

Sample	Thorium ($\mu\text{g/g}$)	Uranium ($\mu\text{g/g}$)
<i>Ilmenite</i>		
Hydroxide fusion	466	13.4
Tetraborate–carbonate fusion	314	ND
<i>Synthetic rutile</i>		
Tetraborate–carbonate fusion	332	ND
<i>Natural rutile</i>		
Tetraborate–carbonate fusion	56.4	25.3
Tetraborate fusion	62.0	53.1
Pyrosulphate fusion	63.4	11.1
Carbonate–tetraborate fusion	47.7	4.9

ND = Not detected.

Table 4

Thorium and uranium concentrations in the original samples obtained using tetraborate fusion/nitric acid leach and cation exchange pretreatment prior to chromatographic analysis

Sample	IC		XRF ^a	
	Thorium ($\mu\text{g/g}$)	Uranium ($\mu\text{g/g}$)	Thorium ($\mu\text{g/g}$)	Uranium ($\mu\text{g/g}$)
Ilmenite	487	15.0	490	10
	462	12.9		
Synthetic rutile	382	12.8	430	15
Zircon	167	184	179	217
Natural rutile	63.0	47.4	53	54
	59.4	48.9		
	59.1	49.6		
	59.5	49.9		
	62.0	53.1		

thorium (2.9% R.S.D.) and 49.8 $\mu\text{g/ml}$ uranium (4.2% R.S.D.).

3.3. Direct sample injection

The cation-exchange pretreatment described above effectively isolated the thorium and uranium from the fusion/digest matrix in a HIBA solution before injection into the liquid chromatograph. The procedure could no doubt have been automated by addition of a sample enrichment pump and six-port column switching valve to the system, in a similar fashion to the preconcentration of thorium and uranium on a HIBA-enriched C_{18} cartridge [14]. The analysis of samples using a direct injection approach would be preferable to the cation-exchange pretreatment; however, as discussed previously, this would require a very large dilution which was impractical at the thorium and (particularly) uranium concentrations present in the original mineral sands. The success of the cation-exchange pretreatment nevertheless indicated that if the thorium and uranium could be fully coordinated with HIBA in the digest solution, then direct injection of the sample would be possible. As the chromatographic detection limits for the thorium and uranium were 3.0 and 5.0 ng/ml , respectively, using a 1000- μl injection, it was

decided to attempt quantitation of the tetraborate fusion/nitric acid digest solutions by direct injection after dilution in HIBA.

The digestion solutions were diluted a further 1:10 and HIBA added to contain a final concentration of 400 mM before injection into the liquid chromatograph. Injection volumes of 1000 μl were required for uranium quantitation in ilmenite and synthetic rutile, while a 250- μl injection was used to quantitate thorium in these samples. Both thorium and uranium could be quantitated in zircon and natural rutile samples after a 500- μl injection. Table 5 summarizes the results and precision obtained by IC using the direct injection/HIBA dilution method and Fig. 4 shows a typical chromatogram obtained for a zircon sample (*i.e.* compare to Fig. 3c obtained using the cation-exchange pretreatment). The results showed excellent agreement to those obtained using the cation-exchange pretreatment, although the precision was generally not as high, particularly for the two cations in the natural rutile sample and also uranium in the ilmenite and synthetic rutile, as these solutes were being detected at concentrations approaching the method detection limits. Also, the direct injection approach was not as robust as the cation-exchange procedure as significant increases in the acid concentration of the fusion/

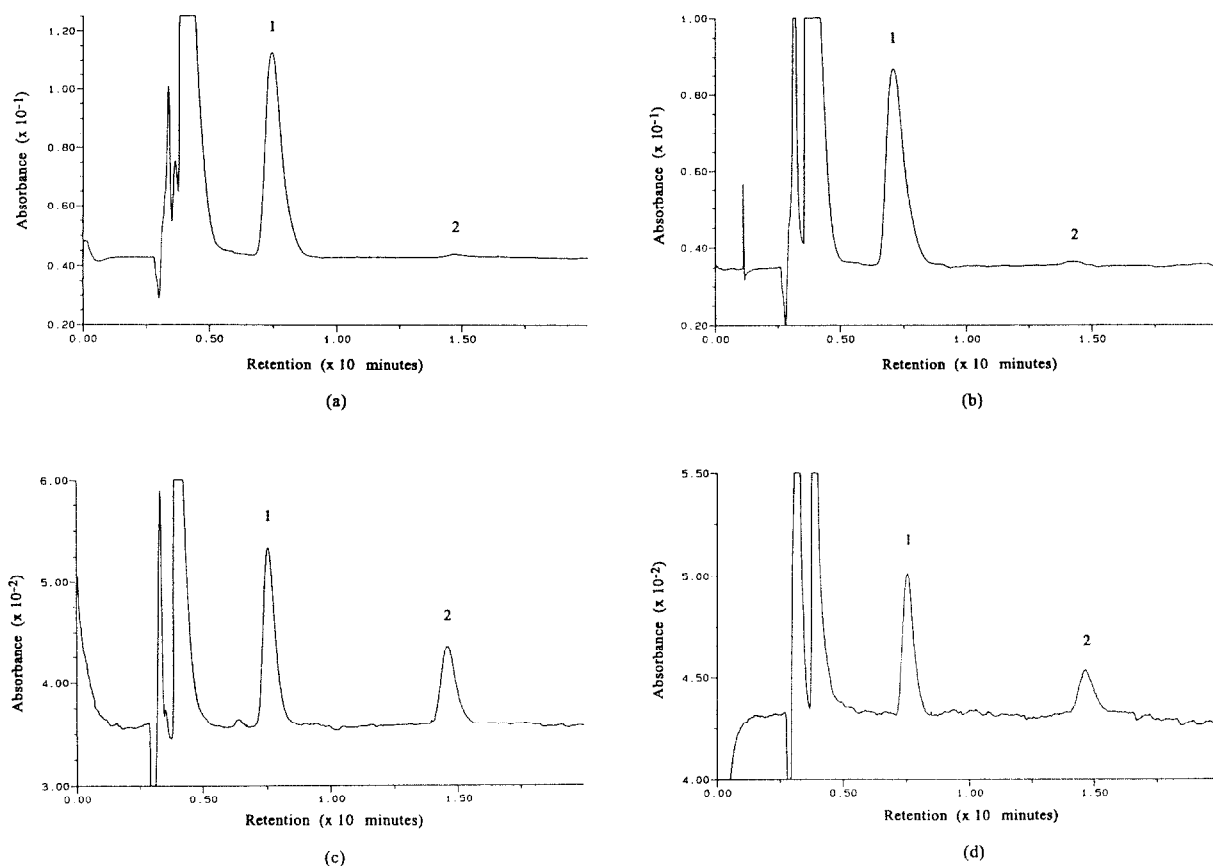


Fig. 3. Chromatograms of ilmenite (a), synthetic rutile (b), zircon (c) and natural rutile (d) prepared by tetraborate fusion/nitric acid digestion and cation-exchange pretreatment. Conditions as for Fig. 1, except injection volume: 200 μ l for (a), 200 μ l for (b), 100 μ l for (c) and 100 μ l for (d); solutes (original concentration): (a) 1 = thorium (462.4 μ g/ml), 2 = uranium (12.9 μ g/ml), (b) 1 = thorium (381.6 μ g/ml), 2 = uranium (12.8 μ g/ml), (c) 1 = thorium (167.2 μ g/ml), 2 = uranium (184.2 μ g/ml) and (d) 1 = thorium (59.4 μ g/ml), 2 = uranium (48.9 μ g/ml).

Table 5

Thorium and uranium concentrations in the original samples obtained using tetraborate fusion/nitric acid leach and direct injection after dilution in HIBA

Sample	Thorium (μ g/g)	Uranium (μ g/g)
Ilmenite	493 (0.4% R.S.D.)	18.3 (8.1% R.S.D.)
Synthetic rutile	382 (0.5% R.S.D.)	8.4 (10.0% R.S.D.)
Zircon	171 (2.13% R.S.D.)	199 (1.6% R.S.D.)
Natural rutile	68.6 (7.4% R.S.D.)	46.9 (9.2% R.S.D.)

R.S.D. obtained from five replicate injections.

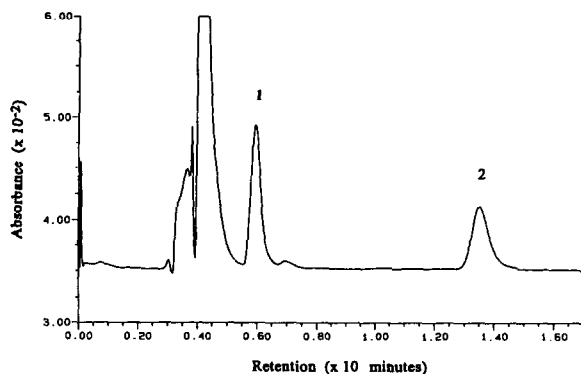


Fig. 4. Chromatogram of zircon prepared by tetraborate fusion/nitric acid digestion and direct injection/HIBA dilution method. Conditions as for Fig. 1, except injection volume: 500 μ l; solutes (original concentration): 1 = thorium (167.2), 2 = uranium (195.8 μ g/ml).

digestion solution resulted in low recoveries for both thorium and uranium.

4. Conclusions

Thorium and uranium can be analyzed in mineral sands by IC using a C_{18} reversed-phase column and an eluent of hydroxyisobutyric acid followed by post-column derivatization with Arsenazo III and visible detection at 658 nm. Sample preparation involved a tetraborate fusion/nitric acid leach followed by either cation-exchange pretreatment or direct injection after dilution in concentrated hydroxyisobutyric acid. The cation-exchange pretreatment resulted in higher precision and could be applied to more acidic sample digests; however, the direct injection approach gave comparable results when using the recommended dissolution procedure and offered significant time savings. The results obtained using the chromatographic method showed excellent agreement with those generated using the significantly more costly techniques of XRF and ICP-MS for ilmenite, synthetic rutile, zircon and rutile mineral sands.

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6. References

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