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Uranium Separations using Extraction Chromatography

by

Helen Carter

A Doctoral Thesis submitted in partial fulfilment of the requirements for
the award of

Doctor of Philosophy
of Loughborough University

March 2000

Research Supervisor: Prof. Peter Warwick

Sponsorship by EPSRC and AEA Technology plc

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ABSTRACT.

In the analysis of environmental samples for uranium and thorium pollutants and at natural levels for the dating of geological samples there was felt a need to develop better uranium and thorium separation procedures to replace the established anion exchange method used at AEA Technology plc. This was the first aim of the PhD research. Separation of uranium from thorium prior to measurement of the isotopes by alpha spectrometry was necessary due to the similar alpha energies of $^{234}\text{U}$ and $^{230}\text{Th}$.

TRU and UTEVA extraction chromatography resins (EIChroM Industries) were investigated as potential replacements to the anion exchange separation method. The resins are claimed by EIChroM to offer the advantage of providing an actinide specific separation while reducing the separation time from 2 to 0.5 days; the volume of acidic waste produced by a factor of 3, therefore, the cost of analysis was reduced.

A uranium and thorium separation procedure using the UTEVA extraction chromatography resin was developed. The uranium and thorium were sorbed by the UTEVA resin from 2M nitric acid. The thorium was then eluted from the resin with 5M hydrochloric acid and the uranium with 0.02M hydrochloric acid. The separation procedure was then evaluated using uraninite ore, coral, granite and lake sediment reference materials. The uranium and thorium concentrations and the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ activity ratio values determined for the reference material were in good agreement with certified values. The presence of plutonium was found to interfere with the measurement of uranium and thorium by alpha spectrometry. This was due to the similar alpha energies of uranium, thorium and plutonium. The co-elution of plutonium with uranium and thorium from the UTEVA resin was prevented by the inclusion of a reduction step using iron (II) sulphamate. The resulting plutonium (III) was not retained by the UTEVA column. The chemical recoveries for the procedure were
similar to those for anion-exchange, but the extraction chromatography procedure provided a more rapid separation using less reagents.

The second aim of the research was to investigate high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) as the measurement step. High resolution inductively coupled plasma mass spectrometry, using a Plasma Trace 2 instrument, was investigated as an alternative measurement step to alpha spectrometry for low level uranium and thorium samples. The instrument was evaluated using reagent blanks, reference materials and speleothem samples. The Plasma Trace 2 instrument advantages were due to its lower detection limits of $10^{-5}$ Bq compared with $0.05$ Bq for alpha spectrometry, and a reduction in the analysis time from 7 days to 1 day. The results obtained for the reference material using the Plasma Trace 2 instrument were in agreement with certified values when corrected for mass bias effects using a standard uraninite solution. However, the high cost of analysis using the Plasma Trace 2 instrument would prevent its use when analysis by alpha spectrometry was possible.

Finally, the third aim was to investigate reported variability in uranium in urine measurements. Experiments were carried out to determine whether the variable uranium recoveries obtained by several laboratories were due to operator error, the sample pre-treatment and separation method used or the TRU resin extraction chromatography columns. This research was undertaken at the request of ELChroM industries. The research identified differing but consistent uranium recoveries for the different sample pre-treatment and separation methods.

These results demonstrate that by adopting the techniques developed by the writer, the limit of detection for uranium and thorium was reduced from $0.05$ Bq to $10^{-5}$ Bq, and the costs in terms of materials and person hours were greatly reduced.
I would like to thank the EPSRC and AEA Technology plc for sponsoring my research and providing me with the opportunity to work towards a PhD. I would like to thank Professor Peter Warwick for his advice and support during my research. Thank you to all the staff in the radiochemistry group at AEA Technology plc for their help and support in particular to my industrial supervisors Doctor John Cobb and Doctor Geoff Longworth.

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| Table 6.15: | Results for method D with real urine solution, $^{233}$U and TR8B batch TRU columns. |
| Table 6.16: | Results for method B with real urine solution, $^{233}$U and TR8B batch TRU resin columns. |
| Table 6.17: | Results for method B with real urine solution, $^{233}$U and TR8B batch TRU resin columns with 1ml of ferrous sulphamate (as method A). |
CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW.
Introduction to Thesis.

The research reported in this thesis had three objectives:

The first objective was to evaluate extraction chromatography resins (TRU and UTEVA) as possible replacements for anion exchange resins for use in the separation of uranium from thorium. The extraction chromatography resins offer the advantage of reducing the separation time (from 2 days to 1/2 day) and the volume of reagents required (volume of nitric from 169 to 69ml and volume of hydrochloric from 69 to 3.8ml per sample). The reductions in time, and in volumes of reagents required, are major advantages over conventional methods used for uranium and thorium separations. The uranium, thorium separation method was used to determine the age of geological materials.

The second objective was to evaluate a high resolution inductively coupled plasma mass spectrometer instrument for the determination of low-levels of uranium and thorium. The instrument claims to measure uranium at the ppq level. The instrument would be valuable for the analysis of samples with low levels of uranium and thorium.

Finally, the third objective was to investigate problems in uranium recovery from urine samples. This latter investigation was in response to a request from ElChroM Industries.

As a valuable outcome of these investigations a procedure was developed which improved the limits of detection of uranium and thorium from 0.05Bq to $10^5$Bq and reduced the time taken, typically, from 80 to 16 person hours for analysis with an associated reduction in the quantity of acidic waste from 138ml to 73ml per sample. The initial investigation of the application of TRU resin, described in chapter 2, are confirmed by the standard procedures used in the measurement of uranium in urine described in chapter 6.

This introduction starts by describing the background to the theory and research undertaken for solvent extraction and anion exchange. This research lead to the
development of a combination of the techniques called extraction chromatography (EC). The chapter also includes an introduction to the theory, a general literature review of extraction chromatography and a literature review of EICChrom products. The chapter also includes an introduction to dating methods used to age geological samples and an introduction to the measurement of uranium in urine.
(1:1) SOLVENT EXTRACTION.

In its simplest form, extraction refers to the transfer of a solute from one liquid phase to another. A solute S will distribute itself between two phases (after shaking and allowing the phases to separate) and, within limits, the ratio of the concentration of solute (K_D) in the two phases will be a constant.

\[ K_D = \frac{[S_{\text{org}}]}{[S_{\text{aq}}]} \]  

Where:
- \( K_D \) is the distribution coefficient.
- \( S_{\text{org}} \) and \( S_{\text{aq}} \) are the concentration of solute in the organic solvent and in the aqueous phase respectively (g/cm³).

The main parameter which characterises the extraction process is its distribution coefficient. The distribution coefficient remains constant over a wide concentration range unless the extraction process is complicated by some side effects: in most cases this coefficient is numerically equal to the ratio of the solubilities of the extracted substance in two phases. For separation of two substances, the difference between their distribution coefficients is of fundamental importance. The ratio of the distribution coefficients of two substances, \( a = K_1/K_2 \), is called their separation coefficient: it provides the criterion by which the possible effectiveness of their separation can be judged. The greater the difference between this ratio and unity, the easier is the separation. If \( K_1 = K_2 \), the separation becomes impossible.

(1:1:1) Literature review for solvent extraction.

As early as 1842 Peligot reported that diethyl ether would extract uranium from aqueous nitric acid solutions [1]. However, sustained investigations into liquid-liquid extraction systems and properties of the actinide elements really began a century later. From the late 1940’s to the early 1980’s plutonium production for nuclear weapons was the principle driver for technology development in the separation of the actinides.
The diethyl ether methods were replaced by less volatile and flammable ketones and phosphates. Methyl Isobutyl Ketone (MIK) has been used to extract uranium from nitrate solutions as a molecular compound of uranyl nitrate. Solvent extraction using MIK has been used extensively in the nuclear industry for large scale separation of uranium from plutonium from spent fuels in the REDOX process [2].

Tri-n-butyl phosphate (TBP) has been widely used for the separation of uranium since Warf [3] observed in 1945 that tri-n-butyl-phosphate (TBP) would extract uranium from aqueous nitric media. The extensive use of TBP is mainly because of its very high distribution coefficient. This enables an almost complete separation of uranium with one extraction. TBP is also non-volatile over a very wide temperature range (b.p. +289°C), is not sensitive to radioactivity and is chemically stable with respect to water and nitric acid. Uranium is extracted from nitrate solutions by TBP in the form of the molecular compound \( \text{UO}_2(\text{NO}_3)_2.2(\text{C}_4\text{H}_9\text{O})_3\text{PO} \). Iron, thorium and protactinium are all co-extracted with uranium from the nitric acid, but iron can be removed by washing the organic phase with dilute nitric acid. Thorium can be complexed with EDTA before extracting the uranium into TBP, leaving thorium in the aqueous phase. Separation of uranium, thorium and protactinium can be achieved in hydrochloric acid since thorium and protactinium are poorly extracted into TBP relative to uranium.

Many different methods have been published for the recovery of uranium from the TBP complex [4-7]. TBP has also been used extensively in the nuclear industry as the solvent in the PUREX process [8].

In the late 1950's and early 1960's acidic organophosphorus extractants were developed. Phosphonic, phosphoric, and phosphinic acid esters containing at least one ionizable proton were extensively investigated as "liquid cation exchangers" for the separation of a variety of metals, but particularly for the lanthanides and trivalent actinides. The example of this type of ligand is bis(2-ethylhexyl)phosphoric acid (HDEHP) [9]. This reagent is perhaps the most
important industrial reagent used for lanthanide separations. Examples of the use of HDEHP include; the extraction of uranium from hydrochloric acid by the HDEHP [10], the extraction of uranium by HDEHP from aqueous diamine solutions [11], the extraction of uranium from phosphoric acid solutions using a HDEHP-TOPO mixture [12,13], and the extraction of uranium from phosphoric acid using a HDEHP-CYANEX-921 mixture [14].

As the lanthanide and trivalent actinide cation radii and extraction coefficients overlap, the HDEHP in toluene system was not effective at separating the lanthanides from the trivalent actinides. The technology was then used to develop TALSPEAK, trivalent actinide lanthanide separation by phosphorus extractants and aqueous complexes [15]. In these the aqueous medium is 1M lactic acid/0.05M diethylenetriaminepentaacetic acid (DTPA) at pH 3. The extractant is 0.3M HDEHP in diisopropylbenzene.

In the early 1980’s attention focused on carbamoylmethylphosphoryl extractants as potential extractants for selected tri, tetra, and hexavalent actinides from nitric acid containing waste solutions [16,17,18]. Previous work with other types of bifunctional extractants lead to the extraction and recovery of tetra and hexavalent actinides [19,20,21], but the extraction of trivalent species, particularly americium, from acidic media, remained difficult. Horwitz et al [22], based on earlier work by Siddall [23,24], developed a new organophosphorus octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) extractant. The CMPO extractant was used to develop a new solvent based extraction process for total actinide recovery, TRUEX [22]. The TRUEX process is compatible with PUREX technology as the solvent consists of a standard PUREX process solvent with CMPO added for trivalent actinide extraction.

The development of an extraction process for the removal and recovery of strontium-90 from waste streams was complicated by its chemistry. Strontium (II) has a relatively low charge density due to its large ionic radius and low charge. As a result the energy associated with bond formation between it and functional groups of many organic extractants is not sufficient to completely
dehydrate the cation and to strip away water molecules associated with the anions that must accompany strontium into the organic phase to maintain electrical neutrality. Thus extraction of strontium inevitably involves the transfer of a complex bearing a number of associated water molecules into the organic solvent. This leads to poor extraction of strontium particularly from acidic nitric media. To compensate for this crown ethers are used for strontium separation. Crown ethers possess a cage-like structure whose dimensions can be tailored to provide a good fit for strontium. Because, complex formation between strontium and such a molecule involves little change in the conformation of the extractant the energetics of the extraction are somewhat more favourable.

The crown ether [25] (bis-4,4' (5') tertbutylcyclohexano-18-crown 6) is in an organic solvent for example, 1-octanol, capable of dissolving a substantial amount of water. This enables transfer of the strontium complex from the aqueous phase into the water-like, yet water immiscible, organic media. This technique has been developed and is known as the SREX process [26].

The disadvantages of solvent extraction methods/separation schemes are that they are time consuming and generate substantial volumes of organic waste.

(1:2) ION EXCHANGE.

Ion-exchange chromatography is based on the equilibrium of solute ions between the solvent and charged sites fixed on the stationary phase.

An ion exchange reaction may be defined as the reversible interchange of ions between a solid phase, the ion exchanger, and a solution phase, the ion exchange being insoluble in the medium in which the exchange is carried out.

\[
M^+A^- + B^- \longleftrightarrow M^+B^- + A^- \quad \text{Equation 1.02.}
\]

Where:

- \(M^+\) is the insoluble fixed cationic complement of the ion exchanger \(M^+A^-\),
- often called simply the fixed ion.
The anions A' and B' are referred to as counter ions, whilst ions in solution which bear the same charge as the fixed anion of the exchanger are called co-ions.

For the purpose of this thesis only the strongly basic anion exchange resins are discussed. The resins are small, amorphous (non crystalline) particles of organic material. Polystyrene resins for ion exchange are made by the copolymerization of styrene and divinyl benzene. The benzene rings can be modified to produce an anion-exchange resin, containing ammonium groups (-NR₃⁺), to which the anions in solution are attracted. The pore size of polystyrene and polyacrylic acid resins effectively limits their use to molecules weighing less than 500. Large molecules cannot penetrate these resins. The structure of a strongly basic anion exchange resin is shown in figure 1.01.

![Structure of a strongly basic anion exchange resin.](image)

Figure 1.01: Structure of a strongly basic anion exchange resin.

**(1:2:1) Literature review for anion exchange.**

Anion exchange columns have been used to separate uranium and thorium [27-35].

Research by Bunney et al [27] demonstrated that the adsorption of uranium on to strongly basic anion exchange resin increased rapidly as the strength of the hydrochloric acid was increased. Strong anionic complexes of the uranyl ion (UO₂Cl₃⁻) and (UO₂Cl₄)²⁻ were formed in aqueous solutions. By varying the strength of the hydrochloric acid separation of uranium, thorium and protactinium
was achieved using an anion exchange column. The uranium, thorium and protactinium were loaded onto the anion exchange column with 12M hydrochloric acid. The thorium was not retained by the column. The protactinium was eluted from the column with 4-5M hydrochloric acid and the uranium was eluted with 0.1M hydrochloric acid. The uranium was separated from iron, reduced to the divalent state, using a chloride form anion exchange column.

Maiti et al [28] have used ion exchange to separate americium, plutonium, uranium and neptunium from the highly radioactive defence waste stored at the Hanford site. A hydrochloric acid anion exchange column was used; the americium was not retained by the column, the plutonium was eluted with 9M hydrochloric acid-ammonium iodide to reduce the plutonium(IV) to plutonium(III), the neptunium was eluted with 4M hydrochloric acid-0.1M hydrofluoric acid and the uranium with 0.5M hydrochloric acid-1M hydrofluoric acid. The concentration and abundance of the separated americium, plutonium, uranium and neptunium was then determined. This information was used to characterize the defence waste prior to the selection of an appropriate waste disposal method.

In the nitrate form uranium was only weakly adsorbed on to strong base anion exchange resins, while thorium formed very stable nitrate complexes (Th(NO₃)₆)²⁻.

Lally et al [29] demonstrated that by combining a hydrochloric and a nitric acid anion exchange column separation of uranium, thorium and iron can be achieved. Initially a hydrochloric acid column was used to separate thorium from uranium and iron. Two separate nitrate columns were then used to separate uranium from iron and to separate thorium from any remaining uranium respectively. The anion exchange separation method for uranium and thorium currently in use at AEA Technology plc is based on this method.

Rodriguez et al [30] used two columns initially. A nitric acid column to separate uranium from the thorium which was absorbed by the column. The thorium was then eluted with 10M hydrochloric acid. The uranium fraction was then further
purified using a hydrochloric acid column. The hydrochloric acid column enabled separation of the uranium from iron and any remaining thorium.

Radenkovic et al [31] used more than one column to separate and purify uranium, plutonium and thorium from environmental samples. Initially the uranium, thorium and plutonium were separated using a nitrate column. The three individual fractions were then purified by placing the uranium fraction on a hydrochloric acid column, the thorium fraction on a nitrate column and the plutonium fraction on a nitrate column with hydrogen peroxide and sodium nitrite.

Parsa et al [32] used a nitrate anion exchange column in combination with solvent extraction for the determination of uranium and thorium in soil. The thorium was eluted with 8M nitric acid and the uranium was then eluted with 3M hydrochloric acid. The solvent extraction step was added to further separate and purify the uranium and thorium fractions.

A combination of anion exchange and solvent extraction was also used by Choukri et al [33]. A hydrochloric acid column was used to separate uranium from thorium. The uranium and iron were then separated by solvent extraction and the thorium fraction purified by placing on the column for a second time after it had been converted to the nitrate form.

Rosholt et al [34,35] used a hydrochloric acid anion exchange column to separate uranium from thorium. The uranium fraction was then purified using solvent extraction.

Korkisch et al [36] used a nitrate anion exchange column with 90% methanol-10% nitric acid solution to separate thorium from uranium, iron, titanium, zirconium, aluminium, cobalt, nickel and copper. An ascorbinate anion exchange column was used at pH 4 to separate thorium ascorbinate complex from the rare earth elements, lanthanum, barium and lead.

Anion exchange with hydrochloric acid-methyl alcohol mixed media was also used by Usuda et al [37] to separate the transplutonium and rare earth elements from uranium or plutonium and aluminium.
Anion exchange in the sulphate form has been used to separate uranium from iron and vanadium [38], to separate uranium from a large excess of bismuth [39], to separate uranium, thorium and the rare earth elements [40, 41, 42, 43, 44], and to separate thorium from the rare earth elements [45].

The disadvantage of the anion exchange technique are that they generate substantial volumes of acidic and resin waste.

(1.3) EXTRACTION CHROMATOGRAPHY.

Extraction chromatography combines the selectivity of solvent extraction with the simplicity of ion chromatography. The technique involves the use of an inert solid support coated with a small quantity of extractant solution. The resulting extraction chromatography resin has the advantages of reducing the separation time, the volume of organic/acidic solutions required for analysis and therefore the volume of acid/organic waste solutions, and the cost of analysis. The theory of extraction chromatography is discussed in this section of the thesis.

Regardless of the method of the extraction chromatography resin preparation or the support-chemistry combination, all extraction chromatography methods share certain features. These are:

First, partitioning is accompanied by the complex chemical changes involved in converting a hydrated metal ion into a neutral, organophilic metal complex as in liquid-liquid extraction.

Second, if no specific interactions occur between the support and molecules of either the extractant selected or complex formed, the chromatographic behaviour of a given ion can be correlated with its behaviour in the corresponding liquid-liquid extraction system.

This enables data obtained when developing liquid-liquid solvent extraction procedures to be used in the selection of conditions for extraction chromatography. Using the ratio of the concentration of metal in the organic
phase to the concentration in the aqueous phase and two column parameters (Vs and Vm). The separation of ions can be estimated using equation 1.03.

\[ k' = \frac{DV_s}{V_m} \]  
\text{Equation 1.03}

Where:
- \( k' \) is the number of free column volumes (FCV) of eluent required to reach peak maximum.
- \( D \) is the ratio of the concentration of metal in the organic phase to the concentration in the aqueous phase.
- \( V_s \) and \( V_m \) are the stationary phase volume and the interstitial or free column volume respectively (cm\(^3\)).

The sorption of an ion by an extraction chromatographic resin is a composite of a number of processes: partition of the extractant molecule between the aqueous and organic phases, formation of the metal complex, and partitioning of the complex formed between the organic and aqueous phases. Considering these processes an expression for the distribution ratio of the metal ion (\( D_{M} \)) between the two phases is given by equation 1.04.

\[
D_{M} = \left( \frac{K_p}{K'_{p}^{m}} \right) B_{i} [A^{-}]^{n} [L]_{\text{org}}^{m}
\]  
\text{Equation 1.04}

Where:
- \( D_{M} \) is the ratio of the concentration of the fully formed metal complex in the organic phase to the concentration of the hydrated metal ion in the aqueous phase.
- \( K_p \) is the distribution constant for the extracted metal complex.
- \( K'_{p} \) is the distribution ratio of the extracted molecule.
- \( B_{i} \) is the formation constant.
- \([A^{-}]\) is the aqueous anion concentration (g/cm\(^3\)).
- \([L]_{\text{org}}\) is the concentration of the extractant available to react with M\(^{n+}\).
- \( m \) and \( n \) are the number of extractant molecules and anions which are present in the extracted complex (g/cm\(^3\)).
In practice, the optimum organic-phase compositions used in liquid-liquid extraction are frequently unsuitable for direct use as a stationary phase in extraction chromatography. For example, the need to maximise the capacity of a chromatography resin often mandates the use of a higher extractant concentration than is feasible in a liquid-liquid system. Equations 1.03 and 1.04 are useful in predicting general trends rather than in defining the optimum conditions for a given separation.

Experience indicates that the easiest method of determining the most suitable conditions for separation is to carry out batch sorption experiments. In these experiments the solution containing the ion(s) of interest is equilibrated with a known weight of extraction resin. Using equation 1.05, the experimental data are used to calculate the weighed distribution ratio values Dw. The Dw value is converted to D (volume distribution ratio) value (using the density of extractant) and then used to calculate k'.

\[
D_w = \left( \frac{A_o-A_s}{W} \right) \div \frac{A_s}{V} \tag{Equation 1.05}
\]

Where:

- \( A_o \) and \( A_s \) are the aqueous concentration of the test element before and after equilibration respectively (g/cm³).
- \( W \) is the weight of the resin (g).
- \( V \) is the volume of the aqueous phase (cm³).
General Literature Review of Extraction Chromatography.

Extraction chromatography was first proposed by Siekierski [46] in 1959 as a possible way of separating metal ions. The research initially concentrated on the choice of the inert solid support material and then on the use of the extractant solution mixtures. Various support/extraction combinations have been proposed and are discussed in this section of the thesis. Molochnikova [47] used filter paper and silica gel impregnated with polyethylene glycol to separate neptunium from americium. Heunisch et al [48] used silica gel coated with 35-40% tri-n-butyl phosphate (TBP) to separate uranium from phosphoric acid.

Hamelin et al [49] used KEL-F support impregnated with tri-n-butyl phosphate (TBP) for the isolation of uranium from plutonium. Cerrari et al [50] used KEL-F supporting tri-n-octylphosphine oxide (TOPO) for a variety of separations: the separation of aluminium, copper, iron and uranium, the separation of vanadium, titanium, and uranium, the separation of manganese, copper, uranium and the separation of nickel, cobalt, iron and uranium.

The advantages of Teflon powder over various other supports in extraction chromatography have been discussed by Moore et al [51]. Filer [52] used polytetrafluoroethylene powder impregnated with 0.45M di(2-ethylhexyl)orthophosphoric acid (HDEHP) for the separation of the trivalent lanthanides from trivalent actinides. The Teflon powder was selected as the inert support because of its exceptional stability to chemical reagents.

Testa et al [53] used microthene-710 (microporous polythene) 50-100 mesh coated various extractants. The resin was coated with tri-n-octylphosphine oxide (TOPO) for the extraction and subsequent separation of uranium from thorium. The uranium and thorium were sorbed onto the resin microthene-TOPO with 4M nitric acid. The thorium was eluted using 3M sulphuric acid and the uranium eluted with 1M hydrofluoric acid.
The resin was coated with 1.5M (HDEHP) in toluene for the separation of yttrium from strontium. The yttrium was sorbed onto the microthene-HDEHP with 0.3M nitric acid and separated from the strontium which was not sorbed. The yttrium was then eluted from the resin using 6M nitric acid.

The resin was coated with 1.5M (HDEHP) in benzene for the extraction of iodine by the microthene-benzene after the iodide in the sample had been oxidized to iodine. The resin was washed with water and the iodine eluted with 0.1M ascorbic acid.

Jarvis et al [54] developed a scheme to separate neptunium and americium from uranium and plutonium using lewatit OC 1023 impregnated with tri-n-butyl phosphate (TBP). The sample containing neptunium, americium, uranium and plutonium was loaded onto the resin with 4M nitric acid. The plutonium was adjusted to the tetravalent state by the addition of 0.1M sodium nitrite. The column was washed with 6M nitric acid which eluted the neptunium and americium. The plutonium was then eluted with 2.5M nitric acid-0.1M ferrous sulphamate. The column was washed with 6M nitric acid to remove any remaining iron and the uranium eluted with de-ionized water.

Mathur et al [55] used octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) adsorbed on chromosorb-102 which has been evaluated as an alternative to the TRUEX process for the separation of the americium, plutonium uranium and the rare earth elements. The sample solution containing americium, plutonium, uranium and the rare earth elements was loaded onto the resin with 3M nitric acid. The americium and rare earth elements were eluted from the resin using 0.04M nitric acid. The plutonium and uranium were eluted with 0.01M oxalic acid and 0.25M sodium carbonate solution respectively.

Al-Ammar et al [56] investigated the use of TBP impregnated macroporous Amberlite XAD-4 for the separation of uranium from impurity elements in nuclear grade uranium compounds.
Lee et al [57] used the chelating resin TAR-XVI which contains the 4-(2-thiazolylazo) resorcinol group. Selective sorption of uranium was achieved by controlling the pH and by the addition of complexing agents. The method enabled the separation of uranium from thorium, zirconium and metals present in geological materials.

The literature review shows that extraction chromatography resins have been developed and used for the separation of a variety of metals from a variety of sample matrices. The bulk of the development work on the use of extractant and resin combinations for selective separation of a number of radionuclides has been carried out by Horwitz and co-workers for EICChroM industries. These resins and their applications are described in detail in the following literature review.
(1:5) EIChroM PRODUCTS LITERATURE REVIEW.

(1:5:1) Introduction to EIChroM products.

EIChroM (Extraction Ion Chromatographic Materials) Industries, Inc., Darien, IL60561, USA, manufacture speciality chromatographic materials. The materials are based on four key technologies:

diphonix resin,
ABEC extraction materials,
crown ethers and speciality extractants,
and inorganic adsorbers.

Each of the extraction chromatography resins employ an organic extractant originally devised for the removal of the selected metal ions from the complicated and highly acidic wastes generated by the processing of nuclear materials. Although all of the reagents are highly selective for their target cation(s), they are not sufficiently specific to extract a single ion. This literature review describes the Sr, TRU, UTEV, RE, Ln, Ni, Pb, tritium, diphonix and ABEC resins and their applications. Separation schemes consisting of one or more of the resins are also discussed. Figure 1:02 shows the element separation schemes developed for the UTEV, TRU, TEVA and Sr resins.
Figure 1.02: Schematic showing the element separation schemes developed for the UTEVA, TRU, TEVA and Sr resins.
(1:5:2) Sr resin.

The strontium (Sr) resin is an extraction chromatography resin for the selective sorption of strontium from acidic nitrate media. The strontium extracted by the Sr resin is easily stripped using dilute acid or de-ionized water.

![Figure 1.03: di-t-butylcyclohexano-18 crown-6.](image)

The crown ether (di-t-butylcyclohexano-18 crown-6) used as the strontium extractant is shown in figure 1.03. The selectivity of the reagent stems, in part, from the close correspondence of the ionic diameter of strontium ($\text{Sr}^{2+} = 2.24 \text{ nm}$) to the cavity size of the crown ether (2.6-3.2 nm). Interference's from potassium and barium can occur when they are present in sufficient quantities this is due to their similar diameters ($\text{K}^+ = 2.66 \text{ nm}$ and $\text{Ba}^{2+} = 2.70 \text{ nm}$) to strontium.

ElChroM Industries have published a procedure for the analysis of strontium 89/90 in water [58,59,60] and the analysis of lead-210 in water [61] using Sr resin.

Research by E.P. Horwitz [25,26,62] has shown that strontium may be efficiently extracted from aqueous solutions containing high concentrations (1-7M) of nitric acid by solutions of various crown ethers dissolved in a number of aliphatic alcohols and ketones. This chemistry was then adapted [63] to produce a novel extraction chromatography resin by sorbing a solution of 1M 4,4'(5')-bis(t-butylcyclohexano)-18-crown-6 in 1-octanol on an inert polymeric substrate. The resulting material [64,65] was evaluated for the effects of matrix constituents (divalent $\text{Ca}^{2+}$, $\text{Sr}^{2+}$, $\text{Ba}^{2+}$, $\text{Ra}^{2+}$, $\text{Pb}^{2+}$, and $\text{UO}_2^{2+}$) and (monovalent $\text{Na}^+$, $\text{K}^+$, $\text{Rb}^+$, $\text{Cs}^+$, and $\text{Tl}^+$) metal ions. The research concluded that the material provides a simple and efficient method for the separation of strontium from a wide variety of
metal ions in nitric acid solution and under appropriate conditions, the resin can also function as either a lead selective or tetravalent actinide (plutonium(IV), neptunium(IV)) selective material.

**Applications of the Sr resin.**

Proposed applications of the Sr resin are shown in figure 1.02. These include Sr separation from a variety of samples, $^{90}\text{Sr} - ^{90}\text{Y}$ separations using the Sr and RE resins (see 1:5:6), separation and isolation of lead from environmental samples, and the separation of radium from barium.

**Strontium separations.**

The Sr resin has been used for the analysis of strontium in biological, environmental and nuclear waste samples [63,66], the characterisation of nuclear waste solutions [67], analysis of geological materials [68], soil samples [69], liquid samples [70], urine [71], calcium carbonate matrices of biological origin [72] and milk samples [73]. The resin has also been used with an automated sequential injection system for the rapid determination of $^{90}\text{Sr}$ [74].

**Radium and barium separation.**

Chabaux [75] showed that the Sr resin may be used to separate radium and barium when measuring the radium content of volcanic rocks by mass spectrometry. The method consists of radium enrichment by cation exchange or co-precipitation with barium sulphate followed by purification using the Sr resin.

**Determination of lead.**

Sloof [76] used Sr resin for the determination of lead in sulphate and phosphate matrices. The samples were loaded onto the column using 2M nitric acid and lead was eluted from the column as an ethylenediaminetetraacetic acid (EDTA) complex using 15 ml of 0.01mol/l Na$_2$EDTA. The research concluded that the combination of chromatographic lead separation and graphite furnace atomic absorption spectrometer (GFAAS) was an accurate method for lead determination.
in phosphogypsum, phosphate ore, phosphoric acid, and in soils, sediments, environmental and biological reference materials. Gale [77] used Sr resin for extracting and purifying lead from difficult matrices such as geological and archaeological samples. Woittiez [78] used the Sr resin for the determination of lead-210 in phosphogypsum and phosphate ore. Vajda [79] described the sequential separation of lead and polonium using the Sr resin. The sample was loaded onto the column in 2M hydrochloric acid. Polonium was stripped from the column with 6M nitric acid. The column was then converted to the chloride form and the lead eluted with 6M hydrochloric acid.

Previous approaches to determine lead have included counting the resin directly by liquid scintillation counting (LSC), stripping the lead with a complexing agent such as ammonium oxalate, and the use of the lead resin (see 1:5:8).
TRU resin is an extraction chromatography resin for the selective sorption of the transuranics from acidic nitrate media. The transuranics extracted by TRU resin are then easily eluted from the column using dilute nitric acid. The resin consists of 0.75M octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO) in tributyl phosphate (TBP) coated onto an inert polymeric support.

![Structure of CMPO](image)

Figure 1.04: Structure of CMPO.

Early research used Amberlite XAD-7 as the inert polymeric support. The resin was used to separate and preconcentrate the actinides from urine [80]. The actinides were sorbed onto the column with 2M nitric acid-0.5M aluminium nitrate (aluminium is added to enhance americium sorption) and eluted from the column with dilute ammonium oxalate solution. The resin's use was limited due to the width of the elution bands which caused significant tailing which precluded the sequential separation of the actinides.

The use of resins chemically indistinguishable from Amberlite XAD-7 but with smaller average particle diameters (Amberchrom CG-71ms) have lead to narrow elution bands and the possibility of sequential actinide elution.

Research by Horwitz et al [81] investigated the effect of nitric and hydrochloric acid concentrations and of macro levels of selected elements on the sorption of actinide ions by the TRU resin. Actinide sorption was shown to be most efficient at high (>1M) nitric acid concentrations, although tetra and hexavalent actinides are strongly retained even from dilute (0.05M) nitric acid solutions. Macro concentrations of several common anions (e.g. PO$_4^{3-}$ and SO$_4^{2-}$) or complexing
agents (e.g. oxalic acid) were shown not to adversely affect the sorption of trivalent actinides, while reducing the sorption of tetravalent actinides. Such, effects, together with oxidation state adjustments, provide the basis for the sequential elution of individual actinides and for actinide isolation from environmental and biological samples.

TRU resin retains americium(III) and other trivalent actinides strongly over a wide range of nitric acid concentrations (0.5-8M). The extremely strong retention of uranium, neptunium and plutonium even at low acidities means that the elution of these ions cannot be effected simply by lowering the aqueous nitric acid concentration. Elution is achieved by using a different acid or a solution of an appropriate complexing agent.

The effect of iron(III) even at low concentrations is pronounced. By reducing the iron(III) to iron(II) with ascorbic acid the effect of the presence of iron on americium sorption is practically negligible. Aluminium is added to reduce interference effects from phosphoric, sulphuric and oxalic acids. The presence of aluminium also enhances the sorption of americium through its salting out effect. Calcium was found to be poorly retained by the TRU resin over a range of nitric acid concentrations and therefore causes little interference with actinide sorption.

(1:5:3:1) Applications of the TRU resin.

The applications of the TRU resin are shown in figure 1.02. The TRU resin has been used to develop methods for the group separation of the actinides from urine [82,83], hydrochloric acid waste streams [84] and soil samples [85]. The resin has also been used to preconcentrate uranium and thorium from soil samples prior to analysis by inductively coupled plasma mass spectrometry (ICP-MS) [86].

(1:5:3:1:1) Americium separation.

Goldstein et al [87] have reported the measurement of americium in air, water and urine samples. The samples were loaded onto the TRU resin column and washed using 1-3M nitric acid solution. The column was then converted to the chloride
form with 10M hydrochloric acid and the americium was eluted with 4M hydrochloric acid. If plutonium analysis is required the plutonium is separated from americium on an anion exchange resin prior to using the TRU resin. Sodium nitrite is added to the load solution to adjust any plutonium present to the quadravalent oxidation state.

1:5:3:1:2 Americium, curium and plutonium separation.

The resin has also been used in separation schemes for americium, curium and plutonium from a variety of matrices including soil, sludge and waste tank samples [88]. A 5ml 2M nitric acid / sodium nitrite load solution was used to adjust the plutonium valence from +3 to +4. The column was rinsed with 20ml of 2M nitric acid. The americium and curium were eluted from the column with 2ml of 9M hydrochloric acid followed by 13ml of 4M hydrochloric acid. The plutonium was then eluted with 15ml of 4M hydrochloric acid in 0.1M hydroquinone.

Research by Rodriguez et al [89] investigated the interferences in the determination of plutonium, americium and curium in radioactive waste. The paper concluded that the determination of $^{241}\text{Pu}$, $^{241}\text{Am}$, $^{242}\text{Cm}$ and $^{244}\text{Cm}$ by extraction chromatography is affected by some interferences (e.g. $^{55}\text{Fe}$ in the analysis of $^{241}\text{Pu}$, and $^{236}\text{Pu}$ and $^{238}\text{Pu}$ in the analysis of $^{241}\text{Am}$ and $^{244}\text{Cm}$).

1:5:3:1:3 Light rare earths, uranium and thorium separations.

Pin et al [90] developed a scheme for separating the light rare-earth elements (LREE), thorium and uranium. The method consists of using a (5mm i.d., 0.25ml) TRU resin column to separate LREE, uranium, and thorium. The sample was loaded onto the column in 2ml of 1M nitric acid and the column washed with 2.5ml of 1M nitric acid and 0.25ml of 0.05M nitric acid. The LREE were then eluted with 0.7ml of 0.05M nitric acid and separated from each other using Ln resin (see 1:5:7). Thorium and uranium were eluted with 1.5ml of 0.25M hydrochloric acid and 1.5ml of 0.1M hydrochloric acid-0.29M hydrofluoric acid respectively.
(1:5:3:1:4) Uranium, thorium, neptunium, plutonium and americium separations.

Boll et al [91] used the TRU resin to develop an actinide separation scheme. The Am$^{3+}$, Cm$^{3+}$, and most M$^{3+}$, M$^{2+}$, and M$^+$ matrix ions were eluted with a 5M hydrochloric acid load/wash fraction. Thorium was then eluted with 1.3M hydrochloric acid. Plutonium and neptunium were eluted with 0.03M oxalic acid/0.5M hydrochloric acid solution. Uranium was eluted with 0.1M ammonium oxalate.

(1:5:3:1:5) Radium.

Burnett et al [92,93] used the TRU resin for the determination of $^{228}$Ra in natural waters. The resin is used to isolate the direct daughter $^{228}$Ac prior to low-level counting. The barium, lead and radium pass directly through the column when loaded in 5ml of 2M nitric acid and rinsed with 5ml of 2M nitric acid. The actinium is retained by the column and can be eluted with 5-10ml of 1M hydrochloric acid. Bismuth is quantitatively retained on the column through the actinium elution and can be eluted with 6M hydrochloric acid. Problems in the measurement of actinium can occur with samples containing thorium and high levels of $^{90}$Sr($^{90}$Y) and $^{212}$Pb. Thorium interference can be eliminated by eluting the actinium with 10-15ml of 3M hydrochloric acid instead of 1M hydrochloric acid. Yttrium interference can be overcome by using 0.5M nitric acid instead of 2M nitric acid to load the sample onto the column. Samples with high $^{212}$Pb relative to the amount of $^{228}$Ac continued to cause problems as increasing the amount of dilute nitric acid to remove lead from the column caused breakthrough of the actinium.


Burnett et al [94] used the TRU resin with ion-exchange for the isolation of protactinium from geological materials. The procedure initially separates the uranium and protactinium from thorium using a TRU resin column. The uranium and protactinium are then separated from each other using a cation-exchange column.
Bunzl et al [95] used the TRU resin to determine $^{90}$Sr in brine. The method utilises the different solubility of yttrium compared to that of strontium, calcium and magnesium in ammonium chloride solutions and uses the TRU resin for purification of the yttrium fraction. The activity of $^{90}$Y is then used to obtain the activity of $^{90}$Sr in the sample.
The UTEVA resin is an extraction chromatography resin for the selective sorption of uranium and tetravalent actinides from acidic nitrate media. The uranium and tetravalent actinides are then easily eluted from the resin using dilute nitric acid. The capacity of the resin for uranium is 37mg of uranium per ml of resin. With a 20% recommended capacity the 2ml columns can extract up to 15mg of uranium. The extractant in UTEVA resin, diamyl amylphosphonate (DAAP) is shown in figure 1.05.

![Structure of diamyl amylphosphonate](image)

Figure 1.05: Structure of diamyl amylphosphonate.

The extractant forms nitrato complexes with actinide elements. The formation of these complexes is driven by the concentration of nitrate in the sample solution. Therefore, the uptake of the actinides increases with increasing nitric acid solution. The uptake from nitric acid is similar for the tetravalent actinides and uranium with $k' > 100$ above 5M nitric acid. Americium is not retained at any nitric acid concentration.

Horwitz et al [96] showed that uranium sorption by the resin was most efficient at high (>1M) acid concentrations. The sorbed uranium can then be eluted using dilute acid. The UTEVA resin has been used to isolate uranium from various environmental samples (e.g. groundwater and soil). Separation schemes for uranium and thorium were also investigated using 2M nitric acid as the eluent, although a scheme using 2M nitric acid-0.5M oxalic acid was found to be simpler and more effective. A uranium, thorium separation scheme using hydrochloric acid is also described. The sample is loaded onto the column in 6M hydrochloric acid which is then used to rinse the column. The thorium is not retained by the
column and therefore is eluted with the 6M hydrochloric acid. The uranium is then eluted using 0.025M hydrochloric acid.

Experiments on the retention of transition metals, alkali and alkaline earth metals by the UTEVA resin showed that nearly all the test elements were removed with only 10 free column volumes (FCV) of 2M nitric acid.

Uranium is efficiently sorbed by the resin from solutions containing a wide range of either nitric or hydrochloric acid concentrations and is readily eluted with dilute acid. As the uranium/neptunium and uranium/thorium separation factors are somewhat better in hydrochloric acid, elution sequences involving a cross over from nitric to hydrochloric acid may offer a means to isolate and sequentially elute several actinides in a single run. This is the basis of the method described by EIChroM industries for the separation of uranium and thorium in water [97] and soil [98] samples. Many other commonly encountered cations (e.g. calcium, iron and sodium) are essentially not retained by the resin, making the resin suitable for the isolation of uranium from a variety of environmental samples.

(1:5:4:1) Applications of the UTEVA resin.

The applications of the UTEVA resin are shown in figure 1.02. Gingell et al [99] used UTEVA resin for the determination of uranium in a range of environmental samples. Taylor et al [100] used UTEVA resin to isolate uranium for $^{238}\text{U}/^{235}\text{U}$ and uranium concentration measurements in soil samples by thermal ionization mass spectrometry (TIMS). The resin has been used by Carney et al [101] to separate the rare earth elements from the actinides. The resin has also been used to separate uranium from thorium, and uranium from plutonium and these applications are discussed below.

(1:5:4:1:1) Uranium and thorium separations.

Adriaens et al [102] investigated the use of UTEVA resin to separate uranium and thorium prior to their determination by isotope dilution secondary ion mass spectrometry (ID-SIMS) and isotope dilution thermal ionization mass
spectrometry (ID-TIMS). The following method involving a UTEVA resin column and an anion exchange column was developed. Initially a UTEVA column was used to separate the uranium and thorium from metals such as iron, lead and bismuth. The samples were loaded onto the UTEVA column with 6M nitric acid which was then used to wash the column. The uranium and thorium were then eluted from the UTEVA column with 0.1M nitric acid. The uranium and thorium were then separated using an anion exchange column. The uranium and thorium fraction was then loaded onto a (Biorad AG1X8) anion exchange column in 9M hydrochloric acid. The uranium and thorium were then separated with the thorium passing straight through column and the uranium then being eluted with 0.1M nitric acid.

(1:5:4:1:2) Uranium and plutonium separations.

Goldstein et al [103] used the UTEVA resin to separate uranium and plutonium from thorium. The uranium and plutonium were then separated using anion exchange. The method was used for air filter, soil, water and urine samples. Croudace et al [104] developed a rapid procedure for plutonium and uranium determination in soil using anion-exchange and UTEVA resin. The plutonium and thorium are isolated on an anion-exchange column prior to passing the uranium fraction through the UTEVA column. The UTEVA separated the uranium from iron and the sample matrix. Initial studies found that the uranium fraction contained organic residues on evaporation and a small anion exchange column was required to remove the organic fraction prior to measurement by thermal ionisation mass spectrometry (TIMS).

Apostolidis et al [105] developed a simple and robust method for the separation of uranium and plutonium from mixed uranium/plutonium/fission product solutions. The plutonium was eluted using a mixture of hydroxylaminehydrochloride and ascorbic acid in dilute nitric acid. Plutonium(IV) was reduced to plutonium(III) which was not retained by the column. The uranium was stripped from the column using a dilute solution of ammonium oxalate. The activities of the
uranium and plutonium fractions were then determined by alpha spectrometry and TIMS without any further pre-treatment.

Goodall et al [106] used UTEVA resin to separate uranium and plutonium from solutions of spent nuclear fuel before their determination by thermal ionisation mass spectrometry. The research developed a single column method for the separation of uranium and plutonium. The method uses a reductant (0.1M ascorbic acid, 3M nitric acid) to strip selectively the strongly retained plutonium (IV) from the column as plutonium(III). After washing with nitric acid to remove any residual ascorbic acid the uranium was then eluted using very dilute hydrochloric acid.
**TEVA resin.**

TEVA resin is an extraction chromatography resin for the selective sorption of tetravalent actinides and technetium and consists of an aliphatic quaternary amine (aliquat 336). As such it has properties similar to those of typical strong base anion exchange resins. However, because the functional groups are in a liquid form rather than fixed to a polymer backbone these groups have greater mobility to co-ordinate around target anions. This means that the uptake of these ions is generally higher, often at much lower acid concentrations.

\[
\begin{align*}
C_8H_{17} & + \quad CH_3 \\
C_{10}H_{21} & \quad N \quad C_{10}H_{21}
\end{align*}
\]

Figure 1.06: Structure of aliquat 336.

**Applications of the TEVA resin.**

The resin has three applications:

In the first application tetravalent actinides (plutonium, thorium and neptunium) are extracted from 2-8M nitric acid by the TEVA resin selectively over uranium and most other elements. The plutonium and thorium can then be stripped as a group with dilute hydrochloric acid (0.5M hydrochloric acid / 0.1M hydroquinone and the neptunium can be removed from the resin with 0.5M hydrochloric acid.

In the second application the technetium was retained strongly by the TEVA resin under dilute (0.1M) nitric acid conditions. The technetium can be removed from the column with 7-9M nitric acid.

In the third application the trivalent actinides are readily separated from lanthanides on the TEVA resin. The actinides are extracted by the column from (2M ammonium thiocyanate-0.1M formic acid) load solution, whereas the
lanthanides elute in the load rinse fractions. The actinides are removed from the column with 0.25M hydrochloric acid. ElChroM have published procedures for the analysis of technetium in water [107] and soil [108] samples and the separation of thorium from neptunium in water [109] using TEVA resin.

Horwitz et al [110] concluded that TEVA resin provided a simple and effective method for the separation and pre-concentration of tetravalent actinides from aqueous solutions. Tetravalent plutonium and neptunium are efficiently sorbed from a wide range of nitric and hydrochloric acid concentrations while thorium (IV) is strongly sorbed from nitric acid solutions. Under the same conditions many commonly encountered cations are essentially not retained by the resin, making the material well suited to the isolation of tetravalent actinides from a variety of sample types. The advantages of using TEVA rather than conventional anion exchange methods are that plutonium and neptunium can be separated in 2-3M nitric acid. The thorium elution is not subject to tailing and the elution of uranium requires less nitric acid. TEVA columns may be used together with TRU and UTEVA columns for the separation of the actinides. These applications are discussed in the sequential column section (section 1:5:13).

The TEVA resin has been used to preconcentrate technetium from soil samples before determination by ICP-MS [111]. The dissolved soil sample was loaded onto the TEVA resin with 0.5M nitric acid and eluted with 8M nitric acid. This procedure separated the technetium from ruthenium and molybdenum which would interfere with the measurement of technetium by ICP-MS.

The TEVA resin has been used to preconcentrate technetium from water samples [112]. The technetium was sorbed onto the TEVA resin after conversion to pertechnetate using hydrogen peroxide. The resin was then washed with 50ml of 1M nitric acid and the technetium eluted from the resin with 30ml of 4M nitric acid.

TEVA resin has also been used to separate technetium from ruthenium for low level determination in soils and sediments [113]. Initially, an anion exchange
column was used as a sample clean up stage. The TEVA resin column was then used to isolate technetium from ruthenium. The sample was loaded onto the column with 10ml of 0.5M nitric acid and washed with 50ml of 0.5M nitric acid. The ruthenium was not retained by the column and eluted in the 0.5M nitric acid load and wash fractions. The technetium was then eluted from the column with 10 ml of 8M nitric acid.

The analysis of technetium-99 in water has been carried out using sequential injection separation system with stopped-flow for the automated analysis of nuclear waste [114]. The technetium was loaded onto the resin in 0.1M nitric acid as the pertechnetate ion. The resin was then washed with 0.1M nitric acid-0.2M hydrofluoric acid to remove plutonium. The technetium was eluted with 6M nitric acid.

The determination of technetium-99 in low-level radioactive waste [115] is carried out following iron (III) hydroxide and carbonate precipitation and separation on a TEVA resin column. The 3-5ml sample load solution was adjusted to pH 1-2 with concentrated hydrochloric acid and loaded onto the TEVA column. The column was then rinsed with 25ml of 0.1M hydrochloric acid and the technetium eluted with 10ml of 6M nitric acid.

The TEVA resin has been used in combination with cation exchange for the determination of technetium in fuel leachates [116]. The cation exchange resin was used to separate the technetium from strontium and caesium. The technetium was then purified using TEVA resin.

Another application of the TEVA resin has been in the purification of fermium from the rare earth fission products (yttrium, dysprosium and holmium) [117]. The TEVA column was used in conjunction with two cation exchange columns. The initial cation exchange column was used to remove trace actinide contamination (e.g. plutonium, berkelium, californium and einsteinium), the second anion exchange column was used to remove divalent cation impurities. The fermium was then separated from $^{91}$Y, $^{166}$Dy and $^{166}$Ho using the TEVA resin.
column. The sample was loaded onto the column in 2M ammonium thiocyanate-
0.1M formic acid solution. The column was then rinsed with 2M ammonium
thiocyanate-0.1M formic acid solution before the fermium was eluted with 0.25M
hydrochloric acid. The $^{91}\text{Y}$, $^{166}\text{Dy}$ and $^{166}\text{Ho}$ are eluted from the column with the
2M ammonium thiocyanate-0.1M formic acid solution.

One disadvantage of using the TEVA columns is the length of time required to
pass through large volumes of samples. To overcome this problem a TEVA disc
has been developed. The TEVA disc is a 47mm glass fibre filter loaded with 0.5g
silica-based TEVA resin, which enables aqueous samples to be passed through the
disc at much faster flow rates than with the resin column [118].
(1:5:6) RE resin.

The RE resin consists of 1 M octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO) in tributyl phosphate (TBP) coated onto an inert polymeric support.

The resin is similar to the TRU resin in that both are composed of the same extractant system (CMPO/TBP). However, the concentration of CMPO is higher in the RE resin, therefore increasing the affinity for rare earth elements (REEs) and yttrium from acidic solutions. When the uptake of selected lanthanides (cerium, europium, dysprosium, erbium) on TRU and RE resin was compared it was found that the uptake was twice as high using the RE resin. The RE resin is suitable to achieve a group separation of the rare earths using 8M nitric acid.

Esser et al [119] investigated the effect of nitric acid molarity on the sorption of caesium, barium and the rare earth elements onto the RE resin. Load and rinse solutions of 2, 4 and 6M nitric acid were investigated. Dilute nitric acid (0.015M) was used to investigate the possibility of separating barium from the rare earths. The results showed that the retention of lanthanum and the heavy REE by the RE resin was sensitive to the molarity of nitric acid used to load the sample solution and to wash the column. The 2M and 4M nitric acid load/wash solutions quantitatively eluted caesium and barium from the RE resin column. Increasing the molarity of the load/wash solutions to 6M nitric acid resulted in 20% of the caesium being retained by the RE column. The light rare earth elements (cerium, praseodymium, neodymium, samarium, europium, gadolinium and terbium) were retained by the RE column when loaded/washed with 2M, 4M and 6M nitric acid.

The sorption of lanthanum was reduced from 100% as the molarity of the nitric acid load/wash solution was increased. The 4M and 6M nitric acid solutions eluted approximately 1% and 17.5% respectively of the lanthanum from the column.
The light rare earth elements and lanthanum were quantitatively eluted from the RE resin column with 0.015M nitric acid. As the heavier rare earth elements (dysprosium, holmium, erbium, thulium, ytterbium and lutetium) increase in atomic number an increase in the percentage of loaded element eluted by the 2M nitric acid load was observed (5% for dysprosium to 100% for ytterbium and lutetium). Increasing the molarity of the load/wash solution to 4M nitric acid resulted in a reduction in the elution of the heavy REEs. Increasing the molarity of the load/wash solution to 6M nitric acid resulted in all the heavy REEs being retained by the RE resin.

Separation of barium from the REEs was achieved by using the RE resin in combination with a 2ml silica-immobilized 8-hydroxyquinoline (silica-8HQ) column. The silica-8HQ column was used to preconcentrate the REEs from the sample solution. The RE resin then separates the REEs from any residual barium in the silica-8HQ-REE fraction. This fraction was loaded onto the RE resin in 6M nitric acid and the REEs eluted with 0.0015M nitric acid.

Applications of the resin have been reported for analysis of REEs in natural waters [119] and in the purification of yttrium for cancer therapy [120].

(1:5:7) Lanthanum (Ln) resin.

The extractant used in Ln resin is di(2-ethylhexyl) orthophosphoric acid (HDEHP). Applications of the Ln resin include its use in methods for the analysis of radium, neodymium, promethium and samarium [121,122].

Pin et al [121] used the Ln resin (column i.d., 4mm packed with 300mg of resin) to separate the light rare earth elements lanthanum, cerium, and praseodymium from neodymium and samarium. The LREEs were loaded onto the column in 3.5ml of 0.05M nitric acid. A fraction containing lanthanum, cerium and praseodymium was then eluted using 3ml of 0.025M hydrochloric acid. The neodymium was eluted with 2ml of 0.25ml hydrochloric acid and the samarium with 1.5ml of 0.75M hydrochloric acid.
Burnett et al [122] investigated the use of the Ln resin for the separation of actinium (for radium determinations) from radium, lead, bismuth and yttrium. Possible interference from thorium was also investigated. The procedure seemed to offer quantitative separation of actinium from most elements which have potentially interfering beta-emitting radionuclides (e.g. lead, bismuth, thorium and yttrium). The sample was loaded and rinsed with 0.095M nitric acid which eluted the radium and lead. The actinium was then eluted with 0.35M nitric acid. Bismuth was then eluted with 2M nitric-0.1M oxalic acid and yttrium with 3M hydrochloric acid.

(1:5:8) Lead resin.

The lead selective resin consists of a 0.75M solution of the macrocyclic polyether bis-4,4'(5')-[tert-butylcyclohexano]-18-crown-6 in isodecanol on an Amberchrom CG-71 md resin support. The resin is used to pre-concentrate and separate lead from acidic media. The resin retains lead efficiently and selectively over a wide range of nitric acid concentrations. The sorbed lead is readily recovered using complexing agents such as ammonium oxalate. The resin has applications for the isolation of lead from geological samples [123].

(1:5:9) Nickel resin.

The nickel resin utilises dimethylglyoxime (DMG) impregnated into the pores of an inert polymer support. In the presence of nickel, Ni-DMG precipitate is formed and contained inside the pores of the resin. Experiments by Warwick et al [124] have investigated the effect of ammonia concentration on the uptake of nickel on the column and, distribution coefficients for a number of other radionuclides found in typical nuclear plant solutions. The results showed that only nickel had a strong affinity for the DMG resin.

(1:5:10) Tritium resin.

The tritium resin [125] is designed to replace distillation for the analysis of routine aqueous tritium samples. The column works by removing potential
interferences in the liquid scintillation counting (LSC) spectrum. Aqueous samples were loaded onto the tritium column which comprises of three resins; diphonix, anion exchange and XAD-7. The diphonix resin removes the cations, the anion exchange resin removes the anions and the XAD-7 resin removes the organically bound carbon$^{14}$ and tritium. The eluent from the column contains the aqueous tritium.

(1:5:11) Diphonix resin.

ElChroM's Diphonix resins were originally developed to address the specific nuclear decontamination requirements of the US nuclear weapons complex. The goal was to develop an ion exchange resin with greater selectivity for the hazardous and radioactive metals and to ensure the usefulness of that resin in acidic solutions.

Diphonix is a polyfunctional resin containing sulphonic and gem-phosphonic acid groups chemically bonded in a styrene-divinylbenzene polymeric network. Diphonix can be regarded as a dual mechanism polymer, with a sulphonic acid cation exchange group allowing for rapid access, mostly non specific, of ions into the polymeric network, and the diphosphonic acid group responsible for the specificity (recognition) for a number of metal cations.

![Structure of the diphonix resin.](image)

Figure 1.07: Structure of the diphonix resin.

The diphonix resin has been studied in detail [126-134] and a review of the resins properties and applications has been published [135]. The research concluded that hexavalent uranium and the tetravalent actinides are strongly retained by the resin over the 0.01 to 10M nitric acid range. The presence of aluminium (III) and
iron (III) were found to affect the uptake of the actinides (and in particular americium). The iron interference was overcome by reducing the iron(III) to iron(II) which was not retained by the resin.

The diphonix resin retains the tetra and hexavalent actinides so strongly that to elute the actinides ≥0.5M solutions of water soluble diphosphonic acid (i.e. compound that contain the same functional group as the resin) are required. The aqueous diphosphonic acid used to elute the actinides must then be decomposed. The resulting solutions contain a high concentration of phosphoric acid which can lead to problems if subsequent separation of the actinides is required.

The resin has been used for the analysis of actinides in environmental samples, treatment of radwaste from nuclear power and in the treatment of mixed wastes [135]. Although the resin was developed to separate actinides it is now realised that its major application is for the copper electrowinning process. Other areas where the unique selectivity of the resin may find applications are in potable water purification (e.g. from lead), in the preparation of special high purity reagents (e.g. in the semiconductors industry), and in the hydrometallurgy and/or electrowinning processes used for other metals besides copper.

Research reported in [136] investigated the behaviour of alkaline earth cations on diphonix resin in the absence and presence of crown ethers. The results of the study were that the presence of certain crown ethers can have a substantial effect on the uptake of the alkaline earth cations by sulphonic and diphosphonic acid based cation-exchange resins, the exact nature of which is dependent on the hydrophobicity of the crown compound. The application of the work is to develop a simple and flexible tandem column scheme for the isolation of radium although considerable work is still required to optimise and demonstrate the applicability to various real samples.

(1:5:11:1) DIPEX or ‘actinide’ resin.

Recently, an extraction chromatographic version of diphonix has been developed [137,138]. The new resin is called ‘dipex’ or ‘actinide resin’. The resin consists
of a new compound bis(2-ethylhexyl) methanediphosphonic acid, where (R= 2-ethylhexyl), supported on an inert polymeric substrate.

![Structure of H₂DEH[MDP]](image)

Figure 1.08: Structure of H₂DEH[MDP].

When compared with Diphonix the resin exhibits stronger affinity for the actinides and superior americium/iron and americium/aluminium selectivity. Other advantages include the resins insensitivity to high concentrations of hydrofluoric acid and that the actinides can be recovered by alcohol stripping and wet oxidation of the stationary phase leaving an easily processed calcium phosphate residue. The resin has been used to preconcentrate actinides from soils and large volumes of water [139].

(1:5:12) ABEC Extraction materials.

Aqueous Biphasic Extraction Chromatography (ABEC) materials are distinctive in their ability to function in the presence of high salt concentrations without the loss of selectivity for the pertechnetate anion. The ability to cope with high salt concentration is necessary for alkaline radioactive waste solutions containing high concentrations of nitrates, nitrites and other salts.

Applications of the materials are in nuclear waste treatment, radio-pharmaceutical purification, rhenium production and preconcentration of dyes used in the food and textile industry.

Aqueous biphasic systems (ABS) consist of two immiscible phases formed when certain water soluble polymers combine either with one another or with certain
inorganic salts in specific concentrations. In ABS the major component of the phases is water and because of the non denaturing environment the systems have been widely employed in biological separations for over 40 years [140]. ABEC materials were developed by adapting the liquid-liquid ABS to a solid chromatographic mode [141]. This was done by grafting high molecular weight monomethylated polyethylene glycol (PEGS) to an inert support and utilising the fact that salt solution mobile phases produce ABS like conditions. Alkaline radioactive waste solutions containing pertechnetate were added to columns of the ABEC resin. In the presence of phase forming anions (e.g. OH\(^-\), CO\(_3\)\(^2-\), citrate\(^2-\), SO\(_4\)\(^2-\), PO\(_4\)\(^3-\) and F\(^-\)) an aqueous biphasic system is formed and the pertechnetate ion is retained by the ABEC column. The pertechnetate was eluted by washing the ABEC column with water (which does not induce biphasic formation).

Advantages of the ABEC include that the polyethylene glycol based aqueous biphasic systems (PEG-ABS) are virtually non toxic and non flammable. They are commercially available in bulk and are inexpensive. The ABEC resin has been used to remove pertechnetate from simulated Hanford waste [142].
(1:5:13) **Sequential methods using EIChroM columns.**

Horwitz et al [143] used TEVA, TRU and UTEVA columns for sequential determination of the actinides. Three schemes are described:

Scheme 1 uses TEVA, UTEVA and finally TRU resin columns for the separation of thorium, neptunium, uranium, plutonium and americium. The TEVA column was used to isolate the thorium and neptunium fractions. The UTEVA resin was used for the isolation of uranium and the TRU resin used to isolate the plutonium and americium fractions.

Scheme 2 uses the same three resins as scheme 1 to separate neptunium from uranium and americium. Separation scheme 2 does not however separate neptunium from plutonium. The plutonium was converted to the tetravalent state using ammonium sulphate and sodium nitrite and the solution loaded onto a TEVA resin column. The thorium was eluted with 6M hydrochloric acid, the plutonium and neptunium were eluted with 0.02M nitric acid/hydrofluoric acid mixture, the uranium and americium were then eluted with 2.5M nitric acid. The uranium and americium were loaded onto the UTEVA resin column for the separation of uranium from americium. The americium was then further purified using the TRU resin column.

Scheme 3 uses TEVA, UTEVA, TRU and Sr resin cartridges in tandem configuration. The sample is, in effect, added to the four columns at once. By careful choice of the load conditions, all the radionuclides of interest can be sorbed in a single pass of the sample. The columns are then split apart into the individual cartridges for recovery of the desired species. The load solution is 2-3M nitric acid made to 3-5M total nitrate with aluminium nitrate. Ferrous sulphamate is used to fix the plutonium and neptunium at (plutonium(III) and neptunium (IV)) while ascorbic acid is used to convert any iron present to iron(II). Thorium and neptunium are removed by the TEVA, uranium by the UTEVA, americium and plutonium by the TRU and strontium by the Sr resin.
Ham [144] used anion exchange followed by TRU then TEVA resin columns for the separation of plutonium, americium and curium in environmental samples. Pilvio et al [145] used UTEVA to separate plutonium, americium and curium from thorium and uranium. The separation of plutonium from americium and curium was performed with TRU resin. The americium and curium were measured together.

Berne [146] developed a method for americium separation from large soil samples (up to 50g). The method uses anion exchange, TRU and then TEVA resin columns. The anion exchange column is used to separate americium from plutonium. The americium is then separated from other actinides using the TRU column. The TEVA column is used to separate the americium from the lanthanides.

Smith et al [147] developed analytical schemes for analysing actinides in soil samples using a series of actinide selective extraction chromatography (TRU, TEVA) and ion-exchange (Diphonix) resins for detection by alpha spectrometry and ICP-MS. The scheme for detection by alpha spectrometry required the sequential isolation of the actinides, whereas for ICP-MS only a group separation of the actinides was required.

Alvarez et al [148] used anion exchange, TRU and then Sr resins for the separation of plutonium, americium and strontium in urine samples.

Moody et al [149] used TRU then TEVA and TRU columns for the pre-concentration and separation of thorium, uranium, plutonium and americium in human soft tissue. The initial TRU column was used to pre-concentrate the actinides. The TEVA and TRU columns were then used in a tandem configuration with the TEVA column first so that the eluate from the TEVA column flowed into the TRU column. The sample was loaded onto the columns with 2.5M nitric acid. The thorium and plutonium were retained on the TEVA column and the americium and uranium retained on the TRU column. The columns were then separated and treated separately. The TEVA column was
washed with 6M hydrochloric acid to elute the thorium and the plutonium was then eluted with 0.5M hydrochloric acid. The TRU column was treated with 0.025M nitric acid to elute the americium while the uranium was eluted with 0.1M ammonium oxalate.

Ware et al [150] reported the determination of $^{90}$Sr, $^{90}$Y, $^{238}$Pu, $^{239/240}$Pu, $^{241}$Am, $^{241}$Cm and $^{243/244}$Cm in environmental and liquid effluent samples. An aliquot of the sample was taken for strontium analysis using the Sr resin. A second aliquot was then analysed using anion exchange followed by TRU resin. The anion exchange resin was used for the separation of uranium, thorium and plutonium. The TRU resin was then used for the separation of americium from curium.

Pin et al [151] separated strontium and the light rare earth elements (LREEs) using the Sr and TRU resins. The Sr and TRU resin columns were operated in a coupled arrangement during loading. The 2M nitric acid load solution was added to the Sr resin column which retained the barium (80%) and strontium (95%). The LREEs were eluted from the Sr resin and retained by the TRU resin column. The columns were then separated and the barium and strontium eluted from the Sr resin with 7M nitric acid and 0.05M nitric acid respectively. The light rare earths were eluted from the TRU resin column with 0.05M nitric acid.

Dietz et al [152] used the Sr and RE resins for the separation of yttrium and strontium for medical applications. The $^{90}$Sr stock solution was loaded onto a Sr resin column in 3M nitric acid. The strontium was sorbed onto the column and the yttrium was eluted with the 3M nitric acid solution. The yttrium solution was then adjusted to a 2M nitric acid solution and added to a RE resin column. Residual strontium and most other impurities were eluted from the column with the 3.6ml of 2M nitric acid. The yttrium was then eluted by increasing the volume of 2M nitric acid (7-18ml).
(1:6) **DATING METHODS.**

(1:6:1) **Introduction to dating methods.**

Radioactive decay is not influenced by temperature, pressure or the chemical environment, making it an excellent method for dating samples. The determination of absolute age is based on the fact that a given radionuclide decays at a known rate and forms a geological clock.

Radiometric dating methods can be divided into three main groups:

The first group involves measuring the decrease in concentration of a radionuclide from an initial level, or measuring the build-up of a stable daughter product. Examples of this type of dating method include uranium/lead, potassium/argon and carbon-14.

The second group is based on the measurement of the degree of restoration of radioactive equilibrium in a radioactive decay series following an initial external perturbation. Examples of this type of dating method are the uranium-series disequilibrium dating methods.

The third group is based on radiation damage to the sample. These techniques utilise changes in matter, for example in the lattice spacing caused by interaction of the matter with radiation passing through it. If the radiation damage increases at a constant rate the number of damages can be used as a measure of the time (radiation age) that the sample was subjected to the radiation. Examples of this type of dating technique are thermoluminescence and electron spin resonance.

(1:6:2) **Choice of dating method.**

A number of factors should be considered when choosing a dating method. These include the type of sample, the amount of sample available, the level of radionuclide present, and the expected age of the sample. The age ranges of a number of radiometric dating methods are shown in table 1.01. The time range of the chosen method must match the probable age of the sample.
Table 1.01: Age range of some dating methods.

<table>
<thead>
<tr>
<th>Dating method</th>
<th>Age range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiocarbon</td>
<td>$7-4.5 \times 10^4$ years</td>
</tr>
<tr>
<td>$^{230}$Th/$^{234}$U</td>
<td>$10^3-5 \times 10^5$ years</td>
</tr>
<tr>
<td>Thermoluminescence</td>
<td>$10^3-10^6$ years</td>
</tr>
</tbody>
</table>

(1:6:3) Uranium-series disequilibrium.

For the purpose of this report uranium-series disequilibrium and in particular the $^{230}$Th/$^{234}$U dating method is discussed. The $^{230}$Th/$^{234}$U method has applications for dating carbonates and in particular speleothem [153,154] and calcite samples [155,156,157] and has also been used to date coral [158-160], molluscs [161,162], bones and teeth [163,164].

(1:6:3:1) Radioactive equilibrium.

Most of the long lived, heavy radioactive elements decay to form daughter products that are themselves radioactive. These decay in turn to form a series or chain, which ends when a stable daughter nuclide is formed. A decay series is said to be in radioactive equilibrium when the ratio of the number of active parent atoms to the number of active daughter atoms is constant. The amount of stable daughter product at the end of the chain will continue to increase with time at a decreasing rate. Because of the relative half lives of the intermediate members of the decay series, normal secular equilibrium amongst them should have long since been established on earth.

The decay series for $^{238}$U is shown in figure 1.09.

(1:6:3:2) Radioactive disequilibrium.

The disequilibrium in speleothem and calcite samples is caused by their formation, thus, the nature and degree of disequilibrium, which exists in a sample frequently offers information regarding it’s geological history. Because of the
Figure 1.09: $^{238}$U decay series.
relatively short half-lives of the intermediate members of the decay series, normal secular equilibrium among them should have long since been established on earth. The disequilibrium in carbonates can be explained by the different chemical behaviour of uranium and thorium. When calcium carbonate forms it usually contains a few parts per million (ppm) of uranium but essentially no thorium. This removal of $^{230}\text{Th}$ from the $^{238}\text{U}$ decay chain results in a total disequilibrium of the $^{230}\text{Th}/^{234}\text{U}$ activity ratio. In cave water and newly formed calcites the $^{230}\text{Th}/^{234}\text{U}$ is almost zero. Alpha decay of the $^{234}\text{U}$ regenerates $^{230}\text{Th}$ with time. The age of the sample can be calculated using equation 1.06.

$$\frac{^{230}\text{Th}}{^{234}\text{U}} = \frac{1-e^{-\lambda_{230}t}}{^{234}\text{U}/^{238}\text{U}} + \left(1 - \frac{1}{^{234}\text{U}/^{238}\text{U}}\right) \left(\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}}\right) 1-e^{(230-234)t}$$

Equation 1.06: Dating equation.

Where:
- $\lambda_{230}$ and $\lambda_{234}$ are the decay constants of $^{230}\text{Th}$ and $^{234}\text{U}$ respectively.
- $^{230}\text{Th}$, $^{234}\text{U}$ and $^{238}\text{U}$ are the measured activities (Bq) in the samples.
- and $t$ is the age of the sample (y).

The unknown $t$ can be computed iteratively using computer programs such as UTAGE [165] and the Solver program in Microsoft Excel. The programs use the Newton Raphson approach in which the age is calculated using an iterative method, an estimate of the age ($t_0$) is used to calculate ($t$) the true age of the sample by the Newton Raphson method of successive approximations. The age can also be estimated using the graphical approach shown in figure 1.10.

Figure 1.10: Graphical solution for equation 1.06.
(1:7) URANIUM IN URINE.

(1:7:1) Introduction to uranium in urine.

The determination of the gross alpha content in urine is used to support radiological protection/occupational hygiene monitoring programmes for radiological workers. These measurements are undertaken to ensure that any dose of radioactivity received by workers is below the annual limit of intake (ALI). Where a worker is found to have been contaminated, urine analysis is also useful for determining whether treatment to eliminate the contamination has been effective.

For occupational exposure the most probable contamination route is by inhalation and where there is a risk of contamination, air sampling will be operational. Previous research [166] has shown that soluble uranium is deposited primarily in the kidneys and the bones. The uranium is excreted from the kidneys relatively quickly and so the important long term storage mechanism is in the bones. Insoluble or sparingly soluble uranium will be deposited in the gastro-intestinal tract and the lungs. Therefore excretion monitoring using urine and faecal samples will provide information on the extent (if any) of internal contamination. To determine if any occupational exposure has occurred the background ‘normal concentration’ levels of uranium in urine from non-occupationally exposed people is required. Information gained from experimental study of the uptake and excretion of uranium by the human body [167,168] has been used to generate biokinetic models [169,170,171] which calculate the mean dose equivalent and the effective dose equivalent.

The annual dietary intake of uranium has been estimated [172] to be 5Bq per year. Whereas the excretion of uranium from a typical uranium worker can be up to 14.6Bq per year [174].

A wide variety of industries use materials that have a natural radioactivity content and so require investigation to establish the radiation exposures to the workforce. This is performed chiefly by analysing data from air sampling. Examples of these
industries include non-nuclear energy production, manufacturing (chemical, ceramic and glass industries), and ore-extraction and refining with research into the contribution to the environment from uranium-ore mining and coal fly ash processes.

(1:7:2) Experimental.

Various methods have been used to measure the gross alpha content in urine but the methods for simultaneous analysis of the isotopes are generally complicated and time consuming. These methods generally consist of pre-concentration, mineralization, radiochemical separation involving, source preparation and counting. Over the years attempts to reduce the length of time (and therefore cost) from sample collection to obtaining the results have been investigated.

Research into reducing the sample preparation stage by eliminating the oxidation step and by using photon electron rejecting alpha liquid scintillation spectrometry (PERALS) counting has been reported [173]. The alpha emitters are counted by liquid scintillation using a PERALS spectrometer. A pulse height discriminator is used to separate the alpha-particle produced pulses from beta and gamma produced pulses. The high background counts associated with liquid scintillation counting were reduced using the PERALS system with typical background levels of 0.01cpm obtained in the 4-7MeV alpha energy region.

To reduce the length of time involved in source preparation alternatives to electrodeposition have been investigated. One of these methods is co-precipitation [174] in which the uranium source is prepared by co-precipitation of the uranium from solution with a small amount of inactive carrier (lanthanum). The method also has the advantage of being able to produce sources in the presence of iron and aluminium. Another source preparation method investigated was chemical stripping using a polymeric membrane containing trioctylphosphine oxide (TOPO) on a stainless steel disc [175]. The disadvantage of the (TOPO) technique was that it required more steps for source preparation and so, although
a cheaper alternative to electrodeposition, a reduction in the source preparation method was not achieved.

The use of extraction chromatography to reduce and simplify the sample separation stage has also been investigated [103].

The use of inductively coupled plasma mass spectrometry (ICP-MS) as an alternative measurement technique to alpha spectrometry has been investigated. ICP-MS is advantageous as it requires small sample volume, is rapid, free from spectral interferences, requires no chemical separation and has a low limit of detection to enable quantification of both uranium and thorium in urine to be made at 'expected normal' concentrations. ICP-MS has been used for the determination of uranium in urine [176,177] and uranium and thorium in urine [178,179] and faecal samples [180]. Thermal ionization mass spectrometry (TIMS) has also been used to determine picogram levels of uranium in human urine [181].

Laboratories must ensure that although quicker and more cost effective, their methods of analysis are reliable and accurate. This can be assessed by taking part in intercomparison studies [182] which test whether the equipment, methods selectivity, efficiency and accuracy, staff, and detection limits are appropriate.

The experimental work reported in section (6:0) of this thesis was undertaken at the request of EICроM Industries. The experiments were designed to investigate the possible causes of variable uranium recoveries from urine samples observed with four gross alpha in urine methods.
CHAPTER 2

STUDIES USING TRU RESIN.
INTRODUCTION TO RESEARCH IN THE USE OF TRU RESINS IN URANIUM AND THORIUM SEPARATIONS.

The TRU resin has been described in section (1:5:3) of this thesis. The research using the TRU resin concentrated on two areas:

In the first area initially the sorption and elution of uranium and thorium were studied. This was done to investigate claims by previous researchers [81,82] that the uranium and thorium were sorbed onto the TRU resin with (>1M) nitric acid and eluted with an appropriate complexing agent (e.g. ammonium oxalate). The molarity of the load solution was then varied (2M, 4M, 6M and 8M nitric acid) and the sorption of uranium and thorium onto the TRU resin was investigated.

The elution of uranium and thorium from the TRU resin was investigated using 0.1M ammonium oxalate and 0.05M nitric acid. The effect of iron on the sorption/elution of uranium was investigated. Finally a 10ml, 2M nitric acid solution was chosen to load the uranium onto the TRU resin column. The uranium was then eluted with 0.1M ammonium oxalate. This experiment was repeated with thorium, americium and plutonium.

In the second area the suitability of the TRU resin for separating uranium from thorium was then investigated. The proposed separation scheme was based on the americium in soil separation scheme developed at AEA Technology plc [183] and the separation scheme developed by Burnett et al [184]. The uranium and thorium were loaded onto the TRU resin with nitric acid. The TRU resin column was converted to the chloride form and washed with 4M hydrochloric acid (which would elute americium from the resin). The thorium was then eluted using 1M hydrochloric acid [184]. The uranium remaining on the column was then eluted with 0.1M ammonium oxalate.

Four experiments are described. The first two experiments investigate the use of 1M hydrochloric acid to elute thorium from the column. The third and fourth experiments investigate the use of 2M hydrochloric acid to elute thorium from the column.
(2:2) INITIAL INVESTIGATION OF SORPTION AND ELUTION ONTO TRU RESIN.

An initial experiment was undertaken to investigate 0.1M ammonium oxalate and 0.05M nitric acid as possible reagents to elute the uranium and thorium from TRU resin. Nitric acid (2M) was used as the load solution. The experiments were carried out using four calcium carbonate solutions and four reagent blank solutions. The calcium carbonate solutions were chosen as the majority of the samples to be analyzed using this method would have a calcium carbonate matrix. The sample preparation method involved the following stages: dissolution; coprecipitation; separation; electrodeposition and counting.

Reagents.

These were; TRU resin, pre-filter resin, deionized water, glass wool, concentrated nitric acid, 2M nitric acid, calcium carbonate, iron (III) carrier which was prepared by dissolving 72.3g of ferric nitrate in deionized water adding 50ml of concentrated nitric acid and making the solution up to 1 litre with deionized water, concentrated ammonia, ascorbic acid, ammonium oxalate, sodium hydrogen sulphate solution (110g NaHSO₄ in 1 litre deionized water), sodium sulphate solution (226g sodium sulphate in 1 litre deionized water), and ethanol. The spike solutions used are listed in table 2.01.

<table>
<thead>
<tr>
<th>Spike</th>
<th>Solution</th>
<th>Specific Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>²³⁶U</td>
<td>7M nitric acid</td>
<td>167mBq/g</td>
</tr>
<tr>
<td>²³³U</td>
<td>7M nitric acid</td>
<td>182mBq/g</td>
</tr>
<tr>
<td>²²⁹Th</td>
<td>7M nitric acid</td>
<td>140mBq/g</td>
</tr>
<tr>
<td>²³²Th</td>
<td>7M nitric acid</td>
<td>132.8mBq/g</td>
</tr>
<tr>
<td>²⁴¹Am</td>
<td>7M nitric acid</td>
<td>60mBq/ml</td>
</tr>
<tr>
<td>²⁴²Pu</td>
<td>7M nitric acid</td>
<td>98.2mBq/ml</td>
</tr>
</tbody>
</table>

Apparatus.

These were: 8 glass columns; 8 (400ml) glass beakers; 50ml screw-topped centrifuge tubes; pH meter; stirrer plate; heat lamp; 8 electroplating cells;
electroplating rig; Bunsen burner and alpha spectrometer.

(2:2:1) Experimental.

Four calcium carbonate solutions were prepared using the following method. A 100ml aliquot of 0.1 M nitric acid was added to a 400ml glass beaker and placed on a stirrer plate and 10g of calcium carbonate added. Concentrated nitric acid was added slowly until all the calcium carbonate had dissolved. The pH of the solution was then adjusted to 1. The samples were then heated until boiling and allowed to cool. Four blank solutions were prepared using the same method without the addition of calcium carbonate.

A 1ml aliquot of the $^{229}$Th spike was added to two of the calcium carbonate test solutions and two of the blank solutions. A 1ml aliquot of the $^{236}$U spike was added to both the remaining two calcium carbonate and two blank test solutions. The samples were labelled as shown in table 2.02.

A 1ml aliquot of iron (III) carrier (10mg/ml) was added to all the test solutions. Watch glasses were placed on top of the beakers and the samples were placed on a hotplate and left to equilibrate for 2 hours. The samples were then allowed to cool.

The uranium and thorium were co-precipitated with ferric hydroxide by the addition of ammonia solution using the following method; ammonia was added to the solution while stirring until the pH reached 7.5. The precipitate was isolated by centrifuging and then washed with 0.05M ammonia solution. The precipitate was dissolved in 5ml 8M nitric acid and made up to 20ml with deionized water. A 200mg amount of ascorbic acid was then dissolved in each of the test solutions.

Eight columns were prepared (four for uranium and four for thorium) using the following method. A glass wool plug was placed at the bottom of the column. The columns used were made from 6mm I/D glass tubing closed off at the lower end to 2mm diameter. A slurry of the pre-filter resin and deionized water was
made and sufficient resin was added to form a 0.5 cm column. A slurry of the TRU resin was added to form a 3 cm column. A glass wool plug was placed at the top of the column. The column was pre-conditioned by washing with 5 ml of 2M nitric acid. The samples were introduced into the columns which were then allowed to drain. The columns were then washed with 10 ml of 2M nitric acid. Samples U1, Th3, U5, Th7 were eluted with 10 ml of 0.1 M ammonium oxalate. Samples U2, Th4, U6, Th8, were eluted with 30 ml of 0.05 M nitric acid.

Table 2.02: Labelling of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spike added</th>
<th>Eluent used</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1 CaCO₃ solution</td>
<td>²³⁵U</td>
<td>0.1 M ammonium oxalate</td>
</tr>
<tr>
<td>U2 CaCO₃ solution</td>
<td>²³⁵U</td>
<td>0.05 M nitric acid</td>
</tr>
<tr>
<td>Th3 CaCO₃ solution</td>
<td>²²⁹Th</td>
<td>0.1 M ammonium oxalate</td>
</tr>
<tr>
<td>Th4 CaCO₃ solution</td>
<td>²²⁹Th</td>
<td>0.05 M nitric acid</td>
</tr>
<tr>
<td>U5 Blank</td>
<td>²³⁶U</td>
<td>0.1 M ammonium oxalate</td>
</tr>
<tr>
<td>U6 Blank</td>
<td>²³⁶U</td>
<td>0.05 M nitric acid</td>
</tr>
<tr>
<td>Th7 Blank</td>
<td>²²⁹Th</td>
<td>0.1 M ammonium oxalate</td>
</tr>
<tr>
<td>Th8 Blank</td>
<td>²²⁹Th</td>
<td>0.05 M nitric acid</td>
</tr>
</tbody>
</table>

(2:2:1:1) Preparation of sources for alpha spectrometry.

The ammonium oxalate and nitric acid eluent fractions were prepared for electrodeposition by adding 1 ml of the sodium hydrogen sulphate solution and evaporating to dryness under a heat lamp. Concentrated nitric acid (1 ml) was added, and the resulting solutions evaporated to dryness. Sodium sulphate plating solution (6 ml) was then added to each fraction. The resulting solution was warmed and transferred with deionized water to an electroplating cell. The total volume in the cell was 50 ml. The electrodeposition cell consists of a stainless steel planchet in a metal cap assembly attached to a plastic container and a platinum electrode.

The electrodeposition cells were placed on an electrodeposition rig and the uranium and thorium plated at 1 amp for 3 and 5 hours respectively. Concentrated ammonia (2 ml) was added one minute before the end of plating. The stainless steel planchet was rinsed with deionized water, and then methanol before being ignited over a Bunsen burner. The discs were then labelled and
counted by alpha spectrometry.

(2:2:1:2) Alpha Spectrometry.

All results for this chapter were obtained by alpha spectrometry. The alpha spectrometry measurements were carried out using a 7401 model alpha spectrometer (Canberra Packard Ltd) fitted with passivated ion implanted planar silicon detectors (PIPS) having an active surface area of 450mm$^2$. The spectrometers were connected to a personal computer fitted with a TRUMP-8k-W3 multi-channel analyser plug in card (EG&G Instruments).

(2:2:2) Results and discussion.

The results from the initial experiment (table 2.03) show that the uranium and thorium were sorbed onto the TRU resin from the 2M nitric acid load solution. The 0.05M nitric acid did not elute any uranium or thorium from the TRU resin column. The 0.1M ammonium oxalate eluted (67%) of the uranium from the TRU resin for the calcium carbonate load solution and the blank solution respectively. The ammonium oxalate solution eluted (9%) of the thorium for the calcium carbonate solution and (50%) of the thorium for the blank solution.

From the results it was decided to repeat the experiment with 2M nitric acid as the load solution using the 0.1M ammonium oxalate solution to elute uranium and thorium from the column.
Table 2.03: Initial sorption and elution experiment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spike added</th>
<th>Reagent used</th>
<th>Tracer recovery (%)</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1 CaCO₃ solution</td>
<td>U²³⁶</td>
<td>0.1M ammonium oxalate</td>
<td>67</td>
<td>2.0</td>
</tr>
<tr>
<td>U2 CaCO₃ solution</td>
<td>U²³⁶</td>
<td>0.05M nitric acid</td>
<td>No U eluted</td>
<td></td>
</tr>
<tr>
<td>Th³ CaCO₃ solution</td>
<td>Th²²⁹</td>
<td>0.1M ammonium oxalate</td>
<td>9</td>
<td>0.6</td>
</tr>
<tr>
<td>Th⁴ CaCO₃ solution</td>
<td>Th²²⁹</td>
<td>0.05M nitric acid</td>
<td>No Th eluted</td>
<td></td>
</tr>
<tr>
<td>U5 Blank</td>
<td>U²³⁶</td>
<td>0.1M ammonium oxalate</td>
<td>67</td>
<td>1.7</td>
</tr>
<tr>
<td>U6 Blank</td>
<td>U²³⁶</td>
<td>0.05M nitric acid</td>
<td>No U eluted</td>
<td></td>
</tr>
<tr>
<td>Th⁷ Blank</td>
<td>Th²²⁹</td>
<td>0.1M ammonium oxalate</td>
<td>50</td>
<td>1.3</td>
</tr>
<tr>
<td>Th⁸ Blank</td>
<td>Th²²⁹</td>
<td>0.05M nitric acid</td>
<td>No Th eluted</td>
<td></td>
</tr>
</tbody>
</table>
(2:3) INVESTIGATION OF SORPTION ONTO TRU RESIN.

The sorption of uranium and thorium onto the TRU resin was investigated using a range of molarities (2M, 4M, 6M and 8M) of the nitric acid load solution. The uranium and thorium were then eluted from the TRU resin using ammonium oxalate.

(2:3:1) Experimental.

Two columns were prepared; one for uranium and one for thorium, as described in section (2:2:1). The columns were pre-conditioned using 10ml of 2M nitric acid. The $^{239}$Th or $^{236}$U spike solutions (2ml) were added to a glass beaker made to a 2M 20ml solution and introduced to the respective columns. The solutions were allowed to drain through the columns before any further solutions were added. Nitric acid (10ml of 2M) was then used to rinse the glass beaker and added to the columns. The load solution and the 10ml of 2M nitric acid were collected as fraction 1. Two separate 3ml aliquots of nitric acid were added to the columns and collected as fractions 2 and 3. Nitric acid (4ml) was then added and collected as fraction 4. The elution of uranium and thorium from the columns was then investigated by adding five separate 3ml aliquots of 0.1M ammonium oxalate. The five 3ml aliquots were labelled fractions 5, 6, 7, 8 and 9. The nine fractions were electrodeposited using the method described in section (2:2:1:1) and counted by alpha spectrometry.

The uranium and thorium experiments were repeated with 4M, 6M and 8M nitric acid loads solutions.

(2:3:2) Results and discussion.

The results for uranium (table 2.04) show that the $^{236}$U was sorbed onto the column from the 2M nitric acid. Increasing the molarity of the nitric acid load solution reduced the amount of uranium observed in the 2M nitric acid load and wash fractions (fractions 1 to 4). The majority of the uranium was then eluted by the first 3ml fraction of 0.1M ammonium oxalate. As the molarity of the load
solution was increased from 2M to 4M, 6M and 8M nitric acid, the amount of uranium eluted by the first 3ml of 0.1M ammonium oxalate (fraction 5) was reduced. The amount of uranium eluted by the second 3ml of 0.1M ammonium oxalate (fraction 6) was increased. At the higher molarities of nitric acid (4M, 6M and 8M) the initial 3ml of ammonium oxalate was required to reduce the molarity of nitric acid on the column and enable uranium elution.

Table 2.04: Investigation of sorption onto TRU resin. Uranium results.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>2M nitric load Count rate (cps)</th>
<th>4M nitric load Count rate (cps)</th>
<th>6M nitric load Count rate (cps)</th>
<th>8M nitric load Count rate (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1-30ml 2M nitric acid</td>
<td>1.10×10^4</td>
<td>4.50×10^3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F2-3ml 2M nitric acid</td>
<td>1.13×10^4</td>
<td>4.50×10^3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F3-3ml 2M nitric acid</td>
<td>1.23×10^4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F4-4ml 2M nitric acid</td>
<td>0.97×10^4</td>
<td>1.66×10^5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F5-3ml 0.1M ammonium oxalate (AO)</td>
<td>0.091</td>
<td>0.0864</td>
<td>0.0905</td>
<td>7.57×10^-2</td>
</tr>
<tr>
<td>F6-3ml 0.1M ammonium oxalate (AO)</td>
<td>9.33×10^4</td>
<td>1.32×10^3</td>
<td>3.43×10^3</td>
<td>4.01×10^-4</td>
</tr>
<tr>
<td>F7-3ml 0.1M ammonium oxalate (AO)</td>
<td>1.27×10^4</td>
<td>2.87×10^4</td>
<td>1.18×10^3</td>
<td>1.58×10^-4</td>
</tr>
<tr>
<td>F8-3ml 0.1M ammonium oxalate (AO)</td>
<td>1.07×10^4</td>
<td>1.43×10^4</td>
<td>8.60×10^-4</td>
<td>1.66×10^-4</td>
</tr>
<tr>
<td>F9-3ml 0.1M ammonium oxalate (AO)</td>
<td>1.17×10^4</td>
<td>9.20×10^-5</td>
<td>2.35×10^-4</td>
<td>8.38×10^-5</td>
</tr>
</tbody>
</table>

The results for thorium (table 2.05) show some initial breakthrough of the thorium when it was loaded onto the column with 2M nitric acid. The amount of thorium eluted from the column with the nitric acid load and washes (fractions 1 to 4) was
reduced as the molarity of the nitric acid was increased from 2M nitric acid. The majority of the thorium was eluted by the first 3ml of 0.1M ammonium oxalate. As the molarity of the load solution was increased from 2M nitric acid then the amount of thorium eluted by the first 3ml of ammonium oxalate was reduced. The amount of thorium eluted by the remaining ammonium oxalate washes (fraction 6 to 9) was increased as the molarity of the nitric acid load solution was increased. As seen with the uranium experiments at the higher molarities of nitric acid (4M, 6M and 8M) the initial 3ml of ammonium oxalate was required to reduce the molarity of nitric acid on the column and enable thorium elution.

Table 2.05: Investigation of sorption onto TRU resin. Thorium results.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>2M nitric load Count rate (cps)</th>
<th>4M nitric load Count rate (cps)</th>
<th>6M nitric load Count rate (cps)</th>
<th>8M nitric load Count rate (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1-30ml 2M nitric acid</td>
<td>7.51x10^{-3}</td>
<td>1.64x10^{-3}</td>
<td>1.66x10^{-3}</td>
<td>1.04x10^{-3}</td>
</tr>
<tr>
<td>F2-3ml 2M nitric acid</td>
<td>5.80x10^{-4}</td>
<td>1.73x10^{-4}</td>
<td>1.33x10^{-4}</td>
<td>5.87x10^{-5}</td>
</tr>
<tr>
<td>F3-3ml 2M nitric acid</td>
<td>1.53x10^{-4}</td>
<td>4.10x10^{-5}</td>
<td>7.42x10^{-5}</td>
<td>1.97x10^{-5}</td>
</tr>
<tr>
<td>F4-4ml 2M nitric acid</td>
<td>1.47x10^{-4}</td>
<td>1.60x10^{-5}</td>
<td>4.09x10^{-5}</td>
<td>3.97x10^{-6}</td>
</tr>
<tr>
<td>F5-3ml 0.1M ammonium oxalate (AO)</td>
<td>0.1186</td>
<td>8.84x10^{-2}</td>
<td>6.30x10^{-2}</td>
<td>0.118</td>
</tr>
<tr>
<td>F6-3ml 0.1M ammonium oxalate (AO)</td>
<td>8.67x10^{-4}</td>
<td>1.11x10^{-3}</td>
<td>1.80x10^{-2}</td>
<td>2.88x10^{-3}</td>
</tr>
<tr>
<td>F7-3ml 0.1M ammonium oxalate (AO)</td>
<td>1.30x10^{-4}</td>
<td>2.50x10^{-4}</td>
<td>5.86x10^{-4}</td>
<td>1.56x10^{-4}</td>
</tr>
<tr>
<td>F8-3ml 0.1M ammonium oxalate (AO)</td>
<td>1.40x10^{-4}</td>
<td>1.24x10^{-4}</td>
<td>1.81x10^{-4}</td>
<td>1.56x10^{-5}</td>
</tr>
<tr>
<td>F9-3ml 0.1M ammonium oxalate (AO)</td>
<td>1.50x10^{-4}</td>
<td>4.17x10^{-5}</td>
<td>0</td>
<td>1.90x10^{-3}</td>
</tr>
</tbody>
</table>
(2:4) INVESTIGATION OF SORPTION ONTO TRU RESIN. 

QUANTITATIVE EXPERIMENTS.

The experiments described in section (2:2:2) were repeated using two uranium and two thorium spike solutions. The second uranium and thorium spike solutions allowed correction of losses due to plating and counting efficiency and allowed quantitative analyses. This enabled investigation of whether all the uranium and thorium was being eluted from the TRU resin column.

(2:4:1) Experimental.

For the uranium experiments 2ml of \(^{238}\)U spike solution were used. For the thorium experiments 2ml of the \(^{232}\)Th spike solutions were used. The uranium experiments were carried out with 2M, 4M and 6M nitric acid load solutions. The thorium experiments were carried out with 2M and 4M nitric acid load solutions. Prior to electrodeposition 2ml of \(^{236}\)U and \(^{229}\)Th were added to the uranium and thorium experiments respectively.

(2:4:2) Results and discussion.

Tables 2.06 and 2.07 show the elution results from the quantitative investigations. The quantitative elution experiment results for uranium (table 2.06) show that all the uranium was sorbed onto the TRU resin column with the 2M, 4M and 6M nitric acid load and wash solutions. The elution experiment results for uranium show that the majority of uranium added to the column was eluted by the ammonium oxalate (fraction 5 for 2M nitric acid load and fraction 6 for the 4M and 6M nitric acid load solutions).

The elution profile results confirms the findings from the qualitative experiments that the majority of the uranium for 2M and (4M and 6M) nitric acid was eluted by 6ml and 9ml of ammonium oxalate respectively. The requirement for more ammonium oxalate for the 4M load can be explained as at the higher acid load solution the uranium is more strongly bound to the resin and the ammonium oxalate solution was required to reduce the acidity of the resin and allow uranium
elution.

The calculated results show that all the uranium added to the TRU resin column was eluted with the ammonium oxalate (101% for 2M nitric acid, 99% for 4M nitric acid and 101% for 6M nitric acid).

Table 2.06: Investigation of sorption onto the TRU resin. Quantitative uranium results.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>2M nitric acid</th>
<th>4M nitric acid</th>
<th>6M nitric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% U eluted</td>
<td>% U eluted</td>
<td>% U eluted</td>
</tr>
<tr>
<td>F1-30ml 2M nitric acid</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F2-3ml 2M nitric acid</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F3-3ml 2M nitric acid</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F4-4ml 2M nitric acid</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F5-3ml 0.1M ammonium oxalate</td>
<td>99</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F6-3ml 0.1M ammonium oxalate</td>
<td>1.4</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>F7-3ml 0.1M ammonium oxalate</td>
<td>0.6</td>
<td>1.1</td>
<td>2.1</td>
</tr>
<tr>
<td>F8-3ml 0.1M ammonium oxalate</td>
<td>0.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F9-3ml 0.1M ammonium oxalate</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The quantitative elution experiment results for thorium (table 2.07) show that the thorium was sorbed onto the column with the 2M and 4M nitric acid load and wash solution with breakthrough of 0.1% and 0.26% respectively.

The corrected results showed that not all of the thorium added to the column was eluted by the 15ml of 0.1M ammonium oxalate. A reduction in the % of the thorium eluted by the ammonium oxalate was seen as the molarity of the load solution was increased from 2M (87%) to 4M nitric acid (66%). This suggests that the thorium was either being retained by the TRU resin column or that thorium has a wider elution profile than uranium. The width of the elution profile for thorium seems to increases as the load solution was increased from 2M to 4M nitric acid.
Table 2.07: Investigation of sorption onto the TRU resin. Thorium quantitative results.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>2M nitric acid load (% Th eluted)</th>
<th>4M nitric acid load (% Th eluted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1-30ml 2M nitric acid</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>F2-3ml 2M nitric acid</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F3-3ml 2M nitric acid</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F4-4ml 2M nitric acid</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F5-3ml 0.1M ammonium oxalate</td>
<td>64</td>
<td>50</td>
</tr>
<tr>
<td>F6-3ml 0.1M ammonium oxalate</td>
<td>17</td>
<td>30</td>
</tr>
<tr>
<td>F7-3ml 0.1M ammonium oxalate</td>
<td>3</td>
<td>1.8</td>
</tr>
<tr>
<td>F8-3ml 0.1M ammonium oxalate</td>
<td>1.7</td>
<td>0.1</td>
</tr>
<tr>
<td>F9-3ml 0.1M ammonium oxalate</td>
<td>1.2</td>
<td>0</td>
</tr>
</tbody>
</table>
(2:5) EFFECT OF IRON EXPERIMENTS.

The effect of iron on the extraction was investigated because 10mg of iron was present in the current pre-concentration step and iron could also be present in geological and environmental samples. The experiments were carried out to determine if the TRU resin separated iron from the uranium and thorium. The presence of iron in the uranium or thorium fractions would inhibit the electrodeposition of uranium and thorium onto the stainless steel disc and produce thick sources which would not be suitable for alpha spectrometry. The effect of iron on the sorption/elution of uranium from a 3ml TRU resin column was investigated quantitatively.

(2:5:1) Experimental.

The 20ml 2M nitric acid column load solution contained 1 ml of $^{238}$U spike solution and 1 or 5ml of the 10mg/ml iron carrier solution. The load solution was added to the column and collected as fraction 1. The column was then washed with 10ml of 2M nitric acid and collected as fraction 2. The uranium was then eluted from the column with 15ml of 0.1M ammonium oxalate and collected as fraction 3. To the uranium fraction 1ml of $^{235}$U spike solution was added prior to electrodeposition.

The experiment was repeated with 200mg of ascorbic acid added to the load solution.

(2:5:2) Results and discussion.

The results for the iron experiments are shown in table 2.08. The results show that iron was present in the 2M nitric acid load and wash solutions (fraction 1 and 2). The presence or absence of iron was detected during the electrodeposition stage. At the end of the electrodeposition step ammonia solution was added and any iron present was precipitated from solution.

The results for uranium elution from the TRU resin column are shown in the ammonium oxalate fraction (fraction 3). These results show that the majority of
uranium was eluted from the column by the ammonium oxalate (100%, 92%, 94%, and 77% for the 10mg iron, 50mg iron, 10mg iron and 0.2g ascorbic acid, and 50mg iron and 0.2g ascorbic acid experiments respectively). In conclusion the TRU resin column separated uranium from iron as the iron was not retained by the TRU resin column.

Table 2.08: Results for iron experiments showing % uranium eluted by ammonium oxalate.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>10mg Fe</th>
<th>50mgFe</th>
<th>10mg Fe and 0.2g AA</th>
<th>50mg Fe and 0.2g AA</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1-20ml 2M nitric acid</td>
<td>Contained iron</td>
<td>Contained iron</td>
<td>Contained iron</td>
<td>Contained iron</td>
</tr>
<tr>
<td>F2-10ml 2m nitric acid</td>
<td>Contained iron</td>
<td>Contained iron</td>
<td>Contained iron</td>
<td>Contained iron</td>
</tr>
<tr>
<td>F3-15ml 0.1M ammonium oxalate</td>
<td>100%</td>
<td>92%</td>
<td>94%</td>
<td>77%</td>
</tr>
</tbody>
</table>
(2:6) INVESTIGATION OF SORPTION AND ELUTION OF URANIUM, THORIUM, AMERICIUM AND PLUTONIUM.

(2:6:1) Experimental.

The experiments described in section (2:2:2) were repeated with 0.5ml of each of the following spike solutions, $^{236}$U, $^{229}$Th, $^{241}$Am and $^{242}$Pu. The 20ml 2M nitric acid test solutions were loaded onto the four TRU resin columns, washed with 10ml of 2M nitric acid which was collected as fraction 1. The radionuclides were then eluted from their respective TRU resin column with 10ml of 0.1M ammonium oxalate and collected as fraction 2. The resulting eight fractions were electrodeposited and counted by alpha spectrometry.

(2:6:2) Results and discussion.

The results for the uranium, thorium, americium and plutonium experiments are shown in table 2.09. These show that the radionuclides (uranium, thorium, americium and plutonium) were sorbed onto the TRU resin from the 2M nitric acid load solution. The radionuclides (uranium, thorium, americium and plutonium) were then quantitatively eluted from the column with 0.1M ammonium oxalate.

Table 2.09: Uranium, thorium, americium and plutonium experimental results.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>% U eluted</th>
<th>% Th eluted</th>
<th>% Am eluted</th>
<th>% Pu eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M nitric acid</td>
<td>0.6%</td>
<td>1.1%</td>
<td>0.1%</td>
<td>6.3%</td>
</tr>
<tr>
<td>0.1M AO</td>
<td>99%</td>
<td>99%</td>
<td>100%</td>
<td>94%</td>
</tr>
</tbody>
</table>

In conclusion the TRU resin preconcentrates the uranium, thorium, americium and plutonium from acidic solutions and separates them from matrix interferences such as iron. The experimental results agree with previous research [82,83] which states that the TRU resin preconcentrates the actinides from acidic solutions. As the method does not separate the uranium, thorium, americium and plutonium, its applications include gross alpha determination of the actinides by alpha spectrometry or individual alpha determination by ICP-MS after preconcentration using the TRU resin.
(2:7) INVESTIGATION OF URANIUM AND THORIUM SEPARATION USING TRU RESIN.

The second aim of the experiments was to investigate the suitability of the TRU resin to separate uranium from thorium. The uranium and thorium were loaded onto the TRU resin in 1M nitric acid. The thorium was eluted from the column with 1M hydrochloric acid after a 4M hydrochloric acid wash. The uranium was eluted from the column with 0.1M ammonium oxalate.

(2:7:1) Uranium and thorium elution with 1M hydrochloric acid.


The TRU resin column was prepared as described in section (2:2:1) and preconditioned with 10ml of 1M nitric acid. The test solution was prepared by adding 2ml of the $^{232}$U/$^{228}$Th spike solution to a 100ml glass beaker. The solution was made up to 15ml with 1M nitric acid. This load solution was added to the column and collected as fraction 1. Three 5ml aliquots of 4M hydrochloric acid added to wash the column were collected as fractions 2, 3 and 4. Three 5ml aliquots of 1M hydrochloric acid were added to elute the thorium from the column and collected as fractions 5, 6 and 7. The uranium was then eluted from the column with three 5ml aliquots of 0.1M ammonium oxalate and collected as fractions 8, 9 and 10. Prior to electrodeposition 2ml of $^{236}$U were added to fractions 8, 9 and 10 and 2ml of $^{229}$Th were added to the remaining fractions. The resulting nine fractions were electrodeposited and counted by alpha spectrometry.

(2:7:1:2) Results and discussion.

The thorium and uranium results for the experiment described in section (2:7:1:1) are shown in figures 2.01 and 2.02 respectively.
Figure 2.01: Experiment as described in (2:7:1:1). Thorium elution profile showing sorption with 1M nitric acid, column washing with 4M hydrochloric acid, and thorium elution initially with 1M hydrochloric acid and finally with 0.1M ammonium oxalate.

Figure 2.02: Experiment as described in (2:7:1:1). Uranium elution profile showing sorption with 1M nitric acid, column washing with 4M hydrochloric acid, 1M hydrochloric acid and finally uranium elution with 0.1M ammonium oxalate.

The results show that the 1M nitric acid load and the 4M hydrochloric acid wash solutions elute 3.5% of the thorium and no uranium from the column. The 1M hydrochloric acid solution elutes 15% of the thorium and no uranium from the column. The 0.1M ammonium oxalate elutes 60% of the thorium and all the uranium from the column. From these experimental results, it was decided to increase the volume of 1M hydrochloric acid to try to elute more of the thorium from the column before the uranium was eluted by the ammonium oxalate.
(2:7:2) **Investigation of thorium elution with 1M hydrochloric acid.**

An experiment was undertaken to investigate the elution of thorium from the TRU resin in greater detail. The experiment involved increasing the volume of 1M hydrochloric acid used to elute the thorium from the resin from 15 to 30ml and collecting the 1M hydrochloric acid in 5ml fractions.

(2:7:2:1) **Experimental.**

The experiment was qualitative with 2ml of the $^{239}$Th spike solution made up to 15ml with 1M nitric acid to produce the load solution. The experiment was then carried out as described in section (2:2:6). Six 5ml aliquots of 1M hydrochloric acid collected as fractions 5-10 were used to elute thorium from the column. A 10ml aliquot of 0.1M ammonium oxalate (fraction 11) were added to elute any thorium remaining on the column. The resulting eleven fractions were electrodeposited and counted by alpha spectrometry.

(2:7:2:2) **Results and discussion.**

The results for the experiment described in section (2:7:2:1) are shown in figure 2.03. These results show that increasing the volume of 1M hydrochloric acid from 15 to 30 ml did not increase the amount of thorium eluted from the column. It was decided that 1M hydrochloric acid was not a suitable eluent for thorium elution. The remaining two experiments investigated the use of 2M hydrochloric acid.
Figure 2.03: Experiment as described in (2:7:2:1). Thorium elution profile showing sorption with 1M nitric acid, column washing with 4M hydrochloric acid, and thorium elution initially with 1M hydrochloric acid and finally with 0.1M ammonium oxalate.
(2:7:3) Investigation of thorium elution with 2M hydrochloric acid.

The use of 2M hydrochloric acid as a possible eluent for thorium from the TRU resin was investigated.

(2:7:3:1) Experimental.

The experiment described in section (2:7:1:1) was repeated with 2M hydrochloric acid in place of 1M hydrochloric acid. The resulting eleven fractions were electrodeposited and counted by alpha spectrometry.

(2:7:3:2) Results and discussion.

The results for the initial experiment with 2M hydrochloric acid are shown in figure 2.04. The elution profile shows 5% of the thorium was eluted by the load and wash solutions as seen in experiment 2:2:6. The 30ml of 2M hydrochloric acid eluted 76% of the thorium from the column with 13% of the thorium eluted by the 0.1M ammonium oxalate. Because the 2M hydrochloric acid increased the percentage of thorium eluted from the column the experiment was repeated with an increased volume of 2M hydrochloric acid to elute the remaining thorium from the column.
Figure 2.04: Experiment as described in (2:7:3:1). Thorium elution profile showing sorption with 1M nitric acid, column washing with 4M hydrochloric acid, and thorium elution initially with 2M hydrochloric acid and finally with 0.1M ammonium oxalate.
Investigation of uranium and thorium separation with 2M hydrochloric acid.

The experiment was performed to investigate the separation of thorium from uranium using the TRU resin. The thorium and uranium were loaded onto the TRU resin in 2M nitric acid and the resin was washed with 4M hydrochloric acid. The thorium was then eluted from the resin using 2M hydrochloric acid. The behaviour of uranium during the load, wash and 2M hydrochloric acid rinse was investigated before its elution with 0.1M ammonium oxalate.

Experimental.

The experiment described in section (2:7:4:1) was repeated with 2 M hydrochloric acid. The load solution was collected as fraction 1. The 15ml of 4M hydrochloric acid were collected as fraction 2. Four 10ml aliquots and two 5ml aliquots of 2M hydrochloric acid to investigate thorium elution were collected as fractions 3-8. The uranium and any remaining thorium were then eluted from the column with two 5ml aliquots of 0.1M ammonium oxalate. The resulting ten fractions were electrodeposited and counted by alpha spectrometry.

Results and discussion.

The results for experiment as described in (2:7:4:1) are shown in figure 2.05. These results show that increasing the volume of 2M hydrochloric acid from 30-50ml did not result in any more thorium being eluted from the column. However, the increased volume of 2M hydrochloric acid caused slight uranium elution from the column. The 0.1M ammonium oxalate eluted 12% of the thorium and 93% of the uranium from the column.

The TRU resin separation experiments showed a thorium breakthrough of 5-10% with the load and wash solutions. The combination of the thorium breakthrough, the broad elution profile for thorium, and the presence of uranium in the thorium fraction lead to the conclusion that the TRU resin was not suitable for the separation of thorium from uranium.
Figure 2.05: Experiments described in (2:7:4:1). Uranium and thorium elution profile experiment.

(2:3) CONCLUSION.

In conclusion, the experiments showed that the TRU resin column was suitable for the sorption and subsequent elution of uranium, thorium, americium and plutonium for gross alpha analysis by alpha spectrometry or individual radionuclide analysis by ICP-MS. As the separation scheme did not remove all the thorium from the column before the uranium was eluted (thorium contamination in the uranium fraction) the proposed separation method using the TRU resin was not suitable for the separation of uranium from thorium. The method could be used in combination with anion exchange methods to separate americium from uranium, thorium and plutonium for analysis by alpha spectrometry. It was decided to investigate the possibility of using the UTEVA resin to separate uranium from thorium.
CHAPTER 3

STUDIES USING UTEVA RESIN.
(3:1) INTRODUCTION TO RESEARCH IN THE USE OF UTEVA RESINS IN URANIUM AND THORIUM SEPARATION.

The UTEVA resin has been described in section (1:5:4) of this thesis. The experiments described here are divided into three sections:

The first experiments described in this chapter of the thesis were carried out to investigate the uranium and thorium separation method proposed by ElChroM [97] using their 2ml UTEVA resin columns.

The second set of experiments were carried out to investigate the uranium and thorium separation method [97] using a 3M nitric acid load solution was studied to investigate the effect, if any, of removing aluminium nitrate from the load solution on the sorption/elution of uranium and thorium.

Finally in the third set of experiments the uranium, thorium separation method was adapted for the separation of americium, plutonium, uranium, and thorium.
The experiments described in this section of the thesis were undertaken to investigate the uranium and thorium separation method described by EIChroM industries [97]. The separation scheme uses a UTEVA resin column to separate uranium from thorium. A schematic of the method is shown in figure 3.01.

Figure 3.01: Schematic of the EIChroM uranium and thorium in water separation method.
The following experiments were undertaken:

Initially, two uranium and thorium spike solutions were added to the load solution to enable quantitative data to be obtained. The experiments were repeated adding the second uranium and thorium spike solutions just before the electrodeposition step to correct for any losses of uranium and thorium. The experiment was carried out four times at Loughborough University and three times at AEA Technology by an independent analyst using a different batch of UTEVA columns. The elution of thorium from the column was studied qualitatively to ensure that the thorium had been eluted from the column.

Experiments with 10, 20, 30 and 50mg of added iron were performed to investigate whether iron affected the separation of uranium and thorium. The 10mg of iron was chosen as this is the concentration used in the ferric hydroxide precipitation step. The effect of 20, 30 and 50mg of iron was also investigated.

The elution profiles of uranium and thorium were studied in greater detail by collecting five 3ml fractions of the 5M hydrochloric acid and the 0.02M hydrochloric acid column washes.

Uraninite experiments with and without added iron were performed to investigate the separation of the natural uranium ($^{238}$U, $^{234}$U) and the thorium ($^{230}$Th) isotopes.

Possible interferences from radium, polonium, americium and plutonium were also investigated.
(3:2:1) Initial Experiment.

This initial experiment investigated the uranium and thorium separation method proposed by EIChroM industries [97] using their 2ml UTEVA columns. The separation method uses a 3M nitric acid load solution from which uranium and thorium are sorbed onto the UTEVA resin. A 15ml 5M hydrochloric acid wash was used to elute the thorium from the column. The uranium was then eluted using 15ml of 0.02M hydrochloric acid. The UTEVA column was then washed with 0.1M ammonium oxalate solution which would elute any remaining uranium and thorium from the column.

Reagents.

These were: UTEVA resin columns, deionized water, nitric acid, hydrochloric acid, aluminium nitrate, ammonium oxalate and iron carrier (10mg/ml) solution. The radioactive tracer solutions used are listed in table 3.01.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Solution composition</th>
<th>Specific activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{229}$Th</td>
<td>7M nitric acid</td>
<td>182mBq/g</td>
</tr>
<tr>
<td>$^{236}$U</td>
<td>7M nitric acid</td>
<td>167mBq/g</td>
</tr>
<tr>
<td>$^{232}$U/$^{228}$Th</td>
<td>7M nitric acid</td>
<td>147mBq/ml</td>
</tr>
<tr>
<td>$^{208}$Po</td>
<td>7M nitric acid</td>
<td>133mBq/ml</td>
</tr>
<tr>
<td>$^{210}$Pb/$^{210}$Po</td>
<td>7M nitric acid</td>
<td>433mBq/ml</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>7M nitric acid</td>
<td>60mBq/ml</td>
</tr>
<tr>
<td>$^{243}$Am</td>
<td>7M nitric acid</td>
<td>1.573Bq/ml</td>
</tr>
<tr>
<td>$^{244}$Pu</td>
<td>7M nitric acid</td>
<td>98.2mBq/ml</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>7M nitric acid</td>
<td>43.08mBq/ml</td>
</tr>
</tbody>
</table>

(3:2:1:1) Experimental.

Test solutions were prepared by adding 2ml of the $^{236}$U, $^{229}$Th, and $^{232}$U/$^{228}$Th spike solutions to a 100ml glass beaker. The spike solutions were then evaporated to dryness under a heat lamp. The resulting residue was re-dissolved in 5ml of 6M nitric acid and 5ml of 1M aluminium nitrate added to produce a 3M nitric acid-0.5M aluminium nitrate solution. The solution was swirled to mix.
A beaker was placed under the UTEVA column and the column allowed to drain. The column was then conditioned with 5ml of 3M nitric acid. The test solution was then added to the column and allowed to drain. The sample beaker was washed with 5ml of 3M nitric acid which was then added to the column. The load and wash fractions were discarded. The following reagents were added to the column sequentially and collected in four 100ml glass beakers labelled fractions 2 to 5: A 5ml aliquot of 9M hydrochloric acid was passed through the column to convert the column to the chloride form (fraction 2). A 15ml aliquot of 5M hydrochloric acid was passed through the column to elute the thorium (fraction 3). A 15ml aliquot of 0.02M hydrochloric acid was passed through the column to elute the uranium (fraction 4). Finally, to elute any uranium/thorium remaining on the column 10ml of 0.1M ammonium oxalate (fraction 5) was passed through the column.

The uranium and thorium fractions were electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry. The experiment was repeated.

(3:2:1:2) Results and discussion.

The results for the initial experiments are shown in table 3.02 and show that the uranium and thorium were sorbed onto the column from the 3M nitric acid load solution and were not eluted by the 9M hydrochloric acid wash (fraction 2). The results show that the thorium was separated from the uranium. An average of 99.5% of the thorium with a standard deviation of 0.7% was eluted by 15ml of 5M hydrochloric acid (fraction 3). An average of 99.5% of the uranium with a standard deviation of 0.7% was eluted by 15ml of 0.02M hydrochloric acid (fraction 4). The results for the ammonium oxalate (fraction 5) show that <1% of the thorium and approximately 1% of the uranium were still sorbed onto the UTEVA column after the 5M and 0.02M hydrochloric acid washes. In conclusion the initial two experiments demonstrated that the method separated thorium from uranium.
Table 3.02: Initial experiment results.

<table>
<thead>
<tr>
<th>Experiment/Fraction</th>
<th>Reagent</th>
<th>%Th in fraction</th>
<th>%U in fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F2</td>
<td>5ml 9M HCl</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>F3</td>
<td>15ml 5M HCl</td>
<td>99</td>
<td>&lt;1</td>
</tr>
<tr>
<td>F4</td>
<td>15ml 0.2M HCl</td>
<td>&lt;1</td>
<td>100</td>
</tr>
<tr>
<td>F5</td>
<td>10ml 0.1M AO</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Experiment 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F2</td>
<td>5ml 9M HCl</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>F3</td>
<td>15ml 5M HCl</td>
<td>100</td>
<td>&lt;1</td>
</tr>
<tr>
<td>F4</td>
<td>15ml 0.2M HCl</td>
<td>&lt;1</td>
<td>99</td>
</tr>
<tr>
<td>F5</td>
<td>10ml 0.1M AO</td>
<td>&lt;1</td>
<td>1.2</td>
</tr>
</tbody>
</table>
(3:2:2) Repeatability of recovery of uranium and thorium.

The reproducibility of the uranium and thorium separation method was investigated by performing the separation experiment seven times to determine the recoveries of uranium and thorium.

(3:2:2:1) Experimental.

To a 100ml glass beaker 2ml of the $^{232}\text{U}^{228}\text{Th}$ spike solution were added and the solution evaporated to dryness under a heat lamp. The resulting residue was re-dissolved in 5ml of 6M nitric acid and 5ml of 1M aluminium nitrate were added to produce a 3M nitric acid-0.5M aluminium nitrate solution. The solution was swirled to mix.

The solution was then loaded onto a pre-conditioned UTEVA column and the separation method described in section (3:2:1:1) followed.

The collected fractions were spiked with 1ml of each of the $^{236}\text{U}$ and $^{229}\text{Th}$ spike solutions. The fractions were electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry. The experiment was repeated seven times.

(3:2:2:2) Results and discussion.

The results for repeatability of recoveries experiments are shown in tables 3.03 and 3.04. The uranium and thorium are sorbed onto the UTEVA resin with the load solution and 9M hydrochloric acid wash. The thorium results (table 3.03) show that an average of 106% of the thorium, with a standard deviation of 6%, was eluted by 15ml of 5M hydrochloric acid (fraction 3) along with approximately 1-2% of the uranium.

The uranium results (table 3.04) show that an average of 102% of the uranium with a standard deviation of 4% was eluted by 15ml of 0.02M hydrochloric acid (fraction 4) along with approximately 1% of the thorium. The results show that the 0.1M ammonium oxalate wash does not elute any thorium from the column but elutes the remaining 1-2% of uranium from the column. The results agree
with the results obtained in the initial experiment described in section (3:2:1:2).
The results indicate that the separation method provides repeatable and
quantitative separation of thorium from uranium.

Table 3.03: Thorium recovery (%).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Fraction 2 5ml 9M HCl</th>
<th>Fraction 3 15ml 5M HCl</th>
<th>Fraction 4 15ml 0.02M HCl</th>
<th>Fraction 5 10ml 0.1M AO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&lt;1</td>
<td>105 ± 5</td>
<td>1.8 ± 5.4</td>
<td>&lt;1</td>
</tr>
<tr>
<td>2</td>
<td>2.1 ± 0.3</td>
<td>93 ± 3</td>
<td>&lt;1</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>3</td>
<td>&lt;1</td>
<td>108 ± 3</td>
<td>1.6 ± 0.3</td>
<td>&lt;1</td>
</tr>
<tr>
<td>4</td>
<td>&lt;1</td>
<td>108 ± 3</td>
<td>1.6 ± 0.3</td>
<td>&lt;1</td>
</tr>
<tr>
<td>5</td>
<td>&lt;1</td>
<td>105 ± 3</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>6</td>
<td>&lt;1</td>
<td>108 ± 2</td>
<td>1.1 ± 0.1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>7</td>
<td>&lt;1</td>
<td>112 ± 4</td>
<td>1.4 ± 0.2</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Table 3.04: Uranium recovery (%).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Fraction 2 5ml 9M HCl</th>
<th>Fraction 3 15ml 5M HCl</th>
<th>Fraction 4 15ml 0.02M HCl</th>
<th>Fraction 5 10ml 0.1M AO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>102 ± 3</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>2</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>95 ± 3</td>
<td>1.3 ± 0.2</td>
</tr>
<tr>
<td>3</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>105 ± 9</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td>4</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>105 ± 9</td>
<td>&lt;1</td>
</tr>
<tr>
<td>5</td>
<td>&lt;1</td>
<td>1.4 ± 0.2</td>
<td>103 ± 4</td>
<td>2.2 ± 0.3</td>
</tr>
<tr>
<td>6</td>
<td>&lt;1</td>
<td>1.2 ± 0.1</td>
<td>102 ± 3</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td>7</td>
<td>&lt;1</td>
<td>1.4 ± 0.3</td>
<td>102 ± 4</td>
<td>1.7 ± 0.2</td>
</tr>
</tbody>
</table>
(3:2:3) Thorium elution profile.

The thorium elution profile was studied without the presence of uranium to ensure that the thorium was not being eluted in the uranium fraction.

(3:2:3:1) Experimental.

To a 100ml glass beaker a 2ml aliquot of the $^{229}$Th spike solution was added and the solution evaporated to dryness under a heat lamp. The resulting residue was re-dissolved in 5ml of 6M nitric acid and 5ml of 1M aluminium nitrate added to produce a 3M nitric acid-0.5M aluminium nitrate solution. The solution was swirled to mix.

The load solution was then placed onto a conditioned UTEVA column and the separation method described in section (3:2:1:1) followed.

Fractions (2-5) were electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry. The experiment was repeated.

(3:2:3:2) Results and discussion.

The thorium results are shown in table 3.05. The results show that the majority (92%) of the thorium was eluted by the 15ml of 5M hydrochloric acid fraction (fraction 3). The remaining thorium was eluted (1.6%) with the 9M hydrochloric acid wash (fractions 2), (1.4%) with the 0.02M hydrochloric acid wash (fraction 4) and (3.3%) with the 0.1M ammonium oxalate wash (fraction 5). In conclusion the experimental results demonstrated that some thorium (1.4%) was eluted with the uranium fraction.

Table 3.05: Thorium elution profile.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Fraction 2 5ml 9M HCl</th>
<th>Fraction 3 15ml 5M HCl</th>
<th>Fraction 4 15ml 0.02M HCl</th>
<th>Fraction 5 10ml 0.1M AO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.8</td>
<td>91</td>
<td>1.6</td>
<td>3.8</td>
</tr>
<tr>
<td>2</td>
<td>1.4</td>
<td>93</td>
<td>1.2</td>
<td>2.8</td>
</tr>
</tbody>
</table>
(3:2:4) Effect of the presence of iron in the load solutions.

The following experiments were carried out to investigate whether the uranium and thorium separation method also separated the uranium and thorium from any iron present. This is important as 10mg of iron are present in the column load solution from the sample pre-concentration step. Iron could also be present in geological and environmental samples. The presence of iron in the uranium and thorium fractions would inhibit the deposition of uranium and thorium onto the stainless steel discs and produce thick sources which are not suitable for alpha spectrometry.

(3:2:4:1) Experimental.

To four 100ml glass beakers, labelled 10, 20, 30 and 50mg of iron, a 2ml aliquot of the $^{232}$U/$^{228}$Th spike solution was added. Iron carriers (10mg/ml) 1,2,3 or 5ml were then added to the labelled beakers and the solutions were evaporated to dryness under a heat lamp. The resulting residues were dissolved in 5ml of 6M nitric acid and 5ml of 1M aluminium nitrate added to produce a 3M nitric acid-0.5M aluminium nitrate solution. The solutions were swirled to mix. Each of the four iron load solutions were added to a separate conditioned UTEVA column and the separation method described in section (3:2:1:1) followed.

To each of the collected fractions (2-5) 1ml of the $^{236}$U and $^{229}$Th spike solutions were added. The fractions were electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry.

(3:2:4:2) Results and discussion.

The results, in table 3.06, show that the presence of 10, 20, 30 and 50mg of iron in the load solution had no affect on the sorption or elution of uranium and thorium. The 10, 20, 30 and 50mg of iron did not affect the electrodeposition of the alpha sources as the iron was not retained by the UTEVA column. The results show percentage thorium recoveries of 103±4, 110±4, 108±4 and 106±3 for the 10, 20,
30 and 50mg of added iron. The results show percentage uranium recoveries of 103±3, 98±4, 99±3 and 104±3 for the 10, 20, 30 and 50mg of added iron. The errors on the uranium and thorium results were calculated using the equation shown in appendix I. In conclusion the method separates iron from the uranium and thorium and therefore would be suitable for use with the electrodeposition method of counting source preparation.

Table 3.06: Effect of the presence of iron in the load solution.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Thorium recovery (%)</th>
<th>Uranium recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10mg iron</td>
<td>103 ± 4</td>
<td>103 ± 3</td>
</tr>
<tr>
<td>20mg iron</td>
<td>110 ± 4</td>
<td>98 ± 4</td>
</tr>
<tr>
<td>30mg iron</td>
<td>108 ± 4</td>
<td>99 ± 3</td>
</tr>
<tr>
<td>50mg iron</td>
<td>106 ± 3</td>
<td>104 ± 3</td>
</tr>
</tbody>
</table>

The alpha spectra for the uranium and thorium with iron present in the load solution are shown in figures 3.02 and 3.03 respectively. The uranium spectra shows the $^{232}\text{U}$ and $^{236}\text{U}$ peaks are well resolved and that there is no thorium present in the spectra.

The thorium spectra shows the $^{229}\text{Th}$ and $^{228}\text{Th}$ peaks are well resolved and that uranium was not present in the spectra.

The spectra show that the peaks are well resolved and therefore the iron was not present on the source.
Figure 3.02: $^{236}$U and $^{238}$U spectra with 10mg of iron. The first peak on the x scale is the $^{236}$U peak which has an energy range of 4.20-4.53MeV, a peak centroid of 4.48MeV and 4714 counts. The second peak is the $^{238}$U peak which has an energy range of 5.12-5.34MeV, a peak centroid of 5.30MeV and 7011 counts.
Figure 3.03: $^{229}$Th and $^{228}$Th spectra with 10mg of iron. The first peak on the x scale is the $^{229}$Th peak which has an energy range of 4.59-5.11MeV, a peak centroid of 4.84MeV and 3835 counts. The second peak is the $^{228}$Th peak which has an energy range of 5.47-5.87MeV, a peak centroid of 5.77MeV and 5893 counts.
(3:2:5) Elution profile.

To determine the elution profiles of thorium and uranium from the UTEVA column in greater detail, 15ml of 5M hydrochloric acid and 0.02M hydrochloric acid were used to wash the column. Each strength acid was collected from the column in five 3ml fractions.

(3:2:5:1) Experimental.

To a 100ml glass beaker a 2ml aliquot of the $^{232}$U/$^{228}$Th spike solution was added. The spike solutions were then evaporated to dryness under a heat lamp. The resulting residue was re-dissolved in 5ml of 6M nitric acid and 5ml of 1M aluminium nitrate were added to produce a 3M nitric acid-0.5M aluminium nitrate solution. The solution was loaded onto a conditioned UTEVA column and allowed to drain. The sample beaker was washed with 5ml of 3M nitric acid which was then added to the column. The load and wash fractions were discarded. The 5ml of 9M hydrochloric acid were collected as fraction 2. The 15ml of 5M hydrochloric acid were collected as five 3ml fractions labelled fraction 3-7. Each 3ml fraction of the 5M hydrochloric acid was added to the column and collected before the next 3ml fraction was added. The 15ml of 0.2M hydrochloric acid were collected in five 3ml fractions and labelled fraction 8-12. The 10ml of 0.1M ammonium oxalate were collected as fraction 13.

To each of the collected fractions 1ml of $^{236}$U and $^{229}$Th were added. The uranium and thorium fractions were then electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry.

(3:2:5:2) Results and discussion.

The elution profile of uranium and thorium (figure 3.04) shows a broad elution profile for thorium with 80% of the thorium eluted by the first 3ml of 5M hydrochloric acid. The remaining 12ml of 5M hydrochloric acid eluted 10.3% of the thorium.
The uranium was eluted quantitatively from the column within the first 3 ml of 0.02M hydrochloric acid. The uranium fraction also contained 9.8% of the thorium. The ammonium oxalate fraction shows that no uranium or thorium were left on the column after the 5M hydrochloric acid and 0.02M hydrochloric acid washes. Approximately 10% of thorium was eluted with the uranium fraction.

Figure 3.04: Uranium and thorium elution profile.
(3:2:6) Uraninite experiment.

This experiment was performed to evaluate the efficiency of the separation of uranium \(^{238}\text{U}, \text{\textsuperscript{234}U}\) from thorium \(^{230}\text{Th}\) in a natural material. The natural material used was a solution of uraninite that was used in the Uranium Series Intercomparison Project [185]. The experiment was performed in the absence and presence of iron. The \(^{238}\text{U}, \text{\textsuperscript{234}U}\) and \(^{230}\text{Th}\) are in secular equilibrium in the uraninite.


A 2ml aliquot of the \(^{238}\text{U}\) spike solution was added to two glass beakers. To one of the glass beakers 1ml of iron carrier (10mg/ml) was then added. The resulting residue was re-dissolved in 5ml of 6M nitric acid and 5ml of 1M aluminium nitrate added to produce a 3M nitric acid-0.5M aluminium nitrate solution. The solution was swirled to mix.

The solutions were loaded onto separate pre-conditioned UTEVA columns and the separation method described in section (3:2:1:1) followed.

To fractions (2,3 and 5) a 1ml aliquot of the \(^{229}\text{Th}\) spike solution was added and to fraction (4) a 1ml aliquot of the \(^{235}\text{U}\) spike solution was added. The fractions were then electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry.

(3:2:6:2) Results and discussion.

The results for the two uraninite experiments are shown in table 3.07. The results show that the same results are obtained with or without the presence of 10mg of added iron. The uranium and thorium were separated from each other and quantitatively eluted from the column. The calculation of the counting errors for the results is shown in appendix 1. The values for the activity values of (143±3) and (144±4) for \(^{238}\text{U}\), (145±3) and (142±3) for \(^{234}\text{U}\) and (146±4) and (146±3) for \(^{230}\text{Th}\) agree with the spike activity value of 140mBq/g. The activity ratio values
of $(1.01 \pm 0.019)$ and $(0.99 \pm 0.016)$ for the $^{238}\text{U}/^{234}\text{U}$ activity ratio and
$(1.009 \pm 0.035)$ and $(1.027 \pm 0.032)$ for the $^{234}\text{U}/^{230}\text{Th}$ activity ratio agree within
experimental errors with the activity ratio of the uraninite ore of 1.

Table 3.07: Uraninite ore results.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$^{238}\text{U}$ activity (mBq/g)</th>
<th>$^{234}\text{U}$ activity (mBq/g)</th>
<th>$^{230}\text{Th}$ activity (mBq/g)</th>
<th>$^{238}\text{U}/^{234}\text{U}$</th>
<th>$^{234}\text{U}/^{230}\text{Th}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>without iron</td>
<td>143±3</td>
<td>145±3</td>
<td>146±4</td>
<td>1.01±0.019</td>
<td>1.009±0.035</td>
</tr>
<tr>
<td>with (10mg) iron</td>
<td>144±3</td>
<td>142±3</td>
<td>146±3</td>
<td>0.99±0.016</td>
<td>1.027±0.032</td>
</tr>
</tbody>
</table>

The uranium and thorium alpha spectra for the uraninite with iron are shown in
figures 3.05 and 3.06 respectively.
The uranium spectra shows that the $^{238}\text{U}$, $^{236}\text{U}$ and $^{234}\text{U}$ peaks are well resolved
and that thorium is not present in the spectra.
The thorium spectra shows that the $^{230}\text{Th}$ and $^{229}\text{Th}$ peaks are well resolved and
that uranium is not present in the spectra.
Figure 3.05. $^{238}$U, $^{236}$U and $^{234}$U spectra for uraninite. The first peak on the x scale is the $^{238}$U peak which has an energy range of 3.84-4.23 MeV, a peak centroid of 4.20 MeV and 8255 counts. The second peak is the $^{236}$U peak which has an energy range of 4.28-4.50 MeV, a peak centroid of 4.48 MeV and 4493 counts. The third peak is the $^{234}$U peak which has an energy range of 4.55-4.76 MeV, a peak centroid of 4.76 MeV and 7983 counts.
Figure 3.06: $^{230}$Th and $^{229}$Th spectra for uraninite. The first peak on the x scale is the $^{230}$Th peak which has an energy range of 4.55-4.78 MeV, a peak centroid of 4.76 MeV and 6573 counts. The second peak is the $^{229}$Th peak which has an energy range of 4.82-5.11 MeV, a peak centroid of 4.91 MeV and 3905 counts.
(3:2:7) Radionuclide interferences.

The behaviour of several potential radionuclide interferences (radium, polonium, americium and plutonium) were investigated to establish if they would co-elute with the uranium and thorium. If present, the radionuclides because of their similar alpha energies shown in table 3.08 could interfere with the alpha spectrometry measurement of the uranium and thorium isotopes.


Four load solutions containing 3M nitric acid-0.5M aluminium nitrate solution were spiked with either 1ml of $^{226}$Ra, 0.5ml of $^{210}$Po/$^{210}$Pb, 2ml of $^{241}$Am, and 2ml of $^{239}$Pu.

These solutions were loaded onto four conditioned UTEVA columns. The UTEVA columns were then washed with the following solutions; 5ml of 3M nitric acid, 5ml of 9M hydrochloric acid, 15ml of 5M hydrochloric acid, 15ml of 0.02M hydrochloric acid and 10ml of 0.1M ammonium oxalate. The combined load and 3M nitric acid fraction, the three hydrochloric acid fractions and the ammonium oxalate fraction were analysed for the presence of the radionuclide interferences. The fractions from the radium experiment were measured by gamma spectrometry.

The fractions from the polonium, americium and plutonium experiments were spiked with 1ml of $^{208}$Po, 0.2ml of $^{243}$Am and 1ml of $^{242}$Pu respectively. The polonium sources were prepared by autodepositing the polonium fractions onto silver discs from dilute hydrochloric acid solution in the presence of ascorbic acid. The americium and plutonium fractions were electrodeposited as described in section (2.2:1:1). The polonium, americium and plutonium sources were then measured by alpha spectrometry.
Table 3.08: Table of alpha energies.

<table>
<thead>
<tr>
<th>Energy (MeV)</th>
<th>Radionuclide</th>
<th>Half-life</th>
<th>$\alpha$-emission probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.954</td>
<td>$^{232}$Th</td>
<td>1.405×10^{10} y</td>
<td>23, 77</td>
</tr>
<tr>
<td>4.013</td>
<td>$^{238}$U</td>
<td>4.468×10^{9} y</td>
<td>23, 77</td>
</tr>
<tr>
<td>4.150</td>
<td>$^{235}$U</td>
<td>7.038×10^{8} y</td>
<td>18, 57</td>
</tr>
<tr>
<td>4.198</td>
<td>$^{233}$U</td>
<td>1.600×10^{7} y</td>
<td>6, 84</td>
</tr>
<tr>
<td>4.368</td>
<td>$^{235}$U</td>
<td>7.54×10^{4} y</td>
<td>23, 76</td>
</tr>
<tr>
<td>4.396</td>
<td>$^{233}$U</td>
<td>2.457×10^{5} y</td>
<td>28, 71</td>
</tr>
<tr>
<td>4.445</td>
<td>$^{235}$U</td>
<td>1.5925×10^{5} y</td>
<td>15, 83</td>
</tr>
<tr>
<td>4.495</td>
<td>$^{238}$U</td>
<td>2.3416×10^{3} y</td>
<td>26, 74</td>
</tr>
<tr>
<td>4.602</td>
<td>$^{226}$Ra</td>
<td>1.600×10^{3} y</td>
<td>6, 94</td>
</tr>
<tr>
<td>4.785</td>
<td>$^{226}$Ra</td>
<td>1.600×10^{3} y</td>
<td>6, 94</td>
</tr>
<tr>
<td>4.621</td>
<td>$^{230}$Th</td>
<td>7.54×10^{4} y</td>
<td>23, 76</td>
</tr>
<tr>
<td>4.688</td>
<td>$^{231}$U</td>
<td>2.457×10^{5} y</td>
<td>28, 71</td>
</tr>
<tr>
<td>4.723</td>
<td>$^{233}$U</td>
<td>1.5925×10^{5} y</td>
<td>15, 83</td>
</tr>
<tr>
<td>4.775</td>
<td>$^{238}$U</td>
<td>2.3416×10^{3} y</td>
<td>26, 74</td>
</tr>
<tr>
<td>4.784</td>
<td>$^{238}$U</td>
<td>2.3416×10^{3} y</td>
<td>26, 74</td>
</tr>
<tr>
<td>4.824</td>
<td>$^{239}$Th</td>
<td>7.340×10^{3} y</td>
<td>9, 56</td>
</tr>
<tr>
<td>4.815</td>
<td>$^{238}$U</td>
<td>2.4113×10^{4} y</td>
<td>11, 15</td>
</tr>
<tr>
<td>4.845</td>
<td>$^{239}$Pu</td>
<td>2.4113×10^{4} y</td>
<td>11, 15</td>
</tr>
<tr>
<td>4.901</td>
<td>$^{240}$Pu</td>
<td>3.735×10^{5} y</td>
<td>23, 76</td>
</tr>
<tr>
<td>4.968</td>
<td>$^{241}$Pu</td>
<td>1.4×10^{3} y</td>
<td>0.002</td>
</tr>
<tr>
<td>5.050</td>
<td>$^{242}$Pu</td>
<td>3.735×10^{5} y</td>
<td>23, 76</td>
</tr>
<tr>
<td>4.897</td>
<td>$^{241}$Pu</td>
<td>1.4×10^{3} y</td>
<td>0.002</td>
</tr>
<tr>
<td>5.106</td>
<td>$^{242}$Pu</td>
<td>3.735×10^{5} y</td>
<td>23, 76</td>
</tr>
<tr>
<td>5.144</td>
<td>$^{243}$Am</td>
<td>7.370×10^{3} y</td>
<td>11, 88</td>
</tr>
<tr>
<td>5.168</td>
<td>$^{249}$Pu</td>
<td>2.4113×10^{4} y</td>
<td>11, 15</td>
</tr>
<tr>
<td>5.124</td>
<td>$^{240}$Pu</td>
<td>3.735×10^{5} y</td>
<td>23, 76</td>
</tr>
<tr>
<td>5.233</td>
<td>$^{243}$Am</td>
<td>7.370×10^{3} y</td>
<td>11, 88</td>
</tr>
<tr>
<td>5.276</td>
<td>$^{244}$Pu</td>
<td>2.4113×10^{4} y</td>
<td>11, 15</td>
</tr>
<tr>
<td>5.264</td>
<td>$^{242}$Pu</td>
<td>3.735×10^{5} y</td>
<td>23, 76</td>
</tr>
<tr>
<td>5.305</td>
<td>$^{240}$Pu</td>
<td>3.735×10^{5} y</td>
<td>23, 76</td>
</tr>
<tr>
<td>5.340</td>
<td>$^{243}$Am</td>
<td>7.370×10^{3} y</td>
<td>11, 88</td>
</tr>
<tr>
<td>5.423</td>
<td>$^{244}$Pu</td>
<td>2.4113×10^{4} y</td>
<td>11, 15</td>
</tr>
</tbody>
</table>

Where the alpha energy in bold print is the most intense $\alpha$-line of a given radioisotope. The above data was obtained from the radiochemical manual [186].
Results and discussion.

Table 3.09 shows the recoveries of the radionuclides in each of the five analysed fractions. The $^{226}$Ra, $^{210}$Po and $^{241}$Am were recovered quantitatively in the combined load and nitric acid wash (fraction 1) which means that if present they would not interfere with the analysis of uranium and thorium. The $^{238}$Pu was present in both the thorium and uranium eluates (fractions 3 and 4). As the $^{239}$Pu has an alpha energy of 5.16 MeV, $^{239}$Pu would not interfere with the alpha spectrometry analysis of uranium and thorium isotopes. The $^{242}$Pu isotope has alpha energy of 4.903 MeV which would interfere with the $^{229}$Th peak. This indicates that the separation procedure would be unsuitable for environmental samples which may contain plutonium isotopes.

Table 3.09: Percentage recoveries of polonium, radium, americium and plutonium.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Fraction 1</th>
<th>Fraction 2</th>
<th>Fraction 3</th>
<th>Fraction 4</th>
<th>Fraction 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15ml 3M HNO$_3$</td>
<td>5ml 9M HCl</td>
<td>15ml 5M HCl</td>
<td>15ml 0.02M HCl</td>
<td>10ml 0.1M AO</td>
</tr>
<tr>
<td>Po</td>
<td>91 ± 3</td>
<td>1.3 ± 0.3</td>
<td>2.7 ± 0.7</td>
<td>&lt;1</td>
<td>2.9 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>101 ± 2</td>
<td>2.3 ± 0.3</td>
<td>1.1 ± 0.2</td>
<td>&lt;1</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>93 ± 5</td>
<td>2.5 ± 0.6</td>
<td>1.4 ± 0.3</td>
<td>&lt;1</td>
<td>3.2 ± 0.7</td>
</tr>
<tr>
<td>Ra</td>
<td>100</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Am</td>
<td>102 ± 6</td>
<td>2.9 ± 0.4</td>
<td>&lt;1</td>
<td>1.9 ± 0.3</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>111 ± 2</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Pu</td>
<td>4.7 ± 0.6</td>
<td>1.7 ± 0.2</td>
<td>41 ± 2</td>
<td>43 ± 2</td>
<td>9.8 ± 0.7</td>
</tr>
</tbody>
</table>

In conclusion the EIChroM proposed separation method separates uranium from thorium. The presence of iron does not affect the separation of the uranium and thorium as the iron was not retained by the UTEVA resin. The radionuclide interference experiments show that radium, polonium and americium were not sorbed by the UTEVA resin. The presence of plutonium in the sample would interfere with the analysis of thorium and uranium as it was present in both fractions. In conclusion the separation scheme was suitable for the separation of uranium and thorium from mixed spike solutions and a uraninite ore reference material.
(3:3) EXPERIMENTS WITH 3M NITRIC ACID LOAD SOLUTION.

The following experiments were carried out to investigate whether using a 3M nitric acid load solution without aluminium nitrate would affect the sorption/elution of uranium and thorium. The experiments enabled the load/wash solution (fraction 1) to be electrodeposited as the presence of aluminium in fraction 1 in the previous experiments prevented the electrodeposition of uranium and thorium.

The following experiments were undertaken:

An initial experiment to investigate whether the absence of aluminium nitrate from the 3M nitric acid load solution affected the separation of uranium and thorium.

Experiments in which iron is added to the column load solution to establish whether the absence of aluminium nitrate affected the separation of uranium and thorium from iron.

Elution profile experiment to study the elution of uranium and thorium in greater detail.

Interferences such as americium and plutonium were investigated to see whether the absence of aluminium nitrate affected their sorption and elution.
(3:3:1) Initial Experiment.

An initial experiment was carried out to establish whether the absence of aluminium nitrate from the 3M nitric acid load solution would affect the separation of uranium from thorium.

(3:3:1:1) Experimental.

A 2ml aliquot of the $^{235}\text{U}$, $^{229}\text{Th}$, and $^{232}\text{U}/^{228}\text{Th}$ spike solutions were added to a 100ml glass beaker. The spike solutions were then evaporated to dryness under a heat lamp. The resulting residue was re-dissolved in 5ml of 6M nitric acid and made up to 10ml with deionized water. The solution was swirled to mix.

A beaker was placed under the UTEVA column and the column allowed to drain. The column was then conditioned with 5ml of 3M nitric acid. The test solution was then added to the column and allowed to drain. The sample beaker was washed with 5ml of 3M nitric acid which was then added to the column. The load and wash fractions were collected as fraction 1. The following reagents were added sequentially to the column and collected in four, 100ml glass beakers labelled fractions 2 to 5. The 5ml 9M hydrochloric acid wash, which was added to convert the column to the chloride form was collected as fraction 2. The 15ml of 5M hydrochloric acid, which was used to elute the thorium, was collected as fraction 3. The 15ml of 0.02M hydrochloric acid was collected as fraction 4. The column was then washed with 10ml of 0.1M ammonium oxalate to remove any remaining uranium or thorium and collected as fraction 5.

To each of the fractions, 1ml of $^{236}\text{U}$ and $^{229}\text{Th}$ spike solutions was added. The fractions were then electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry.

(3:3:1:2) Results and discussion.

The results for the initial experiments are shown in table 3.10. The results show that the 3M nitric acid load solution results agree with those obtained with the 3M
nitric acid-0.5M aluminium nitrate load solution (shown in section 3:2:1:2). The experiment shows that neither uranium or thorium are eluted from the column with the load solution. Separation of uranium from thorium was achieved and thorium was eluted by the 15ml of 5M hydrochloric acid and the uranium was eluted by 15ml of 0.02M hydrochloric acid.

<table>
<thead>
<tr>
<th>Fraction Number</th>
<th>Reagent used</th>
<th>$^{232}$Th in each fraction</th>
<th>$^{232}$U in each fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>15ml 3M HNO₃</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>F2</td>
<td>5ml 9M HCl</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>F3</td>
<td>15ml 5M HCl</td>
<td>105 ± 3</td>
<td>2.3 ± 0.3</td>
</tr>
<tr>
<td>F4</td>
<td>15ml 0.02M HCl</td>
<td>1.1 ± 0.2</td>
<td>103 ± 4</td>
</tr>
<tr>
<td>F5</td>
<td>10ml 0.1M AO</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
(3:3:2) Effect of the presence of iron in the load solutions.

The iron experiments were carried out to establish whether the absence of aluminium nitrate from the 3M nitric acid load solution would affect the separation of iron from uranium and thorium. The importance of studying the presence of iron has been discussed previously in section (3:2:4).

(3:3:2:1) Experimental.

Two test solutions were prepared as described in section (3:3:1:1) with the addition of 1 or 5ml of the 10mg/ml iron solution.

The test solutions were then loaded onto two conditioned UTEVA columns. The sample beaker was washed with 5ml of 3M nitric acid which was then added to the column. The load and wash fractions (fraction 1) were discarded. The method then followed that described in section (3:3:1:1) for the addition and collection of fraction 2 to 5.

To each of the fractions, 1ml of the $^{236}\text{U}$ and $^{229}\text{Th}$ spike solutions was added. The fractions were electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry.

(3:3:2:2) Results and discussion.

The results for the experiments with 10 and 50mg of added iron are shown in table 3.11. The results show that the presence of 10 and 50mg of iron and the absence of aluminium nitrate does not affect the sorption/elution behaviour of the uranium and thorium. Once again, thorium was eluted in fraction 3 and uranium in fraction 4.

Table 3.11: UTEVA EIChroM method with 3M nitric acid load, 10 and 50mg of iron.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Thorium recovery (%)</th>
<th>Uranium recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10mg Iron</td>
<td>106 ± 7</td>
<td>106 ± 4</td>
</tr>
<tr>
<td>50mg Iron</td>
<td>100 ± 5</td>
<td>102 ± 3</td>
</tr>
</tbody>
</table>
(3:3:3) Elution profile.

The elution profile experiment was carried out to establish whether the absence of aluminium nitrate from the 3M nitric acid load solution would affect the elution of uranium and thorium. The elution of uranium and thorium was studied in detail (as in section 3:2:3) with the addition and collection of the 15ml of 5M hydrochloric acid and 0.02M hydrochloric acid in five 3ml fractions. The experiment was carried out with and without the addition of 10mg of iron.

(3:3:3:1) Experimental.

A 2ml aliquot of the $^{233}$U/$^{228}$Th spike solution was added to two 100ml glass beakers. To one of the beakers 1ml of the iron solution (10mg/ml) was added. The spike solutions were then evaporated to dryness under a heat lamp. The resulting residues were re-dissolved in 5ml of 6M nitric acid made to a 10ml volume with deionized water. The solution was swirled to mix.

A glass beaker was placed under each of the UTEVA column, the bottom plug removed, and the columns allowed to drain. The columns were then conditioned with 5ml of 3M nitric acid. The sample load solution was then added to the column and allowed to drain. The sample beaker was washed with 5ml of 3M nitric acid which was then added to the column. The load and wash fractions were collected as fraction 1 for the elution experiment not containing iron and discarded for the experiment that contained iron. The 5ml of 9M hydrochloric acid were collected as fraction 2. The 15ml of 5M hydrochloric acid were collected as five 3ml fractions (labelled fractions 3-7). Each 3ml fraction of the 5M hydrochloric acid was added to the column and collected before the next 3ml fraction was added. The 15ml of 0.2M hydrochloric acid were collected in five 3ml fractions (labelled fractions 8-12). The 10ml of 0.1M ammonium oxalate were collected as fraction 13.

To each of the collected fractions 1ml of $^{236}$U and $^{229}$Th were added. The fractions were then electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry.
(3.3.3.2) Results and discussion.

The elution profile experimental results with and without 10mg of added iron (figures 3.07 and 3.08) showed that the uranium was quantitatively eluted from the column with 6ml of 0.02M hydrochloric acid. The majority of the thorium was eluted from the column with 15ml of 5M hydrochloric acid. These results show that the separation of uranium and thorium was not affected by the absence of aluminium nitrate from the load solution.

Figure 3.07: Uranium and thorium elution profile.

![Graph showing uranium and thorium recovery](image1)

Figure 3.08: Uranium and thorium elution profile with 10mg of iron.

![Graph showing uranium and thorium recovery with iron](image2)
(3.3.4) **Radionuclide interferences.**

The effect of interference experiments were carried out with americium, plutonium and plutonium to establish whether the absence of the aluminium nitrate from the 3M nitric acid load solution affected the sorption/elution behaviour of americium, plutonium and polonium. The interference problems associated with americium and plutonium have been discussed previously in section (3.2.7).

**Experimental.**

Interference test solutions of 3M nitric acid were prepared and spiked with either 2ml of $^{241}$Am, 2ml of $^{239}$Pu or 0.5ml of $^{210}$Po/$^{210}$Pb.

The test solutions were loaded onto two conditioned UTEVA columns which were then sequentially eluted with 5ml of 3M nitric acid (fraction 1), 5ml of 9M hydrochloric acid (fraction 2), 15ml of 5M hydrochloric acid (fraction 3), 15ml of 0.02M hydrochloric acid (fraction 4) and 10ml of 0.1M ammonium oxalate (fraction 5). The combined load and nitric acid fraction, the three hydrochloric acid fractions and the ammonium oxalate fraction were then analysed for the presence of the radionuclide interferences.

The fractions from the americium, plutonium and polonium experiments were spiked with 0.2ml of $^{243}$Am, 1ml of $^{242}$Pu and 1ml of $^{208}$Po respectively. The americium and plutonium fractions were then electrodeposited as described in section (2.2.1:1). The polonium fractions were autodeposited onto silver discs from dilute hydrochloric acid solution in the presence of ascorbic acid. The americium, plutonium and polonium sources were then measured by alpha spectrometry.

(3.3.4.2) **Results and discussion.**

The results of the interference studies are shown in table 3.12. The results show that the plutonium was present in both the thorium and uranium fractions. This
indicated that the column procedure, without the addition of aluminium nitrate to the load solution, would also not be suitable for environmental samples that contain plutonium. The americium and polonium were not retained by the UTEVA resin and so would not interfere with the analysis of uranium and thorium.

The interference experiment results for the 3M nitric acid load solution agree with those obtained for the 3M nitric acid-0.5M aluminium nitrate load solution. This indicates that the absence of aluminium nitrate does not have any affect on the separation of uranium from thorium.

Table 3.12: Percentage recoveries of polonium, americium and plutonium.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Fraction 1 15ml 3M HNO₃</th>
<th>Fraction 2 5ml 9M HCl</th>
<th>Fraction 3 15ml 5M HCl</th>
<th>Fraction 4 15ml 0.02M HCl</th>
<th>Fraction 5 10ml 0.1M AO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Po</td>
<td>101 ± 4</td>
<td>1.4 ± 0.1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Am</td>
<td>110 ± 2</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Pu</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>34 ± 2</td>
<td>56 ± 2</td>
<td>9.7 ± 0.5</td>
</tr>
<tr>
<td>Pu</td>
<td>4.6 ± 0.6</td>
<td>&lt;1</td>
<td>23 ± 1</td>
<td>49 ± 2</td>
<td>22 ± 1</td>
</tr>
</tbody>
</table>

In conclusion the uranium and thorium separation method with 3M nitric acid load solution produced the same results without the presence of aluminium nitrate as those obtained in section (3:2) with the aluminium nitrate present.
(3:4) URANIUM, THORIUM, AMERICIUM, AND PLUTONIUM SEPARATION METHOD.

The uranium, thorium, americium and plutonium separation method was developed by combining and adapting ElChroMs uranium and thorium in water [97] and americium, plutonium and uranium in water [186] methods.

The separation method is based on the use of two columns. Initially the sample solution is passed through a UTEVA resin column which the americium and plutonium pass straight through. The uranium and thorium are sorbed onto the column and are subsequently eluted using the method described in section (3:2).

The americium and plutonium are then separated by passing the solution containing the americium and plutonium through a TRU resin column. The separation scheme is shown in figure 3.09.

(1) Sample load solution
(3M nitric acid-1M aluminium nitrate, ferrous sulphamate and ascorbic acid).

(2) Thorium elution (5M HCl)

(3) Uranium elution (0.02M HCl)

UTEVA
2ml column

(4) Sample load solution. (3M nitric acid-1M aluminium nitrate, ferrous sulphamate and ascorbic acid)

Thorianum

Uranium

TRU
2ml column

Americium
(4M HCl)

Plutonium
(0.1M ammonium oxalate)

Figure 3.09: Separation scheme for uranium, thorium, americium, and plutonium.
The following experiments were undertaken:

An initial experiment to investigate using iron (II) sulphamate to reduce the plutonium to plutonium (III).

The separation method was investigated using varying amounts of iron to ensure that the presence of iron in the sample along with the added iron (from the ferrous sulphamate) would not affect the separation.

The separation method was then adapted by using sulphamic acid and the 10mg of iron present from the co-precipitation step to investigate if this could be used in place of the ferrous sulphamate.

The separation method was carried out separately with plutonium, americium, uranium and thorium spike solutions to investigate their sorption/elution. Finally the separation scheme was evaluated using a solution containing a mixed uranium, thorium, americium and plutonium spike solution.
(3:4:1) Initial experiment with plutonium.

The initial experiment investigated the load solution conditions of the americium, plutonium, uranium separation method to determine whether the 3M nitric acid, ferrous sulphamate and ascorbic acid load solution prevented the plutonium from eluting with the uranium and thorium fractions.

(3:4:1) Experimental.

A 2ml aliquot of $^{239}\text{Pu}$ was added to a 100ml glass beaker and evaporated to dryness under a heat lamp. The resulting residue was re-dissolved in 10ml of 3M nitric acid/1M ammonium nitrate. Ferrous sulphamate, (2ml of 0.6M), was then added and the solution mixed. To the load solution 0.2g of ascorbic acid were added two minutes before the solution was placed on the column.

A UTEVA column was conditioned with 5ml of 3M nitric acid. The sample solution was loaded onto the column and allowed to drain through. Two, 5ml aliquots of 3M nitric acid used to rinse the sample beaker were passed through the column. The load and 3M nitric acid washes were collected as fraction 1. The column was then converted to the chloride form by passing through 5ml of 9M hydrochloric acid. The 9M hydrochloric acid wash was collected as fraction 2. The 15ml of 5M hydrochloric acid, which would elute the thorium from the column, were added to the column and collected as fraction 3. The 15ml of 0.02M hydrochloric acid, which would elute the uranium from the column, were added to the column and collected as fraction 4. A 10ml aliquot of 0.1M ammonium oxalate was then used to elute any plutonium remaining on the column and collected as fraction 5.

Fraction 1 was then added to a TRU column pre-conditioned with 5ml of 2M nitric acid and collected as fraction 6. The column was then washed with 5ml of 2M nitric acid. The $^{239}\text{Pu}^{3+}$ was then oxidised to $^{240}\text{Pu}^{4+}$ to enhance separation from americium by the addition of 5ml of 2M nitric acid-0.1M sodium nitrite solution. The column was then washed with 5ml of 0.5M nitric acid before the column was
converted to the chloride form with 3ml of 9M hydrochloric acid. The column washings were collected as fraction 7. A 20ml aliquot of 4M hydrochloric acid was added to the column to elute any americium and collected as fraction 8. The plutonium was then eluted from the column with 10ml of 0.1M ammonium oxalate and collected as fraction 9.

To each of the collected fractions 1ml of $^{242}$Pu spike solution was added. The fractions were then electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry.

(3:4:1:2) Results and discussion.

The plutonium experimental results are shown in table 3.13. The results show that the addition of ferrous sulphamate and ascorbic acid to the 3M nitric acid load solution reduces the plutonium (IV) to plutonium (III). The plutonium (III) was not retained by the UTEVA column and therefore does not interfere with the analysis of thorium and uranium (as no plutonium is eluted in fractions 3 and 4). The load solution (containing plutonium) was then passed through a TRU column and an average of 99% with a standard deviation of 3% of the plutonium was eluted by the 0.1M ammonium oxalate.

| Table 3.13: Plutonium results for U, Th, Am and Pu separation method |
|-----------------------------|----------------|----------------|
| Experiment                  | % Pu in fraction 9 | % Pu in F2,3,4,5,7 and 8 |
| Experiment 1                | 101 ± 3          | <1              |
| Experiment 2                | 97 ± 3           | <1              |
(3:4:2) Experiment with uranium and thorium.

The experiment described in section (3:4:1:1) was repeated with thorium and uranium spike solutions to ensure that the thorium and uranium were sorbed onto the UTEVA column from the 3M nitric acid-0.5M aluminium nitrate load solution and subsequently eluted with 5M hydrochloric acid and 0.02M hydrochloric acid respectively.

(3:4:2:1) Experimental.

A 0.5ml aliquot of $^{238}$U were added to a 100ml glass beaker. The spike solution was then evaporated to dryness under a heat lamp. The resulting residue was re-dissolved in 10ml of 3M nitric acid, 2ml of 0.6M ferrous sulphamate were added and the solution mixed. Two minutes before the load solution was placed on a pre-conditioned UTEVA column, 0.2g of ascorbic acid were added.

Two, 5ml aliquots of 3M nitric acid used to rinse the sample beaker were passed through the column. The load and 3M nitric acid washes were collected as fraction 1. The 5ml of 9M hydrochloric acid were collected as fraction 2. The 15ml of 5M hydrochloric acid were collected as fraction 3. The 15ml of 0.02M hydrochloric acid were collected as fraction 4. The 10ml of 0.1M ammonium oxalate were collected as fraction 5.

Fraction 3 and fraction 4 were spiked with 0.5ml of $^{229}$Th spike solution and 0.5ml of $^{236}$U spike solution respectively. The fractions were then electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry.

(3:4:2:2) Results and discussion.

The uranium and thorium results in table 3.14 show that the presence of ferrous sulphamate and ascorbic acid in the 3M nitric acid load solution does not affect the sorption and elution of uranium and thorium. An average of 103.5% ($\pm$0.7%) of the thorium was eluted by the 15ml of 5M hydrochloric acid (F3) and an average of 104.5% ($\pm$5%) of the uranium was eluted by 0.02M hydrochloric acid.
These results compare with the recovery of uranium and thorium results observed for the uranium and thorium separation methods shown in sections (3:2 and 3:3).

Table 3.14: Uranium and thorium results for U, Th, Am and Pu separation method.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Fraction 2 5ml 9M HCl</th>
<th>Fraction 3 15ml 5M HCl</th>
<th>Fraction 4 15ml 0.02M HCl</th>
<th>Fraction 5 10ml 0.1M AO</th>
</tr>
</thead>
<tbody>
<tr>
<td>U Expt 1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>108 ± 3</td>
<td>&lt;1</td>
</tr>
<tr>
<td>U Expt 2</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>101 ± 3</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Th Expt 1</td>
<td>&lt;1</td>
<td>104 ± 4</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Th Expt 2</td>
<td>&lt;1</td>
<td>103 ± 4</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
(3:4:3) Iron experiments.

The following experiments with 10mg and 50mg of iron added to the spike solution were undertaken to investigate whether increasing the amount of iron in the load solution would affect the elution of plutonium.

(3:4:3:1) Experimental.

A 2ml aliquot of $^{239}$Pu was added to two 100ml glass beakers labelled 30 and 50mg of iron. Then, 3ml and 5ml of (10mg/ml) iron (III) carrier were added to the respective glass beakers. The spike solutions were then evaporated to dryness under a heat lamp. The resulting residue was re-dissolved in 10ml of 3M nitric acid, 2ml of 0.6M ferrous sulphamate were then added and the solution mixed. Two minutes before the load solution was placed on a conditioned UTEVA column, 0.2g of ascorbic acid were added. The separation method then followed that described in section (3:4:1). To each of the collected fractions 1ml of $^{242}$Pu spike solution was added. The fractions were then electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry.

(3:4:3:2) Results and discussion.

The results of the experiments in which 30 and 50mg of iron were added are shown in table 3.15. These show that increasing the amount of added iron did not affect the sorption and elution of plutonium. An average of 101% (± 3%) of the plutonium was eluted by the 0.1M ammonium oxalate (fraction 9). The plutonium was not eluted in fractions (2 to 8).

Table 3.15: Plutonium results with added iron for U, Th, Am and Pu separation method.

<table>
<thead>
<tr>
<th>Amount of iron (mg)</th>
<th>% Pu in fraction 9</th>
<th>% Pu in F2,3,4,5,7 and 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>100 ± 3</td>
<td>&lt;1</td>
</tr>
<tr>
<td>50</td>
<td>102 ± 3</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
(3:4:4) Plutonium experiment with sulphamic acid and 10 or 50mg of added iron.

As the sample preconcentration method contained iron the following experiments were undertaken to investigate if using the iron present in the iron carrier and a solution of sulphamic acid instead of the ferrous sulphamate solution would reduce the plutonium (IV) to plutonium (III).


Two experiments were carried out with 10mg or 50mg of added iron. A 2ml aliquot of $^{239}$Pu and 1ml and 5ml of (10mg/ml) iron carrier solution were added to two 100ml glass beaker labelled 10 and 50mg of iron. The spike solutions were then evaporated to dryness under a heat lamp. The resulting residues were re-dissolved in 10ml of 3M nitric acid-1M aluminium nitrate solution. Sulphamic acid (2ml of 0.6M) were then added and the solution mixed. Two minutes before the load solution was placed on a conditioned UTEVA column, 0.2g of ascorbic acid were added.

The separation method then follows that described in section (3:4:1:1).

To each of the collected fractions 1ml of $^{242}$Pu spike solution was added. The fractions were then electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry.

(3:4:4:2) Results and discussion.

The results of the experiments in which 10mg or 50mg of iron and sulphamic acid (instead of ferrous sulphamate) were added to the load solutions are shown in table 3.16. The results showed that using the 10mg and 50mg of iron and the sulphamic acid reduced the plutonium to plutonium (III) which was not retained by the UTEVA column. The plutonium was then separated from the iron using a TRU column and eluted with 0.1M ammonium oxalate. The results are in agreement with those obtained using ferrous sulphamate shown in section (3:4:1:2) and (3:4:3:2).
Table 3.16: Plutonium results with 10mg, 50mg iron and sulphamic acid for U, Th, Am and Pu separation method.

<table>
<thead>
<tr>
<th>Amount of iron (mg)</th>
<th>% Pu in fraction 9</th>
<th>% Pu in F2,3,4,5,7 and 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>105 ± 4</td>
<td>&lt;1</td>
</tr>
<tr>
<td>50</td>
<td>101 ± 4</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
(3:4:5) Sulphamic acid and 10mg iron without aluminium nitrate with plutonium and uranium and thorium.

The experiment with sulphamic acid, 10mg of iron carrier and without aluminium nitrate was carried out with plutonium, uranium and thorium spike solutions.

(3:4:5:1) Experimental.

A 0.5ml aliquot of $^{238}$U and 2ml of $^{239}$Pu were added to two 100ml glass beakers. The iron carrier, 1ml of 10mg/ml, was added to each of the beakers and the spike solutions evaporated to dryness under an heat lamp. The resulting residues were re-dissolved in 5ml of 6M nitric acid and made to a 10ml volume with deionized water. Then, 2ml of 0.6M sulphamic acid were added and the solution mixed. Two minutes before the load solution was placed on the column, 0.2g of ascorbic acid were added.

The test solution was loaded onto two conditioned UTEVA columns and allowed to drain through. The separation method then followed that described in section (3:4:1:1). To each of the collected fractions for the plutonium experiment 1ml of the $^{242}$Pu spike solution was added.

To each of the collected fractions from the uranium and thorium experiment 0.5ml of $^{229}$Th and 0.5ml of $^{236}$U spike solutions were added. The fractions were then electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry.

(3:4:5:2) Results and discussion.

The plutonium results with 10mg of iron and sulphamic acid added but without aluminium nitrate added are shown in table 3.17. The results show that the absence of aluminium nitrate did not affect the sorption/elution of plutonium which was eluted from the TRU column by the 0.1M ammonium oxalate (F9). The plutonium was not eluted from the column within fractions 2 to 8.
The results for the thorium and uranium experiment carried out with 10mg of iron, and sulphamic acid added showed that the thorium and uranium were quantitatively recovered from the column with the 5M and 0.02M hydrochloric acid fractions respectively.

The results were not affected by the absence of aluminium nitrate from the load solution.

Table 3.17: Plutonium experiment with 10mg of iron, sulphamic acid and without aluminium nitrate.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>% Pu in fraction 9</th>
<th>% Pu in F2,3,4,5,7 and 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>111±6</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
(3:4:6) Sulphamic acid and 10mg iron with americium with and without aluminium nitrate.

The experiment was undertaken to investigate the effect of the absence and presence of aluminium nitrate on the sorption and elution of americium. The experiment also investigated whether sulphamic acid/10mg iron instead of the ferrous sulphamate solution affected americium's sorption and elution.


Test solutions were prepared by adding 2ml of $^{241}$Am and 1ml of iron (10mg/ml) carrier solution to two 100ml glass beakers. The spike solutions were then evaporated to dryness under a heat lamp. The resulting residues were re-dissolved in 10ml of 3M nitric acid-1M aluminium nitrate solution and 10ml of 3M nitric acid solution. 2ml of 0.6M sulphamic acid were then added to each of the beakers and the solutions mixed. Two minutes before the load solution was placed on the two conditioned UTEVA columns, 0.2g of ascorbic acid were added.

The test solutions were loaded onto the columns and allowed to drain through. The separation method then followed that described in section (3:4:1:1).

To each of the collected fractions 0.2ml of $^{243}$Am spike solution were added. The fractions were then electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry.

(3:4:6:2) Results and discussion.

The americium results are shown in table 3.18. The experimental results show that the americium was not retained by the UTEVA column. This finding agrees with results from the uranium/thorium separation methods described in sections (3:2:7:2) and (3:3:4:2) and shows that the presence of sulphamic acid in the load solution does not affect the behaviour of americium on the UTEVA column. The americium was retained by the TRU column and separated from aluminium, iron
and plutonium. The americium is eluted from the column (before the plutonium) with 4M hydrochloric acid (F8). The experiments with and without the presence of aluminium nitrate in the load solution gave similar results showing that the absence of aluminium nitrate had no affect on the sorption and elution behaviour of the americium spike solution.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>% Am in fraction 8</th>
<th>% Pu in F2,3,4,5,7 and 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment with aluminium nitrate</td>
<td>110 ± 2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Experiment without aluminium nitrate</td>
<td>110 ± 2</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
Sulphamic acid and 10mg iron with uranium, thorium, americium and plutonium mixed spike solution.

The following experiment investigated the developed separation scheme using a load solution containing uranium, thorium, americium and plutonium spike solutions.

Experimental.

Test solutions were prepared by adding 0.5ml of $^{238}$U, 2ml of $^{239}$Pu and $^{241}$Am and 1ml of iron carrier (10mg/ml) solution to 100ml glass beaker. The spike solutions were then evaporated to dryness under a heat lamp. The resulting residues were re-dissolved in 10ml of 3M nitric acid-1M aluminium nitrate solution. Then 2ml of 0.6M sulphamic acid were added and the solution mixed. Two minutes before the load solution was placed on the column, 0.2g of ascorbic acid were added.

A UTEVA column was conditioned with 5ml of 3M nitric acid. The sample solution was loaded onto the column and allowed to drain through. The separation method then followed that described in section (3:4:1:1).

The thorium (fraction 3), uranium (fraction 4), americium (fraction 8) and plutonium (fraction 9) fractions were collected and 0.5ml of $^{229}$Th, 0.5ml of $^{236}$U, 0.2ml of $^{243}$Am, and 1ml of $^{242}$Pu spike solutions were added to the respective fractions. The fractions were then electrodeposited as described in section (2:2:1:1) and counted by alpha spectrometry.

Results and discussion.

The results for the mixed uranium, thorium, americium, and plutonium spike solution are shown in table 3.19. The results show that the separation method elutes the thorium (104%), uranium (113%), americium (109%) and plutonium (99%) in fractions 3,4,8 and 9 respectively.
Table 3.19: Uranium, thorium, americium and plutonium results for mixed spike solution.

<table>
<thead>
<tr>
<th></th>
<th>Thorium</th>
<th>Uranium</th>
<th>Americium</th>
<th>Plutonium</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%) Recovery</td>
<td>104 ± 3</td>
<td>113 ± 4</td>
<td>109 ± 2</td>
<td>99 ± 3</td>
</tr>
</tbody>
</table>

In conclusion the experimental results show that the developed americium, plutonium, uranium and thorium separation method was suitable for the separation of these elements. Replacing the ferrous sulphamate with 10mg of iron carrier and sulphamic acid did not affect the separation and the separation method was able to cope with up to 70mg of iron per sample.
(3:5) CONCLUSION.

In conclusion the ElChroM proposed separation method was shown to be successful in separating uranium from thorium. The presence of iron did not affect the separation of the uranium and thorium as the iron was not retained by the UTEVA resin. The radionuclide interference experiments showed that radium, polonium and americium were not sorbed by the UTEVA resin. The presence of plutonium in the sample would interfere with the analysis of thorium and uranium as it was present in the same elution fractions as these elements. In conclusion the separation scheme was suitable for the separation of uranium and thorium from mixed spike solutions and a uraninite ore reference material. The separation method is further evaluated in chapter 4.

The uranium and thorium separation method with 3M nitric acid load solution produced the same results without the presence of aluminium nitrate as those obtained in section (3:2) with the aluminium nitrate present.

The developed americium, plutonium, uranium and thorium separation method was suitable for the separation of these elements. Replacing the ferrous sulphamate with 10mg of iron carrier and sulphamic acid did not affect the separation and the separation method was able to cope with up to 70mg of iron per sample. The separation method is further evaluated in chapter 4.
CHAPTER 4

EVALUATION OF URANIUM, THORIUM AND URANIUM, THORIUM, AMERICIUM, PLUTONIUM SEPARATION METHODS.
(4.1) INTRODUCTION TO THE EVALUATION OF THE TWO SEPARATION METHODS.

The two separation methods were evaluated using real samples to ensure that separation was not affected by matrix interferences found in environmental/geological samples (and not in the spike solutions).

The uranium and thorium separation method described in section (3.3) was used to determine the concentrations of uranium isotopes ($^{238}\text{U}$, $^{234}\text{U}$) and thorium isotopes ($^{232}\text{Th}$, $^{230}\text{Th}$, $^{228}\text{Th}$) in the following samples. The samples are discussed in greater detail in section (4.2:1).

(i) a solution of a uraninite ore  
(ii) coral reference material  
(iii) Mirhib well water sample  
(iv) Malham Tarn samples  
(v) and Pinarbasi basin samples

The uranium, thorium, americium and plutonium separation method described in section (3.4) was used to determine uranium and thorium concentrations in the following samples. The samples are discussed in greater detail in section (4.2:1).

(i) a solution of a uraninite ore  
(ii) granite reference material  
(iii) sediment reference material  
(iv) Mirhib well water sample  
(v) iron rich calcium carbonate samples A and B.
(4:2) URANIUM AND THORIUM SEPARATION METHOD.

Reagents.

These were; hydrochloric acid, nitric acid, ammonia, iron carrier (10mg/ml), ammonium oxalate, sulphamic acid, UTEVA resin 2ml columns, $^{236}$U (167mBq/g) and $^{229}$Th (192mBq/g) tracer solutions.

(4:2:1) Experimental.

The uranium and thorium separation method developed in section (3:3) of chapter 3 was evaluated using reference materials and environmental samples. The purpose of using the uraninite ore solution, the coral reference material, Mirhrib well water sample, Malham Tarn samples and the Pinarbasi basin sediment samples was to establish that the separation method was suitable for the analysis of uranium and thorium in a wide range of different types of sample matrices.

(4:2:1:1) Solution of uraninite ore.

The uraninite ore was used in the Uranium Series Intercomparison Project (USIP) [185]. The $^{238}$U, $^{234}$U and $^{230}$Th activities of 151mBq/g were known by cross checking against NIST $^{232}$U and $^{229}$Th standards. The USIP established the secular equilibrium between $^{238}$U, $^{234}$U and $^{230}$Th. The analysis was repeated five times to determine whether repeatable results could be obtained. The uraninite ore reference material was also analysed using an established anion exchange method [29] to enable comparison of the two separation methods.

Experimental.

A 0.5ml aliquot of the uraninite solution was diluted to 100ml using 0.1 M nitric acid. To the uraninite solution 0.5g of $^{236}$U and $^{229}$Th internal standard solutions and 1ml of the iron (III) carrier solution were added. The solution was then left to equilibrate overnight.
The uranium and thorium were co-precipitated from solution with iron (III) hydroxide by the addition of ammonia solution. The sample was then warmed to coagulate the precipitate, which was then isolated by centrifuging.

The sample was then ready for separation by either the UTEVA or the anion exchange method.

The following method was used for the UTEVA separation method. The precipitate was dissolved in 5ml of 6M nitric acid and the resulting solution diluted to 10ml with deionized water. The uranium and thorium separation method, developed in chapter 3, section (3:3:1), was then used. A UTEVA resin column was conditioned with 5ml of 3M nitric acid. The sample solution was loaded onto the column and allowed to drain through. A 5ml aliquot of 3M nitric acid used to rinse the centrifuge tube was passed through the column. The column was then converted to the chloride form by passing through 5ml of 9M hydrochloric acid. Thorium was then eluted from the column with 15ml of 5M hydrochloric acid and the uranium was eluted from the column with 15ml of 0.02M hydrochloric acid.

The following anion exchange procedure, as described by Lally et al [29] was used as a comparison for the extraction chromatography procedure.

Uranium and thorium were initially co-precipitated with iron (III) hydroxide. The precipitate was dissolved in 8M hydrochloric acid and the resulting solution was passed through a 1X8 anion-exchange resin pre-conditioned with 8M hydrochloric acid. The thorium passes straight through the column. The uranium and iron are retained, then eluted from the column using 0.2M hydrochloric acid. The uranium and thorium fractions were reprecipitated with ammonia (after the addition of 0.2ml of the iron carrier (10mg/ml) to the thorium fraction). The precipitates were dissolved in 7M nitric acid and further purification was then achieved by passing the uranium and thorium fractions through separate 1X8 anion exchange columns pre-conditioned with 7M nitric acid. The thorium was sorbed onto the thorium column and separated from the iron which was not
retained. The thorium was then eluted from the column with 2M hydrochloric acid. The uranium was sorbed onto the uranium column. The column was washed with 7M nitric acid to remove the iron, and with 8M hydrochloric acid to remove any traces of thorium, before the uranium was eluted with 0.2M hydrochloric acid.

The uranium and thorium fractions from both separation methods were prepared for counting by alpha spectrometry by electrodeposition onto stainless steel discs using the method described in chapter 2 section (2:2:1:1).

(4:2:1:2) Coral reference material.

The coral (RKM5) reference material was obtained from Richard Ku at the University of Southern California. The coral was used in the Uranium Series Intercomparison Project [185] and had a certified uranium concentration and \(^{234}U/^{238}U\) and \(^{230}\)Th/\(^{234}U\) activity ratios. The coral sample was analysed as the geological samples of particular interest (speleothem/calcite samples) would be of similar matrix (calcium carbonate) and the samples would show if the UTEVA columns were able to cope with calcium carbonate based samples.

The analysis was repeated five times to determine whether repeatable results could be obtained.

Experimental.

Approximately 2g of the coral (RKM5) were added to a 250ml glass beaker and then 100ml of deionized water added. The calcium carbonate was then slowly dissolved by the gradual addition of concentrated nitric acid, such that the solution was maintained at pH 1. Appropriate levels of \(^{236}U\) and \(^{229}\)Th solutions and 1ml of the iron (III) carrier solution were added to the supernate which was then left to equilibrate overnight. The solution was boiled prior to precipitation of the iron (III) hydroxide to ensure removal of the dissolved carbonate.

The uranium and thorium were co-precipitated from solution, separated and prepared for alpha spectrometry using the method described in section (4:2:1:1).
(4:2:1:3) **Mirhib well water sample.**

The Mirhib well water sample of known uranium concentration (60ppb) was obtained from Barry Smith at the British Geological Survey (BGS), Keyworth. The sample was analysed to evaluate the accuracy of the separation method. The analysis was repeated to ensure that reproducible results were obtained.

**Experimental.**

A 500ml aliquot of the Mirhib well water sample was placed in a litre glass beaker. Appropriate levels of $^{236}$U and $^{239}$Th solutions and 1ml of the iron (III) carrier solution were added to the supernate, which was left to equilibrate overnight.

The uranium and thorium were co-precipitated from solution, separated and prepared for alpha spectrometry using the method described in section (4:2:1:1). The analysis was repeated.

(4:2:1:4) **Malham Tarn samples.**

Malham Tarn is of interest as it is the highest Marl lake in the country. The tarn is situated 25 miles north-west of Bradford at an altitude of 376.6m. Current research is being carried out on the tarn by Allan Pentecoste and Pietro Coletta who are developing a model for the carbon dynamics of the tarn ecosystem using stable isotopes [188].

The samples analysed from the Malham Tarn area included two water samples and a speleothem sample. The two water samples: a Malham Tarn water sample (100ml) and a Gordale Beck water sample, taken downstream of the tarn, (500ml) were analysed for their uranium and thorium content and their $^{238}$U/$^{234}$U isotope ratios were measured. The speleothem sample was taken from Victoria cave which is located in the Malham Tarn area. The speleothem sample was analysed for $^{238}$U, $^{234}$U, and $^{210}$Th isotopes and its age calculated using the dating equation described in section (1:4:3:2). The uranium and thorium analysis was of
importance as it enabled the speleothem sample to be dated and provided the first uranium isotope ratio measurements on the Malham Tarn area.

**Experimental**

The two water samples were placed in glass beakers and appropriate levels of $^{236}\text{U}$ and 1ml of the iron (III) carrier solution were added and left to equilibrate overnight. The water samples were then analysed using the method described in section (4:2:1:3).

The speleothem sample was prepared for analysis using the following method. Approximately 1g of the speleothem sample was added to a 250ml glass beaker and 100ml of deionized water added. The calcium carbonate was then slowly dissolved by the gradual addition of concentrated nitric acid, such that the solution was maintained at pH 1. Appropriate levels of $^{236}\text{U}$ and $^{229}\text{Th}$ solutions (0.5ml) and 1ml of the iron (III) carrier solution were added to the supernate, which was left to equilibrate overnight. The solution was boiled prior to precipitation of the iron (III) hydroxide to ensure removal of the dissolved carbonate.

The speleothem sample was then analysed using the method described in section (4:2:1:3).


The Pinarbasi basin sediment samples were obtained from Neil Roberts at Loughborough University, Geography department. The samples were from a core sediment sample taken from the Pinarbasi basin, Turkey. The sediment samples consisted of alternating grey to beige calcareous silts with gastropods and diatomites and with a layer of black to dark brown silty humified peat. The samples from the sediment core have been dated by U/Th, stable isotope and Optically Stimulated Luminescence (OSL) methods [189]. The samples analysed in this thesis were taken from varying depths of the sediment core to give further information on the age of the sediment within the core.
Experimental

Approximately 0.5g of the sediment samples were added to 100ml glass beaker. The calcium carbonate was then slowly dissolved by the gradual addition of concentrated nitric acid, such that the solution was maintained at pH 1. Appropriate levels of $^{236}\text{U}$ and $^{229}\text{Th}$ solutions (0.25ml) and 1ml of the iron (III) carrier solution were added to the supernate, which was left to equilibrate overnight. The solution was boiled prior to precipitation of the iron (III) hydroxide to ensure removal of the dissolved carbonate.

The sediment samples were then analysed using the method described in section (4:2:1:3).
(4:2:2) Results and discussion.

(4:2:2:1) Solution of uraninite ore.

Table 4.01 shows the results from the analysis of the uraninite ore. The calculations used to determine $^{238}\text{U}$ activity of 151.32 mBq/g and its associated error of ± 3.43 are shown in appendix 1.

The value of the $^{230}\text{Th}/^{234}\text{U}$ ratio shows that, within experimental errors, the radionuclides are in secular equilibrium. Comparison of the mean values of the $^{234}\text{U}/^{238}\text{U}$ ($0.996 \pm 0.013$) and the $^{230}\text{Th}/^{234}\text{U}$ ($1.021 \pm 0.03$) ratios for the UTEVA resin method with those previously obtained using anion-exchange ($^{234}\text{U}/^{238}\text{U}$, $0.968 \pm 0.013$; $^{230}\text{Th}/^{234}\text{U}$, $1.016 \pm 0.025$) show that the two method give statistically identical results.

The five analyses of the uraninite ore solution show that the separation method produced repeatable results for the $^{238}\text{U}$, $^{234}\text{U}$, $^{230}\text{Th}$ and $^{234}\text{U}/^{238}\text{U}$ and the $^{230}\text{Th}/^{234}\text{U}$ ratios.

(4:2:2:2) Coral reference material.

Table 4.02 shows the results from the analysis of the coral reference material. The results show that the measured values of the uranium (ppm w/w) compare well with the reference value of 3.25 ± 0.10 ppm uranium. The measured $^{234}\text{U}/^{238}\text{U}$ activity ratios compare well with the certified value of 1.098 ± 0.016 and the $^{230}\text{Th}/^{234}\text{U}$ measured ratio compares well with the reference value of 0.709 ± 0.025. Since this ratio is less than 1, the radionuclides are not in equilibrium and the age of the reference material can be calculated. The age of the coral was calculated using the dating equation described in section (1:4:3:2). The average calculated age of the coral of 132600± 3440 years compares well with the reference value of 131000 ± 9000 years.
Table 4.01: Results of the uraninite ore analyses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{238}$U/mBq g$^{-1}$</th>
<th>$^{234}$U/mBq g$^{-1}$</th>
<th>$^{238}$Th/mBq g$^{-1}$</th>
<th>$^{234}$U/$^{238}$U</th>
<th>$^{236}$Th/$^{234}$U</th>
<th>U recovery (%)</th>
<th>Th recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>154.2 ± 3.3</td>
<td>156.9 ± 3.4</td>
<td>154.5 ± 3.1</td>
<td>1.018 ± 0.018</td>
<td>0.984 ± 0.029</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>151.4 ± 2.8</td>
<td>149.7 ± 2.8</td>
<td>153.8 ± 3.9</td>
<td>0.989 ± 0.017</td>
<td>1.028 ± 0.032</td>
<td>81</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>156.8 ± 2.9</td>
<td>150.4 ± 2.8</td>
<td>158.4 ± 3.6</td>
<td>0.959 ± 0.016</td>
<td>1.053 ± 0.031</td>
<td>82</td>
<td>69</td>
</tr>
<tr>
<td>4</td>
<td>151.9 ± 3.4</td>
<td>153.4 ± 3.4</td>
<td>154.7 ± 3.2</td>
<td>1.009 ± 0.021</td>
<td>1.008 ± 0.031</td>
<td>74</td>
<td>79</td>
</tr>
<tr>
<td>5</td>
<td>151.8 ± 3.8</td>
<td>152.4 ± 3.9</td>
<td>156.9 ± 4.3</td>
<td>1.004 ± 0.020</td>
<td>1.030 ± 0.038</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Mean</td>
<td>153.2 ± 2.3</td>
<td>152.6 ± 2.8</td>
<td>155.7 ± 1.9</td>
<td>0.996 ± 0.020</td>
<td>1.021 ± 0.030</td>
<td>83 ± 7</td>
<td>80 ± 7</td>
</tr>
<tr>
<td>Expected value</td>
<td>151</td>
<td>151</td>
<td>151</td>
<td>1</td>
<td>1</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

The error quoted for samples 1 to 5 are counting error the calculation for which is shown in appendix 1. The mean calculated error is shown with ± standard deviation.
Table 4.02: Results of the coral (RKMS) analyses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[U] (ppm, ww)</th>
<th>$^{234}$U/$^{238}$U</th>
<th>$^{230}$Th/$^{234}$U</th>
<th>U recovery (%)</th>
<th>Th recovery (%)</th>
<th>Age/ka</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.40 ± 0.08</td>
<td>1.072 ± 0.026</td>
<td>0.719 ± 0.026</td>
<td>83</td>
<td>80</td>
<td>134</td>
</tr>
<tr>
<td>2</td>
<td>3.30 ± 0.09</td>
<td>1.078 ± 0.027</td>
<td>0.720 ± 0.025</td>
<td>72</td>
<td>71</td>
<td>135</td>
</tr>
<tr>
<td>3</td>
<td>3.33 ± 0.07</td>
<td>1.075 ± 0.020</td>
<td>0.724 ± 0.026</td>
<td>70</td>
<td>61</td>
<td>136</td>
</tr>
<tr>
<td>4</td>
<td>3.16 ± 0.07</td>
<td>1.136 ± 0.023</td>
<td>0.705 ± 0.025</td>
<td>61</td>
<td>68</td>
<td>128</td>
</tr>
<tr>
<td>5</td>
<td>3.23 ± 0.07</td>
<td>1.102 ± 0.026</td>
<td>0.708 ± 0.021</td>
<td>90</td>
<td>80</td>
<td>130</td>
</tr>
<tr>
<td>Mean</td>
<td>3.28 ± 0.09</td>
<td>1.093 ± 0.03</td>
<td>0.715 ± 0.008</td>
<td>75 ± 11</td>
<td>72 ± 8</td>
<td>132.6</td>
</tr>
<tr>
<td>Certified value</td>
<td>3.25 ± 0.105</td>
<td>1.098 ± 0.016</td>
<td>0.709 ± 0.025</td>
<td></td>
<td></td>
<td>131</td>
</tr>
</tbody>
</table>
(4:2:2:3) Mirhib well water sample.

Table 4.03 shows the results of measurements on the water sample. The values of (74 ± 7) and (59 ± 1) ppb agree with the uranium concentration of 60 ppb obtained from previous analysis.

<table>
<thead>
<tr>
<th>U, Th separation method</th>
<th>U (ppb)</th>
<th>$^{234}$U/$^{238}$U</th>
<th>Chemical yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>74 ± 7</td>
<td>1.143 ± 0.01</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>59 ± 1</td>
<td>1.155 ± 0.02</td>
<td>78</td>
</tr>
</tbody>
</table>

(4:2:2:4) Malham Tarn samples.

Table 4.04 shows the results from the analysis of the Malham Tarn samples. The results show the Malham tarn water sample has a $^{234}$U/$^{238}$U ratio of (1.068±0.224). The Gordale beck water sample has a $^{234}$U/$^{238}$U ratio of (1.025±0.092). The $^{234}$U/$^{238}$U activity ratios for the two water samples are approximately 1 which shows that the $^{234}$U/$^{238}$U are in equilibrium.

The speleothem sample has a $^{234}$U/$^{238}$U ratio of 1.178±0.022 and a $^{230}$Th/$^{234}$U ratio of 0.044±0.002. These two ratios were used to calculate the age of the speleothem using the dating equation in section (1:4:3:2). The speleothem has a calculated age of 4883 years and an age range of 4647-5110 years. This value agrees with the expected age of the speleothem which was based on previous research on the Malham tarn area [188].

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[^{238}\text{U}]$ mBq/g</th>
<th>$^{234}$U/$^{238}$U</th>
<th>$^{230}$Th/$^{234}$U</th>
<th>Age (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malham Tarn water</td>
<td>0.006 ± 0.001</td>
<td>1.068 ± 0.224</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Gordale Beck water</td>
<td>0.004 ± 0.001</td>
<td>1.025 ± 0.092</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Speleothem</td>
<td>165.9 ± 3.992</td>
<td>1.178 ± 0.022</td>
<td>0.044 ± 0.002</td>
<td>4883</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(4647-5110)</td>
</tr>
</tbody>
</table>
**Table 4.05: Table 4.05 shows the results from the analysis of the Pinarbasi basin sediment samples. The estimated ages of the samples were obtained from previous analysis of samples from varying depths using U/Th, ^14^C and stable isotope techniques [189]. The analysis of the P10 sample resulted in a calculated age of 30554 years and an age range of (26172-35123) years. This age agrees with the estimated age of the sample of 36000 years. The analysis of the P56 sample resulted in a calculated age of 61539 years and an age range of (53940-70566) years. This age agrees with the estimated age of the sample of 53000 years. The analysis of the Pn94C sample resulted in a calculated age of 50600 years and an age range of (48071-53232) years. This age agrees with the estimated age of the sample of 43000 years. The three analyses of the Bpn94c sample resulted in a calculated ages of 45362, 43308 and 43999 years and age ranges of (41795-49191), (39535-47304) and (41808-46162) years. These values agree with the estimated age of the sample of 53000 years. The three Bpn94c samples give repeatable ages with an average of 44223 ± 1045 years. **

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (cm)</th>
<th>AGE (years)</th>
<th>EST AGE (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P10</td>
<td>178-179</td>
<td>30554</td>
<td>36000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(26172-35123)</td>
<td></td>
</tr>
<tr>
<td>P56</td>
<td>967-968</td>
<td>61539</td>
<td>53000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(53940-70556)</td>
<td></td>
</tr>
<tr>
<td>Pn94c</td>
<td>478-480</td>
<td>50600</td>
<td>43000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(48071-53232)</td>
<td></td>
</tr>
<tr>
<td>Bpn94c</td>
<td>967-968</td>
<td>45362</td>
<td>53000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(41795-49191)</td>
<td></td>
</tr>
<tr>
<td>Bpn94c</td>
<td>967-968</td>
<td>43308</td>
<td>53000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(39535-47304)</td>
<td></td>
</tr>
<tr>
<td>BPn94c</td>
<td>967-968</td>
<td>43999</td>
<td>53000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(41808-46162)</td>
<td></td>
</tr>
</tbody>
</table>

In conclusion the results from analyses of the uraninite, coral, Mirhib well water, Malham Tarn and Pinarbasi basin samples show that the uranium, thorium separation method separates the uranium from thorium and produces accurate and repeatable results. The analysis of the range of samples shows that the separation
method can cope with different sample matrices and that the method can be used for the analysis of a range of environmental samples.
(4:3) URANIUM, THORIUM, AMERICIUM AND PLUTONIUM SEPARATION METHOD.

The uranium, thorium, americium and plutonium separation method developed in section (3:4) of chapter 3 was evaluated using reference materials and environmental samples. The purpose of using the uraninite ore, the granite and the sediment reference materials, the Mirhib well water sample, and the iron rich calcium carbonate samples was to establish that the separation method was suitable for the analysis of uranium and thorium in a wide range of different sample matrices.

(4:3:1) Experimental.

(4:3:1:1) Solution of uraninite ore.

The uraninite ore reference material has been described previously in section (4:2:1:1). The following experiment was carried out to evaluate the separation method. The analysis was repeated three times to determine whether reproducible results could be obtained.

Experimental.

The uraninite ore sample was prepared by diluting 0.5ml of the uraninite solution to 100ml using 0.1 M nitric acid. Then 0.5g of the $^{236}$U and $^{229}$Th internal standards and 1ml of the iron (III) carrier solution were added to the solution which was then left to equilibrate overnight. The uranium and thorium were coprecipitated from solution with iron (III) hydroxide by the addition of ammonia solution. The sample was then warmed to coagulate the precipitate, which was then isolated by centrifuging. The uranium, thorium, americium and plutonium separation method developed in chapter 3 of this thesis was then followed. The precipitate was dissolved in 5ml of 6M nitric acid and the resulting solution diluted to 10ml with deionized water. To the sample solution 2ml of 0.6M sulphamic acid and 0.2g of ascorbic acid were added, the solution was swirled to mix and left to stand for 2 minutes.
A UTEVA column was conditioned with 5ml of 3M nitric acid. The sample solution was loaded onto the column and allowed to drain through. Two, 5ml aliquots of 3M nitric acid used to rinse the centrifuge tube was passed through the column. If americium or plutonium were present they would be in the sample load and 3M nitric acid wash fractions. The UTEVA column was then converted to the chloride form by passing through 5ml of 9M hydrochloric acid. Thorium was then eluted from the column with 15ml of 5M hydrochloric acid and the uranium was eluted from the column with 15ml of 0.02M hydrochloric acid.

The uranium and thorium fractions were prepared for counting by alpha spectrometry by plating onto stainless steel discs using the method described in chapter 2 section (2:2:1:1).

(4:3:1:2) Granite reference material (SARM-1).

The following experiment was carried out to evaluate how the uranium, thorium, americium and plutonium separation method would cope with separating the uranium and thorium from a difficult sample matrix such as granite. The analysis was repeated five times to ensure that reproducible results were obtained.

Experimental.

To approximately 0.5g of granite 0.6 g of $^{236}$U and $^{229}$Th internal standards and 1ml of the iron (III) carrier solution were added. The granite was ashed at 450°C and digested in 20ml of hydrofluoric acid for 48 hours in a teflon dish. A 5ml aliquot of nitric acid and 5ml of perchloric acid were added and the resulting solution was refluxed at 150°C for 3 hours. The solution was evaporated to dryness and the residue was treated twice with 10ml of concentrated nitric acid and evaporated to dryness. The final residue was dissolved in 20ml of 8M hydrochloric acid and the resulting solution diluted to 100ml with deionized water.

The uranium and thorium were co-precipitated from solution, separated and prepared for alpha spectrometry using the method described in section (4:2:2:1).
(4:3:1:3) Sediment reference material (SL-1).

The following experiment was carried out to evaluate the uranium, thorium, americium and plutonium separation methods capability of dealing with difficult sample matrix such as sediment.

Experimental.

To approximately 1g of sediment 0.6 g of \(^{236}\text{U}\) and \(^{229}\text{Th}\) internal standards were added. The sediment was ashed at 450°C and digested in 20ml of hydrofluoric acid for 48 hours in a teflon dish. A 5ml aliquot of nitric acid and 5ml of perchloric acid were added and the resulting solution was refluxed at 150°C for 3 hours. The solution was evaporated to dryness and the residue was treated twice with 10ml of concentrated nitric acid and evaporated to dryness. The final residue was dissolved in 20ml of 8 M hydrochloric acid and the resulting solution diluted to 100ml with deionized water.

The uranium and thorium were co-precipitated from solution, separated and prepared for alpha spectrometry using the method described in section (4:2:2:1).

(4:3:1:4) Mirhib well water sample.

The Mirhib water sample has been described previously in section (4:2:1:3). The following experiment was carried out to evaluate the uranium, thorium, americium and plutonium separation method. The analysis was repeated twice to determine whether that reproducible results could be obtained.

Experimental.

A 500ml aliquot of the Mirhib well water sample was placed into a litre glass beaker. Suitable levels of \(^{236}\text{U}\) and \(^{229}\text{Th}\) solutions and 1ml of the iron (III) carrier solution were added and the solution left to equilibrate overnight.

The uranium and thorium were co-precipitated from solution, separated and prepared for alpha spectrometry using the method described in section (4:2:2:1).
Two iron rich calcium carbonate samples (A and B) were obtained from AEA Technology plc where they had been analysed for uranium and thorium after separation by anion exchange. The samples were analysed to evaluate how the uranium, thorium, americium and plutonium separation method coped with samples containing a large amount of iron. As the uranium, thorium separation method was unable to cope with the amount of iron present, which blocked the UTEVA columns. The samples (A and B) were analysed twice to determine whether reproducible results could be obtained.

Experimental.

Approximately 10g of the samples A and B were added to a 250ml glass beaker and 100ml of deionized water added. The calcium carbonate was then slowly dissolved by the gradual addition of concentrated nitric acid, such that the pH was maintained at pH 1. The sample was centrifuged to remove any acid insoluble residue. Suitable levels of $^{236}$U and $^{229}$Th (0.5ml) internal standards were added and the samples left to equilibrate overnight. The samples were boiled prior to precipitation of iron(III) hydroxide to ensure removal of dissolved carbonate. Sample A and B were analysed twice.

The uranium and thorium were co-precipitated from solution, separated and prepared for alpha spectrometry using the method described in section (4:2:2:1).
(4:3:2) Results and discussion.

(4:3:2:1) Solution of uraninite ore.

The results in table 4.06 show that the uranium, thorium, americium and plutonium separation method separates the uranium and thorium fractions and allows quantitative recovery of the uranium and thorium.

Table 4.06: Results for uraninite ore analyses.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>%U recovery</th>
<th>%Th recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>108 ± 3</td>
<td>104 ± 4</td>
</tr>
<tr>
<td>2</td>
<td>101 ± 3</td>
<td>103 ± 4</td>
</tr>
<tr>
<td>3</td>
<td>113 ± 4</td>
<td>104 ± 3</td>
</tr>
</tbody>
</table>

(4:3:2:2) Granite reference material.

Table 4.07 shows the results from the analysis of the granite reference material. The uranium concentration is 15 ppm (w/w) which compares well with the mean UTEVA measured value of 17.5 ± 0.6 ppm (w/w). The certified thorium concentration of 51 ± 3 ppm (w/w) also compares well with the measured mean UTEVA value of 47 ± 4 ppm (w/w).

(4:3:2:3) Sediment reference material.

Table 4.08 shows the results from the analysis of the sediment reference material. The uranium concentration of (3.89 ± 0.15) ppm (w/w) agrees with the target value of (4.02 ± 0.32) ppm (w/w). The thorium concentration of (12.81 ± 0.44) ppm (w/w) agrees with the target value of (14 ± 1) ppm (w/w).

Table 4.08: Results for sediment reference material.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[U] ppm</th>
<th>[Th] ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SL-I</td>
<td>3.89 ± 0.15</td>
<td>12.81 ± 0.44</td>
</tr>
<tr>
<td>Target value</td>
<td>4.02 ± 0.32</td>
<td>14 ± 1</td>
</tr>
</tbody>
</table>
Table 4.07: Results of the granite (SARM-1) analyses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[U] (ppm; ww)</th>
<th>[Th] (ppm; ww)</th>
<th>$^{234}\text{U}/^{238}\text{U}$</th>
<th>$^{230}\text{Th}/^{234}\text{U}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.706 ± 0.558</td>
<td>51.467 ± 2.076</td>
<td>1.144 ± 0.035</td>
<td>0.903 ± 0.047</td>
</tr>
<tr>
<td>2</td>
<td>17.821 ± 0.401</td>
<td>48.900 ± 1.381</td>
<td>1.044 ± 0.021</td>
<td>0.913 ± 0.033</td>
</tr>
<tr>
<td>3</td>
<td>17.963 ± 0.565</td>
<td>44.820 ± 2.082</td>
<td>1.059 ± 0.031</td>
<td>0.720 ± 0.041</td>
</tr>
<tr>
<td>4</td>
<td>17.065 ± 0.539</td>
<td>40.694 ± 1.434</td>
<td>1.053 ± 0.031</td>
<td>0.809 ± 0.038</td>
</tr>
<tr>
<td>5</td>
<td>18.164 ± 0.661</td>
<td>49.612 ± 1.170</td>
<td>1.108 ± 0.037</td>
<td>0.837 ± 0.036</td>
</tr>
<tr>
<td>Mean</td>
<td>17.544 ± 0.626</td>
<td>47.099 ± 4.326</td>
<td>1.082 ± 0.043</td>
<td>0.836 ± 0.078</td>
</tr>
<tr>
<td>Certified value</td>
<td>15</td>
<td>$^{+4}_{-3}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(4:3:2:4) Mirhib well water sample.

Table 4.09 shows the results from the analysis of the Mirhib well water sample. The uranium concentration values of (55 ± 2) and (61 ± 3) ppb agree with the expected uranium concentration of 60 ppb. The values are also in agreement with the values of (74 ± 7) ppb and (59 ± 1) ppb obtained using the uranium, thorium separation method. The water samples analysed by both the separation methods had negligible levels of thorium present.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>U (ppb)</th>
<th>$^{234}$U/$^{238}$U</th>
<th>Chemical yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>55 ± 2</td>
<td>1.285 ± 0.04</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>61 ± 3</td>
<td>1.208 ± 0.05</td>
<td>82</td>
</tr>
</tbody>
</table>

(4:3:2:5) Iron rich calcium carbonate samples (A and B).

Table 4.10 shows the results from the analysis of samples A and B. The two analyses of sample A gave uranium concentrations of (2.7±0.01) and (2.3±0.11) ppm, $^{234}$U/$^{238}$U activity ratios of (2.53±0.04) and (2.28±0.07), $^{230}$Th/$^{234}$U activities of (0.318±0.018) and (0.415±0.022). The calculated ages of sample A from the two analyses are 39974 and 55093 years. The chemical recovery of uranium and thorium for sample A were 83% and 75% respectively.

The two analyses of sample B gave uranium concentrations of (2.7±0.007) and (2.4±0.007) ppm, $^{234}$U/$^{238}$U activity ratio of (2.762±0.035) and (2.684±0.041), $^{230}$Th/$^{234}$U activity ratio of (0.018±0.001) and (0.012±0.001). The calculated ages of sample B from the two analyses are 1970 and 1310 years. The chemical recovery of uranium and thorium for sample B were 94% and 67% respectively.

The differences in the results obtained for two analyses of samples A and B could be due to detrital contamination which is indicated from the $^{230}$Th/$^{232}$Th ratios. The $^{230}$Th/$^{232}$Th ratios for sample A and sample B of (3486) and (76) respectively were greater than 20 so detrital correction of the samples was required. The detrital contaminants in the samples are responsible for blocking the columns. The values for the two samples of samples A and B are in agreement with values obtained previously using anion exchange as the separation method [190].
Table 4.10: Results for iron rich calcium carbonate samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>[U] ppm</th>
<th>[Th] ppm</th>
<th>$^{235}U/^{238}U$</th>
<th>$^{230}Th/^{234}U$</th>
<th>Age (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>2.7 ± 0.09</td>
<td>0.031± 0.011</td>
<td>2.534±0.043</td>
<td>0.318±0.018</td>
<td>39974 (37349-42571)</td>
</tr>
<tr>
<td>2A</td>
<td>2.3 ± 0.11</td>
<td></td>
<td>2.280±0.065</td>
<td>0.415±0.022</td>
<td>55093 (51568-58841)</td>
</tr>
<tr>
<td>1B</td>
<td>2.7 ± 0.07</td>
<td>0.091±0.009</td>
<td>2.762±0.035</td>
<td>0.018±0.001</td>
<td>1970 (1856-2080)</td>
</tr>
<tr>
<td>2B</td>
<td>2.4 ± 0.07</td>
<td></td>
<td>2.684±0.041</td>
<td>0.012±0.001</td>
<td>1310 (1200-1417)</td>
</tr>
</tbody>
</table>
CONCLUSIONS.

The results from analyses of the uraninite, coral, Mirhib well water, Malham Tarn and Pinabasi basin samples show that the uranium, thorium separation method separates the uranium and thorium producing accurate and repeatable results. The analysis of the range of samples shows that the separation method can cope with different sample matrices and that the method can be used for the analysis of a range of environmental samples.

The results for the uraninite ore, granite and sediment reference materials show that the uranium, thorium, americium and plutonium separation method was suitable for analysis of difficult sample matrix samples.

The results for the iron rich calcium carbonate samples indicate that the U, Th separation method had problems coping with the iron rich calcium carbonate samples A and B which blocked the UTEVA columns. The U, Th, Am and Pu separation method enabled analysis of the two iron rich calcium carbonate samples.

The recoveries for the different chemical matrices show that the recovery of uranium and thorium is dependent on the type of sample matrix. The more complicated matrices e.g. granite and sediment required more complex sample pre-treatment steps. The recovery for uranium for different sample types did not show significant reduction in the uranium recovery but the thorium recovery was reduced from 75% recovery with simple matrix types e.g. uraninite solution and Mirhib water to approximately 50% with granite.

Table 4.11: Recovery for different sample matrices.

<table>
<thead>
<tr>
<th>Sample</th>
<th>U recovery (%)</th>
<th>Th recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uraninite</td>
<td>83</td>
<td>75</td>
</tr>
<tr>
<td>Coral</td>
<td>75</td>
<td>72</td>
</tr>
<tr>
<td>Mirhib water</td>
<td>75</td>
<td>50</td>
</tr>
<tr>
<td>MT speleothem</td>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>Granite</td>
<td>89</td>
<td>47</td>
</tr>
<tr>
<td>Sediment</td>
<td>78</td>
<td>46</td>
</tr>
<tr>
<td>PB sediment</td>
<td>80</td>
<td>60</td>
</tr>
</tbody>
</table>
CHAPTER 5

MEASUREMENT BY PLASMA TRACE 2 INSTRUMENT.
INTRODUCTION TO MASS SPECTROMETRY.

In contrast to alpha spectrometry which uses the interaction of nuclear radiation with matter for alpha detection, the mass spectrometry (MS) method measures the isotopic abundance of a given element directly. In the last two decades mass spectrometry has been enhanced by the incorporation of modern computers, precise and rapidly switching magnetic control system electronics, refinement of ion optics to achieve high transmission and the improvement of highly shielded detectors to detect small ion signals. Therefore, $^{234}$U, and $^{230}$Th, which were traditionally measured by alpha spectrometry, can now be measured by mass spectrometry.

This introduction discusses the Plasma Trace 2 instrument which is described in section (5:1:1) and the factors which affect analysis. The introduction concludes with a literature review of research into uranium and thorium measurement by thermal ionisation mass spectrometry (TIMS), quadrupole inductively coupled plasma mass spectrometry and sector field inductively coupled plasma mass spectrometry.

(5:1:1) Plasma Trace 2 instrument.

The Plasma Trace 2 instrument shown in figure 5.01 is manufactured by Micromass UK Ltd. The instrument uses an inductively coupled plasma torch as an ionisation source. The aqueous samples are introduced to the ionisation source where the analytes in the sample are converted into ions. An ultra-sonic nebulizer (USN) is used which produces a rich spray of small droplets ($<5 \mu m$). The amount of sample reaching the plasma from the nebulizer is increased from 1% (with the usual concentric nebulizers) to about 10% with a USN. The nebulizer used for this work was an ultra-sonic nebulizer (USN-6000 Cetac Ltd).

In the VG plasma trace 2 instrument the sampling interface, the sampler and skimmer, are isolated electrically from the vacuum chamber, to prevent spurious discharges, and biased at high positive potential. This bias provides the necessary
ion accelerating voltage, typically +4kV to +8kV, for formation of the beam for the subsequent analysers. The ions from the ICP pass through the interface despite the high positive voltage of the latter. This indicates that the plasma potential also follows the bias voltage applied to the interface.

After the interface, lenses are used to change the shape of the beam from circular in cross-section to a slit-like cross section that can be imaged on the slit system for efficient ion transmission. The beam then passes through an electrostatic energy analyser that selects only ions within a band of kinetic energies for transmission through the exit slit. These energy resolved ions are then m/z analysed in a magnetic sector. The electrostatic and magnetic analyser provide direction and velocity focusing. Each stage; sampler, skimmer, and ion lens, electrostatic analyser, magnetic analyser and detector, is separated by relatively small slits or apertures and thus has its own pump.

Each mass of interest is detected sequentially using an electron multiplier detector.

The device can also operate in low resolution mode, i.e. with the slits opened wide, to yield flat topped peaks which may prove advantageous for isotope ratio measurements.

In ICP-MS the relatively high background is mainly due to photons from the plasma reaching the photon sensitive detector by way of multiple reflections inside the instrument. In the double-focusing instruments the continuum background is very low, approximately less than 1 count per second. Because of the longer, more complicated ion flight path and the use of narrow slits and lenses, fewer reach the detectors. As the beam is focused efficiently, the ion count rates are comparable to or higher than, those obtained with quadrupoles so better detection limits are obtained with the double focusing instruments (ppq level for actinides).

The instrument's disadvantages are its expense and slower scan speed.
Figure 5.01: Diagram of Plasma Trace 2 instrument.
(5:1:2) Factors that affect analysis.

(5:1:2:1) Resolving power.

The most important parameter of a mass analyser is its resolving power. Mass peaks of ions have no natural line width so that the breadth of a peak is representative of the mass analyser performance. Recorded ion peaks are usually gaussian in shape. Two peaks of equal height, $h$, separated by a mass difference $\Delta M$, are said to be resolved when the height, $h$, of the valley between them is 10% or less of the peak height. For this condition, $M/\Delta M$ equals the peak width at a height that is 5% of the individual peak height. The resolving power is then given by the value $M/\Delta M$, where $M$ is the mass of the lighter peak. This definition of resolving power is called "10% valley resolution". Occasionally a definition of resolving power based on $\Delta h/h = 0.5$ is used.

The mass spectrometry applications govern the required resolving power. The need for high resolution arises when it is necessary to determine accurate masses of molecular or fragment ions of moderate to great complexity. From an accurate mass of the molecular ion the molecular formula of the compound can often be uniquely determined. For uranium and thorium analyses high resolution is not required and the Plasma Trace 2 instrument is run in low resolution mode ($M/\Delta M = 400$).

(5:1:2:2) Resolution Versus Transmission.

The Plasma Trace 2 instrument has resolving powers of 400-10000. For uranium and thorium analysis a resolving power of (400) and transmission of 100% are used as they yield the best detection limits for the instrument. At the low resolution (RP 400) the flat topped peaks observed are ideal for high stability and low level measurements (ppq level for the actinides). The relationship between resolution and transmission is shown in figure 5.02.
Figure 5.02: Transmission versus resolution.

(5:1:2:3) Sensitivity.

Sensitivity refers to the signal size for a particular quantity of sample. The sensitivity depends on the ionisation efficiency of the source, the transmission efficiency of the instrument and the counting efficiency of the detector. Therefore the detectibility depends on the sensitivity and the basic noise level of the detector.

In the presence of a large neighbouring peak, detectibility will also depend on the abundance sensitivity; that is the ratio of the ion current of the tail at the mass of interest to the ion current of the large neighbouring peak. The signal from the tail of a large neighbouring peak may obscure the detectibility of a nearby minor peak. This is a potential problem with $^{230}$Th which in many natural materials may be present in abundancies $10^{-6}$-10$^{-5}$ as high as $^{232}$Th. Therefore, the nature of these low-level peak tails should be understood before efforts can be made to improve the situation.

The half-lives of the radioisotopes of interest are shown in table 5.01. A comparison of the detection limits for a series of radionuclides measured by ICP-MS and radiochemical techniques demonstrated that differences in sensitivity between ICP-MS and the radiochemical techniques was related to the half-life of
The analytes [191]. The ICP-MS measurements showed that the sensitivity was increased as the half-life of the radionuclide was increased. This relationship was modelled by Smith et al [192] who calculated that the half-life cut off between ICP-MS and alpha spectrometry was now below 1000 years.

Different dwell times were used for the $^{234}$U and $^{238}$U isotopes. This was in order to reduce the differences in sensitivity observed for the $^{234}$U ($2.457 \times 10^5$ years) and $^{238}$U ($4.468 \times 10^9$ years). For example, dwell times of 250 ms for $^{234}$U and 1 ms for $^{238}$U were used. The resultant counts were corrected for the dwell time on each isotope.

**Table 5.01: Half-lives of radioisotopes.** The half-life data was taken from the radiochemical manual [186].

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Half-life ($t_{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$U</td>
<td>$4.468 \times 10^9$ years</td>
</tr>
<tr>
<td>$^{234}$U</td>
<td>$2.457 \times 10^5$ years</td>
</tr>
<tr>
<td>$^{236}$U</td>
<td>$2.342 \times 10^7$ years</td>
</tr>
<tr>
<td>$^{230}$Th</td>
<td>$7.540 \times 10^4$ years</td>
</tr>
<tr>
<td>$^{227}$Th</td>
<td>$7.340 \times 10^3$ years</td>
</tr>
<tr>
<td>$^{232}$Th</td>
<td>$1.405 \times 10^6$ years</td>
</tr>
</tbody>
</table>

**(5:1:2:4) Mass bias.**

In mass spectrometry analysis, the observed or measured isotope ratio may deviate from the 'true' value as a function of a difference in mass between the two isotopes. This effect is termed 'mass bias' and may be positive or negative. Corrections can be made for mass bias by measuring a standard of known isotopic composition. The mass bias can be calculated using equation 5.01.

$$ (A/B)_m = (A/B)_t (1 + an) $$  

**Equation 5.01**

Where:

- $a$ is the bias per mass unit.
- $n$ is the mass difference between isotopes A and B.

$(A/B)_m$ and $(A/B)_t$ are the measured isotope ratio and the true isotope ratio respectively.
(5:1:2:5) Dead time.

At high count rates the detector can begin to count fewer events than actually occur. The 'dead time' is the time during which the detector and its associated counting electronics are unable to resolve successive pulses. The problem causes a non linear response by the instrument above a certain count rate typically \((1 \times 10^6 \text{ counts/s})\). The dead time can be calculated using equation 5.02.

\[
C_{\text{true}} = \frac{C_{\text{obs}}}{(1 - C_{\text{obs}} \tau)} \quad \text{Equation 5.02}
\]

Where:

\(\tau\) is the dead time.

\(C_{\text{true}}\) and \(C_{\text{obs}}\) are the true and observed count rates respectively.

(5:1:3) Previous research.


Thermal Ionisation Mass Spectrometry (TIMS) uses mono element excitation with atoms or molecules produced at the hot surface of a metal filament. The uranium and thorium are analysed separately due to their different ionisation efficiencies. Previous research in this area is described in references [193-199].

McDermott et al [193] used thermal ionisation with a single focusing mass spectrometer identified the following problems when measuring \(^{230}\text{Th}\) and \(^{232}\text{Th}\). The first problem occurred when measuring low thorium isotope ratios and was caused by the large contrast in beam intensity between the \(^{230}\text{Th}\) and \(^{232}\text{Th}\) peaks. The \(^{230}\text{Th}\) peak had to be corrected for overlap from the larger \(^{232}\text{Th}\) peak. The precision on the \(^{230}\text{Th}/^{232}\text{Th}\) ratio was better than \(\pm 1.5\%\) (2\(\sigma\)) which was a 3 to 5 fold improvement in the precision when compared with alpha counting. The precision of the technique was found to be limited by the low abundance of \(^{230}\text{Th}\) with background errors contributing 15-20% of the \(^{230}\text{Th}\) peak.

These findings agreed with work reported by Edwards et al [194] who also found that the TIMS technique's limiting factor was the low ionisation efficiency of
thorium of 0.05-0.2% compared with 0.2-1% for uranium. The ionisation efficiency was found to decrease as increasing amounts of thorium were loaded onto the filament [194]. As the amount of $^{232}$Th was increased the ionisation efficiency of $^{230}$Th was found to decrease causing large uncertainties.

Taylor et al [195] determined $^{238}$U/$^{235}$U and uranium concentration in soil samples. Fractionation of the uranium isotopes was observed as the lighter isotope ($^{235}$U) ionises more readily than the heavier isotope ($^{238}$U), so at the start of ionisation the $^{238}$U/$^{235}$U isotope ratio is likely to be lower than in successive measurements.

Cohen et al [196] used TIMS to determine high precision uranium, thorium and radium isotope ratio measurements.

Stirling et al [197] determined $^{230}$Th/$^{238}$U and $^{234}$U/$^{238}$U ratios for dating of corals from Western Australia.

Chen et al determined $^{238}$U, $^{234}$U and $^{232}$Th in seawater [198] and $^{238}$U and $^{235}$U in meteoritic, lunar and terrestrial samples [199].

(5:1:3:2) Quadrupole ICP-MS.

The quadrupole ICP-MS has applications in environmental radiochemistry [200] and geological analysis [201]. In environmental analysis the technique has been used to analyse waters [202, 203], sediments [204, 205], soil [206, 207], coral [208] and, plant tissue [209]. In geological analysis the technique has been used to analyse zircon reference materials [210], basalts [211], ancient ceramic samples [212], chondritic meteorites [213] and, geological reference materials [214, 215].

The technique has been evaluated by comparing it with radiochemical techniques such as neutron activation analysis and alpha spectrometry [216, 192, 212].

The technique also has applications for the analysis of uranium and thorium in nuclear materials [217, 218], in the analysis of biological samples such as urine.
and faeces [180] and for the determination of uranium and thorium in ferroelectric materials for the integrated circuits industry [220].

Most research in isotopic compositions has concentrated on the analysis of $^{238}\text{U}$ and $^{232}\text{Th}$ in the samples. The $^{234}\text{U}$ and $^{230}\text{Th}$ isotopes, which are also required for uranium series measurements have been analysed by Chiappini et al [221] using an ICP-MS with improvements in its interface pumping system and with a MISTRAL high efficiency desolvating nebulizer (Fison Instruments). The instrument had improved detection limits for $^{232}\text{Th}$ and $^{238}\text{U}$ of $1.6 \times 10^{-10}\text{Bq}$ and $5 \times 10^{-10}\text{Bq}$ compared with the detection limit of $1 \times 10^{-4}\text{Bq}$ obtained by alpha spectrometry.

Apart from this research relatively little use has been made of the quadrupole ICP-MS to obtain isotopic compositions because it is difficult to acquire high precision isotopic data because of the peak shapes generally encountered when using the quadrupole instruments. Most isotopic work has been conducted using magnetic sector thermal ionization mass spectrometry (TIMS) because of the superior precision of this technique. Recent research discussed in (section 5:4:3) has concentrated on using double focusing mass spectrometers for isotope measurements.

(5:1:3:3) Double focusing ICP-MS.

In a single focusing magnetic sector instrument there is a lack of uniformity of ion energies, since the accelerating potential experienced by an ion depends on where in the source it is formed. The resulting spread in ionic energies produces a spread in their radii of curvature in the magnetic field. The result is peak broadening and low to moderate resolution. Magnetic/electrostatic sector instruments use magnetic and electric fields to disperse ions according to their momentum and translational energy. A mass spectrum is obtained by scanning the magnetic field strength to bring ions with different $m/z$ ratios sequentially to focus at the detector.

The ICP as a possible ion source for high resolution mass spectrometry was initially investigated by Bradshaw [222] and Morita [223]. The research showed
that the ICP can successfully be coupled to a high-resolution mass spectrometer. The instrument allows the separation and resolution of polyatomic ions and analytes at the same nominal mass.

(5:1:3:3:1) Plasma Trace 2 and Element instruments.

Becker et al [224] compared the two commercially available double focusing ICP-MS instruments the Plasma Trace 2 (Micromass) and the Element (Finnigan, MAT). These instruments are double-focusing sector-field instruments with reverse Nier-Johnson geometry. The performance of the two instruments is similar with respect to high sensitivity, very low noise (<0.2 ions/s) and very low detection limits in the low pg/l range at low resolution for ideal aqueous solutions. The major difference between the two instruments is in the slit system. The Plasma Trace 2 has up to 5 resolution values which allows variable mass resolution by automatic changing of the resolution. The Element instrument has a fixed slit system at three predefined nominal mass resolutions of 300, 3000 and 7500.

Kerl et al [225] used the Element instrument with an ultrasonic nebulizer to analyse uranium metal and waste samples for their $^{235}\text{U}/^{238}\text{U}$ isotopic ratio. The precision of the analysis was 0.07% at 10µg/l and 0.23% at 100ng/l. The mass discrimination effect during the measurement and the dead time of the instrument were found to be 0.1% mass discrimination and 26ns respectively. The precision of determining the $^{235}\text{U}/^{238}\text{U}$ isotopic ratio in a real geological sample was found to be approximately 0.6%. Applications of the technique include ultratrace and isotopic measurement of uranium in radioactive waste solutions. The results obtained using the Element instrument were in agreement with results obtained by alpha spectrometry [225].

Riondato et al [226] determined uranium in human serum using the Element instrument at low resolution. Detection limits of 770 pg/l with a standard deviation of 140 pg/l were observed for uranium.
Prohaska et al [227] analysed the rare earth elements, $^{232}$Th and $^{238}$U in sediment, soil, plants and animal tissue reference materials using the Element instrument. The research found that $^{232}$Th had a memory effect on the instrument and required a 4 minute wash with 10% nitric acid to be removed.

Kim et al [228] compared the results of isotopic analysis of a plutonium isotopic standard solution by double-focusing sector field (Plasma Trace 2) and quadrupole ICP-MS. The accuracy and precision of the plutonium isotopic analysis by double-focusing ICP-MS with an ultrasonic nebulizer was about one order of magnitude greater than that obtained by quadrupole ICP-MS. The measurement of $^{99}$Tc, $^{226}$Ra, $^{232}$Th, $^{237}$Np, $^{238}$U, $^{239}$Pu and $^{240}$Pu in river water and standard solutions has been achieved by double-focusing sector field ICP-MS and USN with detection limits of between 0.002 and 0.02pg/ml. Crain et al [200] compared the Plasma Trace 2 detection limits for $^{238}$U and $^{232}$Th of 20 and 20pg/L [207] with the detection limits for quadrupole ICP-MS of 500 and 800pg/L.

Yamasaki et al [229, 230] used the Plasma Trace 2 instrument with an ultrasonic nebulizer for the analysis of the lanthanoids and actinoids in water samples. The detection limit for uranium and thorium were 0.7ppq and 1ppq respectively.

The advantages of the double focusing instrument are its low background counts and its applications for ultra trace determination of long-lived radionuclides and isotope ratio measurements.


The P54 is a high precision, double focusing instrument with extended geometry.

The major factor limiting the precision of isotopic ratios by ICP-MS is in the instability of the argon plasma. As simultaneous ion detection is important for precise isotope measurements a multi-collector ion detection system (the plasma 54) with 9 Faraday detectors has been developed for the determination of precise isotopic ratios.
The instrument's detection limits are comparable to TIMS so the instrument was not suitable for analysis of the low levels of uranium and thorium (ppq levels).

Walder and Freedman [231] described the use of the P54 instrument for the analysis of $^{235}\text{U}/^{238}\text{U}$ ratios in standard solutions with a precision of 0.014% at the 1mg/l level.

Taylor et al [232] analysed standard solutions for $^{233}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ isotopic ratios with a precision of 0.03% at the 1mg/l level. A set of synthetically prepared mixtures of the uranium isotopes were used to assess the instrument's linearity and mass bias.

Halliday et al [233] used the P54 for the isotopic analysis of $^{238}\text{U}/^{207}\text{Pb}$. The measured ratios of $^{238}\text{U}/^{207}\text{Pb}$ differed greatly from day to day, reflecting differences in the running conditions, in contrast to TIMS where the mass bias is large but generally stays approximately constant. The uncorrected data were commonly more precise than the mass bias corrected data because errors are greatly magnified if each measurement cycle is corrected individually. The effect of mass bias can be corrected by analysing a standard solution of known isotopic composition in a run of samples.

Applications of the P54 instrument suggested by Halliday et al [234] include measurement of the following isotopic ratios; Lu-Hf isotope, Hf-W, Rb/Sr, U/Pb, Re/Os, Lu/Hf, Pd isotope compositions and uranium isotopic analysis. Uranium and thorium isotopic measurements have been reported [234, 235].

In conclusion the P54 instrument has excellent ionization efficiency - greater than 50% - but the transmission is only ≤2%. Improvements in transmission, if possible, will lead to the P54 replacing TIMS for isotope measurements.
(5:1:4) Introduction to experimental work.

The aim of the research reported in this part of the thesis was to determine whether the Plasma Trace 2 instrument was suitable for the low-level measurement of uranium and thorium isotopes.

The instrument was evaluated using reagent and groundwater blanks, coral, speleothem and the uraninite ore solution. After the evaluation, the instrument was then used to analyse further speleothem and calcite samples.

Operation parameters.

The instrument was run in low resolution mode RP 400. The USN was used with a flow rate of 1ml/min. The data collection mode used was peak hopping. The mass spectrometer was used to collect data at a number of fixed mass positions for each isotope. The magnet rapidly stepped to a pre-defined mass and the electric field was then scanned about the mass window of interest.

The advantages of this mode of data acquisition are that the amount of time, 'dwell time', can be varied so the response from a smaller isotope can be collected for a longer period to improve the counting statistics. Another advantage is that time is not wasted collecting data for isotopes which are not of interest. The mode is advantageous where only a small number of isotopes are required (<20), the isotopes of interest are spread across the mass range and where isotope ratio measurements are made.

Table 5.02: Dwell times for uranium and thorium isotopes.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$^{238}$U</th>
<th>$^{234}$U</th>
<th>$^{236}$U</th>
<th>$^{236}$Th</th>
<th>$^{232}$Th</th>
<th>$^{229}$Th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dwell Time (ms)</td>
<td>1</td>
<td>250</td>
<td>1</td>
<td>500</td>
<td>10</td>
<td>100</td>
</tr>
</tbody>
</table>
(5:2) BLANKS.

(5:2:1) Introduction to blank experiments.

To determine the background levels of uranium and thorium that are present in the reagents and the sample preparation and separation stages of the analysis, the following experiments were carried out to investigate whether it was possible to attain the low limit of detection required for uranium series dating of speleothem samples. Previous research had found that the limit of detection for $^{238}\text{U}$ and $^{232}\text{Th}$ was limited by the high levels of uranium and thorium in the reagents [196, 197].

Areas of possible contamination during analysis include deionized water and therefore 18MΩ deionized water was used. The acid solutions used were doubly distilled nitric acid and Aristar hydrochloric acid. New glassware, washed in 50% nitric : 50% deionized water, was used were possible. Where this was not possible low uranium/thorium dedicated glassware was used. The anion exchange resin was washed with deionized water to remove any trace levels of uranium and thorium.

(5:2:2) Experimental.

Reagents.

Doubly distilled aristar nitric acid, deionized water, aristar BDH concentrated nitric acid S.G. 1.42 (70%), Aristar concentrated hydrochloric acid, ammonia concentrated S.G. 0.88 (35%), ferric chloride standard solution for AAS (1ml = 1.0mg iron) laboratory reagent. Biorad AG 1-X8 resin, 100-200 mesh chloride form, UTEVA 2ml columns. The radioactive tracers were $^{229}\text{Th}$ (40.8mBq/g) and $^{236}\text{U}$ (41.1mBq/g) in 7M nitric acid.

(5:2:2:1) Reagent blanks (RB).

The analysis was repeated in triplicate.
Method

To a 500ml glass beaker (100ml of 0.1M) of doubly distilled nitric acid were added. The samples were then spiked by the addition of 1ml of \(^{236}\text{U}\) and 1ml of \(^{229}\text{Th}\). Ferric chloride solution (10ml of 1mg/ml) was then added to each sample. The beakers were covered with watch glasses, placed on a hotplate to equilibrate for 2 hours and then allowed to cool. The ferric hydroxide was then precipitated using ammonia solution. The resulting precipitate was centrifuged and washed with 0.05M ammonia solution.

The uranium and thorium were separated by anion exchange. An anion exchange column was prepared using a (12mm I/D) glass tubing partly closed at the lower end to leave a 4mm hole. A plug of silica wool was gently pushed to the bottom of the column and the ion-exchange resin washed into the column with deionized water to make a 40mm long column. The resin was then pre-conditioned by washing twice with 20ml of 8M hydrochloric acid. The iron precipitate was then dissolved in 5ml of concentrated hydrochloric acid and 5ml of 8M hydrochloric acid added.

A glass beaker was placed under the column to collect the thorium fraction. The load solution was added to the column and allowed to drain. The centrifuge tube was then washed with 10ml of 8M hydrochloric acid which was then added to the column. A further 20ml of 8M hydrochloric acid was then added to wash the column. The iron carrier (0.2ml of 10mg/ml) was then added to the thorium fraction.

A second glass beaker was then placed under the column and the uranium and iron eluted using 50ml of 0.2M hydrochloric acid. The separate uranium and thorium fractions were reduced to a volume of approximately 10ml by boiling gently on a hotplate. The iron hydroxide was then precipitated by the addition of concentrated ammonia. The resulting precipitates were centrifuged and washed with 0.05M ammonia.
A second set of ion-exchange columns was then prepared. For uranium the previously used column was extended by the addition of sufficient ion-exchange resin to form a 100mm column. The column was then pre-conditioned by washing twice with 50ml of 7M nitric acid. The iron precipitate containing the uranium was dissolved using 5ml of concentrated nitric acid and 5ml of 7M nitric acid added. The resulting solution was washed onto the column with 10ml of 7M nitric acid. The column was then washed with 20ml of 7M nitric acid. Any traces of thorium were then eluted with 10ml of 8M hydrochloric acid. The uranium was then eluted using 50ml of 0.2M hydrochloric acid.

For the thorium a 4mm column (6mm ID glass tubing closed off at the end to 2mm diameter) was prepared and pre-conditioned with two, 10ml aliquots of 7M nitric acid. The iron precipitate containing the thorium was dissolved in 2ml of concentrated nitric acid and 3ml of 7M nitric acid added. The resulting solution was washed onto the column with 2ml of 7M nitric acid. The column was then washed with a further 20ml of 7M nitric acid. The thorium was then eluted from the column with 20ml of 2M hydrochloric acid.

(5:2:2:2) Groundwater blanks (GWB).

Method.

The first sample (GW1) was prepared by adding 300ml concentrated nitric acid (doubly distilled) to 300ml of 18MΩ deionized water. A second sample (GW2) was prepared by adding 300ml concentrated nitric acid (analytical grade reagent) to 300ml of 18MΩ deionized water. To each of the samples 1ml of $^{229}$Th and $^{236}$U, and 10ml of (1mg/ml) ferric chloride solution were added and the samples left to equilibrate for two days.

The samples were then put through the uranium and thorium separation method described in section (5:2:2:1) for the reagent blanks.

The reagent blank and groundwater blank samples were analysed by the Plasma Trace 2 instrument with the dwell times shown in table 5.02.
(5:2:3) Results and discussion for reagent blank and groundwater blank samples.

(5:2:3:1) Reagent and groundwater blanks.

The initial results for the $^{238}$U and $^{232}$Th isotopes in the reagent blank and groundwater blanks that have been analysed following sample preparation and separation methods are shown in table 5.03. These results show that the reagent blank and groundwater blanks contain approximately $10^{-4}$ and $10^{-5}$ Bq of $^{238}$U and $^{232}$Th respectively. (The results are quoted in activity units as the various possible sources of $^{238}$U and $^{232}$Th contamination render the measurement of specific activities unachievable). These values will be the limiting factors in the limit of detection for $^{238}$U and $^{232}$Th. Therefore, samples must be corrected for the $^{238}$U and $^{232}$Th content in the reagent blanks.

Table 5.03. $^{238}$U and $^{232}$Th activities in reagent and groundwater blanks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{238}$U (Bq)</th>
<th>$^{232}$Th (Bq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RB1</td>
<td>$3.09 \times 10^{-4}$</td>
<td>$4.37 \times 10^{-5}$</td>
</tr>
<tr>
<td>RB2</td>
<td>$3.57 \times 10^{-4}$</td>
<td>$4.31 \times 10^{-5}$</td>
</tr>
<tr>
<td>RB3</td>
<td>$5.83 \times 10^{-4}$</td>
<td>$3.57 \times 10^{-5}$</td>
</tr>
<tr>
<td>GWB1</td>
<td>$8.01 \times 10^{-4}$</td>
<td>$3.40 \times 10^{-5}$</td>
</tr>
<tr>
<td>GWB</td>
<td>$7.48 \times 10^{-4}$</td>
<td>$3.35 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

(5:2:3:2) Reagent blanks run with speleothem and calcite samples.

The uranium and thorium content of the reagent blanks run with the speleothem and calcite samples are shown in table 5.04. The five reagent blanks show similar activities of $^{234}$U with values ranging from $4.78-8.67 \times 10^{-5}$ Bq, $^{238}$U values ranging from $3.67-5.9 \times 10^{-5}$ Bq, $^{230}$Th values ranging from $1.02-2.00 \times 10^{-4}$ Bq and $^{232}$Th values ranging from $2.42-4.03 \times 10^{-5}$ Bq. The variation in values can be explained by the use of different reagents (although of the same analytical grade) and different glassware. This shows that the reagent blanks contain reproducible levels of uranium and thorium.
The results from the Plasma Trace 2 instrument were converted from counts to activity in Bq units using a specially designed excel spreadsheet.

The following information was put into the spreadsheet; the specific activity of $^{236}\text{U}$ and $^{229}\text{Th}$ spike solutions, the mass of $^{236}\text{U}$ and $^{229}\text{Th}$ spike solutions added to the samples, the $^{236}\text{U}$, $^{234}\text{U}$, $^{238}\text{U}$, $^{229}\text{Th}$, $^{230}\text{Th}$ and $^{232}\text{Th}$ counts, and the dwell times for the uranium and thorium isotopes.

The equations used to calculate the $^{238}\text{U}$ activity of reagent blank samples are shown in appendix 2.

**Table 5.04: Reagent blanks run with speleothem samples.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{234}\text{U}$ (Bq)</th>
<th>$^{238}\text{U}$ (Bq)</th>
<th>$^{230}\text{Th}$ (Bq)</th>
<th>$^{232}\text{Th}$ (Bq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$5.62\times10^{-5}$</td>
<td>$4.41\times10^{-5}$</td>
<td>$1.23\times10^{-4}$</td>
<td>$2.42\times10^{-5}$</td>
</tr>
<tr>
<td>2</td>
<td>$7.06\times10^{-5}$</td>
<td>$4.90\times10^{-5}$</td>
<td>$2.00\times10^{-4}$</td>
<td>$4.03\times10^{-5}$</td>
</tr>
<tr>
<td>3</td>
<td>$8.46\times10^{-5}$</td>
<td>$5.90\times10^{-5}$</td>
<td>$1.77\times10^{-4}$</td>
<td>$3.56\times10^{-5}$</td>
</tr>
<tr>
<td>4</td>
<td>$4.78\times10^{-5}$</td>
<td>$3.67\times10^{-5}$</td>
<td>$1.02\times10^{-4}$</td>
<td>$3.66\times10^{-5}$</td>
</tr>
<tr>
<td>5</td>
<td>$8.67\times10^{-5}$</td>
<td>$3.12\times10^{-5}$</td>
<td>$1.43\times10^{-4}$</td>
<td>$2.98\times10^{-5}$</td>
</tr>
<tr>
<td>Mean</td>
<td>$6.92\times10^{-5}$</td>
<td>$4.40\times10^{-5}$</td>
<td>$1.49\times10^{-4}$</td>
<td>$3.33\times10^{-5}$</td>
</tr>
<tr>
<td>SD</td>
<td>$1.71\times10^{-5}$</td>
<td>$1.08\times10^{-5}$</td>
<td>$3.97\times10^{-5}$</td>
<td>$6.33\times10^{-6}$</td>
</tr>
</tbody>
</table>

**5.2:3:3 Calculation of limit of detection.**

The limit of detection for the Plasma Trace 2 instrument was calculated using the activity of $^{234}\text{U}$, $^{238}\text{U}$, $^{230}\text{Th}$ and $^{232}\text{Th}$ found in the reagent blanks for the speleothem and calcite analyses. The LOD of an analyte may be described as the concentration which gives an instrumental signal significantly different from the 'blank' signal. An example of the calculation used is shown for $^{238}\text{U}$. The limit of detection was calculated using equation 5.03. The LOD for $^{234}\text{U}$, $^{238}\text{U}$, $^{230}\text{Th}$ and $^{232}\text{Th}$ are shown in table 5.05.

$$Y = 3SD + Y_B$$  
Equation 5.03

Where:

- $Y$ is the LOD of $^{238}\text{U}$
- $Y_B$ is the activity of $^{238}\text{U}$ in reagent blanks
SD is the standard deviation

\[ ^{238}\text{U LOD} = (3 \times 1.08 \times 10^{-5}) + 4.4 \times 10^{-5} = 7.642 \times 10^{-5} \text{ Bq} \]

Table 5.05: LOD for \(^{234}\text{U}, ^{238}\text{U}, ^{230}\text{Th}\) and \(^{232}\text{Th}\).

<table>
<thead>
<tr>
<th>Isotope</th>
<th>LOD (Bq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{234}\text{U})</td>
<td>(1.21 \times 10^{-4})</td>
</tr>
<tr>
<td>(^{238}\text{U})</td>
<td>(7.64 \times 10^{-5})</td>
</tr>
<tr>
<td>(^{230}\text{Th})</td>
<td>(2.68 \times 10^{-4})</td>
</tr>
<tr>
<td>(^{232}\text{Th})</td>
<td>(5.23 \times 10^{-5})</td>
</tr>
</tbody>
</table>

In conclusion the results for the analysis of the reagent blanks show that the limits of detection for the uranium and thorium isotopes are in the order of \(10^{-5}\) for the \(^{238}\text{U}\) and \(^{232}\text{Th}\) isotopes and \(10^{-4}\) for \(^{234}\text{U}\) and \(^{230}\text{Th}\) isotopes. The results show that samples analysed by the Plasma Trace 2 instrument after separation by anion exchange need to be blank corrected.
**(5:3) URANINITE ORE SOLUTION.**

**(5:3:1) Experimental.**

A standard solution containing uraninite ore solution, $^{229}$Th and $^{230}$U was prepared for analysis by the Plasma Trace 2 instrument. The standard was analysed three times by the Plasma Trace 2 instrument to ensure that accurate and reproducible uranium ($^{238}$U, $^{234}$U) and thorium ($^{230}$Th) activities were produced. The uraninite ore reference solution has been described previously in sections (4:2:1:1).

**Method.**

The uraninite standard solution was prepared using the reagents listed in table 5.06.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Activity</th>
<th>Weight (g)</th>
<th>Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$U</td>
<td>0.709mBq/g</td>
<td>4.7776g</td>
<td>4ml</td>
</tr>
<tr>
<td>$^{235}$U</td>
<td>0.167Bq/g</td>
<td>2.3872g</td>
<td>2ml</td>
</tr>
<tr>
<td>$^{239}$Th</td>
<td>0.191mBq/g</td>
<td>4.9141g</td>
<td>4ml</td>
</tr>
<tr>
<td>18MΩ deionized water</td>
<td></td>
<td>89.9254g</td>
<td></td>
</tr>
</tbody>
</table>

The resulting solution was then analysed by the Plasma Trace 2 instrument.

**(5:3:2) Results and discussion for the uraninite ore solution.**

The results for the Plasma Trace 2 instrument analysis of the spike solution are shown in table 5.07. The activity of the $^{238}$U, $^{234}$U, and $^{230}$Th in the spike solution is 0.709mBq/g. The value for the three analyses vary between the runs with the $^{238}$U values decreasing from run 1 to 3, the $^{234}$U values increasing from run 1 to 3, and the $^{230}$Th value increasing then decreasing from run 1 to 3. The results seem to indicate that a mass bias effect is seen for the $^{238}$U and $^{234}$U isotopes. The errors on the $^{238}$U, $^{234}$U and $^{230}$Th results vary from 0.1%, 1% and 6%, from 3.8%, 4.9%, and 8%, and from 0.5%, 4.8% and 8.6% respectively.
Table 5.07: Uraninite ore solution results.

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$U (mBq/g)</td>
<td>0.754±0.014</td>
<td>0.716±0.0137</td>
<td>0.708±0.0063</td>
</tr>
<tr>
<td>$^{234}$U (mBq/g)</td>
<td>0.736±0.022</td>
<td>0.744±0.061</td>
<td>0.766±0.036</td>
</tr>
<tr>
<td>$^{230}$Th (mBq/g)</td>
<td>0.713±0.059</td>
<td>0.770±0.042</td>
<td>0.743±0.107</td>
</tr>
<tr>
<td>$^{230}$Th/$^{234}$U</td>
<td>0.969±0.085</td>
<td>1.035±0.102</td>
<td>0.969±0.147</td>
</tr>
<tr>
<td>$^{234}$U/$^{238}$U</td>
<td>0.977±0.034</td>
<td>1.038±0.088</td>
<td>1.083±0.052</td>
</tr>
<tr>
<td>Natural U (ppm)</td>
<td>0.061±0.001</td>
<td>0.058±0.001</td>
<td>0.057±0.001</td>
</tr>
</tbody>
</table>

The natural uranium (ppm) values obtained for the three runs are reproducible with values from run 1 to 3 of 0.061, 0.058, and 0.057 ppm. The activity values (Bq) for the $^{238}$U was converted to concentration (ppm) values using the calculation in appendix 3.

In conclusion the results for the uraninite ore reference material indicate that the measured $^{234}$U/$^{238}$U and $^{230}$Th/$^{234}$U ratios suffered from mass bias effect which produced high $^{234}$U/$^{238}$U and low $^{230}$Th/$^{234}$U ratios. The effect of mass bias was studied in the uraninite/NBS and uraninite/coral experiments.
THE EFFECT OF $^{232}$Th ON $^{230}$Th.

Introduction to experiments to determine the effect of $^{232}$Th on $^{230}$Th.

In the first set of experiments the uraninite ore solution spiked with $^{236}$U and $^{229}$Th was measured by the Plasma Trace 2 instrument. The solution was then diluted and remeasured. This process was repeated so that a range of concentrations of the standard was measured. A concentration range of 0.0204, 0.0409, and 0.4079mBq was chosen in the linear portion of the calibration graph.

The 0.0204, 0.0409, and 0.4079mBq uraninite standard solutions were then spiked with 0, 1, 10, and 20 ppb of $^{232}$Th respectively. This experiment was undertaken to investigate the effect of increasing the $^{232}$Th concentration on the $^{230}$Th counts observed. Previous research using thermal ionization mass spectrometry (TIMS) [194] discussed the problem of the $^{232}$Th peak interfering with the $^{230}$Th peak. The effect was found to increase as the concentration of $^{232}$Th was increased.

Finally the effect of adding 1ppb and 10 ppb of $^{232}$Th to the 0, 0.0204, 0.0409, and 0.4079mBq uraninite solutions was also investigated.

Experimental.

A uraninite ore reference material spiked with $^{236}$U and $^{229}$Th spike solutions was prepared using the following method: A hundred fold dilution of the uraninite ore reference material was prepared by adding 1ml of uraninite standard (150mBq/g) by weight to a 100ml volumetric and making up to the mark with 7M nitric acid. The $^{229}$Th/$^{236}$U/uraninite standard was then prepared by adding to a 100ml volumetric flask 2ml of the hundred fold dilution uraninite standard, 3.5 ml of $^{236}$U (167mBq/g) and 10ml of $^{229}$Th (181.1mBq/g) standard solutions by weight and making up to 100ml with 18MΩ deionized water.
(5:4:3) Results and discussion.

The results in table 5.08 showed that increasing the $^{232}$Th concentration from 0 to 1 ppb had little effect on the $^{230}$Th counts. However, increasing the concentration from 1 to 10 and to 20 ppb increased the observed $^{230}$Th counts. This effect was reduced as the concentration of uraninite was increased from 0.0204 to 0.4079 mBq. The $^{230}$Th counts were obtained during the 500 ms $^{230}$Th dwell time.

<table>
<thead>
<tr>
<th>$^{232}$Th (ppb)</th>
<th>$^{230}$Th counts in 0.0204 mBq Uraninite</th>
<th>$^{230}$Th counts in 0.0409 mBq Uraninite</th>
<th>$^{230}$Th counts in 0.4079 mBq Uraninite</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>45</td>
<td>100</td>
<td>1670</td>
</tr>
<tr>
<td>1</td>
<td>48</td>
<td>87</td>
<td>1682</td>
</tr>
<tr>
<td>10</td>
<td>306</td>
<td>352</td>
<td>2070</td>
</tr>
<tr>
<td>20</td>
<td>452</td>
<td>595</td>
<td>2255</td>
</tr>
</tbody>
</table>

The results in table 5.09 show that while increasing the $^{232}$Th concentration increases the counts observed as expected, increasing the concentration of uraninite from 0 to 0.4079 mBq does not result in a difference in the observed $^{232}$Th counts. The experimental results showed that the analysis of $^{230}$Th can be affected by overlap from $^{232}$Th and suitable correction for this effect may be required. The $^{232}$Th counts were obtained during the 10 ms $^{232}$Th dwell time.

<table>
<thead>
<tr>
<th>$^{232}$Th (ppb)</th>
<th>$^{232}$Th counts in 0 mBq Uraninite</th>
<th>$^{232}$Th counts in 0.0204 mBq Uraninite</th>
<th>$^{232}$Th counts in 0.0409 mBq Uraninite</th>
<th>$^{232}$Th counts in 0.4079 mBq Uraninite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>69193</td>
<td>73829</td>
<td>67036</td>
<td>68156</td>
</tr>
<tr>
<td>10</td>
<td>507571</td>
<td>667774</td>
<td>651009</td>
<td>692255</td>
</tr>
</tbody>
</table>

In conclusion the experiments demonstrate that the presence of $^{232}$Th at the 10 and 20 ppb level affected the observed $^{210}$Th counts. This effect was reduced as the concentration of uraninite was increased from 0.0204 to 0.4079 mBq.
(5:5) URANINITE ORE SOLUTION AND NBS REFERENCE MATERIALS.

The uraninite ore solution and the NBS reference material solutions NBS050 and NBS200 were analysed by the Plasma Trace 2 instrument. These experiments were undertaken to establish if a mass bias effect, observed in the initial uraninite experiment was reproducible. The reference materials have different mass ratios for $^{234}\text{U}/^{238}\text{U}$ of $5.481 \times 10^{-5}$, $2.940 \times 10^{-4}$ and $1.56 \times 10^{-3}$ and for $^{235}\text{U}/^{238}\text{U}$ of $7.253 \times 10^{-3}$, $5.278 \times 10^{-2}$ and $2.513 \times 10^{-1}$ respectively. The experimental results will demonstrate whether the mass bias effect varies over a range of mass ratios. The uraninite ore reference solution was analysed three times with the NBS050 and twice with the NBS200 solutions.

(5:5:1) Experimental.

The uraninite reference solution was analysed on two separate occasions using the PlasmaTrace 2 instrument. Initially the uraninite solution was analysed twice with the NBS200 reference solution. The uraninite solution was then analysed a further three times with the NBS050 reference solution. The $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ ratios were calculated from the $^{234}\text{U}$, $^{238}\text{U}$ and $^{235}\text{U}$ results.

(5:5:2) Results and discussion.

(5:5:2:1) Uraninite ore solution.

The results for the two uraninite samples are shown in table 5.10. The average measured $^{234}\text{U}/^{238}\text{U}$ ratio obtained for the two analyses of the uraninite sample was $5.564 \times 10^{-5}$. When this value was compared with the expected value of $5.481 \times 10^{-5}$ a mass bias of 1.1% was observed. The mass bias for individual measurements ranged from -4 to +6%. However the calculated standard deviation of $\pm 2.828 \times 10^{-6}$ for the $^{234}\text{U}/^{238}\text{U}$ ratio gave a range of 5.823 to $5.26 \times 10^{-5}$ which the expected $^{234}\text{U}/^{238}\text{U}$ value of $5.481 \times 10^{-5}$ fell within.
The average measured $^{235}\text{U}/^{238}\text{U}$ ratios for the two analyses of the uraninite sample was $7.163\times10^{-3}$. When this value was compared with the expected value of $7.253\times10^{-3}$, a mass bias of -1.4% was observed. The mass bias for individual measurements ranged from -4.2 to +2%. However the calculated standard deviation of $\pm1.826\times10^{-4}$ for the $^{235}\text{U}/^{238}\text{U}$ ratio gave a range of 7.346 to $7.253\times10^{-3}$ which the expected $^{235}\text{U}/^{238}\text{U}$ value of $7.253\times10^{-3}$ fell within.

These results show that the $^{234}\text{U}/^{238}\text{U}$ and the $^{235}\text{U}/^{238}\text{U}$ ratios were not consistently positive or negative and that within errors the average values agreed with the expected values.

Table 5.10: Uraninite ore solution results.

<table>
<thead>
<tr>
<th></th>
<th>$^{234}\text{U}/^{238}\text{U}$ measured</th>
<th>$^{234}\text{U}/^{238}\text{U}$ expected</th>
<th>Bias (%)</th>
<th>$^{235}\text{U}/^{238}\text{U}$ measured</th>
<th>$^{235}\text{U}/^{238}\text{U}$ expected</th>
<th>Bias (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>URAN 1</td>
<td>$5.240\times10^{-5}$</td>
<td>$5.481\times10^{-5}$</td>
<td>-4.4</td>
<td>$7.040\times10^{-3}$</td>
<td>$7.253\times10^{-3}$</td>
<td>-2.9</td>
</tr>
<tr>
<td></td>
<td>$5.793\times10^{-5}$</td>
<td>$5.481\times10^{-5}$</td>
<td>5.7</td>
<td>$7.130\times10^{-3}$</td>
<td>$7.253\times10^{-3}$</td>
<td>-1.7</td>
</tr>
<tr>
<td>Average</td>
<td>$5.517\times10^{-5}$</td>
<td>$5.481\times10^{-5}$</td>
<td>0.6</td>
<td>$7.085\times10^{-3}$</td>
<td>$7.253\times10^{-3}$</td>
<td>-2.3</td>
</tr>
<tr>
<td>URAN 2</td>
<td>$5.594\times10^{-5}$</td>
<td>$5.481\times10^{-5}$</td>
<td>2.1</td>
<td>$7.297\times10^{-3}$</td>
<td>$7.253\times10^{-3}$</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>$5.834\times10^{-5}$</td>
<td>$5.481\times10^{-5}$</td>
<td>6.4</td>
<td>$7.396\times10^{-3}$</td>
<td>$7.253\times10^{-3}$</td>
<td>2.0</td>
</tr>
<tr>
<td>Average</td>
<td>$5.263\times10^{-5}$</td>
<td>$5.481\times10^{-5}$</td>
<td>-4.0</td>
<td>$6.951\times10^{-3}$</td>
<td>$7.253\times10^{-3}$</td>
<td>-4.2</td>
</tr>
<tr>
<td>Average/uraninite</td>
<td>$5.540\times10^{-5}$</td>
<td>$5.481\times10^{-5}$</td>
<td>1.1</td>
<td>$7.163\times10^{-3}$</td>
<td>$7.253\times10^{-3}$</td>
<td>-1.4</td>
</tr>
<tr>
<td>SD</td>
<td>$\pm2.828\times10^{-4}$</td>
<td>$\pm1.826\times10^{-4}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(5:5:2:2) NBS standard solutions NBS050 and NBS200.

The results for the two NBS standard solutions are shown in table 5.11.

The $^{234}\text{U}/^{238}\text{U}$ ratio results for the NBS050 reference material showed that when the measured average value of $2.803\times10^{-3}$ was compared with the expected value of $2.940\times10^{-4}$ a mass bias of -4.7% was observed. The three individual $^{234}\text{U}/^{238}\text{U}$ ratio measurements showed a mass bias range of -6.8 to -3.1%. The $^{235}\text{U}/^{238}\text{U}$ average measured ratio of $4.987\times10^{-2}$ when compared with the expected value of $5.278\times10^{-2}$ showed a mass bias of -5.5%. The three individual $^{235}\text{U}/^{238}\text{U}$ measurements showed a mass bias range of -4.3 to 6.9%.
The $^{234}\text{U}/^{238}\text{U}$ ratio results for the NBS200 reference material showed that when the measured average value of $1.499 \times 10^{-3}$ was compared with the expected value of $1.56 \times 10^{-3}$ a mass bias of -7.4% was observed. The two individual $^{234}\text{U}/^{238}\text{U}$ measurements showed a mass bias range of -7.2 to -7.5%. The $^{235}\text{U}/^{238}\text{U}$ average measured ratio of $2.32 \times 10^{-1}$ when compared with the expected value of $2.513 \times 10^{-1}$ showed a mass bias of -7.7%. The two individual $^{235}\text{U}/^{238}\text{U}$ measurements showed a mass bias range of -6.4 to 8.9%.

Table 5.11: NBS standards NBS050 and NBS200.

<table>
<thead>
<tr>
<th></th>
<th>$^{234}\text{U}/^{238}\text{U}$</th>
<th>$^{235}\text{U}/^{238}\text{U}$</th>
<th>Bias (%)</th>
<th>$^{235}\text{U}/^{238}\text{U}$</th>
<th>$^{235}\text{U}/^{238}\text{U}$</th>
<th>Bias (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>measured</td>
<td>expected</td>
<td></td>
<td>measured</td>
<td>expected</td>
<td></td>
</tr>
<tr>
<td>NBS050</td>
<td>$2.819 \times 10^{-4}$</td>
<td>$2.940 \times 10^{-4}$</td>
<td>-4.1</td>
<td>$5.00 \times 10^{-2}$</td>
<td>$5.278 \times 10^{-2}$</td>
<td>-5.3</td>
</tr>
<tr>
<td></td>
<td>$2.739 \times 10^{-4}$</td>
<td>$2.940 \times 10^{-4}$</td>
<td>-6.8</td>
<td>$4.91 \times 10^{-2}$</td>
<td>$5.278 \times 10^{-2}$</td>
<td>-6.9</td>
</tr>
<tr>
<td></td>
<td>$2.850 \times 10^{-4}$</td>
<td>$2.940 \times 10^{-4}$</td>
<td>-3.1</td>
<td>$5.05 \times 10^{-2}$</td>
<td>$5.278 \times 10^{-2}$</td>
<td>-4.3</td>
</tr>
<tr>
<td>Average</td>
<td>$2.803 \times 10^{-4}$</td>
<td>$2.940 \times 10^{-4}$</td>
<td>-4.7</td>
<td>$4.987 \times 10^{-2}$</td>
<td>$5.278 \times 10^{-2}$</td>
<td>-5.5</td>
</tr>
<tr>
<td>SD</td>
<td>$\pm 5.727 \times 10^{-6}$</td>
<td>$\pm 7.095 \times 10^{-4}$</td>
<td>-2.7</td>
<td>$\pm 7.095 \times 10^{-4}$</td>
<td>-4</td>
<td></td>
</tr>
<tr>
<td>NBS200</td>
<td>$1.452 \times 10^{-3}$</td>
<td>$1.56 \times 10^{-3}$</td>
<td>-7.2</td>
<td>$2.289 \times 10^{-1}$</td>
<td>$2.513 \times 10^{-1}$</td>
<td>-8.9</td>
</tr>
<tr>
<td></td>
<td>$1.446 \times 10^{-3}$</td>
<td>$1.56 \times 10^{-3}$</td>
<td>-7.5</td>
<td>$2.351 \times 10^{-1}$</td>
<td>$2.513 \times 10^{-1}$</td>
<td>-6.4</td>
</tr>
<tr>
<td>Average</td>
<td>$1.499 \times 10^{-3}$</td>
<td>$1.56 \times 10^{-3}$</td>
<td>-7.4</td>
<td>$2.320 \times 10^{-1}$</td>
<td>$2.513 \times 10^{-1}$</td>
<td>-7.7</td>
</tr>
<tr>
<td>SD</td>
<td>$\pm 4.243 \times 10^{-6}$</td>
<td>$\pm 4.384 \times 10^{-3}$</td>
<td>-6.9</td>
<td>$\pm 4.384 \times 10^{-3}$</td>
<td>-5.9</td>
<td></td>
</tr>
</tbody>
</table>

In conclusion the results show that the isotope ratio measurements for the $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ are not consistently positive or negative. The $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ ratios for the NBS reference materials were consistently negative.

To overcome this problem a standard solution would have to be analysed with each set of samples to be analysed to correct for the mass bias on the isotope ratio measurements.
(5:6) URANINITE ORE SOLUTION AND CORAL REFERENCE MATERIAL (RKMS).

The coral (RKMS) and uraninite ore solution have been described previously in sections (4:2:1:1 and 4:2:1:2) respectively.

(5:6:1) Introduction to uraninite ore solution and coral reference materials experiments.

The uranium and thorium in the coral and uraninite ore solution were separated using the uranium, thorium separation method described in chapter 3, section (3:5:1), prior to analysis by the Plasma Trace 2 instrument.

A solution of the uraninite ore was also prepared and analysed by the Plasma Trace 2 instrument without separation of the uranium from thorium. These experiments were carried out to determine whether separation of the uranium and thorium was necessary prior to analysis by the Plasma Trace 2 instrument.

From the results the $^{234}$U/$^{238}$U ratio in the uraninite ore solution was determined by direct use of the $^{234}$U and $^{238}$U values. The $^{234}$U/$^{238}$U ratio was also determined by division of the $^{234}$U/$^{236}$U and $^{238}$U/$^{236}$U mass ratios.

From the calculated $^{234}$U/$^{238}$U ratio the uranium isotope activities were calculated using the known added level of $^{236}$U. The $^{230}$Th activity was calculated using the known added level of $^{229}$Th.

The observed mass bias on the uraninite ore solutions $^{234}$U/$^{238}$U and $^{230}$Th/$^{234}$U ratios were then used to correct the coral reference materials $^{234}$U/$^{238}$U and $^{230}$Th/$^{234}$U ratios.
(5:6:2) **Experimental.**

**Reagents.**

The specific activity of the uraninite solution was $147 \pm 2 \text{mBq/g}$ with respect to $^{230}\text{Th}$. The activity was determined from five replicate alpha spectrometry measurements using a NIST $^{229}\text{Th}$ internal standard. The uraninite used was in secular equilibrium with respect to $^{238}\text{U}$, $^{234}\text{U}$ and $^{230}\text{Th}$ to within 0.5%.

The specific activity of the $^{236}\text{U}$ and $^{229}\text{Th}$ used as internal standards for the Plasma Trace 2 instrument measurements were $167 \pm 5$ and $267 \pm 3 \text{mBq/g}$ respectively. The activity was determined from five replicate alpha spectrometry measurements using NIST internal standards. The half-lives used for $^{236}\text{U}$ and $^{229}\text{Th}$ are $2.3416 \times 10^7 \text{ years} (\pm 0.2\%)$ and $7.340 \times 10^4 \text{ years} (\pm 2.2\%)$ respectively \cite{186}.

(5:6:2:1) **Separated uranium and thorium.**

The coral reference material (0.5g) was dissolved using the method described in section (4:2:1:2). The resulting solution was spiked with 0.425ml of $^{236}\text{U}$ and 0.5ml of $^{229}\text{Th}$ spike solutions.

To 0.2ml of the uraninite standard solution, 0.85ml of $^{236}\text{U}$ and $^{229}\text{Th}$ spike solution were added. Iron carrier (1ml of 10mg/ml) was added to the sample solutions which were then left to equilibrate then heated on a hotplate for 30 minutes. The ferric hydroxide was precipitated by addition of ammonia. The resulting precipitate was centrifuged and washed with 50ml of 0.5M ammonia.

Three uraninite samples and two coral reference material samples were prepared and separated using the method described in chapter 3. The spike levels were chosen so that the concentration of the isotopes of uranium and the isotopes of thorium in the coral and uraninite would be at the same level as the $^{236}\text{U}$ and $^{229}\text{Th}$. The uranium and thorium fractions were made to a volume of 50ml with 18M$\Omega$ deionized water and measured using the PlasmaTrace 2 instrument.
(5:6:2:2) Uraninite ore solution without uranium and thorium separation.

The uraninite ore solution was prepared by the addition of 0.4975g of $^{238}\text{U}$, 1.8367g of $^{236}\text{U}$ and 2.1604g of $^{232}\text{Th}$ by weight to a 100ml volumetric flask. The solution was made to a volume of 100ml with de-ionized water. The uraninite solution was analysed on two separate occasions using the PlasmaTrace 2 instrument.

(5:6:3) Results and discussion.

(5:6:3:1) Uraninite ore solution.

The expected mass ratio $^{234}\text{U}/^{238}\text{U}$ for an isotope ratio of 1, calculated using half-lives for $^{234}\text{U}$ and $^{238}\text{U}$ of $2.457\times 10^5$ years ± 0.1% and $4.468\times 10^9$ years ± 0.1% respectively is 0.00005407.

The calculation of the expected mass ratio is shown in appendix 4.

(5:6:3:1:1) Determination of $^{234}\text{U}/^{238}\text{U}$ mass ratio in the uraninite standard by direct $^{234}\text{U}$ and $^{238}\text{U}$ comparison.

The experimentally determined $^{234}\text{U}/^{238}\text{U}$ mass ratio from the Plasma Trace 2 results are shown in table 5.12. The results show values of 0.0000608±0.0000016, 0.0000600±0.0000012, 0.0000584±0.0000016 were obtained for the uranium and thorium not separated (run 1), the uranium and thorium separated (run 1) and the uranium and thorium separated (run 2) respectively.

The determined $^{234}\text{U}/^{238}\text{U}$ mass ratio was calculated by taking the mean of the measurements. The error on the mean was calculated by taking the standard error of the mean at the 95% confidence level using the calculated shown in appendix 5.

The $^{234}\text{U}/^{238}\text{U}$ activity ratio is given by multiplying the mass ratios by the ratio of the specific activities.
The determined/expected $^{234}\text{U}/^{238}\text{U}$ mass ratios values of $1.12 \pm 0.03$, $1.11 \pm 0.02$ and $1.08 \pm 0.03$ were obtained. These ratios (taking into account the upper and lower uncertainties) are 5-15% high, whereas the measurement uncertainty is 2-3%. This implies that there was a significant positive bias on the $^{234}\text{U}/^{238}\text{U}$ ratio. The results also indicated that there was no significant difference in the separated uranium and thorium and non-separated uranium and thorium $^{234}\text{U}/^{238}\text{U}$ ratio.

Table 5.12: $^{234}\text{U}/^{238}\text{U}$ mass ratio.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run</th>
<th>Dilution factor</th>
<th>determined $^{234}\text{U}/^{238}\text{U}$ mass ratio</th>
<th>N° of ratio measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium, Thorium</td>
<td>Run 1</td>
<td>40</td>
<td>0.0000608±0.0000016</td>
<td>13</td>
</tr>
<tr>
<td>Not separated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uranium, Thorium</td>
<td>Run 1</td>
<td>40</td>
<td>0.0000600±0.0000012</td>
<td>14</td>
</tr>
<tr>
<td>Separated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uranium, Thorium</td>
<td>Run 2</td>
<td>40</td>
<td>0.0000584±0.0000016</td>
<td>15</td>
</tr>
<tr>
<td>Not separated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(5.6.3:1:2) Determination of $^{234}\text{U}/^{238}\text{U}$ mass ratio by division of $^{234}\text{U}/^{236}\text{U}$ and $^{238}\text{U}/^{236}\text{U}$ mass ratios.

Table 5.13: $^{238}\text{U}/^{236}\text{U}$ mass ratio.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run</th>
<th>Dilution factor</th>
<th>$^{238}\text{U}/^{236}\text{U}$ mass ratio</th>
<th>N° of ratio measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) U, Th</td>
<td>Run 1</td>
<td>40</td>
<td>41.61 ± 1.17</td>
<td>13</td>
</tr>
<tr>
<td>Not separated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) U, Th</td>
<td>Run 2</td>
<td>40</td>
<td>43.25 ± 0.79</td>
<td>15</td>
</tr>
<tr>
<td>Not separated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.14: $^{234}\text{U}/^{236}\text{U}$ mass ratio.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run</th>
<th>Dilution factor</th>
<th>$^{234}\text{U}/^{236}\text{U}$ mass ratio</th>
<th>N° of ratio measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c) U, Th</td>
<td>Run 1</td>
<td>40</td>
<td>0.00251 ± 0.00008</td>
<td>13</td>
</tr>
<tr>
<td>Not separated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d) U, Th</td>
<td>Run 1</td>
<td>1</td>
<td>0.00269 ± 0.00004</td>
<td>15</td>
</tr>
<tr>
<td>Not separated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e) U, Th</td>
<td>Run 2</td>
<td>40</td>
<td>0.02520 ± 0.00008</td>
<td>15</td>
</tr>
<tr>
<td>Not separated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(f) U, Th</td>
<td>Run 2</td>
<td>1</td>
<td>0.02690 ± 0.00004</td>
<td>10</td>
</tr>
<tr>
<td>Not separated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The $^{234}\text{U}/^{238}\text{U}$ mass ratio was calculated by dividing the $^{234}\text{U}/^{236}\text{U}$ mass ratio by the $^{238}\text{U}/^{236}\text{U}$ mass ratio.
From tables 5.13 and 5.14 the $^{234}\text{U}/^{238}\text{U}$ mass ratio measured in like solutions was calculated by dividing (c) by (a) and (e) by (b); for run 1 and run 2 the $^{234}\text{U}/^{238}\text{U}$ ratios are $0.0000603 \pm 0.0000026$ and $0.0000583 \pm 0.0000021$. The calculation of the error on the $^{234}\text{U}/^{238}\text{U}$ ratio is shown in appendix 6.

Calculating the $^{234}\text{U}/^{238}\text{U}$ ratio in this way eliminated the inclusion of an uncertainty component associated with the $^{238}\text{U}$ internal standard (as does the direct $^{234}\text{U}/^{238}\text{U}$ ratio measurements). The two mass ratios determined by this calculation are almost identical to their equivalent values determined directly; however, taking the ratio of the uranium isotope to $^{238}\text{U}$ increases the uncertainty (to approximately 4%) due to combination of the errors.

Dividing (c) by (d) and (e) by (f) demonstrated the effect of dilution on the $^{234}\text{U}/^{236}\text{U}$ ratio: the diluted/not diluted ratio on run 1 and 2 were $0.93 \pm 0.03$ and $0.94 \pm 0.03$ respectively. This implied that there may be a small effect on the isotope ratios on dilution. Comparing ratios at different dilutions would yield further uncertainty components; ideally the ratios should be determined at the same dilution.

**(5:6:3:1:3) Determination of $^{238}\text{U}$, $^{234}\text{U}$ and $^{230}\text{Th}$ activities using the $^{236}\text{U}$ and $^{229}\text{Th}$ internal standards.**

From the $^{238}\text{U}/^{236}\text{U}$ and $^{234}\text{U}/^{236}\text{U}$ ratios determined in section (5:5:6:3:2) the uranium isotope activities can be calculated knowing the $^{236}\text{U}$ spike levels added. The following calculation was used to calculate the $^{238}\text{U}$ activity.

The specific activity of $^{236}\text{U}$ was 0.167Bq/g, the mass of the $^{236}\text{U}$ spike solution used was 1.8g. The activity of $^{236}\text{U}$ added to the uraninite ore reference solution was 0.3067Bq. The number of atoms of $^{236}\text{U}$ was calculated using the calculation shown in appendix 7. The number of atoms of $^{238}\text{U}$ were then used to calculate the activity of $^{238}\text{U}$.

The uranium isotope activities are shown in table 5.15. The 3% error on the activity of the $^{236}\text{U}$ spike solution was used to determine the error on the uranium activities.
The $^{230}$Th was calculated in a similar way using the $^{229}$Th internal standard. The expected activity of the three radionuclides of interest in the uraninite ore solution is $73 \pm 1\, \text{mBq}$. The expected activity value was calculated using the known weight of uraninite ore solution used and its known specific activity of $147 \pm 2\, \text{mBq/g}$. The specific activity of the uraninite ore solution was determined as described in section (5:6:2). The thorium activity is shown in table 5.15.

Table 5.15: Determined activities for $^{238}$U, $^{234}$U and $^{230}$Th in uraninite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run</th>
<th>$^{238}$U activity / mBq</th>
<th>$^{234}$U activity / mBq</th>
<th>$^{230}$Th activity / mBq</th>
</tr>
</thead>
<tbody>
<tr>
<td>U and Th Not separated</td>
<td>1</td>
<td>$66 \pm 2$</td>
<td>$74 \pm 2$</td>
<td>$69 \pm 2$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>$69 \pm 1$</td>
<td>$74 \pm 2$</td>
<td>$67 \pm 2$</td>
</tr>
</tbody>
</table>

Table 5.16: Ratio of determined to expected activities in the uraninite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run</th>
<th>$^{238}$U determined/expected</th>
<th>$^{234}$U determined/expected</th>
<th>$^{230}$Th determined/expected</th>
</tr>
</thead>
<tbody>
<tr>
<td>U and Th Not separated</td>
<td>1</td>
<td>$0.91 \pm 0.03$</td>
<td>$1.01 \pm 0.04$</td>
<td>$0.94 \pm 0.04$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>$0.94 \pm 0.02$</td>
<td>$1.02 \pm 0.04$</td>
<td>$0.92 \pm 0.03$</td>
</tr>
</tbody>
</table>

The activities determined for the $^{234}$U are the same as the expected activities taking into account uncertainties, whereas both the $^{238}$U and the $^{230}$Th activities are lower than expected (4-12% and 2-11% respectively taking uncertainties into account).

Table 5.17: Activity ratios calculated from determined activities of $^{238}$U, $^{234}$U and $^{230}$Th in uraninite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run</th>
<th>$^{230}$Th/$^{234}$U</th>
<th>$^{230}$Th/$^{238}$U</th>
<th>$^{234}$U/$^{238}$U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium and Thorium Not separated</td>
<td>1</td>
<td>$0.926 \pm 0.044$</td>
<td>$1.033 \pm 0.047$</td>
<td>$1.116 \pm 0.048$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>$0.908 \pm 0.042$</td>
<td>$0.978 \pm 0.037$</td>
<td>$1.078 \pm 0.040$</td>
</tr>
</tbody>
</table>
The $^{230}\text{Th}/^{234}\text{U}$, $^{230}\text{Th}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ activity ratios shown in table 5.17 were calculated using the activities shown in table 5.15. The $^{230}\text{Th}/^{234}\text{U}$ activity ratios are 3-15% lower than expected; the $^{234}\text{U}/^{238}\text{U}$ ratios are 4-16% higher and the $^{230}\text{Th}/^{238}\text{U}$ activity ratio was within the uncertainty of the expected value. (Note: the $^{234}\text{U}/^{238}\text{U}$ ratio result is mathematically identical to the result obtained when dividing by $^{236}\text{U}$).

The $^{234}\text{U}/^{238}\text{U}$ ratio was consistently high (up to 16%) by both calculation methods (direct and relative to $^{236}\text{U}$), whereas the uncertainty was approximately 2-4%. Direct ratio measurement provides the lowest uncertainty but the best precision. The calculated $^{238}\text{U}$ and $^{230}\text{Th}$ activities are low (up to 12%) whereas, the uncertainty is approximately 3%; the activity was correct within uncertainties (3%). The $^{238}\text{U}$ and $^{230}\text{Th}$ activities are consistent with each other resulting in the expected $^{230}\text{Th}/^{238}\text{U}$ activity ratio within uncertainties.

Assuming that the $^{234}\text{U}$ activity was correct (i.e. the expected value was correct), then both the $^{238}\text{U}$ and $^{230}\text{Th}$ activities are low. The low value for $^{238}\text{U}$ was consistent with the observed high $^{234}\text{U}/^{238}\text{U}$ ratio. Conversely, if the $^{238}\text{U}$ and $^{230}\text{Th}$ values are correct (i.e. the expected value was lower than it should be) then the $^{234}\text{U}$ activity was high which could also account for the high $^{234}\text{U}/^{238}\text{U}$ ratio.

(5:6:3:2) Coral reference material (RKM5).


The uncorrected coral reference results are shown in table 5.18. The $^{230}\text{Th}/^{234}\text{U}$ average ratio of 0.635±0.024 was low when compared with the certified value of 0.709±0.025. The $^{234}\text{U}/^{238}\text{U}$ average ratio of 1.201±0.029 was high when compared with the certified value of 1.098±0.029. The calculated age of 105157 (99447-116263) years was low when compared with the certified value of 131000±9000 years. The low $^{234}\text{U}/^{238}\text{U}$ and high $^{234}\text{U}/^{238}\text{U}$ ratios were correct for mass bias effects using the uraninite ore reference material results.
Table 5.18: Uncorrected coral reference results.

<table>
<thead>
<tr>
<th>Uncorrected coral</th>
<th>$^{230}$Th/$^{234}$U</th>
<th>$^{234}$U/$^{238}$U</th>
<th>AGE (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coral 1 run 1</td>
<td>0.668±0.047</td>
<td>1.245±0.0</td>
<td></td>
</tr>
<tr>
<td>Coral 1 run 1</td>
<td>0.610±0.025</td>
<td>1.188±0.018</td>
<td></td>
</tr>
<tr>
<td>Coral 1 run 1</td>
<td>0.627±0.011</td>
<td>1.186±0.023</td>
<td></td>
</tr>
<tr>
<td>Coral 1 run 1</td>
<td>0.635±0.028</td>
<td>1.185±0.026</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>0.635±0.024</td>
<td>1.201±0.029</td>
<td>105157</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(99447-116263)</td>
</tr>
<tr>
<td>Certified Value</td>
<td>0.709±0.025</td>
<td>1.098±0.029</td>
<td>131000±9000</td>
</tr>
</tbody>
</table>


The corrected coral reference results are shown in table 5.19. The average uraninite $^{230}$Th/$^{234}$U and $^{234}$U/$^{238}$U ratios of 0.917±0.043 and 1.097±0.044 were used to correct the coral results. The $^{230}$Th/$^{234}$U ratio, with errors, was between 4 and 12.6% low. The $^{234}$U/$^{238}$U ratio with errors was between 5.3 and 11.4% high. The $^{230}$Th/$^{234}$U ratio was corrected for the average mass bias of -8.3%. The $^{234}$U/$^{238}$U ratio was corrected for the average mass bias of 9.7%. The upper and lower mass bias range of 4 to 12.6% low and 5.3 to 11.4% high for $^{230}$Th/$^{234}$U and $^{234}$U/$^{238}$U respectively were used to obtain the age range. The corrected $^{230}$Th/$^{234}$U and $^{234}$U/$^{238}$U ratios of 0.688 and 1.085 are in agreement with the certified values of 0.709±0.025 and 1.098±0.029 respectively. The calculated age of the coral of 123664 years, age range 113433 to 133407 years, was in agreement with the certified age of 131000±9000.

Table 5.19: Corrected coral reference results.

<table>
<thead>
<tr>
<th>Corrected coral</th>
<th>$^{230}$Th/$^{234}$U</th>
<th>$^{234}$U/$^{238}$U</th>
<th>AGE (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.688</td>
<td>1.085</td>
<td>123664</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(113433-133407)</td>
</tr>
<tr>
<td>Certified Value</td>
<td>0.709±0.025</td>
<td>1.098±0.029</td>
<td>131000±9000</td>
</tr>
</tbody>
</table>

In conclusion the uraninite experiment demonstrated that the uraninite ore reference material showed a mass bias on the $^{230}$Th/$^{234}$U and $^{234}$U/$^{238}$U ratios. The mass bias can be calculated using uraninite ore reference material and then used to correct the samples for mass bias effects.
(5:7) CORRECTION FOR DETRITAL CONTAMINATION.

(5:7:1) Introduction to detrital contamination correction.

Pure carbonate minerals only require a simple sample dissolution step using mild mineral acids. However, the presence of clay minerals (detritus) deposited with the carbonate introduces external $^{238}\text{U}$, $^{234}\text{U}$ and $^{230}\text{Th}$ into the sample when a simple acid dissolution step is used. The isotope $^{232}\text{Th}$ has been used as a contamination index for the correction of detrital contamination.

The correction is based on the assumption that the carbonate phase contains no $^{232}\text{Th}$ and that any $^{232}\text{Th}$ found in the leachate must have come from the detrital component. In addition to the $^{232}\text{Th}$, the detritus contains $^{238}\text{U}$, $^{234}\text{U}$ and $^{230}\text{Th}$ which are unrelated to the age of the carbonate and must be separated out or a correction made as no physical means is available to completely separate the detritus from the carbonate matrix. The sample is assumed to be 'pure' if $^{230}\text{Th}/^{232}\text{Th} > 20$, if less than 20 detrital correction may be required.

The following two dissolution techniques were used to correct for detrital contamination; the leachate only dissolution technique and the total dissolution technique.

The leachate dissolution technique uses dilute nitric acid to dissolve the sample [236, 237] containing various detritus:carbonate ratios. The leachate fraction is then separated from any insoluble detrital residue by centrifuging the sample. The leachate fraction is then analysed for its $^{234}\text{U}$, $^{238}\text{U}$, $^{230}\text{Th}$ and $^{232}\text{Th}$ content. The 'corrected' $^{230}\text{Th}/^{234}\text{U}$ ratio for the carbonates is determined by plotting the $^{234}\text{U}/^{232}\text{Th}$ versus $^{230}\text{Th}/^{232}\text{Th}$ ratios for the leachate samples. The slope of the 'isochron' or line of best fit through the points was the 'corrected' $^{230}\text{Th}/^{234}\text{U}$ ratio.

The 'corrected' $^{234}\text{U}/^{238}\text{U}$ ratio for the carbonate is determined by plotting the $^{238}\text{U}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$ ratios for the leachate samples. The slope of the 'isochron' or line of best fit through the points was the corrected $^{234}\text{U}/^{238}\text{U}$ ratio.
This procedure was tested here by analysing artificial mixtures of the pure speleothem and a naturally occurring detritus that might be expected to occur as a contaminant in chemically precipitated speleothem sample [238, 239].

The leachate dissolution technique has the advantage that even if fractionation of the isotopes from the detritus to the leachate does occur, it does not affect the slopes of the isochrons from which the age of the sample is obtained.

The total dissolution technique followed the leachate dissolution technique but then the detrital component was dissolved using perchloric, hydrofluoric and nitric acids at 200°C overnight, in a pressure bomb, and then added to the leachate fraction. The total dissolution method was evaluated by using artificial mixtures of detritus and carbonate and an impure carbonate of known age [240, 241]. The advantages of the technique are, that because the detritus is completely dissolved along with the carbonate, no assumptions need to be made about the detritus other than homogeneity.

In conclusion successful applications of either the leachate or the total dissolution techniques require that the coeval samples have sufficient range of detritus/carbonate ratios to enable an adequate spread to define the isochron.

**Speleothem reference material (76001) experimental.**

The speleothem reference material (76001), obtained from Richard Ku at the University of Southern California, and two mixtures of the speleothem (76001) and a detrital sample were prepared. The speleothem (76001) has a $^{230}\text{Th}/^{232}\text{Th}$ ratio which is greater than 20 and so the speleothem is classed as pure. The detrital contamination used consisted of wallrock coating of hematite and clay and minor old calcite. The speleothem-detrital mixtures were prepared so that the detrital content of the mixtures were 3% and 7% respectively.

The following experiments were undertaken to enable correction of the detrital content of the speleothem sample.
The speleothem 76001, the speleothem 76001 sample containing 3% detrital contamination and the speleothem 76001 sample containing 7% detrital contamination were analysed using the leachate method.

The speleothem 76001 sample containing 3% detrital contamination and the speleothem 76001 sample containing 7% detrital contamination were also analysed using the total dissolution method.

The $^{234}\text{U}$, $^{238}\text{U}$, $^{230}\text{Th}$ and $^{232}\text{Th}$ values for the leachate and total dissolution techniques were determined using the Plasma Trace 2 instrument. The uraninite ore reference material solution was also analysed by the Plasma Trace 2 instrument to allow correction of the speleothem sample results for mass bias on the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ ratios.

(5:7:2:1) **Leachate dissolution technique.**

Approximately 0.5g of the 76001, 76001-3% and 76001-7% sample mixtures were weighed into 250ml glass beakers. Deionized water (50ml) were added to the samples. Watch glasses were placed on the beakers and the samples swirled and then left to stand. Concentrated doubly distilled nitric acid was added slowly until all the calcium carbonate had dissolved. The pH of the solutions was checked and adjusted to pH 1. The samples were gently boiled on a hot plate for half an hour in order to ensure the complete dissolution of the carbonate by the acid. The solutions were then allowed to cool. The samples were centrifuged to separate the leachate fraction from the residue.

The 76001, 76001-3% and 76001-7% leachate fraction were labelled 76001L, 76001-3%L and 76001-7%L. To each of these samples the $^{229}\text{Th}$ and $^{236}\text{U}$ spike solutions and 1ml of (10mg/ml) iron carrier were added and left to equilibrate.

The samples were then ready for ferric hydroxide precipitation and uranium, thorium separation as described in section (2:2:1:1).
(5:7:2:2) **Total dissolution technique.**

Approximately 0.5g of the 76001-3% and 76001-7% sample mixtures were weighed into 250ml glass beakers. Deionized water (50ml) were added to the samples. Watch glasses were placed on the beakers and the samples swirled and then left to stand. Concentrated doubly distilled nitric acid was added slowly until all the calcium carbonate had dissolved. The pHs of the solutions were checked and adjusted to pH 1. The samples were gently boiled on a hot plate for half an hour in order to ensure the complete dissolution of the carbonate by the acid. The solutions were then allowed to cool. The samples were centrifuged to separate the leachate fraction from the residue.

To the total dissolution samples 76001-3% and 76001-7, 1ml of (10mg/ml) iron carrier was added to the leachate fraction and left until the detrital residue has been dissolved.

The $^{229}$Th and $^{236}$U spikes were added to the 76001-3% and 76001-7 residues in teflon-beakers and evaporated to dryness under infra red lamps.

Perchloric acid (10ml) and hydrofluoric acid (30 ml) were added to the teflon beakers. The teflon beakers were inserted into pressure bombs and heated at 200°C overnight. The bomb containers were removed from the oven, allowed to cool and the containers removed from the bombs. The teflon beakers were placed under heat lamps and evaporated to dryness. Concentrated nitric acid (5ml) was added and evaporated to dryness. This step was repeated. Hydrochloric acid (20ml of 8M) was added to the solution and digested under heat lamps.

The residue fractions for samples 76001-3% and 76001-7 were transferred to the 250ml glass beakers containing their respective leachate fractions and left to equilibrate. The resulting samples were labelled 76001-3%T and 76001-7T.

The samples were then ready for ferric hydroxide precipitation and uranium, thorium separation described in section (2:2:1:1).
(5:7:3) Results and discussion for Speleothem reference material (76001).

(5:7:3:1) Leachate technique.

The speleothem reference material certified results are shown in table 5.20. The results for the (76001) reference material obtained by the leachate dissolution technique are shown in table 5.21. These results, from the Plasma Trace 2 instrument, were not corrected for mass bias. The $^{230}$Th/$^{234}$U and $^{234}$U/$^{238}$U ratios were corrected for mass bias by using the results from the uraninite reference solution. These results are shown in table 5.22.

The leachate results are shown in table 5.21. These results show the uranium concentration was increased from $0.0755 \pm 0.007$ to $0.702 \pm 0.014$ to $0.742 \pm 0.011$ ppm as the detrital content of the sample was increased from 0 to 3 and 7% respectively.

The $^{230}$Th/$^{232}$Th ratio decreased from $210 \pm 23$ for the pure speleothem to $77.82 \pm 3.374$ and $55.87 \pm 2.585$ with 3% and 7% added detritus as the concentration of $^{232}$Th leached from the detritus was increased.

The $^{234}$U/$^{238}$U ratios for 76001L, 7600113%, and 76001L7% of $2.07 \pm 0.03$, $2.123 \pm 0.045$, and $2.079 \pm 0.038$ respectively were higher than the certified 7600L ratio of $1.900 \pm 0.069$.

The $^{230}$Th/$^{234}$U ratios for 76001L, 7600113%, and 76001L7% of $0.290 \pm 0.023$, $0.307 \pm 0.011$ and $0.315 \pm 0.011$ respectively were lower than the certified 76001 value of $0.369 \pm 0.024$.

Table 5.20: Certified values for speleothem reference material.

<table>
<thead>
<tr>
<th>Reference</th>
<th>U (ppm)</th>
<th>$^{234}$U/$^{238}$U</th>
<th>$^{230}$Th/$^{234}$U</th>
<th>Age ($\times 10^3$ y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>76001</td>
<td>$0.841 \pm 0.033$</td>
<td>$1.900 \pm 0.069$</td>
<td>$0.369 \pm 0.024$</td>
<td>$48 \pm 5$</td>
</tr>
</tbody>
</table>
Table 5.21: Results for speleothem and speleothem/detrital mixtures by the leachate dissolution technique.

<table>
<thead>
<tr>
<th>Sample</th>
<th>U (ppm)</th>
<th>234U/238U</th>
<th>230-234U</th>
<th>230-Th/232-Th</th>
</tr>
</thead>
<tbody>
<tr>
<td>76001L</td>
<td>0.755± 0.007</td>
<td>2.07 ± 0.030</td>
<td>0.290 ± 0.023</td>
<td>210.84 ± 23.130</td>
</tr>
<tr>
<td>76001L3%</td>
<td>0.702±0.014</td>
<td>2.123 ± 0.045</td>
<td>0.307 ± 0.011</td>
<td>77.82 ± 3.374</td>
</tr>
<tr>
<td>76001L7%</td>
<td>0.742 ± 0.011</td>
<td>2.079 ± 0.038</td>
<td>0.315 ± 0.011</td>
<td>55.87 ± 2.585</td>
</tr>
</tbody>
</table>

The $^{230}$Th/$^{234}$U leachate corrected ratio of 0.281 was determined by plotting the $^{234}$U/$^{232}$Th ratio values on the x axis and the $^{230}$Th/$^{232}$Th ratio values on the y axis. The corrected $^{230}$Th/$^{234}$U was obtained from the slope of the graph shown in figure 5.03.

Figure 5.03: Isochron plots for Th-230/Th-232 versus U-234/Th-232 for the leachate dissolution technique.

The $^{234}$U/$^{235}$U leachate corrected ratio of 0.281 was determined by plotting the $^{238}$U/$^{232}$Th ratio values on the x axis and the $^{234}$U/$^{232}$Th ratio values on the y axis. The corrected $^{234}$U/$^{238}$U was obtained from the slope of the graph shown in figure 5.04.
(5:7:3:2) Total dissolution technique.

The results for the total dissolution technique are shown in Table 5.22. The results from the total dissolution technique show increased uranium concentrations of 0.777±0.01 and 0.801±0.021 ppm compared with the leachate values of 0.702±0.014 and 0.742±0.001 ppm respectively.

The $^{230}\text{Th}/^{232}\text{Th}$ ratios of 15.724±1.5503 and 15.182±0.6642 for the 76001T3% and 76001T7% show significant detrital contamination as the ratio is below 20 [247].

Table 5.22: Results for speleothem/detrital mixtures by the total dissolution technique.

<table>
<thead>
<tr>
<th>Sample</th>
<th>U(ppm)</th>
<th>$^{234}\text{U}/^{238}\text{U}$</th>
<th>$^{230}\text{Th}/^{234}\text{U}$</th>
<th>$^{230}\text{Th}/^{232}\text{Th}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>76001T3%</td>
<td>0.777±0.01</td>
<td>1.920±0.027</td>
<td>0.312±0.022</td>
<td>15.724±1.5503</td>
</tr>
<tr>
<td>76001T7%</td>
<td>0.801±0.021</td>
<td>1.912 ±0.056</td>
<td>0.350±0.015</td>
<td>15.182±0.6642</td>
</tr>
</tbody>
</table>

The leachate and total dissolution corrected $^{230}\text{Th}/^{234}\text{U}$ ratio of 0.287 was determined by plotting the total dissolution results with the leachate results. The $^{234}\text{U}/^{232}\text{Th}$ ratio values were plotted on the x axis and the $^{230}\text{Th}/^{232}\text{Th}$ ratio values

187
on the y axis. The corrected $^{230}\text{Th} / ^{234}\text{U}$ was obtained from the slope of the graph shown in figure 5.05.

The leachate and total dissolution corrected $^{234}\text{U} / ^{238}\text{U}$ ratio of 2.08 was determined by plotting the total dissolution results with the leachate results. The $^{238}\text{U} / ^{232}\text{Th}$ ratio values were plotted on the x axis and the $^{234}\text{U} / ^{232}\text{Th}$ ratio values on the y axis. The corrected $^{234}\text{U} / ^{238}\text{U}$ was obtained from the slope of the graph shown in figure 5.06.

**Figure 5.05:** Isochron plots for Th-$^{230}$Th-$^{232}$ versus U-$^{234}$Th-$^{232}$ for the leachate and total dissolution techniques.

![Figure 5.05](image1)

**Figure 5.06:** Isochron plots for Th-$^{234}$Th-$^{232}$ versus U-$^{238}$Th-$^{232}$ for the leachate and total dissolution techniques.

![Figure 5.06](image2)
(5:7:3:3) Uraninite ore solution.

The results for the uraninite ore solution analysed by the Plasma Trace 2 instrument are shown in table 5.23. These results show that the average $^{234}\text{U}/^{238}\text{U}$ value of 1.1235±0.0092 was 12.35% higher than the expected value of 1. The average $^{230}\text{Th}/^{234}\text{U}$ value of 0.940±0.020 was 6% lower than the expected value of 1.

These results agree with those obtained in the experiments described in section (5:6:3:1:3) where mass bias of +9.7% and -8.3% was obtained for the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ ratios for the uraninite ore reference material.

The mass bias for $^{234}\text{U}/^{238}\text{U}$ of +12.35% and for $^{230}\text{Th}/^{234}\text{U}$ of -6% were used to correct the 76001L, the leachate corrected and the leachate and total corrected $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ values. The mass bias corrected results are shown in table 5.26.

Table 5.23: Uraninite ore solution.

<table>
<thead>
<tr>
<th></th>
<th>$^{234}\text{U}/^{238}\text{U}$</th>
<th>$^{230}\text{Th}/^{234}\text{U}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.117±0.048</td>
<td>0.925±0.025</td>
</tr>
<tr>
<td>2</td>
<td>1.130±0.047</td>
<td>0.955±0.030</td>
</tr>
<tr>
<td>Average</td>
<td>1.1235±0.0092</td>
<td>0.940±0.020</td>
</tr>
</tbody>
</table>

(5:7:3:4) Determination of the age of speleothem reference material (76001).

The age of the speleothem (76001) was calculated using the dating equation, equation 1.06, described in section (1:4:3:2). The results for the 76001L, the leachate corrected 76001, and the leachate and total corrected 76001 are shown in table 5.25. The calculated age of the 76001L, the leachate corrected 76001 and the leachate and total corrected 76001 of 36037, 34758 and 35674 years respectively are lower than the certified value of 48000±500 years.
Table 5.24: Results for speleothem reference material (76001).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{234}\text{U}/^{238}\text{U}$</th>
<th>$^{230}\text{Th}/^{234}\text{U}$</th>
<th>AGE (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Certified Values</td>
<td>1.90</td>
<td>0.369</td>
<td>48000±500</td>
</tr>
<tr>
<td>76001L</td>
<td>2.07</td>
<td>0.290</td>
<td>36037</td>
</tr>
<tr>
<td>Leachate corrected 76001</td>
<td>2.06</td>
<td>0.281</td>
<td>34758</td>
</tr>
<tr>
<td>Leachate and Total Corrected 76001</td>
<td>2.08</td>
<td>0.287</td>
<td>35674</td>
</tr>
</tbody>
</table>

The results for the mass bias corrected 76001L, the leachate corrected 76001 and the leachate and total corrected 76001 are shown in table 5.26. The mass bias corrected results for $^{234}\text{U}/^{238}\text{U}$ of 1.810, 1.804, and 1.823 and $^{230}\text{Th}/^{234}\text{U}$ of 0.307, 0.298 and 0.304 are in closer agreement with the certified values of 1.90 and 0.369 respectively.

The calculated ages obtained for the mass bias corrected results of 38656, 37341, and 38206 years are in closer agreement with the certified age of 48000±500 years.

Table 5.25: Results for speleothem reference material (76001) corrected for mass bias using uraninite ore solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{234}\text{U}/^{238}\text{U}$</th>
<th>$^{230}\text{Th}/^{234}\text{U}$</th>
<th>AGE (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Certified Values</td>
<td>1.90</td>
<td>0.369</td>
<td>48000±500</td>
</tr>
<tr>
<td>76001L</td>
<td>1.810</td>
<td>0.307</td>
<td>38656</td>
</tr>
<tr>
<td>Leachate corrected 76001</td>
<td>1.804</td>
<td>0.298</td>
<td>37341</td>
</tr>
<tr>
<td>Leachate and Total Corrected 76001</td>
<td>1.823</td>
<td>0.304</td>
<td>38206</td>
</tr>
</tbody>
</table>

In conclusion, the 3% and the 7% detritus/speleothem mixtures and isochron plots enabled corrections to be made to the raw results obtained from the detritally contaminated speleothem samples.
This demonstrates that the true age of an impure sample can be extracted provided it was available at different impurity levels. The $^{234}\text{U}/^{238}\text{U}$ mass bias corrected ratio of 1.8 was in agreement with the certified value of 1.9. The difference between the $^{230}\text{Th}/^{234}\text{U}$ mass bias corrected ratio of 0.3 was still lower than the certified value of 0.369. This difference was responsible for the lower calculated age of the speleothem sample when compared with the certified value. The speleothem sample was analysed by alpha spectrometry and the lower $^{230}\text{Th}/^{234}\text{U}$ ratio observed by Plasma Trace 2 analysis was also found for alpha spectrometry. This indicates that the $^{230}\text{Th}/^{234}\text{U}$ ratio was not due to a fault in the analysis by the Plasma Trace 2 instrument.
(5:8) COMPARISON OF PLASMA TRACE 2 AND ALPHA SPECTROMETRY TECHNIQUES.

(5:8:1) Experimental.

(5:8:1:1) Coral reference material (RKM5).

The coral reference material was analysed by the Plasma Trace 2 instrument and by alpha spectrometry. A 0.5 g aliquot of the coral reference material was prepared for analysis by the Plasma Trace 2 instrument using the method described in section (5:6:2:1).

The coral reference material was also analysed using alpha spectrometry. A 2 g aliquot was used and the coral reference material was dissolved and the uranium and thorium separated using the dissolution/separation method described in section (2:2:1:1).

(5:8:1:2) Speleothem sample (J5629).

A speleothem samples (J5629) was analysed by the Plasma Trace 2 instrument and by alpha spectrometry. The results obtained allow comparison of the two measurement techniques. The speleothem sample was prepared using 0.5 g and 10 g for analysis by Plasma Trace 2 and alpha spectrometry respectively. These samples were then dissolved and the uranium and thorium separated using the dissolution/separation method described in section (2:2:1:1).

The uranium and thorium fractions from the coral and speleothem samples for alpha spectrometry analysis were electrodeposited onto stainless steel discs using the method described in section (2:2:1:2).

The uranium and thorium fractions from the coral and speleothem samples for Plasma Trace 2 analysis were made to a volume of 50 ml with 18 MΩ deionized water.
Results and discussion.

Coral reference material (RKMS).

The results for the coral reference material obtained using alpha spectrometry and the Plasma Trace 2 instrument are shown in table 5.26. The coral results show that measurement by Plasma Trace 2 and by alpha spectrometry are in agreement with each other and also with the certified coral values.

Table 5.26: Alpha spectrometry and Plasma Trace 2 results for the coral reference material (RKMS).

<table>
<thead>
<tr>
<th>Measurement</th>
<th>$^{230}$Th/$^{234}$U</th>
<th>$^{234}$U/$^{238}$U</th>
<th>Age ($\times 10^3$ yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Spectrometry</td>
<td>0.715±0.008</td>
<td>1.093±0.03</td>
<td>133±3</td>
</tr>
<tr>
<td>Plasma Trace 2</td>
<td>0.688±0.03</td>
<td>1.085±0.02</td>
<td>124 (113-133)</td>
</tr>
<tr>
<td>Certified Value</td>
<td>0.709±0.025</td>
<td>1.098±0.029</td>
<td>131±9</td>
</tr>
</tbody>
</table>

Speleothem (J5629).

The results for the speleothem sample obtained using alpha spectrometry and the Plasma Trace 2 instrument are shown in table 5.27. The alpha spectrometry and Plasma Trace 2 results for the (J5629) sample of 207 (range 186-231) years and 193 (range 181-205) years respectively show agreement between the two counting methods.

Table 5.27: Alpha spectrometry and Plasma Trace 2 results for the speleothem sample (J5629).

<table>
<thead>
<tr>
<th>Measurement</th>
<th>$^{234}$U/$^{238}$U</th>
<th>$^{230}$Th/$^{234}$U</th>
<th>Age ($\times 10^3$ yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Spectrometry</td>
<td>1.131 ± 0.032</td>
<td>0.875 ± 0.033</td>
<td>207 186-231</td>
</tr>
<tr>
<td>Plasma Trace 2</td>
<td>1.1662 ± 0.03</td>
<td>0.8583 ± 0.020</td>
<td>193 ± 12</td>
</tr>
</tbody>
</table>

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In conclusion, the results for the coral reference material and the speleothem sample show that the results obtained by the Plasma Trace 2 were comparable with those obtained by alpha spectrometry. The difference between the two measurement techniques was their limit of detection. The limit of detection for alpha spectrometry is dependent on the count time, the background and the counting efficiency of the detectors. The error on the counts by alpha spectrometry is determined by taking the square root of the counts. Therefore, to obtain good counting statistics, the number of counts should ideally be in the 1000's. i.e for 100 counts the error is 10%, for 1000 counts the error is 3.2% and for 10000 counts the error is 1%. The background of the low level detectors used was 10 counts/week for $^{238}$U and their counting efficiency was 30%. For a count time of 1 week to obtain 1000 counts the activity required in the sample (LOD) is 0.05Bq. The LOD can be reduced by increasing the count time. The LOD for the Plasma Trace 2 instrument was dependent on the level of uranium and thorium in the reagents used and was in the $10^{-4}$ to $10^{-5}$ Bq range. The experiments have demonstrated that the Plasma Trace 2 instrument enabled the analysis of lower levels of uranium and thorium.
In conclusion the results from the uraninite experiments showed that the measured $^{234}\text{U}/^{238}\text{U}$ and the $^{230}\text{Th}/^{234}\text{U}$ ratios suffered from mass bias effects which produced low $^{234}\text{U}/^{238}\text{U}$ and high $^{230}\text{Th}/^{234}\text{U}$ ratios.

The $^{230}\text{Th}/^{232}\text{Th}$ experiments demonstrated that the presence of $^{232}\text{Th}$ at the 10 and 20 ppb level affected the observed $^{230}\text{Th}$ counts.

The coral and speleothem reference materials, after correction for mass bias using the uraninite results, were in agreement with the certified values.

The detrital correction leachate and total dissolution techniques enabled correction of detritally contaminated samples.

The comparison of the Plasma Trace 2 and alpha spectrometry results were in agreement with the alpha spectrometry results. Use of the Plasma Trace 2 enabled a lower limit of detection than those obtained by alpha spectrometry and a reduction in the analysis time.
CHAPTER 6

DETERMINATION OF URANIUM IN URINE.
(6:1) INTRODUCTION TO URANIUM IN URINE
EXPERIMENTS.

The work described in this chapter was undertaken at the request of EIChroM Industries. EIChroM requested an investigation into the alleged problem of variable uranium recovery values found by a number of laboratories analysing for gross alpha in urine. The possible causes of the variable recovery may include operator error, problems with the sample preparation method, variations within and between batches of the TRU resin columns and finally the urine samples. The sample preparation/separation methods (methods A, B, C and D) were chosen from a laboratory with no reported uranium recovery problems (method A), a laboratory with frequent reported uranium recovery problems (method B) and laboratories with occasional reported uranium recovery problems (methods C and D). The sample preparation/separation methods were evaluated ‘blind’ without knowledge of which methods had problems.

The following experiments were undertaken:

As precipitation source preparation methods had not been used previously by the author, the initial investigation was undertaken to ensure that the precipitation method was carried out correctly and that reproducible uranium sources were prepared using the cerium fluoride precipitation technique described in method A. A second cerium fluoride technique described by EIChroM and the lanthanum fluoride technique described in methods C and D were also investigated to ensure that similar uranium recoveries were obtained for all three source preparation techniques. These experiments were carried out to choose the precipitation source preparation method for use in the uranium in urine experiments. The four sample preparation/separation methods (Methods A, B, C and D) were evaluated using a synthetic urine sample spiked with $^{233}$U and pre-prepared TRU resin columns.

The four preparation/separation methods were then evaluated using a real urine sample spiked with $^{233}$U and columns from TRU resin batch TR8B. Further
experiments with method B were undertaken to investigate the hydrolysis stage in greater detail.

Finally, the possibility of using electrodeposition as the source preparation step with method A was investigated.
(6:2) SOURCE PREPARATION.

(6:2:1) Experimental.

Initially the sources were prepared using precipitation techniques. This was because the electrodeposition methods can be sensitive to the presence of interferences. These interferences (e.g. iron, aluminium, and organics) can either inhibit deposition of uranium or produce thick sources. The precipitation methods use co-precipitation of the uranium from solution with a small amount of inactive carrier (cerium or lanthanum) to produce the source. Three precipitation methods were evaluated; the cerium fluoride technique as included in method A, the cerium fluoride technique described by ElChroM Industries and a lanthanum fluoride technique included in methods C and D.

Reagents.

All reagents used were of analytical grade. The reagents used were; hydrochloric acid, ammonia, hydrofluoric acid, deionized water, titanium chloride solution (1.9M titanium (III) chloride in 2M hydrochloric acid), titanium (III) chloride (10 wt% solution in 20-30 wt% hydrochloric acid), cerium chloride (50mg/l) solution, cerium carrier (0.155g cerium nitrate hexahydrate in 100ml of deionized water), lanthanum chloride solution (lanthanum oxide 0.117g in 1000ml of 0.2M hydrochloric acid), 0.1M ammonium oxalate, and $^{233}U$ tracer solution (2Bq/ml).

Apparatus.

Whatman cellulose acetate membrane (diameter 25mm, pore size 0.2 μm), ash free filter paper, filter system, vacuum pump, centrifuge, centrifuge tubes, PTFE beakers, glass beakers, watch-glasses, hot-spot furnace, hotplate/stirrers, heat lamps, glass bumping stones, porcelain crucibles, stainless steel discs, 25ml column extender.
Measurement.

The prepared uranium sources were counted by alpha spectrometry and gross alpha counting. The alpha spectrometry determinations were conducted using a 7401 model alpha spectrometer (Canberra Packard) fitted with passivated ion implanted planar silicon detector (PIPS) with an active surface area of 450mm². The spectrometer was connected to personal computer fitted with a TRUMP-8k-W3 multichannel analyser plug in card (EG&G Ortec). Gross alpha determinations were conducted using a FAG low background gas flow proportional counter with a FAG digital ratemeter FHT 1100.


The precipitation technique described in method A was repeated six times.

Method.

Ammonium oxalate solution 0.1M (10ml) was placed in a 150ml PTFE beaker, 1ml of $^{233}$U tracer solution added and the resulting solution diluted to 50ml with deionized water. The solution was stirred gently and its pH adjusted to pH 2 by the addition of concentrated ammonia. Titanium chloride solution (200µl) was then added to reduce the $\text{U (VI)}$ to $\text{U (IV)}$. The resulting solution was yellow and after 10 to 15 minutes a decolorisation of the solution was observed. Cerium chloride solution (1ml) was added while stirring. After one minute 1ml of hydrofluoric acid was added. The solution was then stirred for a minute and left to stand for 15 minutes. The precipitate formed was then isolated by filtering through a Whatman cellulose acetate membrane. The filter and filter paper were rinsed with deionized water. The filter paper was then glued onto a stainless steel disc and dried under a heat lamp. The uranium source was then counted by alpha spectrometry and gross alpha counting.
(6:2:1:2) Cerium fluoride precipitation technique 2.

The precipitation technique described by EIChroM industries was repeated twice.

Method.

Ammonium oxalate solution 0.1M (10ml) was placed in a 150ml PTFE beaker, 1ml of $^{233}$U tracer solution added and the resulting solution diluted to 50ml with deionized water. Titanium (III) chloride, 10wt% solution in 20-30wt% hydrochloric acid, (0.5ml were added to the uranium solution in the 150 ml PTFE beaker and stirred for 15 minutes. Cerium carrier solution (0.2ml) was added to the solution while stirring and after one minute 1ml of hydrofluoric acid was added. The solution was stirred for a further minute and left to stand for 30 minutes. The precipitate formed was isolated by filtering, dried and counted as described in section (6:2:1:1).

(6:2:1:3) Lanthanum fluoride precipitation technique.

The precipitation technique described in methods C and D was repeated five times.

Method.

Ammonium oxalate solution 0.1M (10ml) was placed in a 150ml PTFE beaker, 1ml of $^{233}$U tracer solution added and the resulting solution diluted to 50ml with deionized water. To the uranium solution, 0.1ml of titanium chloride were added while stirring. The pH was adjusted to pH 1.3 with ammonia. Lanthanum chloride solution (1ml) and hydrofluoric acid (1ml) were then added while stirring the solution. The solution was left to stand for 10 minutes then filtered, counted and dried as described in section (6:2:1:1).
(6:2:2) Results and discussion.

(6:2:2:1) Cerium fluoride precipitation technique 1.

The results in table 6.01 for the cerium fluoride co-precipitation method 1 show average count rates of 0.279 and 0.781 cps for alpha spectrometry and gross alpha counting respectively. The standard deviation on the six repeat analyses of ±0.008 and ±0.030 for alpha spectrometry and gross alpha counting respectively show that this source preparation method produces repeatable uranium sources.

Table 6.01: Results for cerium fluoride precipitation technique 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alpha spectrometry</th>
<th>Gross Alpha</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Count rate (cps)</td>
<td>Count rate (cps)</td>
</tr>
<tr>
<td>1</td>
<td>0.274</td>
<td>0.756</td>
</tr>
<tr>
<td>2</td>
<td>0.283</td>
<td>0.823</td>
</tr>
<tr>
<td>3</td>
<td>0.290</td>
<td>0.795</td>
</tr>
<tr>
<td>4</td>
<td>0.275</td>
<td>0.792</td>
</tr>
<tr>
<td>5</td>
<td>0.267</td>
<td>0.738</td>
</tr>
<tr>
<td>6</td>
<td>0.285</td>
<td>0.779</td>
</tr>
<tr>
<td>Mean</td>
<td>0.279</td>
<td>0.781</td>
</tr>
<tr>
<td>SD</td>
<td>±0.008</td>
<td>±0.030</td>
</tr>
</tbody>
</table>

(6:2:2:2) Cerium fluoride precipitation technique 2.

The results in table 6.02 for the cerium fluoride co-precipitation technique 2 show average count rates of 0.281 ±0.007 and 0.774 ±0.035 cps for alpha spectrometry and gross alpha counting respectively. These two results show that uranium sources are being produced with similar efficiency to the first cerium fluoride precipitation technique.

Table 6.02: Results for cerium fluoride precipitation technique 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alpha spectrometry</th>
<th>Gross Alpha</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Count rate (cps)</td>
<td>Count rate (cps)</td>
</tr>
<tr>
<td>1</td>
<td>0.286</td>
<td>0.749</td>
</tr>
<tr>
<td>2</td>
<td>0.276</td>
<td>0.798</td>
</tr>
<tr>
<td>Mean</td>
<td>0.281</td>
<td>0.774</td>
</tr>
<tr>
<td>SD</td>
<td>±0.007</td>
<td>±0.035</td>
</tr>
</tbody>
</table>
(6:2:2:3) Lanthanum fluoride precipitation technique.

The results in table 6.03 for the lanthanum fluoride co-precipitation technique show average count rates of $0.284 \pm 0.007$ and $0.746 \pm 0.035$ cps for alpha spectrometry and gross alpha counting respectively. These results are comparable with those obtained by the two cerium fluoride co-precipitation techniques and demonstrate that this technique produces reproducible uranium sources.

Table 6.03: Results for lanthanum fluoride precipitation technique.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alpha spectrometry Count rate (cps)</th>
<th>Gross Alpha Count rate (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.286</td>
<td>0.718</td>
</tr>
<tr>
<td>2</td>
<td>0.279</td>
<td>0.759</td>
</tr>
<tr>
<td>3</td>
<td>0.285</td>
<td>0.732</td>
</tr>
<tr>
<td>4</td>
<td>0.279</td>
<td>0.748</td>
</tr>
<tr>
<td>5</td>
<td>0.289</td>
<td>0.772</td>
</tr>
<tr>
<td>Mean</td>
<td>0.284</td>
<td>0.746</td>
</tr>
<tr>
<td>SD</td>
<td>$\pm 0.004$</td>
<td>$\pm 0.021$</td>
</tr>
</tbody>
</table>

In conclusion the results demonstrate that all three precipitation techniques produced reproducible uranium sources. Comparison of the means demonstrates no difference between the methods. The initial cerium fluoride precipitation technique was chosen as the source preparation step for the remaining experiments because this precipitation technique simplifies and standardizes the source preparation step.
(6:3) EVALUATION OF THE FOUR SAMPLE PREPARATION/SEPARATION METHODS WITH SYNTHETIC URINE SOLUTION.

The four sample preparation methods have been labelled methods A, B, C, and D for convenience. The basic steps in the four sample preparation/separation methods are shown in table 6.04. Methods A and C are gross alpha determination methods and methods B and D are individual alpha determination methods using alpha spectrometry. As stated all four sample preparation/separation methods were evaluated using $^{233}$U spiked synthetic urine solutions. A 100ml fraction of the synthetic urine solution was analyzed as this was equivalent to a 24 hour urine sample. The following experiments were undertaken:

Method A (section 6:3:1:1) with TRU resin columns from batch TR8B. The analysis was repeated 12 times.

The experiments were then repeated using three TRU resin columns from the following three TRU resin column batches (TR6D, TR7A and TR8C).

Method B (section 6:3:1:2) with a TRU resin column from batch TR8B. The analysis was repeated three times.

Method C (section 6:3:1:3) with a TRU resin column from batch TR8B. The analysis was repeated three times.

Method D (section 6:3:1:4) with a TRU resin column from batch TR8B. The analysis was repeated three times.
Table 6.04: Table showing the main steps in preparation/separation methods A, B, C and D.

<table>
<thead>
<tr>
<th>Method</th>
<th>Method A</th>
<th>Method B</th>
<th>Method C</th>
<th>Method D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of method</td>
<td>Gross Alpha</td>
<td>Individual alpha determination</td>
<td>Gross Alpha</td>
<td>Individual alpha determination</td>
</tr>
<tr>
<td></td>
<td>Mineralization at 900°C.</td>
<td>Mineralization at 500°C.</td>
<td>Mineralization at 500°C.</td>
<td>Mineralization at 500°C.</td>
</tr>
<tr>
<td></td>
<td>Redissolution with 1.4M nitric acid.</td>
<td>Redissolution with concentrated nitric acid then dilution to 1.6M.</td>
<td>Redissolution with 2M nitric acid.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filtration</td>
<td>Filtration</td>
<td>Filtration</td>
<td>Filtration</td>
</tr>
<tr>
<td></td>
<td>Coprecipitation (x2)</td>
<td>Redissolution with concentrated nitric acid/sodium nitrite.</td>
<td>Redissolution with 8M nitric acid.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Redissolution with 4M nitric acid/aluminium nitrate/ferrous sulphamate.</td>
<td>Redissolution with concentrated nitric acid/aluminium nitrate/sodium nitrite.</td>
<td>Separation steps</td>
<td>TRU resin column</td>
</tr>
</tbody>
</table>
(6:3:1) Experimental.

Reagents.

All reagents used were of analytical grade. The reagents used were; nitric acid, hydrochloric acid, ammonia, hydrofluoric acid, phosphoric acid, deionized water, titanium chloride solution (1.9M titanium chloride in 2M hydrochloric acid), titanium (III) chloride (10 wt% solution in 20-30 wt% hydrochloric acid.), cerium chloride (50mg/l) solution, cerium carrier (0.155g cerium nitrate hexahydrate in 100ml of deionized water), lanthanum chloride solution (lanthanum oxide 0.117g in 1000ml of 0.2M hydrochloric acid), 0.1M ammonium oxalate, 2M aluminium nitrate, octanol ferrous (II) sulphate solution (0.3g ammonium sulphate, 0.3g ferrous sulphamate in 10ml of 2M nitric acid), sodium nitrite, iron (III) chloride (59-61% w/v FeCl₃), ²³³U tracer solution (2Bq/ml), ((Biorad AG 1-X8) 100-200 mesh chloride form), TRU resin columns and TEVA resin columns.

A synthetic urine solution was prepared by dissolving 25g of sodium dihydrogen orthophosphate hydrate, 9g of sodium chloride, 7.5g of calcium chloride dihydrate in 980ml of deionized water. Concentrated nitric acid (2-3 ml) was added to ensure the solution was clear, and the solution made to 1000ml with deionized water.
**Method A.**

Method A is a gross alpha determination method consisting of four main steps. Initially the uranium is concentrated from solution by co-precipitation with calcium phosphate. The calcium phosphate precipitate is then mineralized by heating at 900°C in a hotspot oven. The resulting residue is then dissolved using 4M nitric acid and the uranium extracted from the solution using a TRU resin column.

**Method.**

Nitric acid (10ml of 8M) and 1ml of the $^{233}$U (2Bq/ml) tracer solution were added to a 100ml aliquot of the synthetic urine in a 600ml glass beaker. The solution was then heated to boiling on a hotplate. The calcium phosphate was then precipitated with concentrated ammonia and left to stand overnight. The solution was filtered using ash free filter paper and the filter and beaker rinsed with 10% ammonia solution.

The precipitate was transferred to a porcelain crucible and placed in a hotspot furnace. The temperature was increased in steps up to 900°C over a two hour period, ashed at 900°C for 8 hours and then allowed to cool. To achieve complete dissolution in a minimum volume the resulting residue was dissolved in 20ml of 4M nitric acid whilst gently heating.

The resulting solution was then transferred into a 50ml centrifuge tube, the porcelain crucible rinsed once with 5ml deionized water and twice with 5ml of 4M nitric acid. Aluminium nitrate, 10ml of 2M, were added to the centrifuge tube. The solution was shaken, 1ml of the iron (II) sulphate solution added, shaken, left to stand for 10 minutes and then centrifuged at 4500 or 3000 rpm for ten minutes.

The uranium was isolated using a TRU resin column that had been conditioned with 5ml of the 4M nitric acid/0.5M aluminium nitrate solution. The sample was added to the TRU column. The TRU column was then washed with 5ml of 4M
nitric acid / 0.5M aluminium nitrate solution, 5ml of 4M nitric acid then with 10ml of 4M nitric acid. A 150ml PTFE beaker was placed under the column and the uranium eluted from the column with 10ml of 0.1M ammonium oxalate.

Deionized water (40ml) was added to the PTFE beaker and the source prepared using the method described in section (6:2:1:1). The resulting uranium source was then counted using alpha spectrometry and gross alpha counting.


Method A (section 6:3:2:1) was used for the analysis of $^{233}$U spiked synthetic urine solution with TRU resin columns from batch TR8B. The analysis was repeated 12 times.

(6:3:1:1:2) Method A with different batch TRU columns.

The method described in section (6:3:1:1) was used to analyse the $^{233}$U spiked synthetic urine solution using three TRU resin columns from each of the following three TRU resin column batches (TR6D, TR7A and TR8C).
(6:3:1:2) Method B.

Method B differs from method A in that it separates uranium from other alpha emitters. The method has the following steps: initially the uranium is concentrated from solution by evaporation; the resulting residue is then mineralized in a hotspot oven for 6 hours at 500°C; the residue is then re-dissolved, filtered, and the uranium co-precipitated from solution with iron phosphate; the uranium is then passed through an anion exchange column to isolate the uranium, americium, curium and some thorium from the plutonium; a TEVA resin column is then used to separate the uranium, americium, and curium from thorium. Finally, the uranium is separated from americium and curium using a TRU resin column.

Method.

Octanol (5 drops), concentrated nitric acid (10ml), hydrogen peroxide and (5ml), and a few glass anti-bumping stones were added to the synthetic urine solution. The solution was then spiked with 1ml of $^{233}$U tracer solution. The solution was then evaporated to dryness on a hotplate. The resulting residue was cooled then re-dissolved in 50ml of concentrated nitric acid. The solution was transferred to a porcelain crucible and evaporated to dryness, heated at 500°C for 6 hours in a hotspot furnace and then allowed to cool. The residue was dissolved in 100ml of 1.4M nitric acid. A watch glass was added to the top of the crucible and the solution heated for 30 minutes. The solution was then allowed to cool.

Next the solution was filtered through a cellulose acetate membrane. The filtrate was then precipitated with iron phosphate by adding 1ml of ferric iron solution (30mg/ml), 3ml of concentrated phosphoric acid and diluting to 200ml with deionized water. The pH was adjusted to pH 4 with ammonia. The precipitate was allowed to settle and centrifuged at 2000rpm for fifteen minutes. The precipitate was then dissolved in 10ml of concentrated nitric acid, sodium nitrite (0.1g) was added to the solution, stirred, and left to stand overnight this was designated (Solution B.)
Solution B was then passed through a 2ml anion exchange column. The column was conditioned using 20ml of 8M nitric acid. A beaker was placed under the column and the load solution was then added, the centrifuge tube was rinsed with 5ml of 8M nitric acid and the column washed with 5ml of 8M nitric acid. The collected load and wash solutions were designated (solution B\textsubscript{ii}).

Solution B\textsubscript{ii} was loaded onto a 2ml TEVA column preconditioned with 5ml of 8M nitric acid. The column was then washed with 5ml of 8M nitric acid. The resulting solution was designated (solution B\textsubscript{iii}).

Solution B\textsubscript{iii} was loaded onto a TRU resin column conditioned with 5ml of 8M nitric acid. The column was then washed with 5ml of 8M nitric acid, twice with 10ml of 1M nitric acid. A 150ml PTFE beaker was placed under the column and the uranium was then eluted with 10ml of ammonium oxalate solution.

The uranium source was then prepared using the cerium fluoride method described in section (6:2:1:1). The uranium source was then counted by alpha spectrometry and gross alpha counting.
(6:3:1:3) Method C.

Method C like method A is a gross alpha determination method. The sample preparation method involves concentration from solution by evaporation, ashing at 500°C (as method B), then co-precipitation from solution with calcium phosphate, and the uranium extracted using TRU resin (as method A).

Method.

Octanol (5 drops), 1ml of calcium solution (100μg/ml), concentrated nitric acid (10ml), hydrogen peroxide (5ml) and a few glass bumping stones were added to the synthetic urine solution. The solution was then spiked with 1ml of 233U tracer solution. A watch glass was placed on the beaker and the synthetic urine solution heated on a hotplate for 1hour. The watch glass was then removed and the solution evaporated to dryness.

The resulting residue was cooled and re-dissolved in 50ml of 1.4M nitric acid. The solution was transferred to a porcelain crucible, heated at 500°C for 6 hours in a hotspot furnace, and then allowed to cool. The residue was re-dissolved with 10ml of concentrated nitric acid, transferred to a 600ml beaker and diluted to 100ml with deionized water. The beaker was covered with a watch glass and heated gently for 30 minutes on a hotplate then allowed to cool. The sample was filtered through a 47mm porosity, 0.22μm millipore filter and the beaker and funnel and rinsed with a few ml of deionized water.

The resulting filtrate solution was then made to a volume of 100ml with deionized water and the phosphate precipitated by the addition of 25ml of concentrated ammonia solution. The precipitate was allowed to settle for 15 minutes and then centrifuged for 15 minutes at 2000rpm. The precipitate was then dissolved in 2ml of concentrated nitric acid, 15ml of 2M aluminium nitrate and 1ml of iron (II) sulphate solution were then added, the solution shaken, and left to stand for 15 minutes.

The uranium was then separated using the TRU resin column. The column had
been conditioned using 5ml of 1M nitric acid. The sample was added and the column washed with 5ml of 1M nitric acid. The column was next washed with two 5ml of 1M nitric acid. A 150ml PTFE beaker was placed under the column and the uranium eluted with 10ml of 0.1M ammonium oxalate.

The uranium source was then prepared using the cerium fluoride method described in section (6.2:1:1). The uranium source was then counted by alpha spectrometry and gross alpha counting.
(6:3:1:4) Method D.

Method D like method B uses three columns to separate uranium, thorium, and plutonium so that individual alpha determinations can be made. The sample preparation method has similarities to methods B and C. The uranium is then concentrated from solution by evaporation, ashed in a hotspot furnace at 500°C, re-dissolved in nitric acid, filtered, coprecipitated from solution using calcium phosphate and then iron phosphate steps. The uranium is then isolated using anion exchange, TEVA resin and TRU resin columns.

Experimental.

Concentrated nitric acid (10ml), hydrogen peroxide (1ml), calcium chloride solution (2ml), and $^{233}$U tracer (1ml) were added to the synthetic urine solution. The beaker was then placed on a hotplate, the solution evaporated to dryness and allowed to cool. Concentrated nitric acid (200ml) were then added, the solution transferred to a porcelain crucible and evaporated to dryness. The residue was then heated at 500°C for 5 hours in a hotspot furnace and allowed to cool. 2M nitric acid (100ml) were added to the residue, a watch glass added to the crucible and the solution heated to boiling for 30 minutes. The solution was filtered using a cellulose acetate filter with a porosity of 0.45 μm, transferred to a 600ml beaker and diluted to 500ml with deionized water. The solution was stirred while 40ml of concentrated ammonia were added. The resulting precipitate was left overnight and then centrifuged for 10 minutes at 2500 rpm. The residue was dissolved in 50ml of 4M hydrochloric acid and 0.2 ml of the calcium chloride solution added.

The uranium was co-precipitated with iron phosphate using the following procedure: the sample was diluted to 100ml with deionized water. Phosphoric acid 1M (0.5ml) and iron (III) chloride (0.1ml) added and the pH adjusted to pH 4; the sample was centrifuged and the residue dissolved with 40ml of 8M nitric acid, the solution was then passed through an anion exchange column to separate the uranium from plutonium.
The anion exchange resin was prepared using the following method. Anion exchange resin (100g) was placed in a litre beaker and 800ml of deionized water added, the resin stirred occasionally and left for 48 hours. The water was then removed 800ml of 1M nitric acid added and the resin stirred occasionally for 4 hours. The 1M nitric acid was removed, the resin covered with 8M nitric acid, sodium nitrite (0.1g) added and the resin left to stand for 3 hours. The anion exchange column was prepared by adding 1.6-1.8ml of the resin to a 40mm height, 10mm diameter column. The sample was loaded and the column washed with 10ml 8M nitric acid. This solution contained uranium, americium, curium and some thorium. This solution was designated (solution D.).

Solution D, was then loaded onto a TEVA resin column conditioned with 5ml of 8M nitric acid. The column was then rinse with 5ml 8M nitric acid. The combined load and wash solutions contained uranium, americium and curium. This solution was designated (solution Dii).

Solution Dii was then loaded onto a TRU Resin column conditioned with 5ml of 8M nitric acid. The column was then washed with 5ml of 8M nitric acid. The load and wash solutions contained the americium and curium. The column was then washed with 10ml of 1M nitric acid. A 150ml PTFE beaker was placed under the column and the uranium eluted from the column with 10ml of 0.1M ammonium oxalate.

The uranium source was then prepared using the cerium fluoride precipitation method described in section (6:2:1:1). The uranium source was then counted by alpha spectrometry and gross alpha counting.
(6.3.2) Results and discussion.

(6.3.2.1) Method A.

(6.3.2.1.1) Method A with TR8B batch TRU columns.

The results for method A with the TR8B batch of TRU resin columns are shown in table 6.05. These results show average uranium recoveries from the synthetic urine solution of 87% and 86% by alpha spectrometry and gross alpha counting respectively. The results obtained by both counting techniques are in agreement. The results show that the uranium recoveries from synthetic urine using method A with columns from batch TR8B are repeatable with standard deviations of ± 7% and ± 6% obtained for alpha spectrometry and gross alpha counting respectively.

Table 6.05: Results for method A with synthetic urine, $^{233}$U and TR8B columns.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alpha spectrometry Recovery (%)</th>
<th>Gross Alpha Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>84</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>77</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>94</td>
<td>91</td>
</tr>
<tr>
<td>5</td>
<td>88</td>
<td>88</td>
</tr>
<tr>
<td>6</td>
<td>92</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>89</td>
<td>88</td>
</tr>
<tr>
<td>8</td>
<td>95</td>
<td>89</td>
</tr>
<tr>
<td>9</td>
<td>92</td>
<td>92</td>
</tr>
<tr>
<td>10</td>
<td>87</td>
<td>84</td>
</tr>
<tr>
<td>11</td>
<td>93</td>
<td>92</td>
</tr>
<tr>
<td>12</td>
<td>77</td>
<td>74</td>
</tr>
<tr>
<td>Mean</td>
<td>87</td>
<td>86</td>
</tr>
<tr>
<td>SD</td>
<td>±7</td>
<td>±6</td>
</tr>
</tbody>
</table>

Tables 6.06, 6.07 and 6.08 show the uranium recoveries for method A using different batches of column resins.

The results for TR6D batch columns are shown in table 6.06. These results show average uranium recoveries from the synthetic urine solution of 81±16% and 73±11.5% for alpha spectrometry and gross alpha counting respectively. These results agree with the uranium recoveries of 87±7 and 86±5 for alpha spectrometry and gross alpha counting respectively obtained in previous experiments using TRU resin batch TR8B.

Table 6.06: Results for method A with synthetic urine, $^{233}$U and TR6D batch TRU columns.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alpha spectrometry Recovery (%)</th>
<th>Gross Alpha Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>89</td>
<td>77</td>
</tr>
<tr>
<td>2</td>
<td>91</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>62</td>
<td>60</td>
</tr>
<tr>
<td>Mean</td>
<td>81</td>
<td>73</td>
</tr>
<tr>
<td>SD</td>
<td>±16</td>
<td>±12</td>
</tr>
</tbody>
</table>

The results for TR7A batch columns are shown in table 6.07. These results show average uranium recoveries from the synthetic urine solution of 72±23% and 67±17% for alpha spectrometry and gross alpha counting respectively. The results from the two measurement techniques are in agreement and indicate that the TR7A resin columns have reproducible but lower uranium recovery than the 80% recoveries obtained with the TR8B and TR6D batches.

Table 6.07: Results for method A with synthetic urine, $^{233}$U and TR7A batch TRU columns.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alpha spectrometry Recovery (%)</th>
<th>Gross Alpha Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>88</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>Mean</td>
<td>71.5</td>
<td>67</td>
</tr>
<tr>
<td>SD</td>
<td>±23</td>
<td>±17</td>
</tr>
</tbody>
</table>

The results for TR8C batch columns are shown in table 6.08. These results show that the first and third column from batch TR8C gave an average uranium
recovery from the synthetic urine solution of 78±11% and 75±13 for alpha spectrometry and gross alpha counting respectively. These results agree with the uranium recoveries of approximately 80% obtained for the other TRU column batches.

The uranium recovery for the second column from the TR8C batch of approximately 23% was much lower than the expected 80%. This low uranium recovery indicates that there was a particular problem with column 2. Further experiments using TRU columns from this batch would be needed to establish whether the results for columns 1 and 3 or the result for column 2 were representative for this particular batch of columns.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alpha spectrometry Recovery (%)</th>
<th>Gross Alpha Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70</td>
<td>66</td>
</tr>
<tr>
<td>2</td>
<td>23</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>86</td>
<td>84</td>
</tr>
<tr>
<td>Mean (with sample 2)</td>
<td>60</td>
<td>57</td>
</tr>
<tr>
<td>Mean (without sample 2)</td>
<td>78</td>
<td>75</td>
</tr>
<tr>
<td>SD (with sample 2)</td>
<td>±33</td>
<td>±32</td>
</tr>
<tr>
<td>SD (without sample 2)</td>
<td>±11</td>
<td>±13</td>
</tr>
</tbody>
</table>

The initial conclusion from these experiments are that method A reproducibly extracts 80% of the uranium from the synthetic urine solution using TRU resin columns from batch TR8B.

The experiments with the synthetic urine solution and different batches of TRU resin columns indicated that there was little difference between the batches of TRU resin columns. The experimental results for the TR8C batch indicate that within column batches problems with particular columns may occur.
(6:3:2:2) Method B.

The results obtained for method B are shown in table 6.09. These results show that for the synthetic urine solution and the TR8B batch of TRU resin columns average uranium recoveries of 38±7 and 37±5% were observed by alpha spectrometry and gross alpha counting. These values are reproducible but lower than the average uranium recoveries of 87±7% and 86±6% obtained with method A. This reduction in the uranium recovery was due to losses in either the sample preparation or sample separation stages.

Table 6.09: Results for method B with synthetic urine, $^{233}$U and TR8B columns.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alpha spectrometry Recovery (%)</th>
<th>Gross Alpha Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45</td>
<td>37</td>
</tr>
<tr>
<td>2</td>
<td>36</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>32</td>
<td>28</td>
</tr>
<tr>
<td>Mean</td>
<td>38</td>
<td>37</td>
</tr>
<tr>
<td>SD</td>
<td>±7</td>
<td>±5</td>
</tr>
</tbody>
</table>

(6:3:2:3) Method C.

The results obtained for method C with the synthetic urine solution and TRU columns from batch TR8B are shown in table 6.10. These results show an average uranium recoveries of 93±6% and 94±3% obtained by alpha spectrometry and gross alpha counting respectively. The standard deviations of ±6% and ±3% show that reproducible uranium results were obtained. These results are in agreement with those obtained by method A (87±7 and 86±6). The results show that the sample preparation method used in method C enables 93% of the uranium to be extracted from the synthetic urine solution by the TRU resin column. This experiment demonstrates that the similar sample preparation method used in method B was not responsible for the low uranium recovery obtained with method B.
The results obtained for method D are shown in table 6.11. These results show that the uranium recoveries of 75±1% and 69±4% obtained by alpha spectrometry and gross alpha counting respectively are in agreement with those obtained by method A (87±7 and 86±6) and method C (93±6% and 94±3%). The uranium recoveries were slightly lower but this would be expected as the sample separation method used in method D has more steps (3 columns) and so more opportunities for uranium losses.

In conclusion these results show that methods A, C and D with the TR8B TRU resin columns are capable of reproducibly extracting 70-90% of the uranium from the synthetic urine solution.

The results show that both the sample preparation methods are capable of preparing the synthetic urine solution so 80% could subsequently be extracted by the TRU resin.

The lower uranium recoveries for method D can be explained as the separation...
step contains 3 columns in comparison with the 1 column used with methods A and C.

The results for method B with the TR8B resin columns show that the method reproducibly extracts 37% of the uranium from the synthetic urine. This lower recovery of uranium from the synthetic urine indicates a possible problem within method B. The problem was likely to be with the separation stage of the method as the similar sample preparation methods described in methods C and D had comparable recoveries with method A. The separation stage and in particular the anion exchange column stage of method B was the most likely source of uranium loss as this was the step in which method B differed from method D.
Evaluation of the Four Sample Preparation/Separation Methods with Real Urine Sample.

Sample preparation/separation methods (A, B, C and D) were evaluated three times using a real urine solution (spiked with $^{233}$U) and TR8B batch TRU resin columns.

(6:4:1) Experimental.

The urine stock solution was prepared by combining twelve 24 hour urine samples in 1% v/v nitric acid. The urine stock solution was spiked with 15ml of the $^{233}$U (2Bq/ml) tracer solution, stirred and left to equilibrate for 48 hours. After stirring, four 1500ml aliquots were taken and analysed by each of the four sample preparation/separation methods. This sampling procedure was repeated three times. The 1500ml aliquot size was chosen as this is the average volume for a 24 hour urine sample. The sample preparation methods used are described in section (6:2:2).

Slight alterations to the methods were made with 150ml of concentrated nitric acid added to the urine sample for methods B, C, and D. Hydrogen peroxide (75ml) were added to the urine for method C and D with (15ml) added for method B.
(6:4:2) Results and discussion.

The experimental results for methods A, B, C and D are shown in tables 6.12, 6.13, 6.14 and 6.15.

(6:4:2:1) Method A.

The results for method A with real urine solution are shown in table 6.12. These standard deviations of ±4% and ±7% for alpha spectrometry and gross alpha counting respectively show that reproducible uranium recoveries were obtained. The average uranium recoveries were reduced by 12% from 87% to 75%.

In conclusion method A was capable of reproducibly analysing the synthetic and real urine solutions with high uranium recoveries.

Table 6.12: Results for method A with real urine solution, $^{233}$U and TR8B batch TRU columns.

<table>
<thead>
<tr>
<th>Method A</th>
<th>Alpha spectrometry Recovery (%)</th>
<th>Gross Alpha Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>78</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>71</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>76</td>
<td>80</td>
</tr>
<tr>
<td>Mean</td>
<td>75</td>
<td>76</td>
</tr>
<tr>
<td>SD</td>
<td>±4</td>
<td>±7</td>
</tr>
</tbody>
</table>

(6:4:2:2) Method B.

The results for method B with the real urine solution and TR8B batch TRU resin columns are shown in table 6.13. These results show an average uranium recovery of 29±1 and 26±2 for alpha spectrometry and gross alpha counting respectively. The standard deviations of ±1 and ±2 for the three analyses demonstrate that reproducible recoveries of uranium were obtained with method B.

A reduction of 8% in the uranium recovery was observed when results for the real urine solution (29%) were compared with those obtained for the synthetic urine solution (37%). This effect was also observed with method A.
Table 6.13: Results for method B with real urine solution and TR8B batch TRU columns.

<table>
<thead>
<tr>
<th>Method B</th>
<th>Alpha spectrometry Recovery (%)</th>
<th>Gross Alpha Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>28</td>
<td>26</td>
</tr>
<tr>
<td>Mean</td>
<td>29</td>
<td>26</td>
</tr>
<tr>
<td>SD</td>
<td>±1</td>
<td>±2</td>
</tr>
</tbody>
</table>

(6:4:2:3) Method C.

The results for method C with the real urine solution and TR8B batch TRU resin columns are shown in table 6.14. The three analyses generated only two results as the second real urine sample blocked the TRU resin column. The remaining two analyses generated a mean uranium recovery of 68±1 and 69±2 for alpha spectrometry and gross alpha counting respectively. The standard deviations of ±1 and ±2 for the two analyses demonstrate that reproducible recoveries of uranium were obtained with method C.

A reduction of 25% in the uranium recovery was observed when results for the real urine solution (68%) were compared with those obtained for the synthetic urine solution from (93%). This effect was also observed to a lesser extent with methods A and B.

Table 6.14: Results for method C with real urine solution and TR8B batch TRU columns.

<table>
<thead>
<tr>
<th>Method C</th>
<th>Alpha spectrometry Recovery (%)</th>
<th>Gross Alpha Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>Sample blocked column</td>
<td>Sample blocked column</td>
</tr>
<tr>
<td>3</td>
<td>69</td>
<td>67</td>
</tr>
<tr>
<td>Mean</td>
<td>68</td>
<td>69</td>
</tr>
<tr>
<td>SD</td>
<td>±1</td>
<td>±2</td>
</tr>
</tbody>
</table>

(6:4:2:4) Method D.

The results for method D with the real urine solution and TR8B batch TRU resin columns are shown in table 6.15. These results show an average uranium recovery of 44±6 and 41±6 for alpha spectrometry and gross alpha counting.
respectively. The standard deviations of ±6 and ±6 for the three analyses demonstrate that reproducible recoveries of uranium were obtained with method D.

A reduction of 31% in the uranium recovery was observed when results for the real urine solution (44%) were compared with those obtained for the synthetic urine solution of (75%). This effect was also observed with method C and to a lesser extent with methods A and B.

Table 6.15: Results for method D with real urine solution, $^{233}\text{U}$ and TRU batch TRU columns.

<table>
<thead>
<tr>
<th>Method D</th>
<th>Alpha spectrometry Recovery (%)</th>
<th>Gross Alpha Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44</td>
<td>41</td>
</tr>
<tr>
<td>2</td>
<td>38</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>46</td>
</tr>
<tr>
<td>Mean</td>
<td>44</td>
<td>41</td>
</tr>
<tr>
<td>SD</td>
<td>±6</td>
<td>±6</td>
</tr>
</tbody>
</table>

In conclusion the results for the real urine solution showed a reduction in the percentage of uranium recovery for all the four preparation/separation methods when compared with the percentage uranium recovery obtained with the synthetic urine solution.

Method A differs from the other three methods having a more vigorous ashing (900 °C) step (table 6.04). The method was capable of preparing the synthetic and real urine solutions for subsequent extraction of the uranium by TRU resin column.

Methods B, C, and D have similar sample preparation methods (table 6.04), the lower ashing temperature (500°C) and the addition of weak acid and heat to hydrolyse the pyrophosphates in the sample. The results show that the sample preparation method was suitable for the preparation of the synthetic urine solution.

The sample preparation method with the real urine solution caused a significant reduction in the uranium recovery for methods B and D. Method B and D are very similar and therefore may be expected to have similar uranium recoveries.
The lower uranium recoveries obtained for method B may be explained by differences in the preparation of the anion exchange column.

Although a reduced recovery with the real urine sample was observed with method C the addition of ferrous sulphamate/aluminium nitrate at the hydrolysis stage was observed to improve the uranium recovery when compared with methods B and D. It was decided from these results to further investigate method B by lengthening the mineralization time (from 6 hours to 18 hours) and by the addition of ferrous sulphamate during the hydrolysis step.
(6:4:3) Investigation of hydrolysis step. Method B.

The following experiments were carried out to investigate the hydrolysis step in method B in greater detail. This was achieved by comparing 6 and 18 hour ashing times and by the addition of ferrous sulphamate to the hydrolysis solution.

(6:4:3:1) Experimental.

A second urine stock was prepared by collecting eight 24 hour urine samples and spiking with 8ml of $^{233}$U (2Bq/ml) spike solution.

Eight, 1500ml aliquots were taken and analysed by the following four methods.

Two aliquots were analysed following the method described in section (6:3:2:2).

Two aliquots were analysed following the method described in section (6:3:2:2) but using an 18 hour ashing time.

Two aliquots were analysed following the method described in section (6:3:2:2) but with the addition of 1ml of ferrous sulphamate after the hydrolysis with 1.44M nitric acid.

Two aliquots were analysed following the method described in section (6:3:2:2) but with an 18 hour ashing time and with the addition of 1ml of ferrous sulphamate after the hydrolysis with 1.44M nitric acid.

With all eight experiments care was taken at the hydrolysis step to ensure that the molarity of the nitric acid was maintained at 1.44M.
(6:4:3:2) Results and discussion.

The results for the further investigation of method B are shown in tables 6.16 and 6.17.

The results for method B with 6 and 18 hour ashing times and the real urine solution 2 are shown in table 6.16. The alpha spectrometry results show average uranium recoveries of 29±6% for the 6 hour and 35% for the 18 hour ashing. The results show that increasing the ashing time from 6 to 18 hours slightly increased the percentage uranium recovered from the real urine solution (7%). The 6 hour results agree with those obtained from previous analysis of the initial real urine stock solution of approximately 27% (section 6:4:2:2).

Table 6.16: Results for method B with real urine solution. $^{233}$U and TR8B batch TRU resin columns.

<table>
<thead>
<tr>
<th>Sample / Method</th>
<th>Alpha spectrometry Recovery (%)</th>
<th>Gross Alpha Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6hr ashing step</td>
<td>33</td>
<td>27</td>
</tr>
<tr>
<td>6hr ashing step</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>18hr ashing step</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>18hr ashing step</td>
<td>35</td>
<td>27</td>
</tr>
</tbody>
</table>

The results in table 6.17 show the effect of the addition of ferrous sulphamate solution to method B with 6 and 18 hour ashing times.

The 6 hour ashing time results indicate that the addition of ferrous sulphamate to the hydrolysis solution increases the uranium recovery from the real urine solution. The average uranium recovery of 56±5.7% shows a 27.5% increase from the 28.5% obtained without the ferrous sulphamate.

The 18 hour ashing time results indicate that the addition of ferrous sulphamate to the hydrolysis solution had no effect on the uranium recovery from the real urine solution. The average uranium recovery of 34±4% agrees with the 35% obtained for 18 hour ashing time without the ferrous sulphamate.
Table 6.17: Results for method B with real urine solution, $^{233}$U and TR8B batch TRU resin columns with 1ml of ferrous sulphamate (as method A).

<table>
<thead>
<tr>
<th>Sample / Method</th>
<th>Alpha spectrometry Recovery (%)</th>
<th>Gross Alpha Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6hr ashing step</td>
<td>52</td>
<td>48</td>
</tr>
<tr>
<td>6hr ashing step</td>
<td>60</td>
<td>55</td>
</tr>
<tr>
<td>18hr ashing step</td>
<td>36</td>
<td>30</td>
</tr>
<tr>
<td>18hr ashing step</td>
<td>31</td>
<td>24</td>
</tr>
</tbody>
</table>

In conclusion the results obtained for method B with real urine solution 2 are in agreement with those obtained in previous section (section 6:4:2:2) for method B and real urine solution 1. The results show that ensuring the volume of 1.4M hydrochloric acid was maintained during the hydrolysis step had no effect the uranium recovery.

Increasing ashing time from 6 to 18 hours increased the uranium recovery by (8%).

The addition of ferrous sulphamate with a 6 hour ashing period increased the uranium recovery from 29% to 56%. The addition of the ferrous sulphamate gave method B comparable recoveries to method C of 68%. The values from method B are slightly lower (10%) but this was expected as its separation stage was more complicated (has 3 columns) compared with (1 column) for method C and so more stages from which uranium could be lost.

Increasing the ashing time with the addition of ferrous sulphamate to 18 hours did not increase the percentage of uranium recovered from 29%.
(6:5) INVESTIGATION OF ELECTRODEPOSITION AS THE SOURCE PREPARATION STEP.

(6:5:1) Experimental.

To investigate the possibility of using electrodeposition as the source preparation step, three mock urine samples were prepared and separated using method A described in section (6:3:1:1).

The resulting uranium fractions were electrodeposited using the method described in section (2:2:1:2) and counted by alpha spectrometry.

(6:5:2) Results and discussion.

When the 2ml of ammonia were added to the electrodeposition cell prior to ending the electrodeposition, the ammonia caused the co-precipitation of iron from solution. The presence of iron in the electrodeposition solution means that the counting sources can not be produced by electrodeposition as the presence of iron inhibits uranium deposition onto the stainless steel disc and produces a thick source. Electrodeposition was not a suitable source preparation step with method A.
CONCLUSION.

Method A’s sample preparation and separation method was suitable for the reproducible analysis of uranium in synthetic and real urine solutions.

Method B’s sample preparation method was improved with the addition of 1 ml of ferrous sulphamate. The substitution of the anion exchange method for that described in method D would ensure that the method was suitable for the analysis of uranium in synthetic and real urine solutions.

Method C’s sample preparation method was suitable for the reproducible analysis of uranium synthetic urine solutions.

Method D’s sample preparation method was suitable for the reproducible analysis of uranium from the synthetic urine solution. The method suffered from a reduction in the uranium recovery with the real urine solution although reproducible results were still obtained. This problem could be solved by the addition of 1 ml of ferrous sulphamate during the hydrolysis step.

In conclusion the sample preparation method described in method A was more effective at breaking down the pyrophosphates in the real urine solution than the preparation method described in methods B, C and D.

The results for the four sample preparation/separation methods showed a reduction in the uranium recovery with the real urine solution. This difference in uranium recovery would not be a problem if the samples were spiked with a radioactive tracer solution before analysis to correct for any differences in the recovery with different samples. All four methods showed consistent recoveries for the three analyses of the synthetic and real urine solutions. The results obtained by these experiments were in agreement with the observations reported by the respective laboratories that the different recoveries were due to differences in the sample preparation/separation methods and the samples analysed and not due to problems with the extraction resins or errors by the analysts.
The variable composition of urine is the most likely cause of the variation in uranium recovery. This was seen by the consistent but different recoveries of uranium for the synthetic and stock 'real' urine solutions.
CHAPTER 7

CONCLUSIONS.
The three objectives of the investigation were achieved and, as an outcome, a measurement procedure was developed which improves the limits of detection of uranium and thorium from $0.5$ to $10^{-5}$ Bq and reduces the person hours required per analysis by a factor of 80%. The amount of acidic waste generated is reduced by 50% typically.

The first objective, the evaluation of uranium and thorium separation procedure using UTEVA resin produced a result which indicated that chemical recoveries for the procedure were similar to those obtained by anion exchange but the extraction chromatography procedure provided a more rapid separation method using less reagents.

The second objective, the investigation of high resolution inductively coupled plasma mass spectrometry as an alternative measurement step to alpha spectrometry for low-level uranium and thorium samples produced a result which indicated that the technique was valid but that unless low-level measurements were required cheaper methods exist.

The third objective, the investigation into variability in uranium in urine measurements indicated that apparent inconsistencies in uranium recovery were due to variations in the samples and that consistent results are obtained for consistent samples.
(7:2) TRU RESIN.

(7:2:1) Objective 1.

The initial sorption and elution experiments with the TRU resin demonstrated the resins suitability for the sorption of uranium, thorium, americium and plutonium from nitric acid and their subsequent elution with 0.1M ammonium. This shows the TRU resins suitability for gross alpha analysis by alpha spectrometry or individual radionuclide analysis by ICP-MS.

The suitability of the TRU resin for separating uranium from thorium was then investigated. The proposed separation scheme was based on the americium in soil separation scheme developed at AEA Technology plc [183] and the separation scheme developed by Burnett et al [184]. The uranium and thorium were loaded onto the TRU resin with nitric acid. The TRU resin column was converted to the chloride form and washed with 4M hydrochloric acid (which would elute americium from the resin). The thorium was then eluted using 1M hydrochloric acid [184] and 2M hydrochloric acid. The uranium remaining on the column was then eluted with 0.1M ammonium oxalate.

In conclusion the separation scheme did not remove all the thorium from the column before the uranium was eluted causing thorium contamination in the uranium fraction. Therefore the proposed separation method using the TRU resin was not suitable for the separation of uranium from thorium. The separation method could be used in combination with anion exchange methods to separate americium from uranium, thorium and plutonium for individual measurement by alpha spectrometry.

(7:2:2) Objective 3.

The TRU resin column application for the analysis of uranium in urine was investigated in chapter 6. This work was in response to EICChroM Industries who requested an investigation into the alleged problem of variable uranium recovery values found by a number of laboratories analysing for gross alpha in urine. The
possible causes of the variable recovery may include operator error, problems with the sample preparation method, variations within and between batches of the TRU resin columns and finally the urine samples. The sample preparation/separation methods (methods A, B, C and D) were chosen from a laboratory with no reported uranium recovery problems (method A), a laboratory with frequent reported uranium recovery problems (method B) and laboratories with occasional reported uranium recovery problems (methods C and D). The sample preparation/separation methods were evaluated ‘blind’ without knowledge of which methods had problems.

In conclusion the sample preparation method described in method A was more effective at breaking down the pyrophosphates in the real urine solution than the preparation method described in methods B, C and D.

The results for the four sample preparation/separation methods showed a reduction in the uranium recovery with the real urine solution. This difference in uranium recovery would not be a problem if the samples were spiked with a radioactive tracer solution before analysis to correct for any differences in the recovery with different samples. All four methods showed consistent recoveries for the three analyses of the synthetic and real urine solutions. The results obtained by these experiments were in agreement with the observations reported by the respective laboratories that the different recoveries were due to differences in the sample preparation/separation methods and the samples analysed and not due to problems with the extraction resins or errors by the analysts. In conclusion the variable composition of urine is the most likely cause of the variation in uranium recovery. This was seen by the consistent but different recoveries of uranium for the synthetic and stock ‘real’ urine solutions.
(7:3) UTEVA RESIN.

(7:3:1) Objective 1.

The first experiments described in chapter 3 of the thesis were carried out to investigate the uranium and thorium separation method proposed by EIChroM [97] using their 2ml UTEVA resin columns. The uranium and thorium separation method [97] was also investigated using a 3M nitric acid load solution to determine the effect, if any, of removing aluminium nitrate from the load solution on the sorption/elution of uranium and thorium. Finally, the uranium, thorium separation method was then adapted for the separation of americium, plutonium, uranium, and thorium.

In conclusion the EIChroM proposed separation method separated uranium from thorium. The presence of iron did not affect the separation of the uranium and thorium as the iron was not retained by the UTEVA resin. The radionuclide interference experiments showed that radium, polonium and americium were not sorbed by the UTEVA resin. The presence of plutonium in the sample would interfere with the analysis of thorium and uranium as it was present in both fractions. In conclusion the separation scheme was suitable for the separation of uranium and thorium from mixed spike solutions and a uraninite ore reference material.

The uranium and thorium separation method with 3M nitric acid load solution produced the same results without the presence of aluminium nitrate as those obtained in section (3:2) with the aluminium nitrate present.

An americium, plutonium, uranium and thorium separation method was developed by combining the uranium, thorium separation method [97] with EIChroMs americium, plutonium and uranium separation method [187]. The method differed from the uranium thorium separation method as the load solution contained ascorbic acid and ferrous sulphamate which converted the plutonium (IV) to plutonium (III) which was not retained by the UTEVA column. The method was evaluated using uraninite ore and spike solutions.
The two separation methods were further evaluated in chapter 4 using real samples to ensure that separation was not affected by matrix interferences found in environmental and geological samples (and not in the spike solutions). The results from analyses of the uraninite, coral, Mirhib well water, Malham Tarn and Pinabasi basin samples showed that the uranium, thorium separation method separated the uranium and thorium producing accurate and repeatable results. The results for the uraninite ore, granite and sediment reference materials show that the uranium, thorium, americium and plutonium separation method was suitable for analysis of difficult sample matrix samples and that the separation methods are suitable for the analysis of a range of environmental samples.

The two developed separation methods offered the advantages of reducing the separation time and the volume of reagents required.
Objective 2.

The research also evaluated a high resolution inductively coupled plasma mass spectrometer instrument (PlasmaTrace 2) for the measurement of low-levels of uranium and thorium. As the manufacturers claimed the instrument could measure uranium at the ppq level.

The instrument was evaluated using reagent and groundwater blanks, uraninite ore solution, coral and speleothem reference materials. After the evaluation, the instrument was then used to analyse further speleothem and calcite samples.

In conclusion the results from the uraninite ore solution experiments showed that the measured $^{234}U/^{238}U$ and the $^{230}Th/^{234}U$ ratios suffered from mass bias effects which produced low $^{234}U/^{238}U$ and high $^{230}Th/^{234}U$ ratios. The uraninite ore solution was used to correct samples ratio measurements for mass bias effects. The coral and speleothem reference materials, after correction for mass bias using the uraninite results, were in agreement with the certified values. A procedure for samples run was devised ensuring that enough blanks were analysed between the samples and uraninite ore solution so as to ensure carryover of the uranium and thorium did not affect later analysis and the baseline has returned to normal. The uraninite ore solution was analysed with sample to enable correction of mass bias effects and ensure that any reduction in sensitivity during an analysis run would not affect the results obtained.

The $^{230}Th/^{232}Th$ experiments demonstrated that the presence of $^{232}Th$ at the 10 and 20 ppb level affected the observed $^{230}Th$ counts.

The detrital correction leachate and total dissolution techniques enabled correction of the 35 and 7% detritally contaminated speleothem reference material. This demonstrated that the true age of the impure sample can be extracted provided it was available at different impurity levels.

The Plasma Trace 2 instrument was compared with alpha spectrometry for the analysis of coral and speleothem reference materials. The results show agreement.
between the two measurement techniques. The difference between the two techniques was in the limit of detection obtained. The Plasma Trace 2 instrument enabled a lower limit of detection ($10^{-5}$Bq) than those obtained by alpha spectrometry (0.05Bq) and a reduction in the analysis time from 7 days to 1 day. However the high cost of analysis using the PlasmaTrace 2 instrument would prevent its use when analysis by alpha spectrometry was possible.

In conclusion the thesis succeeded in its aims to develop and evaluate the separation methods and to evaluate the PlasmaTrace 2 instrument for the measurement of low-levels of uranium and thorium.
CHAPTER 8

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APPENDIX 1.

Calculation of the $^{238}\text{U}$ activity and its associated error.

Calculation of the corrected $^{238}\text{U}$ count rate and its associated errors.

The $^{238}\text{U}$ counts, count time (s), background counts and background count time (s) were used to calculate the corrected $^{238}\text{U}$ count rate. The $^{238}\text{U}$ count rate (cpm) was calculated using the following equation.

\[
^{238}\text{U count rate (cpm)} = \frac{^{238}\text{U counts}}{^{238}\text{U count time/60}}
\]

\[
= \frac{4559}{183759.84/60}
\]

\[
= 1.489 \text{ cpm}
\]

The count error on the $^{238}\text{U}$ count rate was then calculated.

\[
\text{Count error on } ^{238}\text{U count rate} = \left(\frac{^{238}\text{U counts}}{^{238}\text{U count time/60}}\right)^{1/2}
\]

\[
= \left(\frac{4559}{183759.84/60}\right)^{1/2}
\]

\[
= 0.022 \text{ cpm}
\]

The $^{238}\text{U}$ background count rate (cpm) was calculated.

\[
^{238}\text{U background count rate (cpm)} = \frac{^{238}\text{U background counts}}{^{238}\text{U background count time/60}}
\]

\[
= \frac{11}{55971.58/60}
\]

\[
= 0.012 \text{ cpm}
\]

The error on the $^{238}\text{U}$ background count rate was calculated.

\[
\text{Error on } ^{238}\text{U background count rate} = \left(\frac{^{238}\text{U background counts}}{^{238}\text{U background count time/60}}\right)^{1/2}
\]

\[
= \left(\frac{11}{55971.58/60}\right)^{1/2}
\]

\[
= 0.004 \text{ cpm}
\]

The corrected $^{238}\text{U}$ count rate was calculated.

\[
\text{Corrected } ^{238}\text{U count rate} = \left(\frac{^{238}\text{U count rate}}{^{238}\text{U background count error}}\right) - ^{238}\text{U background count error}
\]

\[
= 1.489 - 0.012
\]

\[
= 1.477 \text{ cpm}
\]
Calculation of the error on the corrected $^{238}U$ count rate.

Error on the corrected $^{238}U$ count rate = $\left( (^{238}U_{\text{cre}})^2 + (^{238}U_{\text{bkdc}})^2 \right)^{1/2}$

$= ((0.022)^2 + (0.004)^2)^{1/2}$

$= 0.022$ cpms

Where:

$^{238}U_{\text{cre}}$ is the error on the $^{238}U$ count rate and

$^{238}U_{\text{bkdc}}$ is the error on the $^{238}U$ background count rate.

Calculation of the $^{238}U$ activity.

The $^{238}U$ activity was then calculated.

$^{238}U$ activity = \frac{ \left( \frac{^{238}U \text{ corrected count rate}}{ \text{mass of } ^{238}U \text{ added (g)}} \right) \times \left( ^{236}U \text{ spike added (g)} \times \left( ^{236}U \text{ spike activity (DPM/g)} \right) \right) \times \left( \frac{1000}{60} \right) \right)}{ \left( ^{238}U \text{ corrected count rate} \right)}

= ((1.477\times0.6004\times10.044)/(0.60903\times1.421)) \times (1000/60)

= 151.3$ mBq/g

The $^{235}U$ and $^{236}U$ peaks overlap therefore the $^{236}U$ counts needs to be corrected for the associated $^{235}U$ counts. The $^{235}U$ is assumed to be in the natural ratio with $^{238}U$. Similarly the $^{228}Th$ peak needs to be corrected for approximately 5% of $^{224}Ra$ peak ingrowing under $^{228}Th$ peak.

The $^{236}U$ counts were corrected using the $^{235}U$/$^{238}U$ activity ratio of 1:21.7. Therefore

$^{235}U$ counts = $^{238}U/21.7$

$^{236}U$ counts corrected = $^{236}U_{\text{net}} - ^{238}U_{\text{net}}/21.7$
**Calculation of the error on $^{238}\text{U}$ activity.**

The error $^{238}\text{U}$ activity was calculated using the following equation.

Error on $^{238}\text{U}$ (mBq/g) = $(\frac{^{238}\text{Ue}}{^{238}\text{U}})^2 + (\frac{^{236}\text{Ue}}{^{236}\text{U}})^2 + (\frac{^{236}\text{Ua}}{^{236}\text{U}})^2)^{1/2} \times ^{238}\text{Ua} $

= $(\frac{0.022}{1.477})^2 + (\frac{0.022}{1.421})^2 + (\frac{0.072}{10.044})^2)^{1/2} \times 151.33$

= 3.43 mBq/g

Where:
- $^{238}\text{Ue}$ and $^{236}\text{Ue}$ are the errors on the $^{238}\text{U}$ and $^{236}\text{U}$ corrected count rates respectively (cpm).
- $^{238}\text{U}$ and $^{236}\text{U}$ are the corrected count rates of $^{238}\text{U}$ and $^{236}\text{U}$ respectively.
- $^{238}\text{Ua}$ is the activity of $^{238}\text{U}$ (mBq/g).
- $^{236}\text{Ua}$ is the activity of $^{236}\text{U}$ (mBq/g).
- and $^{236}\text{Uae}$ is the error on the $^{236}\text{U}$ activity.
APPENDIX 2.

Calculation of the 238\textsuperscript{U} activity in the reagent blank.

Initially the activity of 236\textsuperscript{U} added to the reagent blank sample was calculated using the following equation.

\[
\text{Activity of } 236\textsuperscript{U} = \text{Specific activity of } 236\textsuperscript{U} \times \text{Weight of } 236\textsuperscript{U} \text{ added to RB1 added to RB1}
\]

The average of the 236\textsuperscript{U} counts was then calculated. The average of the 238\textsuperscript{U} counts was then calculated.

The normalized 236\textsuperscript{U} counts were then calculated.

\[
\text{Normalized } 236\textsuperscript{U} \text{ counts} = \frac{236\textsuperscript{U} \text{ counts } \times 250}{236\textsuperscript{U} \text{ dwell time}}
\]

The normalized 238\textsuperscript{U} counts were then calculated.

\[
\text{Normalized } 238\textsuperscript{U} \text{ counts} = \frac{238\textsuperscript{U} \text{ counts } \times 250}{238\textsuperscript{U} \text{ dwell time}}
\]

The 238\textsuperscript{U} activity in the reagent blank was then calculated.

\[
238\textsuperscript{U} \text{ (Bq)} = \frac{(\text{Normalized } 238\textsuperscript{U} \text{ counts } \times 238\textsuperscript{U} \text{ activity added to RB1 } \times (1.244 \times 10^4))}{\text{Normalized } 236\textsuperscript{U} \text{ counts } \times (2.397 \times 10^6)}
\]

Where:

- The specific activity of 238\textsuperscript{U} is $1.244 \times 10^4$ dps/g.
- The specific activity of 236\textsuperscript{U} is $2.397 \times 10^6$ dps/g.
APPENDIX 3.

Conversion of activity (mBq/g) to concentration (ppm) units.

The activity of $^{238}\text{U} \text{(mBq/g)}$ was converted to a concentration value (ppm) using the following calculation.

$$^{238}\text{U} \text{(ppm)} = \frac{(^{238}\text{U} \text{(mBq/g)} \times 60) / (0.7463 \times 1000)}$$

The error on the $^{238}\text{U} \text{(ppm)}$ was calculated using the following equation.

$$\text{Error on } ^{238}\text{U} \text{(ppm)} = \frac{(\text{Error on } ^{238}\text{U} \text{(mBq/g)} \times 60) / (0.7463 \times 1000)}$$
APPENDIX 4.

Calculation of expected $^{234}\text{U}/^{238}\text{U}$ mass ratio.

The expected $^{234}\text{U}/^{238}\text{U}$ mass ratio was calculated by initially calculating the number of atoms of $^{234}\text{U}$ and $^{238}\text{U}$.

$$N = \frac{A}{(\ln2/\tau_{1/2})}$$

Where:

- $N$ is the number of atoms.
- $A$ is the activity (Bq).
- $\tau_{1/2}$ is the half life (y).

For $^{234}\text{U}$; $\tau_{1/2}$ is $2.457 \times 10^5$ years, $A$ is $0.147\text{Bq}$, $N$ is calculated using

$$N = \frac{0.147}{(0.693 \times 2.457 \times 10^5)} = 52107.115 \text{ atoms}$$

For $^{238}\text{U}$; $\tau_{1/2}$ is $4.468 \times 10^9$ years, $A$ is $0.147\text{Bq}$, the $N$ is calculated using

$$N = \frac{0.147}{(0.693 \times 4.468 \times 10^9)} = 947556332.1 \text{ atoms}$$

The masses of the $^{234}\text{U}$ and $^{238}\text{U}$ were then calculated using the calculated number of atoms of $^{234}\text{U}$ and $^{238}\text{U}$.

$$\text{mass} = N \times \text{RMM.}$$

$$^{234}\text{U mass} = 52107.115 \times 234 = 12193061g$$

$$^{238}\text{U mass} = 947556332.1 \times 238 = 2.255184 \times 10^{11}g$$

The $^{234}\text{U}/^{238}\text{U}$ mass ratio was then calculated by dividing the $^{234}\text{U}$ mass by the $^{238}\text{U}$ mass.

$$^{234}\text{U}/^{238}\text{U mass ratio} = \frac{12193061g}{2.255184 \times 10^{11}g} = 0.00005407.$$
APPENDIX 5.

Error calculation.

The error on the results was calculated using the equation below.

\[ \text{Error} = t \left( \frac{s}{(n-1)} \right)^{1/2} \]

Where:
- \( t \) is the 2 sided confidence factor which depends on the \((n-1)\), the number of degrees of freedom and the degree of confidence required (95%).
- \( n \) is the number of measurements.
- \( s \) is the standard deviation of the measurements.

APPENDIX 6.

Calculation of the error on the isotope ratio measurements.

The error on the ratio was calculated using the equation below.

\[ \text{Error} = \left( \frac{a^2}{B^2} + \left( \frac{(A^2 \times b^2)}{B^4} \right) \right)^{1/2} \]

Where:
- \( A \) is the determined \( ^{234}\text{U}/^{238}\text{U} \) mass ratio.
- \( B \) is the expected \( ^{234}\text{U}/^{238}\text{U} \) mass ratio.
- \( a \) is the error on the determined \( ^{234}\text{U}/^{238}\text{U} \) mass ratio.
- \( b \) is the error on the expected \( ^{234}\text{U}/^{238}\text{U} \) mass ratio.

The error on the \( ^{234}\text{U}/^{238}\text{U} \) mass ratio for the uranium and thorium not separated (run 1) was calculated below.

\[ \begin{align*}
&= \left( \frac{1^2}{73^2} \right) + \left( \frac{\left(69^2 \times 2^2\right)}{73^4} \right)^{1/2} \\
&= \left( \frac{1.877 \times 10^{-4}}{1.706 \times 10^{-4}} \right)^{1/2} \\
&= 0.03
\end{align*} \]
APPENDIX 7.

Calculation of $^{238}$U activity using the $^{236}$U activity.

The number of atoms of $^{236}$U was calculated using the activity and half-life of $^{236}$U.

\[
\text{number of atoms of } ^{236}\text{U} = \frac{0.3067}{(0.693 \times (2.3416 \times 10^7))}
\]
\[
= \frac{0.3067}{0.693 \times 2.3416 \times 10^7}
\]
\[
= 10362462.84 \text{ atoms.}
\]

The mass of $^{236}$U was then calculated.

\[
\text{mass of } ^{236}\text{U} = 10362462.84 \times 236
\]
\[
= 2445541230 \text{ g.}
\]

The $^{238}$U/$^{236}$U mass ratio of 41.61 was then used to calculate the mass of $^{238}$U.

\[
\text{mass of } ^{238}\text{U} = 41.61 \times 2445541230
\]
\[
= 1.018 \times 10^{11} \text{ g.}
\]

The number of atoms of $^{238}$U were then calculated.

\[
\text{number of atoms of } ^{238}\text{U} = \frac{1.018 \times 10^{11}}{238}
\]
\[
= 427558699.9 \text{ atoms.}
\]

The activity of the $^{238}$U was then calculated using the calculation below.

\[
A = N \times \left(\frac{0.698}{t_{1/2}}\right)
\]
\[
A = 427558699.9 \times \left(\frac{0.698}{4.468 \times 10^8}\right)
\]
\[
\text{activity of } ^{238}\text{U} = 0.0668 \text{ Bq}
\]
Determination of uranium and thorium in geological materials
using extraction chromatography

Helen E. Carter, Peter Warwick, John Cobb and Geoff Longworth

* Environmental Radiochemistry Research Group, Chemistry Department, Loughborough
University, Leicestershire, UK LE11 3TU
* Analytical Services Group, AEA Technology plc, 551 Harwell, Didcot, OXON,
UK OX11 0RA

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A procedure has been developed for the determination of uranium and thorium in geological samples using
extraction chromatography. Following sample preparation, uranium and thorium are pre-concentrated by
precipitation with iron(III) hydroxide and then separated using UTEVA resin. The separated uranium and thorium
are electrodeposited onto stainless-steel discs and then measured by alpha spectrometry. The procedure was
evaluated using uranium ore, coral and granite reference materials. The uranium and thorium concentrations and
the 234U/238U and 232Th/238U activity ratio values determined for the reference materials were in good agreement
with the certified values. The presence of plutonium was found to interfere with the separation, but the inclusion
of a reduction step in the uranium/metal sulfate eliminated the problem. Chemical recoveries for the procedure are
similar to those for an anion-exchange procedure, but the extraction-chromatography procedure provides a more
rapid separation using less reagents.

1. Introduction

Measurements of the relative abundances of naturally occurring radionuclides, such as the isotopes of uranium, thorium
and radium, in the natural decay series originating with 238U, 235U
and 232Th, have been used to study a wide variety of problems
in, for example, geology, hydrology and archaeology. Natural
separation of parent and daughter nuclides, due to differing
geochemical behaviour, leads to radioactive disequilibrium
(indicated by a daughter-parent isotope activity ratio not equal
to one) which may be used as an indicator of the timescale of
past geochemical events.

An example of such use is in the dating of calcites such as speleothem. When dating, it is assumed that thorium is not
incorporated into the calcite on formation and the rate of the
resulting ingrowth of 230Th from its parent 234U, governed by its
half-life, is used to determine the age of the calcite.

Alpha spectrometry has been used to measure the activities of
234U, 235U, 238U, 232Th, 237Th and 233Th. Chemical separation of
uranium from thorium is required prior to measurement due to
overlap between the alpha energies of the 234U and 230Th. Many
methods have been reported for the separation of uranium and
thorium from geological materials and are usually based on
liquid-liquid extraction or anion-exchange chromatography. Disadvantages associated with these procedures include
the use of large volumes of organic solvents and acids resulting
in large volumes of generated waste, and the procedures are
labour intensive and time consuming.

In the early 1980s, Horwitz and co-workers at Argonne
National Laboratory developed new reagents for liquid-liquid
extraction of the actinides. Reagents were then developed
for the separation of actinides by extraction chromatography
(reversed phase partition chromatography). This technique
uses an inert polymeric support impregnated with a selective
liquid extractant to form a solid sorbent which canthen be
loaded into a column. The use of extraction chromatography
reduces both the volume of reagents used and the separation
time. The UTEVA reagents are commercially available from
ElChrom Industries Inc. (8205 S. Darton, IL 60561, USA).

This paper reports the use of an extraction chromatography
resin comprising diaminopyridine as the extractant to separate
uranium and thorium from geological materials and compares its performance to an anion-exchange procedure. Previous work using the UTEVA resin has shown that uranium is extracted by the resin at nitric acid concentrations of 1 mol l−1 and greater. The uranium can then be eluted from the resin using 0.01 mol l−1 nitric acid. The separation of thorium from uranium has also been investigated using a nitric acid load solution to separate the uranium and thorium from matrix interferences present in environmental samples due to, for example, aluminium, iron or calcium. Thorium and uranium are then eluted from the column using 6 mol l−1 hydrochloric acid and 0.025 mol l−1 hydrochloric acid, respectively. Horwitz et al. also used the UTEVA resin in conjunction with other extraction chromatography resins to separate thorium, neptunium, uranium, plutonium and americium for the characterization of nuclear waste solutions.

Uranium and thorium separation schemes for water and soil
samples have been published by ElChrom Industries. These
along with the separation method for americium, plutonium
and uranium in water, were used to develop the uranium and thorium separation method described in this paper.

2. Experimental
2.1. Reagents

All reagents used were of analytical-reagent grade and 18 MΩ
demineralized water was used throughout. The following reagents
were used: hydrochloric acid (9, 8, 5 and 0.02 mol l−1), nitric
acid (density = 1.42 g cm−3 and 3 mol l−1), ammonia solution
density = 0.88 g cm−3), 10 mg cm−3 iron carrier solution (iron(III) nitrate in 5% v/v nitric acid), 0.1 mol l−1
ammonium oxalate.

The extraction chromatography resins used were pre-
packaged UTEVA resin columns with a bed volume of 2 cm3.

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The radioactive tracer solutions used were: $^{222}\text{Rn}$ (192 mBq g$^{-1}$), $^{228}\text{Th}$ (167 mBq g$^{-1}$) and $^{232}\text{U}$/$^{228}\text{Th}$ (147 mBq cm$^{-3}$) of each radionuclide in secular equilibrium. The solutions were in approximately 7 mol$^{-1}$ nitric acid. Interference studies were conducted using $^{208}\text{Po}$ (133 mBq cm$^{-3}$), $^{210}\text{Po}$/$^{210}\text{Pb}$ (433 mBq cm$^{-3}$), $^{244}\text{Am}$ (60 mBq cm$^{-3}$), $^{243}\text{Am}$ (1.572 Bq cm$^{-3}$), $^{242}\text{Pu}$ (98.2 mBq cm$^{-3}$) and $^{239}\text{Pu}$ (43.08 mBq cm$^{-3}$).

2.2. Instrumentation

Alpha spectrometry measurements were carried out using a 7401 model alpha spectrometer (Canberra Packard Ltd., Pangbourne, Berkshire, UK) fitted with passivated ion implanted planar silicon detectors (PIPS) having an active surface area of 450 mm$^2$. The spectrometers were connected to a personal computer fitted with a TRUMP-8k-W3 multi-channel analyser plug in card (EG&G Instruments, Wokingham, Berkshire, UK).

The electrodeposition of uranium, thorium, plutonium and americium onto stainless-steel discs was carried out using a 7401 model alpha spectrometer (Canberra Packard Ltd., Pangbourne, Berkshire, UK) capable of maintaining a constant current of 1 A was used for the electrodepositions. Polonium was autodeposited onto silver discs from dilute hydrochloric acid solution in the presence of ascorbic acid.

Gamma spectrometry measurements were carried out using germanium detectors (EG&G Instruments) coupled to a computerized analytical system. Stored spectra were analysed using Super Sabre software (AEA Technology plc, Didcot, Oxfordshire, UK) for photopeak identification and quantification.

2.3. Method development

Initially, the elution behaviour of uranium and thorium from the UTEVA resin was investigated qualitatively using the procedure described by ELKIN and HORTON. Load solutions comprising 10 cm$^3$ of 3 mol L$^{-1}$ nitric acid spiked with either 238U or 239Pu were prepared. These solutions were loaded onto separate UTEVA columns pre-conditioned with 5 cm$^3$ of 3 mol L$^{-1}$ nitric acid. The following solutions were passed through each column: 5 cm$^3$ of 3 mol L$^{-1}$ nitric acid (fraction 1); 5 cm$^3$ of 9 mol L$^{-1}$ hydrochloric acid (fraction 2); five 3 cm$^3$ aliquots of 5 mol L$^{-1}$ hydrochloric acid (fractions 3 to 7); five 3 cm$^3$ aliquots of 0.02 M hydrochloric acid (fractions 8 to 12) and 10 cm$^3$ of 0.1 M ammonium oxalate (fraction 13). Each separate column fraction was collected and prepared for electrodeposition. The resulting sources were measured by alpha spectrometry. The results showed that the $^{222}\text{Th}$ was present in the 5 mol L$^{-1}$ hydrochloric acid (fractions 3 to 7) and the $^{232}\text{U}$ was present in the 0.02 mol L$^{-1}$ hydrochloric acid (fractions 8 to 12). The experiment was repeated quantitatively using a resin load solution containing $^{232}\text{U}$ and $^{235}\text{Th}$ in secular equilibrium. The 15 cm$^3$ fractions of 5 mol L$^{-1}$ and 0.02 mol L$^{-1}$ hydrochloric acid were collected and spiked with either $^{228}\text{Th}$ or $^{233}\text{U}$, respectively, prior to electrodeposition to determine the plating and counting efficiencies of thorium and uranium. The results showed that the recoveries of uranium (101.8 ± 2.9%) and thorium (90.1 ± 2.6%) were almost quantitative in their respective fractions.

2.4. Interferences

The proposed sample pre-concentration step was to co-precipitate uranium and thorium with iron(III) hydroxide from a solution of the dissolved sample. Therefore, the effect of the presence of iron in the load solution was investigated by adding 1, 2, 3 or 5 cm$^3$ of iron(III) carrier solution. The 5 mol L$^{-1}$ and 0.02 mol L$^{-1}$ hydrochloric acid fractions were quantitatively analysed for uranium and thorium, respectively. The elution profile of a load solution containing 10 mg of iron(III) showed uranium (109.6 ± 3.2%) was recovered from the column in fraction 8 and thorium (100.8 ± 3.1%) was recovered in fractions 3, 4 and 5. Table 1 shows uranium and thorium recoveries when varying amounts of iron(III) were added to the load solution. These results show that the chemical recoveries of uranium and thorium were unaffected by the presence of between 10 and 50 mg of iron.

The behaviour of several potential radionuclide interferences was investigated. Load solutions were prepared spiked with either $^{226}\text{Ra}$, $^{219}\text{Po}$, $^{241}\text{Am}$ or $^{239}\text{Pu}$. These were loaded onto the column which was then sequentially eluted with 5 cm$^3$ of 2 mol L$^{-1}$ nitric acid, 3 cm$^3$ of 9 mol L$^{-1}$ hydrochloric acid, 15 cm$^3$ of 5 mol L$^{-1}$ hydrochloric acid and 10 cm$^3$ of 0.1 mol L$^{-1}$ ammonium oxalate. The combined load and nitric acid fraction, the three hydrochloric acid fractions and the ammonium oxalate fraction were analysed for the presence of the radionuclide interference. $^{226}\text{Ra}$ was measured directly by gamma spectrometry whereas $^{219}\text{Po}$, $^{241}\text{Am}$ and $^{239}\text{Pu}$ were measured by alpha spectrometry following spiking with $^{228}\text{Po}$, $^{239}\text{Am}$ and $^{235}\text{Pu}$, respectively.

Table 2 shows the recoveries of the radionuclides in each of the analysed fractions. The $^{226}\text{Ra}$, $^{219}\text{Po}$ and $^{241}\text{Am}$ activities were recovered quantitatively in the combined load and nitric acid wash (fraction 1). The $^{239}\text{Pu}$ was present in both the uranium and thorium eluates (fractions 3 and 4). This indicated that the column procedure would not be suitable for environmental samples that may contain plutonium isotopes. However, for many geological samples plutonium is unlikely to be present.

Co- elution of plutonium with uranium and thorium from the UTEVA resin can be prevented by its reduction to Pu(III) using iron(II) sulfamate. This was investigated using load solutions comprising $^{239}\text{Pu}$ and varying amounts of iron(III) carrier solution, to which 0.6 g of sulfamic acid and 0.2 g of ascorbic acid were added. Table 3 shows that the $^{239}\text{Pu}$ was present in the combined load and nitric acid wash (fraction 1: Fl). This

<table>
<thead>
<tr>
<th>Amount Fe/mg</th>
<th>U recovery (%)</th>
<th>Th recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>103.4 ± 2.7</td>
<td>102.5 ± 3.7</td>
</tr>
<tr>
<td>20</td>
<td>105.2 ± 3.7</td>
<td>105.9 ± 7.0</td>
</tr>
<tr>
<td>30</td>
<td>98.4 ± 3.9</td>
<td>110.0 ± 3.5</td>
</tr>
<tr>
<td>50</td>
<td>98.2 ± 3.4</td>
<td>107.5 ± 3.6</td>
</tr>
<tr>
<td>70</td>
<td>102.2 ± 3.3</td>
<td>100.2 ± 3.0</td>
</tr>
<tr>
<td>50</td>
<td>103.5 ± 3.4</td>
<td>106.1 ± 3.1</td>
</tr>
</tbody>
</table>

Table 1 The effect of the presence of iron(III) on U and Th recoveries

<table>
<thead>
<tr>
<th>Fraction</th>
<th>$^{238}\text{U}$</th>
<th>$^{235}\text{U}$</th>
<th>$^{232}\text{U}$</th>
<th>$^{233}\text{U}$</th>
<th>$^{234}\text{U}$</th>
<th>$^{236}\text{U}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Po</td>
<td>101.1 ± 2.6</td>
<td>1.4 ± 0.1</td>
<td>&lt;1</td>
<td>1.4 ± 0.2</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>$^{210}\text{Po}$</td>
<td>90.3 ± 3.1</td>
<td>1.3 ± 0.3</td>
<td>27.8 ± 0.7</td>
<td>&lt;1</td>
<td>2.9 ± 0.5</td>
<td>&lt;1</td>
</tr>
<tr>
<td>$^{210}\text{Po}$</td>
<td>100.6 ± 1.2</td>
<td>2.3 ± 0.3</td>
<td>1.1 ± 0.2</td>
<td>&lt;1</td>
<td>2.6 ± 0.2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>$^{210}\text{Po}$</td>
<td>93.3 ± 5.0</td>
<td>2.5 ± 0.4</td>
<td>1.4 ± 0.3</td>
<td>&lt;1</td>
<td>3.2 ± 0.7</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ra</td>
<td>100</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>$^{234}\text{Am}$</td>
<td>110.0 ± 2.9</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>$^{234}\text{Am}$</td>
<td>110.0 ± 2.3</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>$^{239}\text{Pu}$</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Table 2 Percentage recoveries of Po, Ra, Am and Pu

$^{272}$ Analyst. 1999, 124, 271-274
indicated that the reduced plutonium did not interact with the resin.

The effect of the presence of the sulfamic acid and ascorbic acid on the uranium and thorium separation was investigated using the uraninite ore solution to which 1 cm³ of iron(III) carrier solution was added. The results showed that the thorium and uranium were recovered quantitatively in their expected fractions. Therefore, iron(III) sulfamate could be used for separation of uranium and thorium from samples where plutonium is suspected to be present.

2.5. Analytical procedure

After dissolution of the geological material (see section 2.6), 1 cm³ of iron(III) carrier solution was added to the sample solution. Uranium and thorium were co-precipitated from the solution with iron(III) hydroxide by the addition of ammonia solution (density = 0.880 g cm⁻³). The sample was warmed to coagulate the precipitate, which was then isolated by centrifuging. The precipitate was then dissolved in 5 cm³ of 6 mol ¹⁻ nitric acid and the resulting solution was diluted to 10 cm³ with deionized water. For samples expected to contain plutonium, 0.6 g of sulfamic acid and 0.2 g of ascorbic acid were dissolved in the resulting solution.

A UTEVA resin column was pre-conditioned with 5 cm³ of 3 mol ¹⁻ nitric acid. The sample solution was loaded onto the column and allowed to drain through. A 5 cm³ aliquot of 3 mol ¹⁻ nitric acid used to rinse the centrifuge tube was passed through the column. The column was then converted to the chloride form by passing through 5 cm³ of 9 mol ¹⁻ hydrochloric acid. Thorium was eluted from the column with 15 cm³ of 5 mol ¹⁻ hydrochloric acid and then uranium was eluted from the column with 15 cm³ of 0.02 mol ¹⁻ hydrochloric acid.

The uranium and thorium fractions were prepared for counting by alpha spectrometry by electrodeposition onto stainless-steel discs. The electrodepositions for uranium and thorium were carried out at 1 A for 3 and 5 h, respectively.

2.6. Procedure test

The procedure was tested using the following materials: a solution prepared from a uraninite ore, a coral (RKMS), and a granite (SARM-1). The uraninite ore and coral were used in the Uranium Series Intercomparison Project.¹⁰

2.6.1. Sample preparation of uraninite ore. The uraninite ore sample was prepared by diluting 0.5 cm³ of the uraninite solution to 100 cm³ using 0.1 mol ¹⁻ nitric acid, 0.5 g of ²³⁵U and ²³²Th internal standards and 1 cm³ of the iron(III) carrier solution were added to the solution, which was then left to equilibrate overnight.

2.6.2. Sample preparation of coral. Approximately 2 g of the coral (RKMS) were added to a 250 cm³ glass beaker and then 100 cm³ of distilled water were added. The calcium carbonate was then slowly dissolved by the gradual addition of nitric acid (density = 1.42 g cm⁻³), such that the solution was maintained at pH 1. The sample was centrifuged to remove any acid insoluble residue. Suitable levels of ²³⁵U and ²³²Th internal standards and 1 cm³ of the iron(III) carrier solution were added to the supernate, which was then left to equilibrate overnight. The solution was boiled prior to precipitation of iron(III) hydroxide to ensure removal of dissolved carbonate.

2.6.3. Sample preparation of granite. 0.6 g of ²³⁵U and 0.6 g of ²³²Th internal standards and 1 cm³ of the iron(III) carrier solution were added to approximately 0.5 g of the granite. The granite wasashed at 450 °C and digested in 20 cm³ of hydrofluoric acid for 48 h in a Teflon dish. A 5 cm³ aliquot of nitric acid and 5 cm³ of perchloric acid were added and the resulting solution was refluxed at 150 °C for 3 h. The solution was evaporated to dryness and the residue was treated with 10 cm³ of nitric acid (density = 1.42 g cm⁻³) and evaporated to dryness. The final residue was dissolved in 20 cm³ of 8 mol ¹⁻ hydrochloric acid and the resulting solution diluted to 100 cm³ with deionized water.

2.7. Ion-exchange method for separation of uranium from thorium

To compare the results from the UTEVA resin method, thorium and uranium were also separated from similar samples using a method based on the use of an ion-exchange resin.¹⁰

3. Results

3.1. Uraninite

Table 4 shows the results, and the repeatability, of the measurements on the uraninite reference material. The errors in the ²³⁵U/²³⁴U ratio shows that, within experimental errors, the radionuclides are in equilibrium. Comparison of the mean values of the ²³⁵U/²³⁴U (0.996 ± 0.02) and ²³⁵Th/²³⁴U (1.021 ± 0.03) ratios for the UTEVA resin method with those for the anion-exchange method (²³⁵U/²³⁴U, 0.968 ± 0.013; ²³⁵Th/²³⁴U, 1.016 ± 0.025) shows that the methods gave statistically identical results.

3.2. Coral

Table 5 shows the results of measurements on the coral reference material. The results show that the measured values of uranium (ppm w/w) compare well with the reference value of 3.25 ± 0.10 ppm uranium. The measured ²³⁵U/²³⁴U activity ratios compare well with the certified value of 1.098 ± 0.016 and the ²³⁵Th/²³⁴U measured ratio compares well with the reference value of 0.709 ± 0.025. Since this ratio is less than 1, the radionuclides are not in equilibrium and the age of the coral reference material can be calculated.²⁰ The measured age of the coral compares well with the reference value of 131,000 ± 9000 years.

3.3. Granite

Table 6 shows the results of measurements on the granite reference material. The uranium concentration is 15 ppm (w/w)

---

Table 3

<table>
<thead>
<tr>
<th>Amount of Ammonium (Femg)</th>
<th>F₁⁺</th>
<th>F₂⁻</th>
<th>F₃⁻</th>
<th>F₄⁺</th>
<th>F₅⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>105.1 ± 3.8</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>30</td>
<td>99.6 ± 2.5</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>50</td>
<td>102.4 ± 2.9</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>70</td>
<td>101.1 ± 4.4</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>90</td>
<td>100.9 ± 2.5</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>110</td>
<td>96.8 ± 3.0</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

* F₁⁺ = 10 cm³ of 3 M nitric acid loaded solution and 5 cm³ of 3 M nitric acid wash. * F₂⁻ = 5 cm³ of 9 M hydrochloric acid. * F₃⁻ = 15 cm³ of 5 M hydrochloric acid. * F₄⁺ = 15 cm³ of 0.02 M hydrochloric acid. * F₅⁻ = 10 cm³ of 0.1 M ammonium oxalate.
which compares well with the mean UTEVA measurement of 17.544 ± 0.626. The certified thorium concentration of 51 ± 3 ppm (ww) also compares well with the mean UTEVA measurement of 47.098 ± 4.326 ppm (ww).

4. Conclusions

The proposed method, which uses UTEVA resin to separate uranium from thorium in geological materials, has been evaluated using coral, uraninite and granite reference materials. The results of the measurements have been compared to those obtained by a method based on the use of an ion-exchange resin. The UTEVA resin results compared favourably with both the ion-exchange results and the certified values. The use of the UTEVA resin provides a quicker separation which uses less reagents than the ion-exchange resin method.

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