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ANALYSIS FOR THE RADIONUCLIDES OF THE URANIUM AND THORIUM DECAY CHAINS WITH SPECIAL REFERENCE TO URANIUM MINE TAILINGS

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ABSTRACT

A detailed review is made of the experimental techniques that are available, or are in the process of development, for the determination of ^{238}U, ^{235}U, ^{234}U, ^{231}Pa, ^{232}Th, ^{230}Th, ^{228}Th, ^{228}Ra, ^{226}Ra, ^{223}Ra, ^{210}Po and ^{210}Pb. These products of the uranium and thorium decay chains are found in uranium mine tailings. Reference is also made to a procedure for the selective phase extraction of mineral phases from uranium mine tailings.

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CONTENTS

1. INTRODUCTION

Although there is now an extensive literature on uranium mine tailings (see bibliographies by the US Department of Energy [USDOE 1958-1982]), there is minimal information on their geochemistry. A prerequisite to any proposed study in this area is the establishment of a suitable scheme for the analysis of the radionuclides of the uranium and thorium decay chains. Sill *et al.* [1974] developed a scheme based on pyrosulphate fusion for the analysis of uranium and thorium and their daughters in soils. This scheme was applied later to tailings [Sill 1977a,b]. The pyrosulphate fusion method has a number of drawbacks. All volatile components, for example ^{210}Po, are lost. The resulting solution is difficult to treat owing to the high sulphate levels. This problem is exacerbated by the high sulphate concentration in the tailings from the milling process and the high calcium concentration from the subsequent neutralisation. Accordingly, an altemative approach using acid digestion was developed.

A number of techniques are available for the subsequent radionuclide analysis using either alpha or gamma spectrometry and beta counting, the choice being dependant on the type of expertise and equipment available.

The three natural decay chains associated with uranium ores are [Busigin *et al.* 1979; Strominger *et al.* 1958]

4(n) series $^{232}\mathrm{Th} \longrightarrow {}^{208}\mathrm{Pb}$ stable
4(n+3) series $^{235}\mathrm{U} \longrightarrow {}^{207}\mathrm{Pb}$ stable
4(n+2) series $^{238}\mathrm{U} \longrightarrow {}^{206}\mathrm{Pb}$ stable

The sequence of alpha decay for the three series is illustrated in figure 1.

The chemistry of uranium and thorium is sufficiently different to preclude the common occurrence of these materials. Thorium is found in nature only as relatively insoluble Th(IV) [Langmuir 1980], whereas uranium occurs as soluble U(VI) and as less soluble U(IV). Thus although thorianite (ThO_2) is isomorphous with uraninite, UO_2 and uranothorite deposits are known [IAEA 1962]; thorium and uranium usually occur as separate ore bodies. No mixed uranium/thorium ore bodies have been found in Australia. Thus in the Australian context, the ^{232}Th (4n) decay series is of lesser significance and attention is focused primarily on the ^{238}U and ^{235}U series.

The concentration of each isotope is related to its decay rate, or its activity, by the equation

$$\frac{-dN}{dt} = \lambda N \ ,$$

where N is the number of atoms and λ is the decay constant. The constant λ is usually reported as the half-life $t_{1/2}$, that is the time for an initial quantity of radioactive material to decay to half its initial amount, so that

$$\lambda = \frac{\ln 2}{t_{1/2}} \ .$$

Uranium ore bodies in the Alligator Rivers region of Australia are 10^9 years old; provided that the ore remained undisturbed, the decay chains would have reached secular equilibrium so that

$$\frac{dN_1}{dt} = \frac{dN_2}{dt} = \frac{dN_n}{dt}$$

Under these conditions, the decay rate, or activity A, of each isotope in the chain will be equal and the ratio of the activities of any pair of isotopes within the decay chain will be unity.

Few geological systems remain totally closed and, over geological time, there are fluctuations from equilibrium [Ivanovich and Herman 1982]. In addition, when the ore is passed through a treatment plant, the equilibrium will be grossly disturbed. Most of the uranium daughters from a uranium ore body end up in the waste material known as tailings. A study of the distribution of these daughters and the extent of the disequilibria in the decay chain will help to characterise the tailings and may help to quantify the leachability of the radioactive elements from this waste material.

Some of these isotopes are short-lived and need not be considered. The important isotopes are ^{238}U, ^{235}U, ^{234}U, ^{231}Pa, ^{232}Th (if present), ^{230}Th (a daughter of ^{238}U), ^{228}Th, ^{228}Ra, ^{226}Ra, ^{223}Ra, ^{210}Po and ^{210}Pb.

The following maximum levels have been reported at a number of tailings sites [AAEC 1985]:

	U		^{232}Th	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po
Site	mg g^{-1}	Bq g^{-1}	Bq g^{-1}				
Rum Jungle	0.337	7.5	0.059	13	63	63	52
Rock Hole	0.272	6.1	0.081	63	210	220	200
Moline	0.178	4.0	0.074	21	96	110	89
Mary Kathleen	-	-	0.962	0.1	5.2	1.5	9.3
Nabarlek	0.253	5.7	0.100	59	104	130	130
Ranger	0.289	6.5	0.070	16	8	34	33

Although the uranium has been stripped from the host rock, the activity of the ^{234}U should be in equilibrium with that of the ^{238}U and the ^{235}U will be present in 0.72 per cent mass abundance or 3.98 per cent activity abundance of the ^{238}U. The concentrations of ^{232}Th and its daughters are very low. The uranium daughters in tailings will be in gross excess of the parent uranium, but should be in approximate secular equilibrium with each other.

In addition to the total quantities of each isotope, information is also required on the location of the isotope within the heterogeneous host matrix. Other workers have concentrated on separating the host matrix in terms of particle size; for example, some found that radium tended to concentrate in the fines [Seeley 1977; Raicevic 1979; Levins *et al.* 1982]. An alternative approach, adopted in the present study, is to separate the tailings on mineralogical/chemical grounds. This technique has been well developed by soil scientists with the combinations of leachants chosen to match the particular soil under examination.

2. TOTAL DISSOLUTION OF TAILINGS

2.1 Chemistry for the Total Dissolution of Tailings

The total dissolution of uranium mine tailings involves the destruction of insoluble silicates and the dissolution of the remaining material through oxidation. There are four basic methods to achieve this, selection being dependent on which components are being quantitatively determined:

(i) high temperature open vessel digestion;

(ii) low temperature open vessel digestion;

(iii) bomb digestion; and

(iv) fusion.

2.1.1 High temperature open vessel digestion

In this method, the tailings are oxidised with nitric acid and the insoluble silicates removed as volatile fluorosilicates by the addition of hydrofluoric acid. Elevated temperatures up to 200°C are achieved by using perchloric acid, a dehydrating solvent which has a boiling point of 200°C. Where the analysis of the isotopic composition is to be by the isotope ratio method, the isotope standards, ^{232}U, ^{236}U, ^{228}Th or ^{229}Th and ^{223}Ra or ^{224}Ra, are added at the beginning of the procedure.

Because the majority of Australian uranium ores are in an acid host rock having low calcium and magnesium levels, there is very little insoluble material left at the end of this procedure for either ore or un-neutralised tailings. The high calcium levels in neutralised tailings may present a problem owing to the formation of insoluble calcium fluorides. This material may be solubilised with boric acid. If the resistate levels are significant, it is necessary to revert to fusion techniques.

The advantages of this method are the relative ease of oxidation and removal of insoluble silicate as volatile silicon tetrafluoride. The disadvantages are the partial loss of other volatile chemicals such as polonium and the fact that silicate concentrations cannot be estimated.

2.1.2 Low temperatures open vessel digestion

This method is similar to the previous method of digestion with the exception that perchloric acid is not used as a dehydrating solvent. Although the digestion process is slower, there is no loss of volatile polonium. The silicate concentration cannot be determined.

2.1.3 Bomb digestion

This method is similar to the low temperature digestion method with the exception that the reaction is carried out in a small pressure vessel. The pressure vessel is held at 150°C for one hour in an air oven. The fluorosilicate precipitate may be dissolved in boric acid after opening the bomb.

The method has several advantages: all products are retained in solution; there is no loss of volatile material; and the method is relatively rapid.

2.1.4 Fusion

This is the classical method for determining silica, alkaline oxides and alkaline earth oxides in rocks [Vogel 1939]. The sample is fused with a mixture of lithium tetraborate and lithium metaborate. The cold melt may then be dissolved in hydrochloric acid for subsequent silica and cation analysis. The method has the advantage of supplying the silica concentration, but the ability to remove such volatile chemicals as polonium, lead and bismuth is variable.

For intractable silicates, Sill [1961] described a procedure in which the solid was first fused with potassium fluoride to break down the intractable silicates (*e.g.* monazite) before transposing the melt to sulphate by forming the pyrosulphate with a second fusion. Complete dissolution is readily obtained at the expense of almost total loss of silica.

The potassium fluoride/pyrosulphate fusion method has a number of disadvantages. Potassium salts are generally less soluble than the corresponding sodium salts and much less soluble than lithium salts. The potassium salts tend to precipitate in strong acids, especially $KClO_4$ following $HClO_4$ oxidations. There are a number of common insoluble sulphates and sulphate interferes in subsequent ion-exchange separations.

Provided that organic matter is absent or thoroughly digested, an alternative approach, worthy of development, would be the fusion of lithium fluoride followed by transposition with perchloric acid.

2.2 Procedure for the Total Dissolution of Tailings

2.2.1 High temperature open vessel acid digestion

(i) Weigh 0.2-0.5 g of material into a Teflon beaker.

(ii) If subsequent analysis is by the isotope ratio method, add an appropriate amount of tracer solution so that the activity the tracer isotope is similar to the expected activity of the major isotopes of the element being analysed.

(iii) Add 30 mL of concentrated HNO_3 and 5 mL of concentrated $HClO_4$ per gram of sample and evaporate to white fumes.

(iv) Add 30 mL of concentrated HF per gram of sample and evaporate to white fumes.

(v) Repeat step (iv) until all materials is dissolved or the amount of intractable material is constant.

(vi) Heat to dryness, that is the cessation of white fumes.

(vii) Add 30 mL of concentrated HCl per gram of sample and evaporate to dryness.

(viii) Dissolve in the minimum volume of 6 *M* HCl. Boil gently to dehydrate and flocculate the gelatinous silica if it is present. If the gelatinous silica cannot be flocculated, proceed directly to the separation steps where flocculation will be achieved during the solvent extraction of iron.

(ix) If there is any intractable residue or flocculated silica, centrifuge to separate the solution phase. Wash the residue with small volumes of 6 *M* HCl, centrifuge and add the washings to the solution phase. Repeat until the residue is free of colour.

(x) Set aside the residue for fusion, if considered necessary, and proceed to the appropriate separation scheme for the solution.

2.2.2 Low temperature open vessel acid digestion

(i) Weigh 0.2-0.5 g of material into a Teflon beaker.

(ii) If subsequent analysis is by the isotope ratio method, add an appropriate amount of tracer solution so that the activity of the tracer isotope is similar to the expected activity of the major isotopes of the element being analysed.

(iii) Add 30 mL of concentrated HNO_3 per gram of sample and evaporate to dryness.

(iv) Add 15 mL of concentrated HNO_3 and 15 mL concentrated HF per gram of sample and evaporate to dryness.

(v) Repeat step (iv) until all material is dissolved or the amount of intractable material is constant.

(vi) Add 30 mL of concentrated HCl per gram of sample and evaporate to dryness.

(vii) Dissolve in the minimum volume of 6 *M* HCl. Boil gently to dehydrate and flocculate the gelatinous silica if it is present. If the gelatinous silica cannot be flocculated, proceed directly to the separation steps where flocculation will be achieved during the solvent extraction of iron.

(viii) If there is any intractable residue or flocculated silica, centrifuge to separate the solution phase. Wash the residue with small volumes of 6 *M* HCl, centrifuge and add the washings to the solution phase. Repeat until the residue is free of colour.

(ix) Set aside the residue for fusion, if considered necessary, and proceed to appropriate separation scheme for the solution.

2.2.3 Bomb digestion

(i) Soak the polytetrafluoroethylene (PTFE) liner overnight in concentrated nitric acid, wash well in hot water and rinse with demineralised water.

(ii) Weigh accurately about 0.2 g of rock sample (<200 mesh) into the PTFE liner. If subsequent analysis is by the isotope ratio method, add an appropriate amount of tracer solution so that the activity of the tracer isotope is similar to the expected activity of the major isotopes of the element being analysed. Dry under an infrared lamp, or on a boiling water bath.

(iii) Add 1 mL of concentrated HNO_3, making certain that the sample is well wetted.

(iv) Add 3.6 mL of 40% HF.

(v) Close and seal the decomposition vessel.

(vi) Heat in an air oven for 50 minutes at 150°C.

(vii) Cool to room temperature (in a Petri dish of water if time is at a premium).

(viii) Open the decomposition vessel and wash the contents into a 250 mL PTFE beaker with demineralised water.

(ix) Add 1.3 g of solid boric acid.

(x) Dilute to 50 mL with demineralised water and heat to 50°C to dissolve the fluoride precipitate.

(xi) Add 10 mL of concentrated HCl and evaporate to dryness.

(xii) Dissolve the residue in 10-30 mL of 6 *M* HCl and proceed to the appropriate separation scheme.

2.2.4 Fusion of refractory material

(i) Weigh accurately 0.2-2.5 g of material into a 50 mL platinum dish and add 15 mL concentrated HNO_3 per gram of sample. If subsequent analysis is by the isotope ratio method, add an appropriate amount of tracer solution so that the activity of the tracer isotope is similar to the expected activity of the major isotopes of the element being analysed.

(ii) Evaporate to dryness gently on a water bath or hot plate at low heat.

(iii) Add 5 g of fusion mixture per g of sample. The fusion mixture is 12 parts of lithium tetraborate to 22 parts of lithium metaborate. Additional fusion mixture should be added if fusion is not complete.

(iv) Gently heat the mixture to remove the last traces of water and HNO_3. Add a few drops of concentrated HBr to the mixture to prevent the cooled melt from sticking to the dish. Fuse the mixture in a muffle furnace at 1000-1100°C.

(v) Allow to cool.

(vi) Transfer the plug of cold melt to a glass beaker and add 50 mL of 6 *M* HCl. Boil gently to dissolve the melt and hydrolyse any condensed phosphates. Add more 6 *M* HCl to dissolve any chlorides that may crystallise on cooling. Proceed to the appropriate separation scheme.

3. ISOTOPIC ANALYSIS OF URANIUM MINE TAILINGS

3.1 Introduction

There are 12 elements in the combined uranium and thorium decay chains. Of these, the isotopes of Ac, Fr, At, Bi and Tl have only a transitory existence and are environmentally unimportant. Radon is a gas and requires *in situ* determination. Of the remainder, isotopes of U, Th and Po may be determined by established alpha spectrometry techniques. Lead as ^{210}Pb may be determined either by gross beta counting its daughter ^{210}Bi or by alpha spectrometry of its grand-daughter ^{210}Po. The routine determination of ^{231}Pa by alpha spectrometry needs further study.

The determination of ^{226}Ra is usually made by allowing in-growth of its daughter radon; this is a very limited technique. There is scope for the development of a rapid and direct measurement of radium isotopes by alpha spectrometry and beta counting. This would allow the determination of ^{224}Ra, ^{223}Ra and ^{228}Ra, as well as the normally determined ^{226}Ra. With the exception of ^{228}Ra and ^{210}Pb, the following procedures for isotopic determination are carried out by alpha spectrometry because of the precision that may be achieved.

In the combined uranium decay chains there are 15 major alpha emitters and 7 in the thorium chain. Most of the alpha emissions occur with a major (~75%) and minor (≤ 25%) peak in the energy spectrum. Thus the total alpha spectrum is quite complex and cannot be resolved without the prior chemical separation of a particular element. The following scheme is designed for either quantitative separation and recovery (Pa, Po and Pb), or the qualitative separation and recovery (U and Th) in the presence of an artificial standard, or of in-growth of a daughter standard (Ra). The final form of the element is that of an 'infinitely' thin film on the polished surface of a counting planchette.

The overall scheme is illustrated in figure 2. Advantage has been taken of the effectively unlimited supply of tailings for analysis. This has allowed two or three samples to be digested for the complete suite of elements. To ensure that the samples are essentially identical, each sample should be split from a bulk sample obtained by multiple sample combination and riffling. The first sample is for U, Pa, Th, and all Ra isotopes. The second is for ^{210}Po, and ^{210}Pb analysis but it may also be used for the determination of ^{226}Ra by a radon emanation technique.

After digestion for the U, Pa. Th, Ra scheme, the solution is converted to a strong hydrochloric acid medium (6 *M* or greater) and the iron removed by solvent extraction with di-isopropyl ether. Silica is also removed at this stage. Protoactinium may then be removed quantitatively by solvent extraction with di-isobutyl carbinol. The aqueous phase, as a chloride solution, is passed through a strong base anion exchange column in the Cl- form. The uranium and polonium are retained on the column as chloro complexes but the thorium and radium pass straight through. The uranium and polonium may be eluted separately from the column and recovered for analysis. The thorium/radium solution is converted to a strong nitric acid medium and passed through a new strong base anion exchange column in the NO_3^- form. The thorium is retained on the column as a nitrate complex but the radium passes straight through. The thorium may subsequently be eluted from the column and recovered for analysis. The radium may be recovered from the wash.

After digestion for the Po, Pb scheme, the Po is extracted into chloroform, leaving the Pb in the aqueous phase. The Po is recovered from the chloroform phase and transferred to an aqueous phase suitable for the spontaneous deposition of Po onto a silver disc. After quantitative removal of the Po, the ^{210}Pb may be quantitatively found by precipitation of lead dichromate and determining the beta activity. The ^{226}Ra concentration may then be determined by a radon emanation method from the remaining aqueous phase.

3.2 Uranium and its Isotopes

3.2.1 Chemistry for the analysis of uranium

Uranium may be separated from a multielement solution by a number of methods such as ion-exchange, solvent extraction, chromatography, sequential precipitation, volatilisation and electrolysis; the choice is determined by such factors as yield, effectiveness of separation, and chemical form [Booman and Rein 1962]. The following method is a combination of ion-exchange and solvent extraction techniques and was chosen for the effectiveness of separation and the convenience of processing batches of five or six samples at a time.

The first step is to remove most of the iron by solvent extraction with di-isopropyl ether. The step removes most of the potential ion-exchange column load and allows the use of smaller columns. This step also flocculates any gelatinous silica If the assay is to include protoactinium then it may now be extracted directly into a mixture of di-isobutylcarbinol (dimethyl heptanol) and xylene. The uranium, thorium and radium remain in the aqueous solution.

The solution is then passed through a strong base anion exchange column in the Cl- form [Kraus and Nelson 1955; Rieman and Walton 1970]. The chloro-uranium complex, together with the chloro complexes of most of the transition metals and groups 4d and 5b metals, is strongly adsorbed onto the column. The alkali, alkaline-earth and group 3b metals, and the lanthanides, Mn, Ni and Th, do not form strong chloro complexes in hydrochloric acid and hence pass straight through the column. The column may then be washed with 9 *M* HCl to remove entrained impurities. The solution and washings should be retained for subsequent Th and Ra analysis. This process has separated the uranium from the alkali and alkaline-earth metals and in particular Ca and Mg, which are the major components of the host matrix, and the daughters of radium and thorium which interfere with the alpha spectrum.

The uranium is stripped from the column with 0.1 to 1 *N* HCl. Chloro complexes of such metals as Re, Os, Ir, Pt, Au, Hg, Pa and Po(IV) remain adsorbed on the column. No separation is perfect, so a final solvent extraction step is required to limit the contaminants to acceptable levels.

The solution is converted to nitrate, saturated with magnesium nitrate and the uranium is extracted into methyl isobutyl ketone (MIBK) as a nitrate complex. Methyl isobutyl ketone was selected as the organic phase on the grounds of low aqueous solubility, reasonable stability and extensively proved suitability [Booman and Rein 1962]. The uranium may be back-extracted into the aqueous phase with distilled water. In the case of a manganese-rich sample, the back-extraction should be carried out between pH 1.5 and 3 to limit manganese co- and back-extraction.

The uranium is electrodeposited onto a stainless steel planchette as the hydroxide through the electrolytic production of hydroxyl ion at the cathode. Originally, electrodepositions were carried out in solutions of ammonium chloride, sulphate, nitrate or oxalate buffered into the neutral pH region [Booman and Rein 1962]. These are also ideal conditions for the electrodeposition of any other metal with an insoluble hydroxide, and the co-deposited interference tends to degrade the spectra. Sill *et al.* [1974] noted that the inteference is reduced by lowering the pH range to 2 - 5 using the acid of the selected ammonium salt.

A number of electrolytes were investigated including organic acids with a pk_a of about 2, such as monochloroacetic acid. The most suitable electrolyte was a solution of ammonium acetate dissolved in nitric acid with the pH adjusted to about 2.

The cathodic reduction generates OH^- and NH_4^+. The reduction of NO_3^- is catalysed by uranium. As electrolysis proceeds there is a steady rise in pH, the extent of which is controlled by the acetic acid which acts as a buffer. The pH must not rise above 5. The acetic acid forms a weak uranium complex which minimises the loss of material through adsorption onto the walls of containers.

The cathode should be a polished stainless steel planchette and the anode a stout piece of platinum wire. The electrode gap should be about 12 mm. Optimum plating conditions are a starting voltage of $\geq$ 10 V and a starting current of 300 to 400 mA, and not greater than 400 mA for a 16 mm plating diameter. Plating is usually complete after 1 and a half hours from a 12 mL solution. For larger volumes it is advisable to increase the electrode gap and to extend the plating time proportionately.

Within the uranium decay series ^{238}U has the highest mass to activity ratio of 1.34 ug/dpm*. To obtain spectra with good resolution uranium sources should be $<$ 20 dpm as severe degradation of the spectra starts at activities of 80 dpm or more owing to the formation of finitely thick films. If necessary, the final uranium solution could diluted with the electrolyte buffer and an aliquot plated to keep the activity within the ideal range. Alternatively the sources may be moved farther from the detector's surface than the usual 6-7 mm to reduce the counting efficiency.

All electroplated sources should be heated in a yellow reducing flame until the plated area turns blue. improves the deposit and volatilises any tramp polonium which can contaminate the detector.

3.2.2 Procedure for the analysis of uranium

(i) If the material is already in solution as the chloride proceed to step (iii). Otherwise evaporate dryness, add 30 mL of concentrated HCl and a few drops of concentrated HNO_3 and evaporate

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* dpm = disintegrations per minute

dryness. Dissolve the residue in a minimum volume of 6 *M* HCl, boil gently to dehydrate and precipitate the excess silica.

(ii) If there is no silica precipitate, or if the silica precipitate is obviously gelatinous, proceed to step (iii). Otherwise, centrifuge or filter to separate and retain the solution. Wash the residue with 6 *M* HCl until it is pale yellow to white in colour. Combine the washings and solution.

(iii) If protoactinium is to be included in the assay, it should be extracted with di-isobutyl carbinol solution (see section 3.3) before proceeding to the next stage.

(iv) Dilute in the ratio 1:1 with concentrated HCl to bring acid strength up to 9 *M*. Extract once or twice with 10 mL of di-isopropyl ether which has been equilibrated with 9 *M* HCl and retain the aqueous phase.

(v) If necessary, centrifuge or filter to remove any flocculated silica. Wash the residue with 6 *M* HCl until it is pale yellow to white in colour. Combine the washings and aqueous phase. Evaporate the solution to 25 to 50 mL unless chloride salts begin to precipitate.

(vi) Apply the solution to the top of a 5 g column of a 100 to 200 mesh strong base anion exchange resin (*e.g.* Dowex 1-X8 or Bio-Rad AGI-X8) previously washed with 15 bed volumes (100 mL) of 9 *M* HCl. Retain the radium and thorium fraction.

(vii) Wash with 10 to 15 bed volumes (70 - 100 mL) of 9 *M* HCl. Combine the washings with the thorium and radium fraction.

(viii) Elute the uranium from the column with 10 bed volumes (70 mL) of 1 *M* HCl.

(ix) Evaporate the uranium eluate to dryness.

(x) Add 1 to 2 mL of concentrated HNO_3 and evaporate to dryness. The uranium is now in the nitrate form.

(xi) Dissolve in 1 to 5 drops of concentrated HNO_3, warming gently if necessary. Add 10 mL of saturated $Mg(NO_3)_2$ solution which has been pre-extracted with MIBK. Note that the frequently used $Al(NO_3)_3$ salt can be contaminated with uranium. Also some Al passes through the purification steps and is precipitated onto the planchette. Add 1 to 2 drops of cresol red indicator and adjust immediately to the yellow colour with 5 *M* NH_4OH.

(xii) Extract three times with 10 mL lots of MIBK. Bulk the organic phases in a glass beaker. Allow the entrained aqueous phase to settle.

(xiii) Decant the organic phase into a clean extraction flask taking care to exclude the aqueous phase. The aqueous phase may be washed with a small amount of MIBK to increase recovery.

(xiv) Back-extract four times with 10 mL lots of distilled water and bulk the water extracts.

(xv) Warm to volatilise the entrained MIBK. If the solution shows signs of turbidity, pass it through a 0.45 μm filter. Evaporate to dryness.

(xvi) Add 5 to 10 drops of concentrated $HClO_4$ and evaporate to dryness to remove any entrained organic contamination. If the residue is to be stored before electrodeposition, moisten with a few drops of concentrated $HClO_4$. This ensures that the uranium remains in solution and does not plate out onto the glass because of hydrolysis.

(xvii) Prepare an electrolyte buffer solution of 0.20 *M* ammonium acetate in 0.26 *M* HNO_3. Assemble a clean electrodeposition cell with a new stainless steel planchette and a new Viton 'O' ring (see para. (xxi) and figure 3). Add about 0 mL of electrolyte to the cell and clean the planchette by anodising it for 1 to 2 minutes (that is until the solution turns yellow). Discard the electrolyte and rinse the cell with fresh electrolyte buffer.

(xviii) Dissolve the evaporate in 5 mL of electrolyte buffer and pour into the electrodeposition cell. Rinse the beaker with a further 5 mL of electrolyte buffer and add the washings to the electrodeposition cell.

(xix) Electrodeposit for 1.5 hours onto the stainless steel planchette at 300 to 400 mA for a 16 mm plating diameter and a starting voltage of $>$10 V. Check the pH every 30 minutes using Merck narrow range pH paper and maintain it to less than 5.0 by adding 8 *M* HNO_3 dropwise. Provided that the electrolyte is reasonably free of contaminants, pH adjustment will not normally be necessary.

CAUTION: The electrodeposition should be carried out in a fume cupboard to control the hazard arising from respirable aerosols containing alpha emitters.

(xx) At the end of the electrolysis store the electrolyte in the original beaker until counting is satisfactorily completed. Wash the planchette with distilled water, adding the washings to the stored electrolyte. Wash the planchette with isopropyl alcohol, air-dry and flame in a yellow (reducing) flame until the deposit turns blue. If an unsatisfactory electrodeposit is produced, the U may be recovered by sitting a drop of concentrated HNO_3 on the deposit and washing it into the retained electrolyte as soon as the original surface is revealed. The resulting solution will be contaminated with the components of the stainless steel and platinum. A round-ended glass rod can be used to rub off the deposit.

(xxi) Rinse the electrodeposition cell in hot water then soak it overnight in concentrated HNO_3. Rinse in hot water before use. Store the platinum anode in concentrated HNO_3 and flame briefly to red heat before use.

3.2.3 Alpha spectrometry for uranium

Table 2 lists the particle energies and intensities for alpha decay of the natural uranium isotopes ^{238}U, ^{235}U and ^{234}U, and for the artificially-produced uranium isotopes ^{236}U and ^{232}U which may be used as isotopic standards. The right-hand column give the percentage particle intensity for ^{235}U in natural uranium based on a natural abundance of 0.72 per cent and an activity of 3.98 per cent of ^{238}U.

Figure 4 shows the theoretically pure spectrum for the isotopes of natural uranium. Included in the diagram as broken curves are the spectra for ^{236}U and ^{232}U. The dotted curves indicate spectra of the uranium daughters which could interfere with the uranium spectra. It has been assumed that the activity ratios of the isotopic standards are equal to that of the natural uranium (a rare event!), that the ^{238}U and ^{234}U isotopes are in secular equilibrium, and that ^{235}U is present at the natural abundance of 0.72 per cent. The particle intensities of the impurities are notional.

A common feature of the spectra is a sharp high energy leading edge and a tail on the low energy trailing edge. The tail becomes more pronounced with thicker deposits on the planchette.

The ^{238}U peak at 4.196 MeV (77 per cent) is free of overlapping peaks. Resolution of the lower energy minor peak at 4.147 MeV (23 per cent) is possible with a well-prepared specimen.

The ^{235}U spectrum is split into a number of low-intensity peaks over the range 4.2 to 4.6 MeV. This, and the low abundance of this isotope, makes this method unsuitable for a quantitative analysis of ^{235}U.

The alpha spectrum for ^{236}U has a major peak at 4.494 MeV (76 per cent) and a low energy minor peak at 4.445 MeV (24 per cent). Resolution of the low energy minor peak is possible with a well-prepared specimen. The spectrum is located centrally between the ^{238}U and ^{234}U spectra. The low energy tail of the ^{236}U spectrum straddles the ^{235}U spectrum and should be taken into account if this isotope is to be used as the standard. The ^{235}U contribution will be approximately four per cent of the ^{238}U peak area. The ratio of the major and minor peak heights should be 3.2 to one. Variation from this ratio is indicative of the presence of impurities.

The alpha spectrum for ^{210}Bi, with the major peak at 4.654 MeV, cannot be observed under these conditions. The major decay mode for this isotope is by beta emission, with only 1.3×10^{-4} per cent decay occurring by alpha emission.

The alpha spectrum for ^{234}U has a well-defined major peak at 4.776 MeV (72 per cent) and low energy minor peak at 4.724 MeV (28 per cent). Resolution of the minor peak is possible with a well-prepared specimen. The low energy side of the spectrum should be inspected for the presence of ^{230}Th with a major peak at 4.688 MeV (76 per cent) and a minor peak at 4.621 MeV (24 per cent). In the ore, this isotope would have been in approximate secular equilibrium with its parent ^{234}U. After extraction of the uranium from the ore, the ^{230}Th is in gross activity excess over its parent. As an impurity, it could cause an enhanced ^{234}U tail.

Unfortunately the ^{226}Ra with a major peak at 4.785 MeV at 94.5 per cent intensity, is almost coincident with the spectrum for ^{234}U. Radium and thorium do not form chloro complexes that may be retained on the strong base anion exchange column so, provided that the column was washed well, there should be no radium or thorium present. If the major and minor peaks for the ^{234}U spectrum can be resolved, then the presence of ^{226}Ra is indicated if the ratio of the heights of the major and minor peaks increases from 2.57. If this is the case, the spectrum should be examined for the low energy radium peak of intensity 5.5 per cent at 4.602 MeV. The spectrum for ^{234}U may then be corrected to bring ratio of the major and minor peaks of ^{234}U back to 2.57:1.

The alpha spectrum for ^{227}Ac with major peaks at 4.950 and 4.938 MeV has not been included in fig because, under these conditions of analysis, it is highly unlikely to be observed for several reasons. As a dau of ^{235}U it will have a maximum intensity of approximately four per cent of the ^{238}U intensity. The che separation processes will have significantly reduced this intensity. The principal decay mode is by beta emi with only 1.4 per cent decay occurring by alpha emission.

The isotope ^{231}Pa is a daughter of ^{235}U. The principal mode of decay is by alpha emission as a series o intensity peaks across the range 5.022 to 4.729 MeV. It is doubtful whether this isotope could be detecte uranium spectrum for a number of reasons. It is a low intensity source with respect to ^{238}U, the ^{231}Pa spectr very diffuse, and the chemical separation process will have reduced its intensity..

The alpha spectrum for ^{232}U has a well-defined major peak at 5.320 MeV (68 per cent) and a low energy peak at 5.263 MeV (32 per cent). Resolution of the major and minor peaks is possible with a well-pre specimen. The spectrum does not interfere with the spectra of ^{238}U, ^{235}U or ^{234}U. There are two po interferences ^{210}Po and ^{228}Th. The ^{210}Po is a daughter of ^{238}U and, unless it has been removed by che separation, it will be present in gross activity excess over the ^{238}U. The alpha spectrum for ^{210}Po is a single at 5.305 MeV which is 15 keV below the major ^{232}U peak. The resolution of most alpha detectors is 25 k greater, consequently these two peaks cannot be resolved. Fortunately ^{210}Po may be quantitatively removed chemical separation process. If the major and minor peaks of the ^{232}U spectrum can be resolved, the presence of ^{210}Po is indicated when the ratio of of the major and minor peaks exceeds 2.125:1. Correcti ^{210}Po may be made either by correcting the peak heights back to the ideal ratio, or by flaming the planchette heat to volatilise the ^{210}Po. This tends to thicken the deposit.

The other interference with the ^{232}U peak is the presence of ^{228}Th. This isotope is a daughter of ^{232}U present in any aged ^{232}U standard. The alpha spectrum for ^{228}Th has a well-defined major peak at 5.423 Me per cent) and a low energy minor peak at 5.341 MeV (27 per cent). Thus although the major peaks of ^{232} ^{228}Th are clearly resolved, the minor peak of ^{228}Th is incorporated into the ^{232}U peak. If ^{228}Th is presen activity of the ^{232}U peak should be corrected for the ^{228}Th minor peak by determining the activity of the major peak and then the activity of the ^{228}Th minor peak from the ratio of the ^{228}Th major to minor intensities.

Another source of error in the ^{232}U spectrum is caused by the injection of ^{228}Th by alpha recoil in detector from previous counting of strong, aged ^{232}U sources. This may be minimised by using weak ^{232}U sc The extent of contamination may be checked by running regular background spectra. Corrections f contamination may be made either from the background spectra or by inspecting the spectra for the high daughters of ^{228}Th, such as ^{216}Po with a peak at 6.779 MeV and an intensity of 100 per cent. A small bias 10 V reverse polarity to the detector (-ve) on the source plate minimises this effect.

The alpha emissions of the remaining isotopes of the uranium decay chains occur with particle energies 5.5 MeV and do not interfere with the uranium spectrum.

3.3 Protactinium-231

3.3.1 Chemistry for the analysis of protactinium

The chemistry and methods for analytical recovery of protactinium have been discussed in detail by [1964] and Smith and Barnett [1965]. Protactinium has a strong tendency to hydrolyse and form intractable c which readily plate out on glassware. This can lead to low chemical recovery. The problem is overco complexing the protactinium with fluoride or sulphate at low pH. The following precautions are neces maintain the protactinium in solution:

(a) The solutions must be highly acidic and contain either hydrofluoric or sulphuric acid.

(b) In hydrochloric acid media the acid concentration should be at least 6 *M* or greater and stal assured only for one to two days, *i.e.* the time taken to complete the analysis.

(c) Protactinium should be held in organic phases for the minimum time possible.

(d) All separations of protactinium must be carried out in strongly acidic media and the aqueous containing the protactinium should be kept in plastic ware if possible.

(e) Separations should be kept as simple as possible.

(f) The number of fresh glass surfaces should be kept to a minimum.

Because the alpha spectra of uranium and protactinium do not overlap, advantage may be taken of the low activity concentration of uranium in uranium mine tailings, thus avoiding quantitative separation of the uranium and protactinium. Unfortunately there is no suitable yield tracer for protactinium so it is necessary to achieve 100 per cent recovery. As this cannot be guaranteed by an electrodeposited finish, an evaporative finish was selected. The adopted method is as follows.

The 6 *M* HCl solution obtained following the initial digestion procedure is dosed with HF to a concentration of 0.05 *M*. The iron is then extracted into isopropyl ether. The fluoride ion complexes the protactinium and blocks co-extraction of the protactinium. Next, the fluoride ion is complexed by the addition of 0.1 *M* Al^{3+} as $AlCl_3$ which releases the protactinium to the solution. The protactinium is then extracted selectively and quantitatively into a solution of 50 per cent di-isobutylcarbinol (dimethylheptanol) in xylene from the 6 *M* HCl medium. The organic extract is separated from the aqueous phase and evaporated to a small volume before transferring it to a lacquered stainless steel planchette where it is evaporated to dryness. The planchette should be flamed to red heat before counting to remove the organic materials and any tramp polonium.

The other actinides do not co-extract to any significant degree. Some metals will co-extract, notably iron, aluminium and niobium, and may cause the evaporated deposit to be quite bulky. Because of the diffuse nature of the protactinium spectrum, the loss of resolution due to a bulky deposit can usually be tolerated provided that it can be shown that the amount of uranium as co-extracted ^{234}U is insignificant. If the deposit is unacceptably bulky, the extract may be washed with 6 *M* HCl containing 4 wt %/vol oxalic acid to remove the iron and niobium, but this causes the loss of some Pa.

This method appears to be suitable for the quantitative estimation of protactinium in ores and tailings, that is to say at levels considerably higher than normal background. Because there is no isotopic yield tracer, total recovery should be checked by testing each class of matrix by the method of standard additions, using pure ^{231}Pa. In addition to alpha spectrometry, the prepared sources may also be checked for gross alpha activity by gas proportional counting provided that a set of standards has been prepared for each class of matrix. The beta-emitting isotope ^{234}Pa (a grand daughter of ^{238}U with a $t_{1/2}$ of 6.7 h) will be present and may be counted for beta activity on the same planchette with high efficiency. For samples less than one month old, the ^{234}Pa level would supply useful information on the behaviour of the parent ^{234}Th within the system being studied.

3.3.2 Procedure for the analysis of protactinium

Carry out steps (i) and (ii) of the procedure for the analysis of uranium following total digestion of the sample described in section 3.2.2. A total dissolution employing hydrofluoric acid at some point is preferred. The sample should now be in 6 *M* HCl solution and devoid of turbidity from suspended silica. Do not store the sample for a prolonged period.

(i) Add enough concentrated HF to bring the F^- concentration up to 0.05 *M* (0.002 mL HF per mL of sample).

(ii) Extract the iron once or twice, depending on the iron level, with 10 mL lots of di-isopropyl ether which has been first equilibrated with 9 *M* HCl and retain the aqueous phase in a Teflon beaker.

(iii) Add enough solid $AlCl_3$ to bring the Al^{3+} up to 0.1 *M* (0.013 g per mL of sample). Heat the solution on a water bath until all of the $AlCl_3$ has dissolved and all traces of ether have evaporated.

(iv) Dilute in the ratio 1:1 with concentrated HCl and extract the Pa with three 10 mL lots of 50 vol.% di-isobutyl carbinol in xylene. Retain the aqueous phase for the analysis of uranium, thorium and radium if required.

(v) Bulk the organic phases. If there is a high iron content in the sample, wash once or twice with 10 mL lots of 6 *M* HCl containing 4 wt %/vol. oxalic acid.

(vi) Transfer all the organic phase to a small Teflon beaker ensuring that none of the aqueous phase is entrained. Evaporate to $<$ 1 mL in two stages; first, the lower boiling xylene will evaporate followed by the di-isobutyl carbinol.

(vii) Paint a mirror-finish, stainless steel planchette with a clear, dilute PVC varnish or glue. Mask the perimeter with a wax pencil. Transfer the evaporate dropwise onto the planchette, evaporating each drop to dryness with an infrared lamp. Wash the Teflon beaker with one or two drops of di-isobutyl carbinol which has previously been equilibrated with 9 *M* HCl. Transfer the washings dropwise to the planchette and evaporate to dryness. Slowly heat the planchette to dull red heat in a cool yellow flame.

(viii) Determine the ^{234}Pa by alpha spectrometry or by gross alpha counting and compare against standard sources. Beta counting may be employed in the presence and absence of a 4 to 5 mg cm^{-2} Al foil as an alpha particle absorber. Gross beta counting efficiencies may be estimated with a pure uranium source that is more than six months old

3.3.3 Alpha spectrometry for protactinium

Table 3 lists the particle energies and intensities for tne alpha decay of ^{231}Pa; the only alpha-emitting isotope of protactinium in the natural uranium and thorium decay chains. The spectrum for ^{231}Pa shown in figure 5 is somewhat dispersed but, fortuitously, there are no interferences with its main part. The three main peaks are located at 4.950 MeV (22.8 per cent), 5.011 MeV (25.4 per cent) and 5.028 MeV (20 per cent). On the low energy side there is a minor peak at 4.736 MeV (8.4 per cent). This peak cannot be resolved from that for ^{234}U at 4.776 MeV nor that for ^{226}Ra at 4.785 MeV. It is unlikely that radium will be present. There may be tramp uranium and the spectrum should be examined for the presence of ^{238}U as an indicator of the presence of ^{234}U. If ^{238}U is present then an appropriate correction should be made for the ^{234}Pa peak at 4.736 MeV. The spectrum is quantitative when it is compared against that for the isotopic standards.

3.4 Thorium and its Isotopes

3.4.1 Chemistry for the analysis of thorium

The chemistry for the analytical recovery of thorium has been discussed in detail by Grimaldi [1961]. The alkali metals, alkaline-earth metals including Ra, the group 3b metals, the lanthanides, Mn, Ni and Th do not form chloro-complexes in strong hydrochloric acid and remain in solution during the ion-exchange separation of the uranium as the chloro-uranium complex. Of the metals now remaining in solution, only Th, Tc, Re, Ce(IV), Au, Pt and Pd form nitrate complexes which adsorb strongly onto a strong-base anion exchange column [Faris and Buchanan 1964; Rieman and Walton 1970]. On converting the thorium to the nitrate in strong nitric acid and passing the solution down a strong-base anion exchange column, the thorium is adsorbed onto the column, whereas the alkali metals, alkaline-earth metals including radium, the group 3b metals, the lanthanides, Mn and Ni pass through the column in solution. After washing out entrained solution from the column with nitric acid, the thorium and trace elements listed above may be eluted with strong hydrochloric acid.

An effective final purification step may be achieved by solvent extraction using 2-thenoytrifluoroacetone (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione), TTA, in xylene as the organic phase [Grimaldi 1961]. This particular reagent is selective for thorium at low pH ranges and is very stable.

The optimum pH range for the electrodeposition of thorium is 1.5 to 5 [Ko 1954; Barring 1966; Puphal and Olsen 1972; Roman, 1980], which is very similar uranium, and the same electrolyte buffer may be used. Thorium does not catalyse the reduction of NO_3^- and the pH rise during the course of the reaction is much slower compared to that for uranium electrodeposition.

3.4.2 Procedure for the analysis of thorium

(i) Evaporate the 9 *M* HCl solution and washings from the uranium extraction to about 20 mL.

(ii) Add 20 mL of concentrated nitric acid and evaporate to about 10 mL. Repeat this procedure two or three times until the solution is colourless. The thorium is now in the nitrate form.

(iii) Dilute in the ratio 1:1 with water to reduce the acid strength to 8 *M*.

(iv) Apply the solution to the top of a 1.5 g (~ 1.8 mL) strong base anion exchange column (*e.g.* Dowex 1-X8 or Bio-Rad AGI-X8) in the NO_3 form which has been washed with 15 bed volumes (25 to 30 mL) of 8 *M* HNO_3. Retain solution as radium fraction.

(v) Wash with 10 to 15 bed volumes (20 to 30 mL) of 8 *M* HNO_3, adding washings to the radium fraction.

(vi) Elute thorium with 10 bed volumes (20 mL) of 6 *M* HCl.

(vii) Evaporate to dryness.

(viii) Add approximately ten drops of $HClO_4$ and five of concentrated HNO_3 and evaporate to dryness to remove the trace organic material. If the residue have very little bulk, then proceed to step (xvi), otherwise continue through step (ix).

(ix) Dissolve the residue in 10 to 30 mL of electrolyte buffer with the pH adjusted to 1.2 with 1 *M* HNO_3 using thymol blue as the indicator. Transfer the solution to a 50 to 100 mL extraction flask.

(x) Prepare a solution of 0.2 *M* thenoytrifluoroacetone in xylene (TTA solution).

(xi) Solvent extract three times with 10 mL of TTA solution. Bulk the organic phases in a glass beaker and allow to settle. Decant the organic phase into a clean extraction flask. The settled aqueous phase may be washed with TTA solution to increase the recovery.

(xii) Back-extract three times with 10 mL of 2 *M* HNO_3.

(xiii) Evaporate the aqueous back-extractant to dryness.

(xiv) Add about ten drops of $HClO_4$ and a few drops of concentrated HNO_3 and evaporate to dryness to remove any co-extracted organic matter. If the residue is to be stored for two or more days before electrodeposition, add a few drops of concentrated $HClO_4$. This ensures that the residue remains moist and acid (pH $<$ 2) and does not hydrolyse or plate out onto the glass.

(xv) Prepare an electrolyte buffer solution of 0.20 *M* ammonium acetate in 0.22 *M* HNO_3. Assemble a clean electrodeposition cell (see step (xix) and figure 4) with a new stainless steel planchette and Viton 'O' ring. Add 10 mL of electrolyte to the cell and clean the planchette by anodising for one to two minutes (that is until the solution turns yellow). Discard the electrolyte and rinse the cell with fresh electrolyte buffer.

(xvi) Dissolve the evaporate in 5 mL of electrolyte buffer. Add one drop of 8 per cent HF to the solution. Rinse the beaker with a further 5 mL of electrolyte buffer and add the washings to the electrodeposition cell.

(xvii) Electrodeposit for two hours onto the stainless steel planchette at 400 to 500 mA for a 16 mm plating diameter (but not greater than 500 mA), and a starting voltage of $>$ 11 V. Check the pH every 30 minutes using Merck narrow range pH paper and maintain the pH to less than 5.0 by adding 8 *M* HNO_3 dropwise. Provided that the electrolyte is reasonably free of contaminants, pH adjustment will not be necessary.

CAUTION: The electrodeposition should be carried out in a fume cupboard to control the hazard arising from respirable aerosols containing alpha emitters.

(xviii) At the end of the electrolysis save the electrolyte in the original beaker until counting is satisfactorily completed. Wash the planchette with distilled water, adding the washings to the stored electrolyte. Wash the planchette with isopropyl alcohol, air-dry and submit for alpha spectral analysis. If the electrodeposit is unsatisfactory, the Th may be recovered by putting a drop of concentrated HNO_3 on the deposit then washing the drop into the stored electrolyte as soon as the original surface is revealed. The resulting solution will be contaminated with the components of the stainless steel and platinum and should be cleaned by passing the solution through another NO_3^- anion column.

(xix) Rinse the electrodeposition cell in hot water. Soak it overnight in concentrated HNO_3. Soak the platinum anode in concentrated HNO_3 for one hour before use. Rinse the cell and the anode with hot and distilled water before assembly.

3.4.3 Alpha spectrometry for thorium

Table 4 lists the particle energies and intensities for alpha decay of the natural thorium isotopes ^{232}Th, ^{230}Th, ^{228}Th and ^{227}Th and for the artificially produced isotope ^{229}Th which may be used as isotopic standards. Figure 6 shows a theoretically pure spectrum for the natural thorium isotopes in the ^{238}U, ^{235}U and ^{232}Th decay series. The broken curve represents the spectrum of ^{229}Th, an isotope which may be used as a standard for isotopic ratio work. The dotted curves are the spectra of uranium and thorium daughters which may interfere with the thorium spectrum. The curves for the natural thorium isotopes ^{232}Th, ^{230}Th and ^{228}Th have been plotted as percentage particle intensity for the alpha decay of a particular isotope. The spectrum of ^{227}Th is shown as percentage activity relative to ^{230}Th. The particle intensities of the impurities are notional.

The majority of the spectra are characterised by a sharp high energy leading edge and a tail on the low energy trailing edge. However, ^{229}Th, ^{214}Bi and ^{227}Th have significant minor peaks at energies above the major peak, so the high energy leading edge for the spectra of these isotopes is broadened.

The ^{232}Th spectrum, with a major peak at 4.010 MeV (77 per cent) and a low energy minor peak at 3.953 MeV (23 per cent), is free of any overlapping peaks from the other thorium isotopes and from the uranium or thorium daughters. As the parent of the ^{232}Th series, it is of minor importance in uranium ores. The very low rate of decay of ^{232}Th discourages the use of this isotope as a thorium yield tracer; ^{229}Th or ^{228}Th is preferred

The ^{230}Th spectrum has a well-defined major peak at 4.686 MeV (76 per cent) and a low energy minor peak at 4.621 MeV (24 per cent). Of the uranium isotopes, only ^{234}U is a likely cause of interference on the high energy side. However, thorium is in gross activity excess over uranium in tailings; further purification steps will have reduced the ^{234}U to insignificance. Evidence for the presence of ^{234}U would be indicated by a peak for ^{238}U at 4.196 MeV. The other possible interference on the high energy side would be from ^{226}Ra, the immediate daughter of ^{230}Th, at 4.786 MeV. Fortunately, the extreme chemical differences of Ra and Th guarantees analytical separation of these materials.

The alpha spectrum for ^{210}Bi, with a major peak at 4.654 MeV, cannot be observed under these conditions. The major decay mode for this isotope is by beta emission, with only 1.3×10^{-4} per cent decay occurring by alpha emission.

Thorium-229 is an artifically-produced isotope which could be used as a yield tracer. The alpha spectrum for ^{229}Th is anomalous, the major peak at 4.845 MeV (56.2 percentage) having a series of minor peaks on the high energy side leading to a rather broad spectrum, and with trace overlap with the ^{230}Th spectrum on the low energy side. Spectra for ^{227}Ac and ^{231}Pa, daughters of ^{235}U, also occur in this region. The alpha spectrum for ^{227}Ac, with major peaks at 4.940 and 4.938 MeV, has not been included in the diagram because under these analytical conditions it is highly unlikely to be observed. As a daughter of ^{235}U it will have a decay activity about four per cent of the ^{230}Th decay activity. The principal decay mode is by beta emmission with only 1.4 per cent decay occurring by alpha-emission. This activity is further reduced by the chemical separation processes. The principal mode of decay of ^{231}Pa is by alpha emission with a series of low intensity peaks across the range 5.022 MeV to 4.729 MeV. It is doubtful also whether this isotope could be detected in a thorium spectrum because of the diffuse nature of the ^{231}Pa spectrum, it is a low activity source with respect to ^{230}Th activity, and the chemical separation is needed to remove this element from the thorium spectrum.

Good spectral resolution is required when ^{229}Th is used as a yield tracer. The spectrum abuts that for ^{230}Th and a minor peak at 4.688 MeV (0.15 per cent) for ^{229}Th is totally unresolvable from the ^{230}Th spectrum.

The daughter of ^{229}Th is ^{225}Ac with a half-life of ten days. The spectrum for ^{225}Ac is diffuse, having a major peak at 5.829 MeV (52 per cent), a minor peak at 5.793 MeV (29 per cent) and a series of lower energy peaks which are unresolvable from the spectrum for ^{224}Ra, the daughter of ^{228}Th. If both thorium isotopes are present, it will be necessary to do some careful spectral stripping.

The ^{228}Th spectrum has a well defined major peak at 5.423 MeV (73 per cent), a low energy minor peak at 5.341 MeV (27 per cent) and three minor peaks in the range 5.14 to 5.21 MeV (0.61 per cent total). Resolution of the major and minor peaks should be possible with a well-prepared specimen. As a daughter of ^{232}Th, ^{228}Th is not normally found in uranium ores. The absence of natural ^{228}Th can be confirmed by the absence of ^{232}Th. This allows ^{228}Th to be used as a yield tracer. There are two natural impurities which could interfere with the ^{228}Th spectrum - ^{210}Po and ^{214}Bi. The alpha spectrum for ^{210}Po is a single peak at 5.305 MeV. Polonium is separated in the analytical scheme and can be quantitatively recovered. However, it is an element which tends to travel. Absence of tramp ^{210}Po is confirmed if the intensities of the ^{228}Th peaks are in the ratio 71.37 : 28.63.

The spectra for ^{214}Bi is anomalous, with a major peak at 5.448 MeV (53.9 per cent), a high energy minor peak at 5.512 MeV (39.2 per cent) and a trace minor peak at 5.268 MeV (5.8 per cent). The major peak interferes with the leading edge of the ^{228}Th spectrum. Fortunately, only 0.04 per cent of the decay is by alpha emission, so normally corrections for this isotope may be ignored.

Thorium-228 has two parents, natural ^{232}Th and the artificially-produced ^{232}U. If ^{228}Th is used as a yield tracer, the source of the isotope should be ascertained because the high energy peak of ^{232}U interferes with the low energy tail of ^{228}Th. For a well-resolved spectrum, the presence of ^{232}U is readily identified by the low energy minor peak for ^{232}U at 5.264 MeV (31 per cent).

Thorium-228 has a half-life of 1.9 y and the immediate daughter ^{224}Ra will start to grow in following the last separation procedure before electrodeposition. Radium-224 has a well-defined major peak at 5.684 MeV (94.5 per cent) and a minor peak at 5.447 MeV (5.5 per cent). The minor peak is completely unresolvable from the ^{228}Th major peak at 5.424 MeV and will enhance the ^{228}Th count. The ^{228}Th count may be corrected by subtracting 5.5/94.5 times the count of the ^{224}Ra major peak.

The alpha spectrum for ^{227}Th is a diffuse series of low energy peaks, the major peaks being at 6.038 MeV (24.5 per cent), 5.978 MeV (23.4 per cent) and 5.757 MeV (20.3 per cent). As a daughter of ^{235}U, its percentage abundance will be low and the spectrum will be lost among spectra of the daughters of the other thorium isotopes. One interfering spectrum is that of ^{212}Bi which has a major peak at 6.051 MeV (69.9 per cent) and a high energy minor peak at 6.090 MeV (27.2 per cent). This isotope is a daughter of ^{228}Th and will not normally be present in uranium mine tailings. However, it will be present in aged solutions of ^{228}Th which are used as yield tracers.

3.5 Radium and its Isotopes

3.5.1 Chemistry for the analysis of radium

The chemistry for the analytical recovery of radium has been discussed in detail by Sedlet [1966]. The most common way of determining radium concentrations is by the radon emanation method. The technique involves the quantitative collection of radon (usually considered as the single isotope ^{222}Rn) which is the gaseous daughter of radium (again usually considered as the single isotope ^{226}Ra). This is the basis of the American Society for Testing Materials (ASTM) method for determining ^{226}Ra in water [ASTM 1975; Rushing *et al.* 1964].

A useful variation on the ASTM technique is to allow the radon to emanate into a toluene solution containing a scintillant, then determine the radium concentration by liquid scintillation counting [Cooper and Wilks 1981; Twining 1983]. Unfortunately, the emanation method is slow, requiring an in-growth time of 20 days to reach full equilibrium between ^{222}Rn and its parent ^{226}Ra. The method is not readily applicable to the measurement of the other radium isotopes via their short-lived radon daughters nor to mixtures of radium isotopes. The advantage of the radon emanation method is that because the ^{222}Rn is also in equilibrium with its daughters, the alpha count is four times that of the originating parent. This allows the detection limit to be set at around 0.3 dpm. The detection limit for the emanation into toluene is about 2 dpm. Gamma-ray emmission techniques may be used. This is a very rapid technique but the detection limit is about 60 dpm; it could be lower if the ^{226}Ra spectrum is relatively clean.

The complete suite of alpha-emitting radium isotopes (^{228}Ra is a beta emmitter) by alpha spectrometry has been analysed by laying down a thin film of radium sulphate with a barium sulphate carrier [Sedlet 1966; Sill *et al.* 1974; Sill 1983]. The presence of the carrier invariably degrades the spectrum through self-adsorption, but it has the advantage that losses of daughters through recoil or, in the case of radon, gaseous diffusion, are minimal. This allows the in-growth of daughters to be used as part of the quantitative determination.

Radium metal, unlike uranium, thorium, protactinium, actinium, polonium, lead and bismuth, has a very large negative electrochemical potential and is therefore unstable in the presence of water at any pH. The oxide is very soluble [Pourbaix 1966]; for this reason there have been very few attempts to electrodeposit radium, and the few that have been reported usually employed an aqueous/organic solution with high cell voltages. Haissinsky [1937] used an acetone solution. Sorret and Tauveron [1972] employed an isopropanol/HCl solution, electroplating at 600 V and 12 mA onto platinum. Koide and Bruland [1975] used a similar electrolyte and cathode but were able to reduce the plating voltage to 40 V and the current to 100 to 150 mA by using higher HCl concentrations. Sill *et al.* [1974] observed the partial deposition of ^{224}Ra while electrodepositing ^{228}Th onto stainless steel from aqueous solutions at 12 V and 500 mA. Roman [1984] observed a similar result and developed a method for the near quantitative electrodeposition of radium onto stainless steel from an ammonium acetate/nitric acid solution with pH 8 - 9 at 12 V and 500 to 600 mA. The deposit was stable, and resistant to mechanical abrasion and mild chemical attack. The radon daughters grew into full equilibrium activity in the film. The nature of the film is not understood but it appears to include platinum removed from the anode. The development of this electrodeposition technique allows analysis of the complete suite of radium isotopes by high resolution alpha spectrometry and beta counting. The following scheme was successfully developed for uranium tailings, ores and soils with a detection limit set at about 3 dpm.

Uranium, protactinium, thorium and polonium interfere with the alpha spectrum of the radium isotopes and their daughters, so they must be completely removed from the solution. Radium-224 is part of the ^{232}Th decay chain and will only be present in minor amounts. If the assay is to include ^{224}Ra, then ^{232}U or ^{228}Th cannot be used as a yield tracer if the same sample is being analysed for uranium or thorium; because ^{224}Ra is a daughter of these yield tracers, it to will produce an anomalously high ^{224}Ra result. If ^{224}Ra is known to be absent, or present at a known level, then it may be used as a yield tracer.

After dissolution of the sample, uranium, protactinium and polonium (IV) and the majority of transition metals may be removed as chloro-complexes on a strong base anion exchange column in the Cl$^-$ form. The radium and thorium pass straight through the column. Thorium is then removed as the nitrate complex on a strong base anion exchange column in the NO_3^- form, leaving actinium and radium isotopes as the only remaining significant alpha emitting nuclides of the uranium and thorium series. Isotopes of francium, astatine, bismuth and polonium will also remain in solution or grow in. Some of these isotopes are alpha-emitters or decay to alpha-emitting daughters. These isotopes are either insignificant or well resolved in the alpha spectrum and may be used for spectral stripping analysis. The alkali metals, the alkaline-earth metals and the group 3b elements are the remaining major stable elements in this fraction.

The radium may be separated from the bulk of the remaining contaminants by co-precipitation with barium sulphate at pH 1 in the presence of lanthanum. The lanthanum is a holdback carrier and prevents the co-precipitation of ^{227}Ac, ^{225}Ac (the in-growing daughter of ^{225}Ra and granddaughter of the tracer ^{229}Th) and residual traces of thorium. The sulphate precipitate is metathesised to the carbonate salt. The radium can then be separated from the barium using the following method developed by Gleason [1979].

The barium/radium carbonate precipitate is dissolved as a complex of cyclohexylenediaminetetraacetic acid (DCYTA) in boric acid at pH 5. The complex is added to a strong acid cation exchange column in the Na^+ form at pH 5. The column is then adjusted to pH 8.5 with saturated boric acid/sodium hydroxide solution. The radium complex is strongly held by the column. The alkali earths, particularly barium, are washed from the column by repeated elution with a DCYTA/boric acid solution adjusted to pH 8.5. The DCYTA is then stripped from the column by converting the column to its acid form with HBr. This also removes any traces of lead. The radium is eluted from the column with 9 *M* HCl to produce a radium fraction pure enough for aqueous electrodeposition onto a stainless steel planchette from an ammonium acetate/nitrate electrolyte which is initially at pH 5 but rises to a pH between 8 and 9 as the electrolysis proceeds. The ^{226}Ra, ^{223}Ra and ^{224}Ra isotopes are determined by alpha spectrometry. The isotope ^{228}Ra may be determined by beta counting the ^{228}Ac daughter.

3.5.2 Procedure for the analysis of radium

(i) If the solution is the eluent from the uranium/thorium scheme, proceed directly to step (ii). If the material is not already in solution, it should be digested using any of the techniques listed in section 2. The fusion digestion will volatilise unknown amounts of polonium, lead, and bismuth. Before digestion, add the requisite amount of the yield tracer ^{224}Ra in the form of aged ^{228}Th.

Alternatively, add the requisite amount of the yield tracer ^{223}Ra which has been freshly milked from an actinium-227 'cow', and standardised by evaporation onto a stainless steel planchette, and counted by alpha spectrometry. Unless uranium and thorium are to be included in the analytical scheme, do not add ^{232}U, ^{236}U or ^{229}Th as yield tracers.

Following digestion ensure that all the uranium, protactinium, polonium and thorium isotopes are removed by the methods described in sections 3.2 to 3.4. The time of the thorium/radium separation must be noted.

(ii) Evaporate the solution produced in step (i) to dryness on a water bath. Add 2 mL of HNO_3 and evaporate to dryness. Repeat twice and redissolve in 50 mL of 0.1 *M* HNO_3.

(iii) Add 1 mL of 9 *M* H_2SO_4 and three to four drops of 0.18 *M* $La(NO_3)$ in 0.1 *M* HNO_3. Chill the solution in a refrigerator for 30 minutes.

(iv) Add dropwise 0.5 mL of 0.73 *M* $BaCl_2$ in 0.1 *M* HNO_3. Age the $Ba/RaSO_4$ precipitate by warming on a water bath, then cool to room temperature.

(v) Decant the supernatant and transfer the precipitate to a centrifuge tube with 25 mL of 10 per cent sodium carbonate solution. Heat the tube in a boiling water bath for at least one hour. Remove the solution from the water bath and allow to cool. Centrifuge the $Ba/RaCO_3$ precipitate.

(vi) Decant the supernatant and dissolve the precipitate in a few drops of 6 *M* $HClO_4$ and sit the tube in a water bath to discharge the CO_2.

(vii) Prepare a solution of 0.05 *M* DYCTA/boric acid buffered to pH 5 by combining equal volumes of 0.1 *M* Na_2DCYTA and saturated boric acid, first adding a drop of methyl red indicator and then adding 10 *M* NaOH dropwise until the colour just turns yellow.

(viii) Add 10-15 mL of the buffered 0.05 *M* DYCTA/boric acid solution to the barium/radium perchlorate solution and adjust the pH to 5 with 10 *M* NaOH.

(ix) Prepare a 1.5 g strong acid cation exchange column (*e.g.* Dowex 50-X8 or BioRad AG50-X8) in the Na^+ form by washing with 15 bed volumes (30 mL) of saturated NaCl solution. Rinse with five bed volumes (10 mL) of distilled water and then with 20 mL of saturated boric acid.

(x) Add the barium/radium solution to the column. Wash the column with five bed volumes (10 mL) of saturated boric acid, adjusted to pH 8.5, with 10 *M* NaOH using a drop of thymol blue as the indicator.

(xi) Wash the column with 10 to 15 bed volumes (20-30 mL) of buffered 0.05 *M* DCYTA/boric acid solution which has been adjusted to pH 8.5 with 10 *M* NaOH.

(xii) Wash the column with 20 mL of 0.5 *M* HBr.

(xiii) Elute the radium from the column with ten bed volumes (20 mL) of 9 *M* HCl. Evaporate the eluent to dryness on a water bath.

(xiv) Prepare an electrolyte buffer solution of 0.21 *M* ammonium acetate in 0.06 *M* HNO$_3$. Assemble a clean electrodeposition cell (see figure 4) with a new stainless steel planchette and a new Viton 'O' ring, and a clean platinum anode positioned 12 cm from the stainless steel cathode. Add approximately 10 mL of electrolyte to the cell and clean the planchette by anodising with a 400 mA current for one to two minutes (that is until the solution turns yellow). Discard the electrolyte and rinse the cell with fresh electrolyte buffer.

(xv) Dissolve the radium residue in a few drops of 50 per cent acetic acid and dilute with 5 mL of electrolyte. Pour this solution into the electrodeposition cell. Rinse the beaker with an additional 5 mL of electrolyte buffer and add the washings to the cell.

(xvi) Electrodeposit for three hours onto the planchette at a starting voltage greater than 1'5 V and a current between 400 and 500 mA. The pH will rise from about 5 to between 8 and 9 over a period of 15 minutes. The temperature will rise to about 60°C during the electrodeposition. The deposit is improved by inclining the cell at a small angle to the vertical to assist the release of hydrogen bubbles. Small volumes of electrolyte should be added to compensate for evaporative losses and to keep the anode immersed.

CAUTION: The electrodeposition should be carried out in a fume cupboard to control the hazard arising from respirable aerosols containing alpha emitters.

(xvii) At the end of the electrolysis, save the electrolyte in the original beaker until counting is satisfactorily completed. Rinse the planchette in the cell with distilled water, adding the washings to the stored electrolyte. Wash the planchette with isopropyl alcohol and air-dry. heat the planchette gently in a yellow (reducing) flame until the plated area turns blue. Submit for alpha spectrometry immediately and note the time that counting is commenced.

(xviii) Rinse the electrodeposition cell in hot water and store in concentrated HNO$_3$ for at least 24 hours before re-use. Store the platinum anode in concentrated HNO$_3$ for at least 24 hours and flame briefly to red heat before use.

3.5.3 Alpha spectrometry for radium

Table 5 lists the particle energies and intensities for alpha decay of the natural radium isotopes ^{226}Ra, ^{224}Ra and ^{223}Ra. The isotope ^{228}Ra in the ^{232}Th decay chain decays by beta emission (0.055 MeV). This energy level is too weak for conventional detection and ^{228}Ra is usually determined from the beta activity of the daughter ^{228}Ac (2.18 MeV maximum, $t_{1/2} = 6.1$ h) after an appropriate in-growth period.

Figure 7 shows the theoretically pure spectrum for the natural alpha-emitting radium isotopes. Included in the spectrum are dotted curves for parents and daughters which may interfere with the spectrum. The particle intensities for the impurities are notional. The intensity of the peaks for ^{223}Ra have been drawn to indicate their natural activity abundance level of 3.9 per cent with respect to ^{226}Ra, based on the natural abundance ratios of ^{235}U to ^{238}U and the assumption that the daughters are in secular equilibrium with their grandparents. The spectral intensity of ^{224}Ra, a daughter in the ^{232}Th decay chain, is notional because of the wide variations that can occur in the ratio of ^{232}Th to ^{238}U.

The alpha spectrum for ^{226}Ra has a well-defined peak at 4.785 MeV (94.5 per cent) and a minor peak at 4.602 MeV (5.5 per cent). Resolution of the major and minor peaks is possible with a well-prepared specimen. The spectrum does not interfere with any of the spectra for the other radium isotopes and daughters. The major interference is ^{234}U, with a major peak at 4.776 MeV. This cannot be resolved from the radium spectrum and uranium must be removed totally from the solution before electrodeposition. The presence of uranium is indicated by inspecting the spectrum for the presence of ^{238}U at 4.196 MeV. The isotope ^{230}Th, with a major peak at 4.688 MeV, interferes with the low energy tail of the ^{226}Ra peak. The low energy tail of the major peak for ^{229}Th at

4.845 MeV overlaps the major peak for ^{226}Ra from the high energy side. Thorium-229 is not normally present but may have been added as a yield tracer for thorium. In either case, thorium should be removed before electrodeposition. All of the daughters of ^{226}Ra (^{222}Rn, ^{218}Po, ^{214}Po and ^{210}Po) are alpha emitters with relatively short half-lives, and are detectable within a few days of depositing the film. Fortunately none of the peaks for these isotopes interfere with the ^{226}Ra spectrum.

The alpha spectrum for ^{224}Ra has a well-defined peak at 5.686 MeV (95.1 per cent) and a minor peak at 5.449 MeV (4.9 per cent). This isotope is a daughter of the ^{232}Th series and is usually present in very small amounts in uranium mine tailings. However, if aged ^{232}U and/or ^{228}Th had been added as a yield tracer, then ^{224}Ra will be present at near secular equilibrium activity. A major interference in the ^{224}Ra spectra is the major peak for ^{223}Ra at 5.715 MeV. Radium-223, which is part of the ^{235}U series, will be present at 3.9 per cent of the ^{226}Ra level.

The alpha spectrum for ^{223}Ra is somewhat diffuse, with a major peak at 5.715 MeV (52.5 per cent), a second major peak at 5.606 MeV (26 per cent), two minor peaks at 5.745 MeV (9.5 per cent) and 5.537 MeV (9.2 per cent), a small peak at 5.432 MeV (2.3 per cent) and 20 other peaks between 5.012 and 5.870 MeV at less than one per cent. The major interferences are from ingrowing ^{222}Rn at 5.490 MeV which will interfere with the the minor peak for ^{223}Ra at 5.537 MeV and, as noted above, the spectra for ^{224}Ra which is embedded in the ^{223}Ra spectra.

The ^{224}Ra and ^{223}Ra spectra cannot be resolved by the majority of alpha detectors and it is necessary to employ spectral stripping techniques based on the spectra for the rapidly ingrowing daughters. The alpha-emitting daughters for the three natural radium isotopes are given in table 6.

In practice, it is preferable to count three groups of radium peaks:

(i) ^{226}Ra alone between 4.55 and 4.80 MeV,

(ii) ^{223}Ra (98.8%) + ^{224}Ra (100%) + slowly in-growing ^{222}Rn between 5.35 and 5.75 MeV, and

(iii) ^{223}Ra (1.2%) + ^{218}Po (100%) + rapidly in-growing ^{212}Bi between 5.80 and 6.15 MeV.

The ^{226}Ra activity is obtained directly from the first group. The ^{224}Ra activity is obtained from the second group by stripping out the ^{222}Rn and ^{223}Ra peaks. The ^{222}Rn is stripped out by measuring the activity of the equilibrium granddaughter ^{214}Po at 7.687 MeV, and the ^{223}Ra is stripped out by measuring the activity of the equilibrium great granddaughter ^{211}Bi at 6.622 MeV.

The third group of peaks supplies the ^{218}Po activity which may be used to check on the ^{226}Ra activity but it is necessary to strip out the ^{212}Bi and ^{223}Ra peaks. The ^{212}Bi is stripped out by measuring the activity of the daughter ^{212}Po at 8.785 MeV after a minimum counting period of six hours, taking into account the percentage contribution of each peak. The ^{223}Ra contribution is obtained from the calculations in group (ii), again taking into account the percentage contribution. The ^{218}Po will be in equilibrium with its parent ^{222}Rn.

If ^{229}Th was used as a yield tracer in the original sample, the spectrum should be examined for the presence of its great granddaughter ^{221}Fr at 6.340 MeV (83.4 per cent). The ^{221}Fr will be in equilibrium with its parent ^{225}Ac, which has a multiplicity of peaks in the range 5.6 to 5.85 MeV. Approximately 20 per cent of this ^{225}Ac activity will interfere with the ^{223}Ra, ^{224}Ra and ^{222}Rn peaks between 5.55 and 5.75 MeV, and approximately 80 per cent of the ^{225}Ac activity will interfere with the ^{218}Po and ^{212}Bi peaks between 5.75 and 5.85 MeV. Actinium-225 is the principal contaminant in this region and causes the groups (ii) and (iii) peaks to lose resolution. The interference is minimised by using a lanthanum holdback carrier during the chemical purification of the specimen.

There are two possible yield tracers - ^{223}Ra and ^{224}Ra - each of which has a number of advantages and disadvantages. Radium-223 is the great granddaughter of ^{235}U and is present in uranium ores at an activity abundance of 3.9 per cent of the ^{238}U. Consequently, if ^{223}Ra is used as a yield tracer, the spectra must be corrected for the naturally present material. Radium-223 has a short half-life (11.43 d) which must be taken into account in the calculations. The ^{223}Ra source, an actinium-227 'cow', is not always readily available.

If ^{223}Ra is used as the tracer, the planchette must be stored for 15 days to allow the ^{224}Ra contribution to decay to an insignificant level. The planchette should then be flamed to remove ^{222}Rn before counting.

As noted above, ^{224}Ra forms part of the ^{232}Th decay series. In Australian uranium ores, isotopes in the ^{232}Th series are present in trace amounts only (see examples in section 1). This is not necessarily true of groundwaters and is totally untrue of mineral beach sands. When ^{228}Th is present in measurable quantities, it will reach secular equilibrium with its daughter ^{224}Ra within a few days. In this case, the ^{224}Ra will act as an internal tracer, the recovery being determined from the ^{228}Th assay. In the absence of natural ^{228}Th, ^{224}Ra may be supplied as the in-grown daughter of calibrated ^{228}Th which has been aged for a few weeks, or as the ingrown granddaughter of calibrated ^{232}U which has been aged for several years.

When ^{224}Ra is used as the yield tracer, the alpha spectrum should be determined immediately after plating and mild flaming to obtain maximum counts and to minimise the in-growth of ^{222}Rn. The ^{224}Ra yield is obtained by the following steps:

(i) Subtract the ^{222}Rn contribution, which may be estimated from the spectrum of its equilibrium daughter ^{218}Po at 6.002 MeV.

(ii) Subtract the ^{223}Ra contribution, which may be estimated from the single alpha peak of its equilibrium daughter ^{215}Po at 7.386 MeV.

(iii) Correct the ^{224}Ra activity for decay from the time of separation from its parent ^{228}Th on the ion-exchange column.

(iv) Relate the ^{224}Ra to the ^{228}Th or ^{232}U assay.

This method relies on the assumption that the ^{228}Th/^{224}Ra activity ratio at the time of separation is unity. If this is in question, for example a sequential selective leaching scheme may disturb the equilibrium, then the solution should be left to stand for several days to allow the thorium to re-equilibrate with the radium before thorium-radium separation is attempted.

The use of ^{224}Ra has two advantages over ^{223}Ra as a yield tracer. First, the specimen can and should be counted immediately after plating. Second, the ^{224}Ra decays to negligible levels within 22 days, compared with 69 days for ^{223}Ra. This enables the ^{228}Ra to be measured after three weeks with minimal contribution from beta-emitting daughters of the natural radium isotopes. If, however, ^{229}Th is used as a yield tracer for thorium, the sample must be stored for 89 days to allow the beta-emitting ^{225}Ra (0.32 MeV) to decay to negligible levels.

When the planchette is counted for ^{228}Ra, it should first be flamed for at least five minutes to remove radon and most of the in-grown beta emitters lead and bismuth. The source should be counted through an aluminium screen of density at least 13 mg cm^{-2} to absorb all alpha particles less than 10 MeV and all beta particles less than 0.1 MeV. If ^{225}Ra is present, owing to the use of ^{229}Th, and the specimen has not been aged for 90 days, then the intervening absorber should be at least 100 mg cm^{-2} thick. In either case, the ^{228}Ra activity is determined by taking 10 minute counts over a period of six hours and plotting the activity versus time. The remaining short-lived, unsupported beta-emitting isotopes decay rapidly over the first hour or two. The beta activity then follows a plateau for about three to four hours before increasing as a result of the ingrowth of daughters. The plateau activity is due solely to ^{228}Ac which is in equilibrium with the ^{228}Ra. If the number of counts is insufficient, the source should be flamed and the procedure repeated as often as is required.

The efficiency of the beta counter is determined from a standard evaporated ^{228}Ra source, prepared by milking radium from a 60 year old or more ^{232}Th solution, and counted through an Al absorber of the same density.

3.6 Polonium-210

3.6.1 Chemistry for the analysis of polonium

Of the seven polonium isotopes that occur in the natural uranium and thorium alpha-decay chains, only ^{210}Po is observed in uranium mine tailings. The half-lives of the remaining six isotopes ^{218}Po, ^{216}Po, ^{215}Po, ^{214}Po, ^{212}Po and ^{211}Po are too short to be environmentally significant or be measured on a chemically isolated polonium sample. This produces a very simple alpha spectrum of a pure polonium source.

The chemistry for the analytical recovery of polonium was reviewed by Sedlet [1964]. Polonium is fairly volatile and temperatures in excess of 150°C should be avoided. Dissolutions with perchloric acid as a solvent (boiling point 200°C) are suitable only if the solution is not allowed to go to dryness. Fusions are unacceptable. The preferred method of dissolution of the sample is either by bomb digestion, or with successive nitric acid, hydrofluoric acid and perchloric acid digestion using an open vessel on a water bath. Digestions should not be carried out in platinum vessels as there is a high probability that significant amounts of polonium might plate out on the platinum.

Initially, attempts were made to isolate the uranium, protoactinium, polonium, thorium and radium sequentially from a single sample by ion exchange. Polonium (IV) is held strongly on a strong base anion exchange column as a chloro complex along with the uranium, protoactinium, iron, zirconium and rare earths. After removal of the uranium with 0.1 *M* HCl, the polonium is stripped from the column with 10 *M* HNO_3. This method presents two problems. First, polonium has a labile valency and Po(IV) will readily reduce to Po(III) and Po(II), possibly with the help of trace organics which leach from the ion-exchange resin. The lower valency states of polonium do not form chloro complexes and result in a net variable loss of polonium as Po(III) and Po(II) from the ion-exchange column. The second problem is that the 10 *M* HNO_3 degrades the resin by oxidation and, in the process, traps the polonium on the resin in a non ion-exchangeable form, so that not all of the polonium can be recovered from the resin. One solution is to use ^{208}Po as a yield tracer, but this isotope is not readily available and is relatively expensive for use in routine work.

In view of the problems associated with the ion-exchange route, we have determined polonium and lead from a sub-sample obtained by riffling. After digestion of the sample, an essentially quantitative determination of the polonium may be achieved by the spontaneous deposition of Po(II) onto silver from weakly acidic solutions [Sedlet 1964; Flynn 1968]. The method is subject to interference from oxidising agents such as Fe(III) and Cr(VI), some chelating agents and elements that co-deposit on the silver.

Iron (III) and chromium (VI) may be removed by solvent extraction with di-isopropyl ether. Provided that there is a complete absence of chelating or oxidising agents, especially HNO_3, the polonium and lead can be retained in the aqueous phase as the chloro complex in strong acid media. Protactinium, which auto-deposits onto anything above pH O, is retained in the organic phase and the low pH ensures that there is no loss of polonium through adsorption onto the glass.

The polonium is then separated from the lead by extracting it into diethylammonium diethyldithiocarbamate (DDTC) in chloroform. The lead remains in the aqueous phase. The organic phase is then destroyed leaving the polonium as a residue which may be taken up in dilute acid from which the polonium is auto-deposited onto a silver planchette.

Ascorbic acid may be added at the deposition stage to reduce and complex residual Fe(III) and Cr(VI). Excess ascorbic acid does not interfere with the plating efficiency and sufficient ascorbic acid should be added at the start of the deposition to ensure a pale clear solution. Plating efficiency is improved by a number of factors:

(a) Hydrochloric acid is used in preference to HNO_4.

(b) The pH is maintained at or just below 2.

(c) The temperature is maintained between 80 and 90°C.

(d) The solution volume is limited to <50 mL

(e) The solution is stirred gently to aid diffusion of the Po to the Ag surface.

With these optimised conditions, quantitative recoveries of polonium may be obtained in the presence of a wide range of ions [Flynn 1968]. The chalcogenides, tellurium and selenium, co-deposit with the polonium but do not interfere with the quantitative recovery.

3.6.2 Procedure for the analysis of polonium

(i) Dissolve the solid, either by the low temperature open vessel digestion method or by the bomb digestion technique. If the sample is an extract from a selective leaching scheme, evaporate to dryness on a water bath. Add 1-2 mL of concentrated $HClO_4$ and 10-30 mL of concentrated HNO_3. Evaporate to near dryness. Do not allow to fume.

(ii) Add 10-20 mL of 6 *M* HCl and centrifuge. Retain supernatant. Wash the solid (insoluble silicate) with 10 mL of 6 *M* HCl, centrifuge and add washings to supernatant

(iii) Transfer solution to an extraction flask and extract twice with 10 mL lots of di-isopropyl ether which has been equilibrated with 9 *M* HCl. Quantitatively recover the aqueous phase.

(iv) Centrifuge and retain the supernatant. Wash any precipitate with 9 *M* HCl, centrifuge and add washings to supernatant

(v) Add concentrated HCl to bring the acid strength up to 7 *M*.

(vi) Prepare a fresh solution of 1 per cent DDTC in $CHCl_3$. Store in a refrigerator before use.

(vii) Extract the polonium from the aqueous phase with 10 mL lots of the DDTC solution until the organic phase is colourless. Shake for one to two minutes only and separate the phases as soon as possible. Retain the aqueous phase for ^{210}Pb assay.

(viii) Evaporate the organic phase to dryness on a water bath and digest three to four times with 5 mL of concentrated HNO$_3$ and two to three drops of concentrated HClO$_4$. Evaporate to near dryness and dissolve in 50 mL of 0.1 m HCl.

(ix) Adjust the pH to between 1 and 2 with 5 *M* HN$_4$OH.

(x) Add a magnetic stirrer bar and heat with stirring to 80-90°C.

(xi) Clean a 25 mm diameter silver disc with metal polish then degrease it in trichloroethylene. Stick the disc with silicone cement to a 25 mm diameter polythene rod, as shown in figure 8. Store the assembly in 0.1 *M* HCl on a water bath for 24 hours. Check the cleanliness of the surface and the integrity of the bond. Rinse with acetone.

(xii) Place the disc assembly face down in the polonium solution and about one to two centimetres above the stirrer bar.

(xiii) Add 0.2 g of ascorbic acid.

(xiv) Stir for 3 h at 80-90°C.

(xv) Withdraw the disc assembly, and wash with dimineralised water and isopropyl alcohol. Remove the disc from the assembly using a scalpel, taking care not to distort the disc. Determine the alpha activity.

(xvi) The discs can be used repeatedly by dipping them in concentrated HNO$_3$ to remove any visible deposit, washing, drying and polishing.

6.3 Alpha spectrometry for polonium

The polonium concentration may be determined by gross alpha counting. Alpha spectrometry is necessary only s a means of checking source purity and estimating recoveries when using ^{208}Po as a yield tracer. It is advisable avoid routine or prolonged counting of polonium sources by alpha spectrometry because, at the low pressures mployed (<100 μm Hg), Po slowly volatilises from the source and drifts to the surface barrier detector where it dsorbs onto the gold-plated surface. The alpha spectrum for ^{210}Po cannot be resolved from that of ^{228}Th, hence amp polonium on a detector causes spurious ^{228}Th estimations. With a half-life of 138 days, polonium ontamination takes a long time to decay to insignificance.

The main interference arises from the co-deposition of bismuth. There are four bismuth alpha emitters: ^{214}Bi $_{1/2}$ = 19.91 min); ^{212}Bi ($t_{1/2}$ = 60.55 min); ^{211}Bi ($t_{1/2}$ = 2.13 min); and ^{210}Bi ($t_{1/2}$ = 5.013 d). In the absence of eir immediate parents, ^{214}Bi ^{212}Bi and ^{211}Bi decay to insignificance within 24 hours. Bismuth-212 is a daughter f ^{232}Th and is not normally found in uranium tailings. It would be present if aged ^{228}Th were used as a yield acer. In the deposited form, it is unsupported and decays to insignificance within 24 hours. Bismuth-210 decays rincipally by beta emission (> 99 per cent) and, under these conditions, the alpha spectrum for this isotope annot be observed. Thus interference from bismuth isotopes can be reduced to insignificance by storing the repared sample for 24 hours.

Thorium isotopes co-deposit to a minor extent, presumably due to the formation of hydrolytic colloids at the pH evels employed. Their presence requires the use of alpha spectrometry for routine assay.

Metals with an E_h higher than silver in the electrochemical series have a tendency to plate out, leading to ource thickening and spectral degradation. The DDTC extraction partly solves this problem. Unlike the heavy netals copper, silver, mercury, antimony, thallium, molybdenum (VI), palladium and platinum, and the halcogenides selenium and tellurium, none of the other significant actinides co-extract. Of the heavy metals only opper presents a significant problem since it also co-deposits, causing surface degradation, but it does not block he polonium deposition.

The preferred method for polonium analysis is to use a split sample containing no added uranium or thorium yield tracers. The iron should be removed by extraction with di-isopropyl ether and the polonium extracted with DDTC. The activity is then determined by gross alpha counting. Because of a higher background, the detection limit is not as low as counting by alpha spectrometry. Use should be made of ^{208}Po tracer at regular intervals to verify 100 per cent recovery, particularly when a new class of sample is assayed for the first time.

The alpha spectrum for ^{210}Po and ^{208}Po is given in figure 9. The spectrum consists of single peaks for ^{210}Po (5.305 MeV) and ^{208}Po (5.114 MeV). The two peaks are separated by 191 keV and should be resolvable. Counting efficiency is determined by counting standard sources that have been made by evaporating small aliquots of standard ^{210}Po onto silver discs. This equalises the backscatter effect.

3.7 Lead-210

3.7.1 Chemistry for the analysis of lead

There are seven lead isotopes in the three natural decay chains for uranium and thorium. Three of these isotopes, ^{208}Pb, ^{207}Pb and ^{206}Pb, are the stable end products of the chains, the remainder are beta emitters (see table 7). The isotopes ^{214}Pb, ^{212}Pb and ^{211}Pb have relatively short half-lives of 10 hours or less and, after separation, are undetectable in uranium tailings after a few days. Lead-210 with a half-life of 22 years is the only lead isotope that needs to be considered as environmentally significant.

Lead-210 decays by beta emission with a major peak at 0.0165 MeV (80.2 per cent) and a minor peak at 0.0630 MeV (19.8 per cent). These energies are too low for conventional beta-counting equipment. Accordingly, the activity is usually determined from either the more energetic beta emission of the ingrown daughter ^{210}Bi (1.161 MeV) or the alpha emission of the in grown granddaughter ^{210}Po (5.305 MeV).

A number of routes have been developed, most of which require an initial chemical separation of the lead from its daughters and parents. This may be achieved by either ion exchange [Korkish and Feik 1964], solvent extraction [Gorsuch 1959; Jaworowski 1963; Aronson and Hammond 1964; Petrow and Cover 1965] or electrodeposition [Harrison et al. 1955; Millard 1963]. The lead is deposited onto a planchette and the daughters allowed to grow in. The disadvantages of these routes are the long times required for in-growth. For ^{210}Bi counting, 75 per cent in-growth is achieved after 10 days, whereas for ^{210}Po, only 14 per cent is achieved after 30 days and 50 per cent after three months.

A modification to the above techniques is the auto-deposition of ^{210}Bi onto Ni [Blanchard 1966]. The disadvantages of this approach are that ^{210}Po is quantitatively co-deposited, and ^{210}Pb is partially deposited and requires absorber corrections. A delay in counting results in the formation of additional ^{210}Bi from the co-deposited ^{210}Pb.

Unless the specimen has had recent unusual treatment, the ^{210}Bi will be in activity equilibrium with the ^{210}Pb. The following method takes advantage of the pre-existing equilibrium and removes most of the drawbacks described above.

The lead and bismuth are jointly solvent extracted from the other actinides, co-precipitated and counted. By this time, the ^{210}Bi is already fully grown in and fully supported by the long-lived parent. This eliminates the need for a long in-growth period. After allowing three days for any ^{212}Pb to decay to insignificance, the source may be counted at any time, even weeks, after preparation.

If, on receipt of the sample, the ^{210}Bi is suspected of being out of equilibrium with the ^{210}Pb, the sample should be stored for several weeks before analysis. The method is unsuitable for studying disequilibria between ^{210}Bi and ^{210}Pb.

If the sample is not derived from the polonium assay, it should be digested by any standard technique. The digestion must not be carried out in platinum vessels because lead and polonium alloy with platinum. After obtaining an aqueous solution, the lead and bismuth content should be determined by atomic absorption spectrometry (AAS) or an equivalent method. Stable lead should then be added to ensure that the final precipitate is between 20 and 25 mg of $PbCrO_4$ and that the mass of stable lead exceeds that of stable bismuth by at least 100:1.

The iron is extracted with di-isopropyl alcohol from a > 6 *M* HCl aqueous solution. Polonium is then extracted with DDTC in $CHCl_3$ from a > 7 *M* HCl aqueous solution. The lead and bismuth remain in the aqueous phase as chloro-complexes. The chloro-complexes are destroyed by diluting the aqueous phase to around 1.8 *M* HCl. The lead and bismuth can then be quantitatively extracted with DDTC into $CHCl_3$. The organic phase is destroyed leaving lead and bismuth residues, which are taken up in acetic acid. Lead and bismuth chromate is then precipitated by addition of ammonium chromate at pH 5. The precipitate is recovered, loaded onto a planchette and counted.

After counting, the precipitate is dried at 105°C, ignited to 550°C and weighed to determine the chemical ecovery of ^{210}Pb.

If the sample contains too much stable lead to allow the ^{210}Pb level to be measured to the required detection mit, the bismuth must be selectively extracted from the lead. In this event, it is necessary to apply a decay orrection starting from the time of chemical separation.

.7.2 Procedure for the analysis of lead specimens

(i) If the solution is the Pb aqueous phase from a Po assay, proceed directly to step (iv). If the material is not already in solution, dissolve the solid by any of the acid digestion techniques given in section 3.2. Do not use a platinum vessel.

(ii) If the solution sample is not already in 6 *M* HCl, evaporate to dryness and dissolve in 10 mL of 6 *M* HCl. If there is a silica precipitate, centrifuge, decant and save the supernatant. Wash the precipitate with 10 mL of 6 *M* HCl, centrifuge and add the washings to the supernatant. Make up to a known volume. Remove a 1 mL aliquot, add 6 mL of water and determine the total Pb and Bi level by AAS or an equivalent method. If necessary, add Pb as PbCl solution to ensure at least a 100 fold excess of lead over bismuth.

(iii) Transfer the solution to an extraction flask and extract twice with 10 mL lots of di-isopropyl ether which has been equilibrated with 9 *M* HCl. Quantitatively recover the aqueous phase. Centrifuge and retain the supernatant. Wash any precipitate with 9 *M* HCl, centrifuge and add washings to the supernatant. Add concentrated HCl to bring the acid strength up to 7 *M*. Prepare a fresh solution of one per cent DDTC in $CHCl_3$. Store in a refrigerator before use. Extract with 10 mL lots of the DDTC solution until the organic phase is colourless. Shake for one to two minutes only and separate the phases as soon as possible. Retain the organic phase for ^{210}Po assay if required.

(iv) Dilute the aqueous phase with three times its volume with water. Extract with 20 mL lots of one per cent DDTC in $CHCl_3$ until the organic phase is colourless.

(v) Quantitatively recover the organic phase. Combine all the extracts and evaporate to dryness. Add 10 to 20 mL of concentrated HNO_3 and evaporate to dryness.

(vi) Add 1 mL of concentrated $HClO_3$ and 10 mL of HNO_3. Evaporate to white fumes. Dissolve the residue in 10 mL of water.

(vii) If there is a white precipitate ($PbSO_4$) repeat step (vi) until the precipitate is completely dissolved.

(viii) Dilute to 20 to 50 mL. Add 5 mL of 6 *M* acetic acid and 10 mL of 6 *M* ammonium acetate. Measure the pH and adjust to 5 with 1 *N* NH_4H.

(ix) Heat to near boiling and add 2 mL of saturated $(NH_4)_2CrO_4$ solution. Heat to near boiling for 60 minutes before allowing to cool.

(x) Filter through a 25 mm, 0.45 μm pore membrane filter. Rinse with demineralised water and isopropyl alcohol.

(xi) Lightly coat a stainless steel planchette with an alcohol-miscible cement. Transfer the filter, wet with isopropyl alcohol, onto the planchette and allow to dry. The filter must not curl up at the edges.

(xii) Set aside for 12 to 18 hours and then count the betas in a low background gas-flow proportional counter with a 4 to 8 g cm^2 Al absorber above the source.

(xiii) After determining the activity, wet the source with isopropyl alcohol. Remove the filter from the planchette and transfer it to a silica crucible. Ignite at 550°C to constant weight. The conversion factor from $PbCrO_4$ to Pb is 0.6411.

3.7.3 Gross beta counting for lead

For the recommended method, the lead activity is determined from the beta activity of the fully in-grown ^{210}Bi Bismuth-210 is a beta emitter with a single peak at 1.161 MeV. The activity is normally determined by gross beta counting. Ideally, the granddaughter ^{210}Po will have been separated before assay, so only in-growing polonium wil contribute alpha activity from the prepared beta source. In any event, the precipitate should be counted through a 4-8 mg cm^2 Al absorber to absorb both the alpha particles from the in-growing ^{210}Po and the weak beta particles from ^{210}Pb. The activity is determined relative to a standard source. The standard source must be counted through an aluminium absorber of the same density.

4. SEQUENTIAL EXTRACTION SCHEME FOR URANIUM MINE TAILINGS

4.1 Mineral Phases in Uranium Mine Tailings

Uranium mine tailings are composed of a random mixture of minerals which include quartz, feldspars, types I, II and III clays, and crystalline and amorphous metal oxides, and the surfaces of the materials are coated with highly adsorptive films. Before deposition in the tailings dam, the material had been leached either with an alkali if the material was basic, or with an acid oxidising solution (sulphuric acid/manganese dioxide or sulphuric acid/hydrogen peroxide) if the rock was acidic. Past practice was to dump the tailings without further treatment, but nowadays a Australian uranium mines the tailings are neutralised before disposal. Thus, in addition to variations in the mineralogy of the ore, there are variations in chemical treatment and disposal.

Previous phase separations have centered around the removal of radium [Yagnik et al. 1980; Benes et al. 1982] There have been no mineralogically based chemical separations of tailings. This technique has been wel developed for soils and although there are a number of selective phase separation schemes, there is no generalised scheme which can cover all eventualities; consequently, a scheme must be tailored to the particular requirements of the work. In drawing up such a scheme, the number of extraction steps should be kept as small as possible without losing the required detail. The inclusion of unnecessary steps overload the subsequent analysis and may result in a blurring of the boundaries between phases. Prior information may indicate that some phases are no present. Separation of some phases may not be required. The phases present in uranium mine tailings are shown in table 8.

The organic phase was not substantial enough to justify the inclusion of an organic extraction. Associated work indicated that an allophane and imogolite extraction step, using the method of Hashimoto and Jackson [1960], was unnecessary. Technically, it was very difficult to ensure reproducibility and there was minimal association between the radionuclides and these materials. The selected phases are discussed below.

(a) Water soluble

This material is in solution in the pore and interstitial water of wet tailings and reprecipitates when air dried The material is recovered by washing the tailings with a gross excess of water. To preserve the integrity of the material, a very gentle washing action is employed; typically this is achieved by periodically inverting the container Shaking or agitation must be avoided. The solid is recovered by filtration or centrifugation. Some oozes ma require piston squeezing against a filter.

(b) Ion-exchangeable

This material ion-exchanges reversibly with exchange sites on the solid matrix. The Ra^{2+} cation capacity of low sulphate tailings is typically 25 meq g^{-1} of tailings [Levins *et al.* 1978]. Accordingly, the ion-exchanging catio should be much greater. The cation of choice is Ca^{2+} since it suppresses the dissolution of calcium sulphat which precipitates during the lime neutralisation process. Chloride is the anion of choice since it will not comple the radionuclides at dilute concentrations.

(c) Alkaline-earth sulphates and carbonates

This is a significant phase in the tailings of neutralised acid and alkaline ores. Selective extraction i accomplished with an excess of 1 *M* ammonium acetate adjusted to pH 4.8 with acetic acid [Alexiades an Jackson 1966]. A 24 hour extraction is usual, although in a fine-grained material (*e.g.* <2 μm) six hours would b sufficient. Solution may be enhanced by heating gently to temperatures below 75°C. The heating should b stopped at the first sign of dissolution of iron oxides, which is indicated by a yellow coloured solution.

d) Manganese oxide

If pyrolusite (MnO_2) is used as the oxidant in the treatment plant, it is discharged into the tailings stream at about 120 mg L^{-1}. The $Mn(OH)_2$ precipitates, during neutralisation, along with the other hydrous oxides; it oxidises back towards MnO_2 by aerobic oxidation in the tailings dam. Manganese oxide is a sufficiently strong adsorber to be regarded as a separate phase. It may be extracted selectively by shaking for one hour with freshly prepared 0.1 *M* $NH_2OH.HCl$ adjusted to pH 2 with HNO_3 [Chao 1973]. This procedure dissolves some of the amorphous iron as well.

(e) Amorphous iron and ferrihydrite

The amorphous iron/ferrihydrite fraction cannot be separated quantitatively from the manganese fraction. However, if Caro's acid is used as the oxidant in the treatment plant or an if alkaline ore is being treated, the manganese phase is insignificant, and the principal adsorbers are the amorphous and crystalline iron oxides. The amorphous iron oxides may be leached with Tamm's acid oxalate solution (10.92 g of oxalic acid and 16.11 g of ammonium oxalate in 1 L of water with the pH adjusted to 3 with HCl) at room temperature, and stand in the dark for four hours [Tamm 1932; Schwertmann 1964]. Tamm's acid oxalate solution is not completely specific to amorphous iron. The solution dissolves any manganese oxides, iron-rich chlorite and biotite. Illite may also be susceptible to this reagent. The solution dissolves small amounts of the crystalline iron oxides magnetite (Fe_3O_4) and maghemite (Fe_2O_3) [Baril and Britton 1967]. Chao and Zhou [1983] reported that 20 per cent of synthetic magnetite is dissolved by the solution in four hours.

(f) Crystalline iron minerals

The remaining manganese and iron oxides and the hydroxides may be extracted selectively by refluxing with freshly prepared 0.04 *M* $NH_2OH.HCl$ in 25 vol.% acetic acid for three hours or more. The residual solid should be a uniform white or grey colour [Chester and Hughes 1967]. Minerals of the jarosite and plumbo-gummite family will also be dissolved.

The manganese, amorphous iron and crystalline iron phases may be grouped together in a single phase and extracted in total by the Chester and Hughes reagent.

(g) Pyrite

The presence of pyrite will be known from the geological assay of the ore. If present in the original ore, it will pass through the mill and into the tailings. Pyrite may be extracted selectively from the tailings at this stage by oxidation with 30 per cent H_2O_2 in 1 *M* CH_3COONH_4 in 6 per cent HNO_3 [Gupta and Chen 1975].

(h) Resistate

The resistate is comprised of clays, chlorites, quartz and detrital minerals and can be assayed by total dissolution using any of the methods discussed earlier.

4.2 Procedure for Selective Phase Extraction

If necessary, before proceeding to selective phase extraction, air-dry the sample below 50°C, then riffle and sub-sample.

(a) Water soluble

Weigh 2 g of material into a stoppered 100 mL container. Add 100 mL of boiled, demineralised water. Stopper and leave for 24 hours with occassional inversion. Allow to settle, decant and pass the supernatant through a 0.2 μm filter. Acidify to pH 1 with concentrated HNO_3 or HCl. Add tracers and evaporate to dryness on a water bath. Store in a desiccator.

(b) Ion-exchangeable

To the wet residue from step (a) add 80 mL of unbuffered 0.1 *M* NH_4Cl. Stopper and leave for two hours with occasional inversion. Allow to settle, decant and pass the supernatant through a 0.2 μm filter. Acidify to pH 1 with concentrated HNO_3 or HCl. Add tracers and evaporate to dryness on a water bath. Store in a desiccator.

(c) Alkaline-earth sulphates and carbonates

To the wet residue from step (b) add 80 mL of 1 *M* ammonium acetate adjusted to pH 4.8 with acetic acid.

Shake gently for 24 hours. Centrifuge, decant and pass the supernatant through a 0.2 µm filter. Wash the residue with 0.1 M NH_4Cl to remove residual acetate. Add the washings to the supernatant and acidify to pH 1 with concentrated HNO_3 or HCl. Add tracers, and evaporate to dryness on a water bath. Store in a desiccator.

(d) Manganese oxide

To the wet residue from step (c) add 80 mL of fresh 0.1 M $NH_2OH.HCl$ in 0.01 M HNO_3. Shake for one hour. Centrifuge, decant and pass through a 0.2 µm filter. There is no need to wash the residue. Acidify the supernatant to pH 1 with concentrated HNO_3 or HCl. Add tracers, and evaporate to dryness on a water bath. Store in a desiccator.

(e) Amorphous iron and ferrihydrite

To the wet residue of step (b) or (c) add 80 mL of Tamm's acid oxalate solution (10.92 g oxalic acid, 16.11 g ammonium oxalate in 1 L of water with the pH adjusted to 3 with HCl) at room temperature, and stand in the dark for four hours. Centrifuge, decant and pass through a 0.2 µm filter. There is no need to wash the residue. Add tracers, and evaporate to dryness on a water bath. Store in a desiccator.

(f) Crystalline iron minerals

To the wet residue from steps (b), (c), (d) or (e) add 80 mL of fresh 0.04 M $NH_2OH.HCl$ in 25 per cent acetic acid and reflux for three hours. If necessary, add a fresh charge of $NH_2OH.HCl$ and repeat until the residue is a uniform white to grey. Allow to cool. Centrifuge, decant and pass through a 0.2 µm filter. Add tracers, and evaporate to dryness on a water bath. Store in a desiccator.

(g) Pyrite

To the wet residue from step (f) add 80 mL of a solution of 30 per cent H_2O_2 in 1 M ammonium acetate and 6 per cent HNO_3. Allow to cool. Centrifuge, decant and pass through a 0.2 µm filter. Add tracers, and evaporate to dryness. Store in a desiccator.

(h) Digestion

Digest residue by any procedure selected from section 2.2.

Before an extracted phase is subjected to radionuclide analysis, add 20 mL of concentrated HNO_3 and evaporate to dryness. If charring is evident, add 10 mL of concentrated $HClO_4$ and a further 20 mL of concentrated HNO_3. Evaporate to dryness. Repeat until no charring is evident. If polonium is being assayed, the evaporations must not be allowed to go completely to dryness. For U, Th and Ra assays, add 20 mL of concentrated HCl and evaporate to dryness. Dissolve the residue in a minimum volume of 6 M HCl and proceed as detailed in the appropriate section for the selected assay.

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6. REFERENCES

AAEC [1985] - Progress report of The Environmental Science Division. In *Divisional Progress Reports for the Period 1 July 1983 - 30 June 1984*. AAEC/PR83-84, Chapter 3.

Alexiades, C.A., Jackson, M.L. [1966] - Quantitative clay mineralogical analysis of soils and sediments. *Clays Clay Miner.*, 14: 35-68.

Aronson, A.L. and Hammond, P.B. [1964] - Fast analysis for Pb210 in biological specimens. *Nucleonics* 22(2):90.

ASTM [1975] - Tentative test method for radium-226 in water. American Society for Testing Materials, Publication D 3454-75 T.

Baril, R., Britton, G. [1967] - Anomolous values of free iron in some Quebec soils containing magnetite. *Can. J. Soil Sci.*, 47: 261.

Barring, N.E. [1966] - Electrodeposition of actinide and lanthanide elements. Aktiebolaget Atomenergi Report AE-217.

ones, P., Sebesta, F., Sedlacek, J. [1982] - Environmental migration of radium and other contaminants present in liquid and solid wastes from the mining and milling of uranium. *Progress Report of the Research Contract No 2893/RB.* Technical University of Prague.

lanchard, R.L. [1966] - Rapid determination of lead-210 and polonium-210 in environmental samples by deposition on nickel. Anal. Chem., 38(2) 189-192.

ooman, G.L., Rein, J.E. [1962] - Uranium. In *Treatise on Analytical Chemistry. Part II. Analytical Chemistry of the Elements*, Vol. 9 (eds. I.M. Kolthoff and P.J. Elving). Interscience, New York.

usigin, A., Van De Vooreen, A.W., Lin Pai, H. and Philips, C.R. [1979] - Development of instrumentation for the measurement of radon, thoron and their daughters in uranium mines and in the environment. *Miner. Sci. Eng.*, 11(4) 193-206.

hao, T.T. [1972] - Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. *Soil Sci. Soc. Am. Proc.*, 36:764-768.

hao, T.T., Zhou, L. [1983] - Extraction techniques for the selective dissolution of amorphous iron oxides from soils and sediments. *Soil Sci. Soc. Am. J.*. 47:225-232.

hester, R., Hughes, M.J. [1967] - A chemical technique for the separation of ferromanganese minerals, carbonate minerals and adsorbed trace elements for pelagic sediments. *Chem. Geol.*, 2:249-262.

ooper, M.B., Wilks, M.J. [1981] - An analytical method for radium (^{226}Ra) in environmental samples by the use of liquid scintillation counting. Australian Radiation Laboratory Report. ARL/TR040.

aris, J.P., Buchanan, R.F. [1964] - Anion exchange characteristics of elements in nitric acid media. *Anal. Chem.*, 36:1157-1158.

lynn, W.W. [1968] - The determination of low levels of polonium-210 in environmental materials. *Anal. Chim. Acta*, 43:221-227.

leason, G. [1979] - An improved ion exchange procedure for the separation of barium from radium. *Proc. 23rd Conf. on Analytical Chemistry in Energy Technology*, Gatlinburg, Tennessee, October 1978. Published as *Radioelement Analysis Progress and Problems* (ed. W.S. Lyon), Ann Arbor Science, Ann Arbor, Michigan.

rimaldi, F.S. [1961] - Thorium. In *Treatise on Analytical Chemistry.* Part II. *Analytical Chemistry of the Elements*, Vol. 5 (eds. I.M. Kolthoff and P.J. Elving). Interscience, New York.

Gorsuch, T.T. [1959] - Radiochemical investigations on the recovery for analysis of trace elements in organic and biological materials. *Analyst*, 84:135-173.

Gupta, S.K., Chen, K.Y. [1975] - Portioning of trace metals in selective chemical fractions of nearshore sediments. *Environ. Lett.*, 10(2):129-158.

Haissinsky, M. [1937] - Electrolysis of salts of Ba and of Ra in acetone. *J. Chim. Phys.*, 34:321.

Harrison, A.D.R., Lindsey, A.J., Phillips, R. [1955] - The electrolytic separation from thorium nitrate of thorium C (^{212}Bi) and thorium B (^{212}Pb) in chloride solutions. *Anal. Chim. Acta*, 13:459-464.

Hashimoto, I., Jackson, M.L. [1960] - Rapid dissolution of allophane and kaolinite-halloysite after dehydration. *Clays Clay Miner.*, 7:102-113.

IAEA [1962] - Geology of uranium and thorium. *IAEA Bibliographic Series*, No.4. IAEA, Vienna.

Ivanovich, M., Harmon, R.S. [1982] - Uranium Series Disequilibrium: Applications to Environmental Problems. Clarendon Press, Oxford.

Jaworowski, Z. [1963] - The determinaton of lead-210 and bismuth-210 in biological material. *Nukleonika*, 8:333.

Ko, R. [1954] - The electrodeposition of plutonium from acid solution. USAEC Report HW-32673.

Kocher, D.C. [1981] - Radioactive decay tables - a handbook of decay data for application to radiation dosimetry and radiological assessments. U.S. Department of Energy, Technical Information Center Report DOE/TIC-11026.

Koide, M., Bruland, K.W. [1975] - The electrodeposition and determination of radium by isotopic dilution in sea water and in sediments simultaneously with other natural radionuclides. *Anal. Chim. Acta*, 75: 1-19.

Korkisch, J., Ahluwalia, S.S. [1966] - Separation of uranium by combined ion exchange-solvent extraction. *Anal. Chem.*, 38:497-500.

Korkisch, J., Feik, F. [1964] - Separation of lead by anion exchange. *Anal. Chem.*, 36:1793.

Kraus, K.A., Nelson, F. [1955] - Anion exchange studies of the fission products. *Proc. 1st International Conf. on the Peaceful Uses of Atomic Energy*, United Nations, New York, 7:113-125.

Langmuir, D, Herman, J.S. [1980] - The mobility of thorium in natural waters at low temperatures. *Geochim. Cosmochim. Acta*, 44(11)1753-1766.

Levins, D.M., Ring, R.J., Dunlop, G.A. [1982] - Reducing the environmental impact of uranium mine tailings by physical segregation and separate disposal of potentially hazardous fractions. *Proc. NEA Workshop on Uranium Ore Processing/Tailings Conditioning for Minimising Long-term Environmental Problems in Tailings Disposal*, Colorado, USA, 28-30 October. Published as *Uranium Mill Tailings Management*, OECD, Paris.

Millard, H.T. [1963] - Quantitative radiochemical procedure for analysis of polonium-210 and lead-212 in minerals. *Anal. Chem.*, 35:1017-1023.

Petrow, H.G., Cover, A. [1965] - Direct radiochemical determination of lead-210 in bone. *Anal. Chem.*, 37(13)1659-1660.

Pourbaix, M. [1966] - Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon, Oxford.

Puphal, K.W., Olsen, D.R. [1972] - Electrodeposition of alpha emitting nuclides from a mixed oxalate-chloride electrolyte. *Anal. Chem.*, 44: 284-289.

Raicevic, D. [1979] - Decontamination of Elliot Lake tailings. *Can. Inst. Min. (CIM) Bull.*, 72(808)109-115.

Rieman, W. III., Walton, H.F. [1970] - Ion Exchange in Analytical Chemistry. Pergamon Press, Oxford.

Roman, D. [1980] - The electrodeposition of thorium in natural materials for alpha spectrometry. *J. Radioanal. Chem.*, 60:317-322.

Roman, D. [1984] - The electrodeposition of radium on stainless steel from aqueous solutions. *Int. J. Appl. Radiat. Isot.*, 35(10)990-992.

Rushing, D.R., Garcia, W.J., Clark, D.A. [1964] - The analysis of effluents and environmental samples from uranium mills and of biological samples for radium polonium and uranium. In *Radiological Health and Safety in Mining and Milling of Nuclear Materials*, Vol II, pp.187-212, IAEA, Vienna.

Schwertmann, U. [1964] - Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalate-Losung. *Z. Pflanzenernaehr*, Bodenkd., 105(3)194-201.

Sedlet, J. [1964] - Actinium, astatine, francium, polonium and protactinum. In *Treatise on Analytical Chemistry*. Part II. *Analytical Chemistry of the Elements*, Vol.6, (ed. I.M. Kolthoff and P.J. Elving). Interscience, New York.

Sedlet, J. [1966] - Radon and radium. In *Treatise on Analytical Chemistry*, Part II. *Analytical Chemistry of the Elements*, Vol.4 (ed. I.M. Kolthoff and P.J. Elving). Interscience, New York.

Seeley, F.G. [1977] - Problems in the separation of radium from uranium ore tailings. *Hydrometall.*, 2(3)249-264.

Sill, C.W. [1961] - Decomposition of refractory silicates in ultramicroanalysis. *Anal. Chem.*. 33(12)1684-1686.

Sill, C.W. [1977a] - Determination of thorium and uranium isotopes in ores and mill tailings by alpha spectrometry. *Anal. Chem.*, 49(4)618-621.

Sill, C.W. [1977b] - Simultaneous determination of ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra and ^{210}Pb in uranium ores, dusts and mill tailings. *Health Phys.*, 33:393-404.

Sill, C.W. [1983] - Determination of radium-226 by high resolution alpha spectrometry. CONF-830495-7.

Sill, C.W., Puphal, K.W., Hindman, F.D. [1974] - Simultaneous determination of alpha-emitting nuclides of radium through californium in soil. *Anal. Chem.*, 46(12)1725-1737.

Smith, G., Barnett, G.A. [1965] - The quantitative electrodeposition of tracer protactinium. *J. Inorg. Nucl. Chem.*, 27:975-978.

Sorret, C., Tauveron, N. [1972] - Preparation of thin U films by electrodeposition application to Th and Ra. CEA-R-4297.

Strominger, D., Hollander, J.M., Seeborg, G.T. [1958] - Table of isosopes. *Rev. Mod. Phys.*, 30(2,pt.2)585.

Tamm, O. [1932] - Uber die Oxalatmethode in der Chemischen Bodenanalyse. *Meddelanden Fran Statens Skogsforsoksanstanct*, Stockholm, 27:1-20.

Twining J.R. [1983] - AAEC private communication.

USDOE [1958-1982] - Radioactive Waste Processing and Disposal Bibliographies. Office of Scientific and Technical Information. US Department of Energy, Oak Ridge. The bibliographies include information on uranium mill tailings: TID-3311, 698 citations [1958]; TID-3555, 696 citations [1960]; TID-3555-S1, 874 citations [1962]; TID-3311-S1, 989 citations [1964]; TID-3311-S2, 1012 citations [1966]; TID-3311-S3, 2249 citations [1972]; TID-3311-S4, 464 citations [1973]; TID-3311-S5, 345 citations [1974]; TID-3311-S6, 2140 citations [1975]; TID-3311-S7, 1841 citations [1976]; TID-3311-S8 (NUREG-0643), 4144 citations [1977]; TID-3311-S9 (NUREG-0944), 3598 citations [1980]; DOE/TIC-3311-S10, 3700 citations [1981]; DOE/TIC-3311-S11, 3382 citations [1982]; DOE/TIC-3311-S12, 4314 citations [1983]. In 1982 the US Department of Energy initiated a new bibliographic series on uranium mill tailings. The first issue was DOE/TIC-3393, 335 citations [1982]; Supplement 1, containing 192 citations, was released in March 1985.

Vogel, A.I. [1939] - A Text-book of Quantitative Inorganic Analysis, 1st edition. Longmans, London.

Yagnik, S.K., Baird, M.H.I., Banerjee, S. [1980] - An investigation of radium extraction from uranium mill tailings. *Hydrometall.*, 7:61-75.

TABLE 1
ALPHA SPECTRA FOR URANIUM MINE TAILINGS

[After Kocher 1981]

Table 1 lists the principal energies for the major radionuclides that may be found in uranium mill tailings. The list covers the parents and daughters of the ^{238}U and ^{235}U decay series; excluded are daughters formed by minor (< 1 per cent) decay paths. Included in the table are the energies for the artificial isotopes ^{236}U, ^{232}U and ^{228}Th. These artifical isotopes may be used as standards in isotope ratio analysis.

Major Peaks						Series	Isotope	$t_{1/2}$
MeV	%	MeV	%	MeV	%			
4.196	77	4.147	23	4.093	0.23	^{238}U	^{238}U	4.468×10^{9} y
4.396	55	4.364	11	4.217	5.7	^{235}U	^{235}U	7.038×10^{8} y
4.494	74	4.445	26	4.332	0.26		^{236}U	2.342×10^{7} y
4.687	76	4.621	23	4.476	0.12	^{238}U	^{230}Th	7.7×10^{4} y
4.776	72	4.724	28	4.605	0.35	^{238}U	^{234}U	2.445×10^{5} y
4.785	94.5	4.601	5.5			^{238}U	^{226}Ra	1600 y
4.845	56.2	4.901	10.2	4.899	9.7		^{229}Th	7340 y
5.011	25.4	4.950	22.8	5.028	20	^{235}U	^{231}Pa	3.276×10^{4} y
		5.057	11	4.736	8.4			
5.305						^{238}U	^{210}Po	138.4 d
5.320	68.6	5.263	31.2	5.139	0.28		^{232}U	72 y
5.423	72.7	5.340	26.7	5.212	0.36		^{228}Th	1.913 y
5.486	100					^{238}U	^{222}Rn	3.832 d
5.715	52.5	5.606	24.2	5.537	9.2	^{235}U	^{223}Ra	11.43 d
6.002	100					^{238}U	^{218}Po	3.05 min
6.038	24.5	5.978	23.4	5.757	20.3	^{235}U	^{227}Th	18.718 d
		5.709	8.2	5.713	4.9			
6.623	83.5	6.678	16.23			^{235}U	^{211}Bi	2.13 min
6.819	79.6	6.552	12.9	6.425	7.5	^{235}U	^{219}Rn	3.96 s
7.386	100					^{235}U	^{215}Po	1.778×10^{-3} s
7.687	99					^{238}U	^{214}Po	1.64×10^{-4} s

TABLE 2
ALPHA SPECTRA OF URANIUM ISOTOPES

[After Kocher 1981]

Isotope	Particle Energy (MeV)	Particle Intensity (%)	Particle Intensity as % Activity ^{238}U
^{238}U	4.196	77	
	4.147	23	
	4.035	0.23	
^{235}U	4.598	5.0	0.23
	4.556	4.2	0.18
	4.502	1.7	0.06
	4.435	0.7	0.03
	4.414	2.10	0.2
	4.396	55	2.9
	4.370	16	0.9
	4.364	11	0.8
	4.344	1.5	0.07
	4.325	4.6	0.15
	4.271	0.4	0.03
	4.219	0.9	0.06
	4.217	5.7	0.29
	4.150	0.9	0.03
^{236}U	4.494	74	
	4.445	26	
	4.332	0.26	
^{234}U	4.776	72.4	
	4.724	27.4	
	4.605	0.24	
^{232}U	5.320	68.6	
	5.264	31.2	
	5.139	0.28	

TABLE 3
ALPHA SPECTRA OF PROTACTINIUM-231

[After Kocher 1981]

Isotope	Particle Energy (MeV)	Particle Intensity (%)
^{231}Pa	5.057	11.0
	5.031	2.5
	5.028	20.0
	5.011	25.4
	4.9984	1.4
	4.974	0.4
	4.950	22.8
	4.933	3.0
	4.851	1.4
	4.736	8.4
	4.712	1.0
	4.680	1.5
	4.642	0.1
	4.631	0.1

TABLE 4
ALPHA SPECTRA OF THORIUM

[After Kocher 1981]

Isotope	Particle Energy (MeV)	Particle Intensity (%)
^{232}Th	4.010	77
	3.953	23
	3.830	0.2
^{230}Th	4.688	76.3
	4.621	24.4
	4.476	0.12
^{229}Th	5.052	1.6
	5.050	5.2
	5.033	0.24
	4.979	3.17
	4.968	5.97
	4.929	0.1
	4.901	10.2
	4.861	0.18
	4.853	56.2
	4.837	4.8
	4.833	0.29
	4.815	9.3
	4.809	0.22
	4.798	1.27
	4.761	0.63
	4.688	0.15
^{228}Th	5.423	72.7
	5.341	26.7
	5.212	0.36

Isotope	Particle Energy (MeV)	Particle Intensity (%)
^{227}Th	6.038	24.5
	6.009	2.9
	5.978	23.4
	5.960	3.0
	5.916	0.78
	5.901	0.17
	5.866	2.42
	5.808	1.27
	5.796	0.31
	5.762	0.23
	5.757	20.3
	5.713	4.89
	5.709	8.20
	5.700	3.63
	5.693	1.50
	5..668	2.06
	5.613	0.22
	5.600	0.17
	5.586	0.18

TABLE 5
ALPHA SPECTRA OF RADIUM ISOTOPES

[After Kocher 1981]

Isotope	Particle Energy (MeV)	Particle Intensity (%)
^{226}Ra	4.785	94.45
	4.602	5.55
^{224}Ra	5.685	95.1
	5.449	4.9
^{223}Ra	5.870	0.85
	5.858	0.32
	5.745	9.5
	5.715	52.5
	5.606	24.2
	5.537	9.2
	5.501	1.0
	5.435	2.27
	5.367	0.13
	5.339	0.13
	5.288	0.16

TABLE 6
ALPHA-EMITTING DAUGHTERS FOR THE THREE NATURAL RADIUM ISOTOPES

From ^{226}Ra (^{238}U)				From ^{224}Ra (^{232}Th)				From ^{223}Ra (^{235}U)			
Isotope	MeV	Frac. (%)	$t_{1/2}$	Isotope	MeV	Frac. (%)	$t_{1/2}$	Isotope	MeV	Frac. (%)	$t_{1/2}$
^{222}Rn	5.490	100	3.82 d	^{220}Rn	6.288	100	55 s	^{219}Rn	6.819	80	4.0 s
^{218}Po	6.002	100	3.05 min	^{216}Po	6.779	100	146 ms	^{215}Po	7.386	100	1.78 ms
^{214}Po	7.687	100	164 μs	^{212}Bi	6.051	69.9	60.6 min	^{211}Bi	6.623	84	2.13 min
^{210}Po	5.305	100	138.4 d	^{212}Po	8.785	100	0.3 μs				

TABLE 7

THE LEAD ISOTOPES OF THE ^{238}U, ^{235}U and ^{232}Th DECAY SERIES

[After Kocher 1981]

Isotope	Decay Series	Decay Mode	Half-life	Particle Energy (max. MeV)	Particle Intensity (%)	Natural Abundance (%)
^{214}Pb	^{238}U	beta	26.8 min	0.185	8	
				0.490	6	
				0.672	48	
				0.729	42.5	
				1.024	6.3	
^{212}Pb	^{232}Th	beta	10.64 h	0.158	5.22	
				0.334	85.1	
				0.573	9.9	
^{211}Pb	^{235}U	beta	36.1 min	0.264	0.66	
				0.541	5.0	
				0.968	1.3	
				1.373	93.0	
^{210}Pb	^{238}U	beta	21 y	0.0165	80.2	
				0.063	19.8	
^{208}Pb	^{232}Th	stable				52.3
^{207}Pb	^{235}U	stable				22.6
^{206}Pb	^{238}U	stable				23.6

TABLE 8

PHASES IN URANIUM MINE TAILINGS

	Acid Ore				Alkaline Ore
Phase	Mn Oxidant		Caro's Acid Oxidant		
	Acid	Neutralised	Acid	Neutralised	
Water soluble	X	X	X	X	X
Ion-exchangeable	X	X	X	X	X
Ca/Ba sulphate/carbonate		X		X	X
Manganese oxide	X	X			
Amorphous hydrous oxides	X	X	X	X	X
Crystal. hydrous oxides	X	X	X	X	X
Pyrite	X	X	X	X	
Resistate	X	X	X	X	X

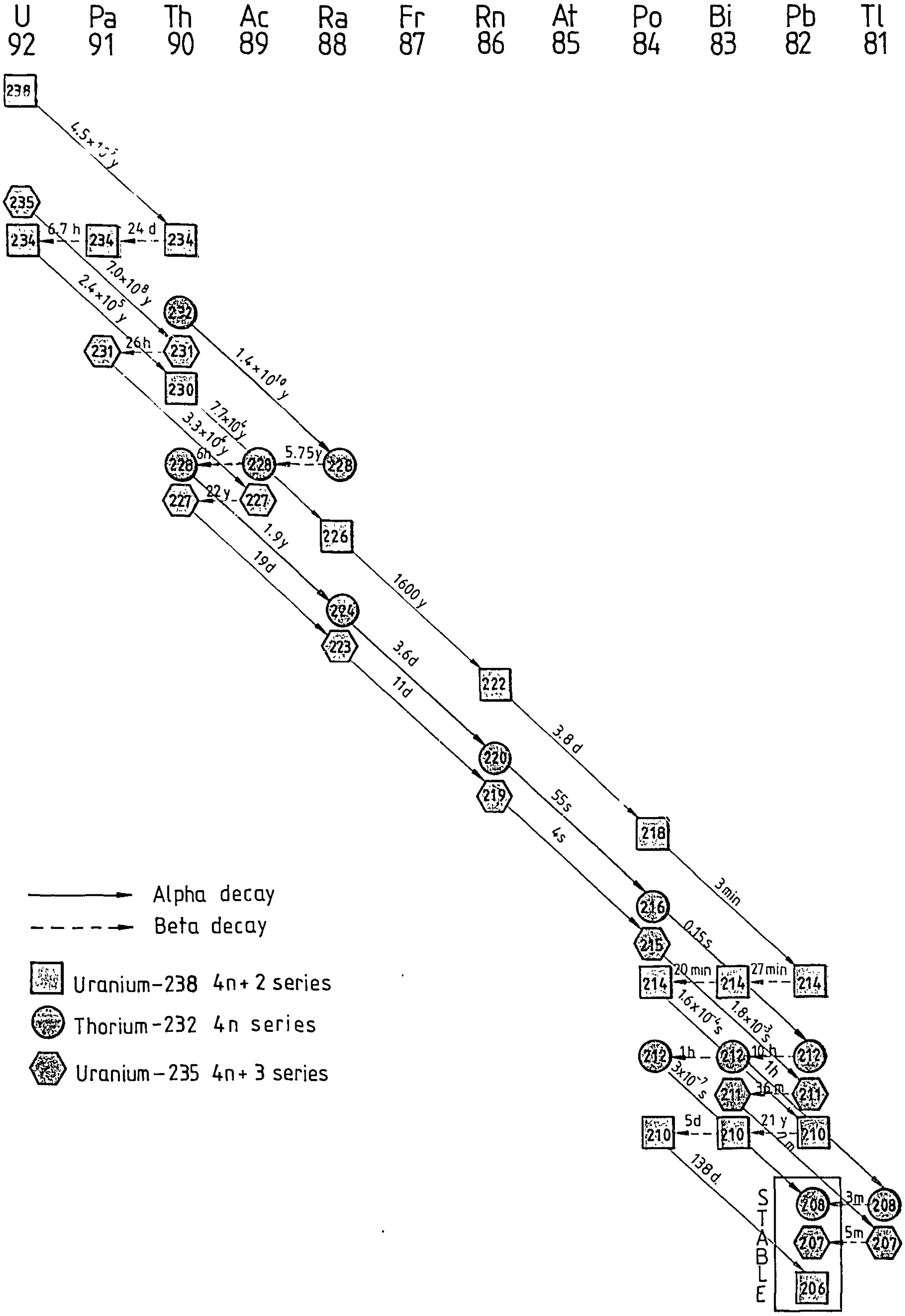


Figure 1 Natural uranium and thorium decay chains.

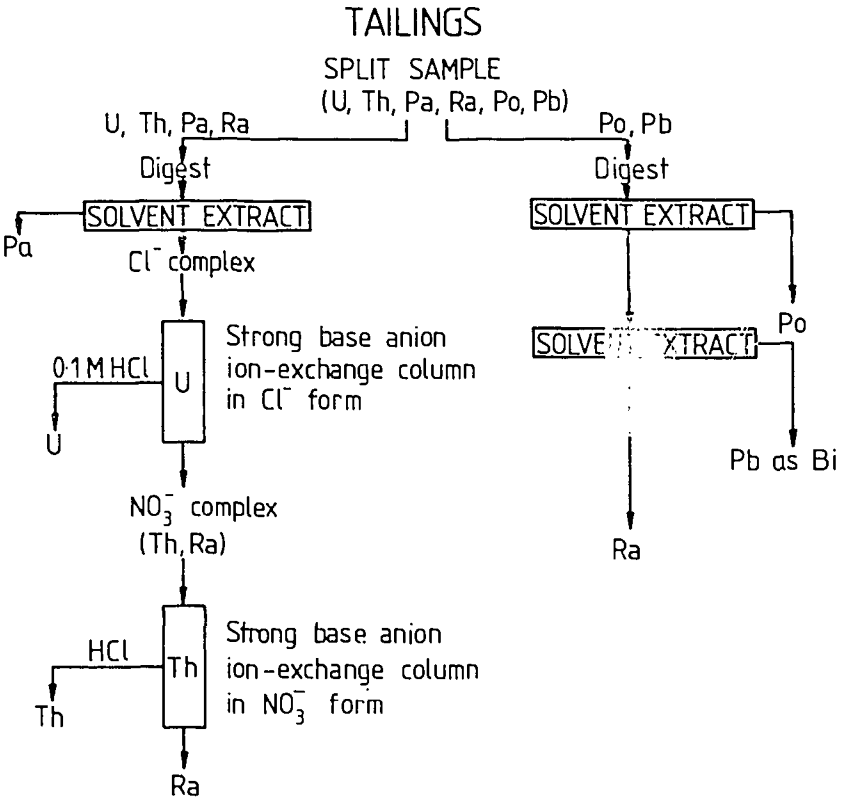
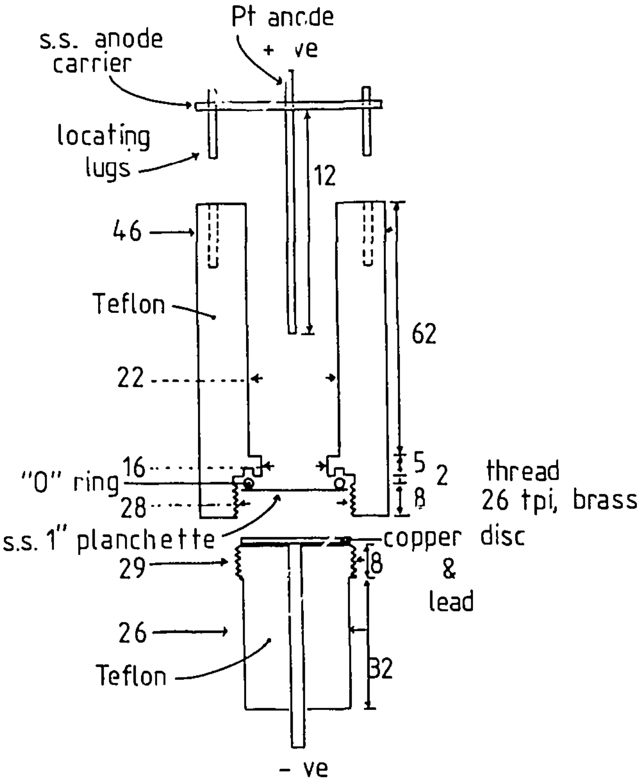


Figure 2 General scheme for the isotopic analysis of uranium mill tailings.



Dimensions in mm.

Figure 3 Electrodeposition cell.

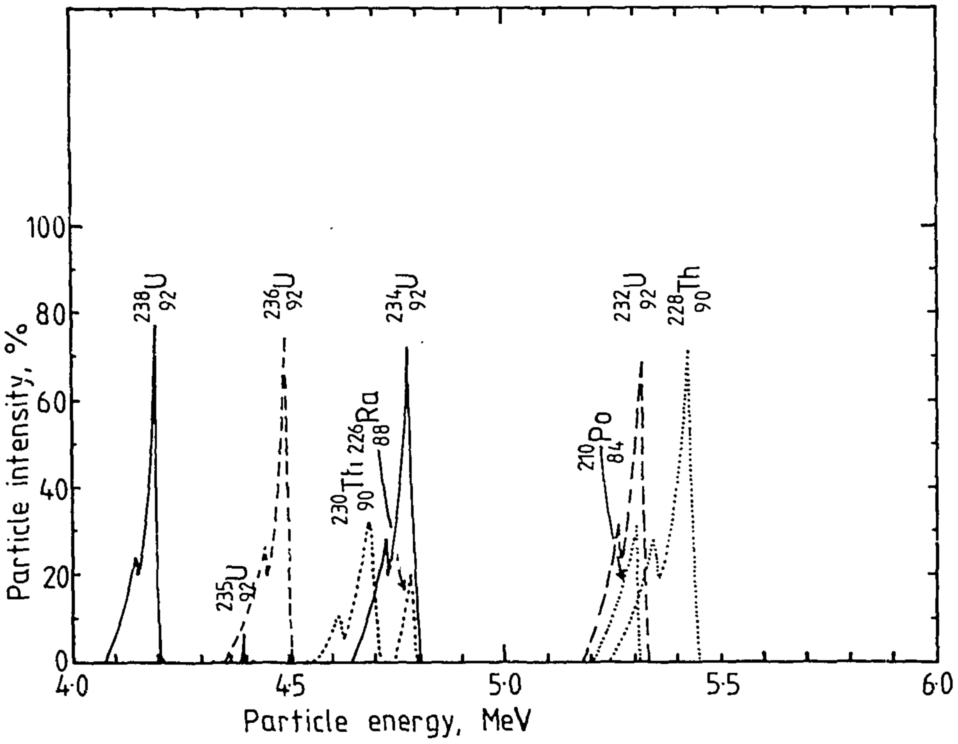


Figure 4 Idealised alpha spectra for uranium.

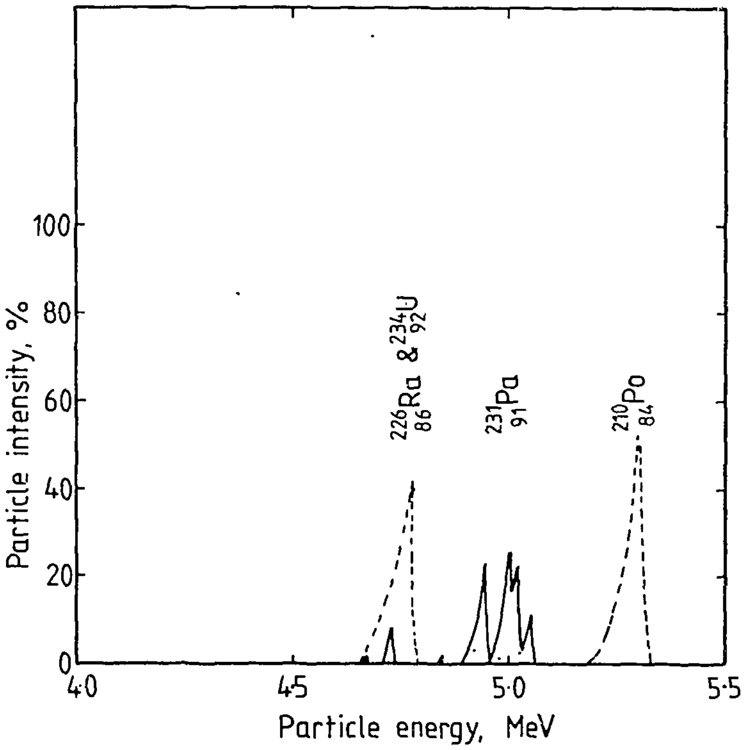


Figure 5 Idealised alpha spectra for protactinium.

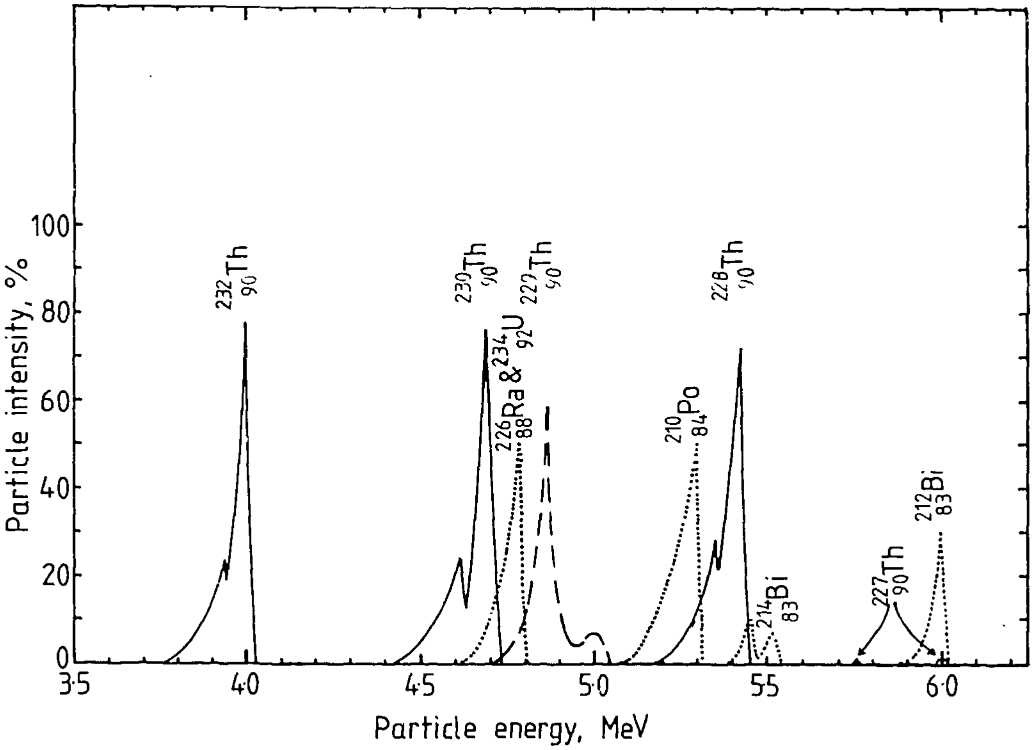


Figure 6 Idealised alpha spectra for thorium

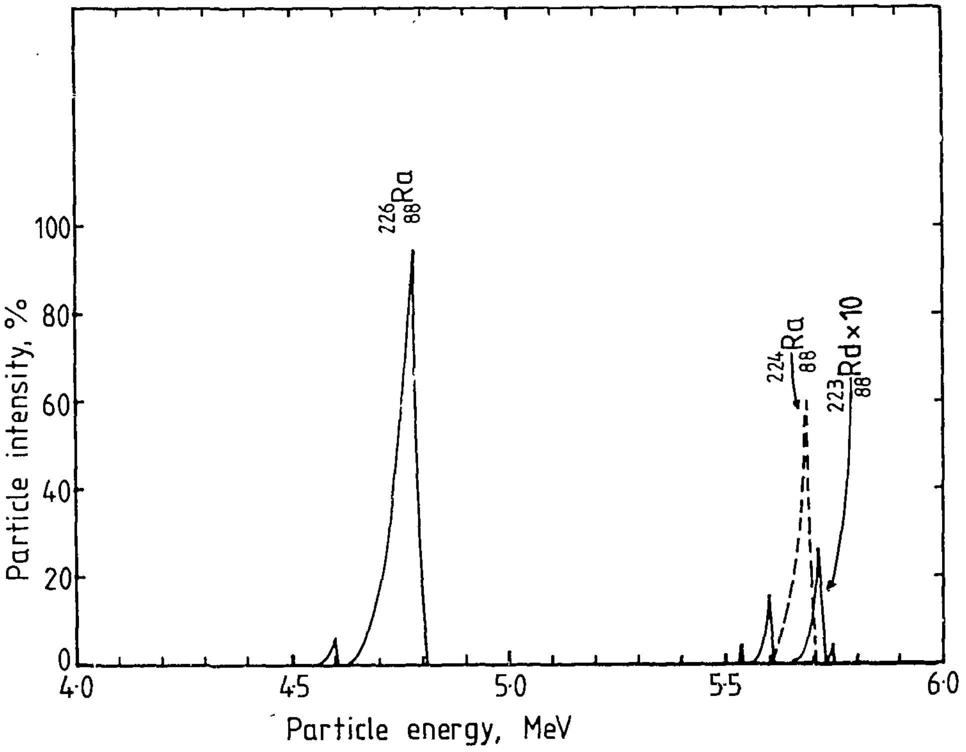


Figure 7 Idealised alpha spectra for radium

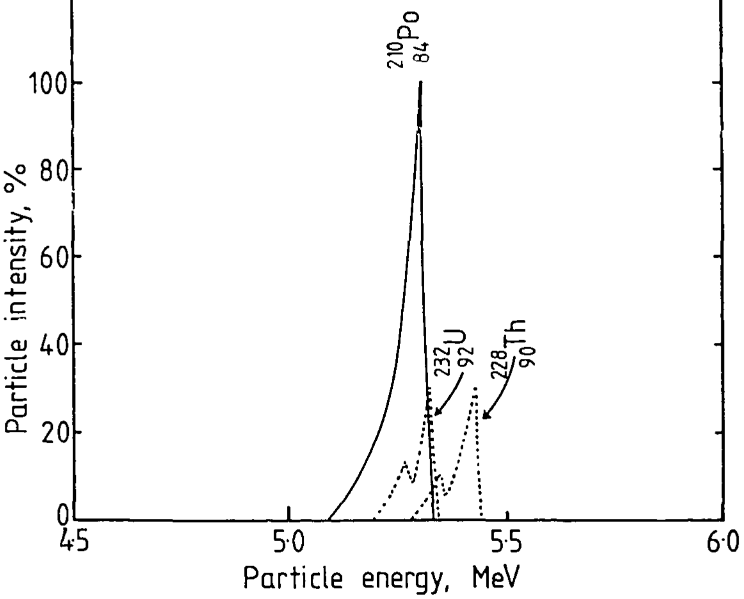


Figure 8 Idealised alpha spectra for polonium

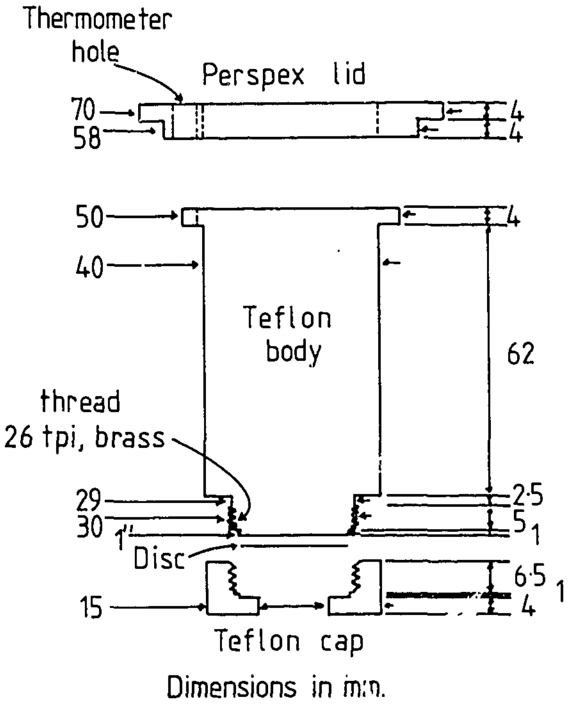


Figure 9 Autodeposition cell.