



Research Report 7

# Routine analysis of naturally occurring radionuclides in environmental samples by alpha-particle spectrometry

P. Martin and G. Hancock

Supervising Scientist for  
the Alligator Rivers Region

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ALPHA-PARTICLE SPECTROMETRY**

*P. Martin and G. Hancock*

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**Paul Martin and Gary Hancock**

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## ABSTRACT

The high sensitivity and wide range of applicable sample types make alpha-particle spectrometry a powerful technique for the determination of low-level activities in environmental samples. Radiochemical techniques are described here for the determination of the following alpha-emitting nuclides:

$^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{234}\text{U}$   
 $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{228}\text{Th}$   
 $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$ , and  
 $^{210}\text{Po}$ ,

together with a method for the determination of  $^{210}\text{Pb}$  by beta counting. In addition, the beta-emitters  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{227}\text{Ac}$  can be determined within a few months of their separation from the sample digest via measurement of their alpha-emitting daughters.

After addition of a suitable tracer and dissolution of the sample, a chemical separation scheme is utilised which allows the sequential separation and analysis of all of the above nuclides on the same sample digest. This scheme has been developed with the aim of achieving consistent high chemical yields while minimising analysis time.

Sample pretreatment criteria, tracer isotope selection and spectral analysis procedures for each element are discussed, and typical spectra shown. A set of computer programs used for the calculation of results are also described.

## 1. INTRODUCTION

The aim of this publication is to provide a description of procedures for radiochemical analysis of environmental samples as currently in use at the Alligator Rivers Region Research Institute (ARRRI).

This Institute conducts research into the environmental effects, including the radiological impact on man, of uranium mining in the Alligator Rivers Region. Consequently, environmental radioactivity measurements are primarily concerned with those members of the uranium, thorium and actinium decay chains with half-lives of the order of a few days or longer. Figures 1-3 show the members of these three decay chains, together with their half-lives and modes of decay. A fourth series (the  $4n+1$  series), whose members are often used as isotopic tracers, is shown in Figure 4.

Analysis for these radioactive isotopes commonly employ one or more of the following techniques:

- alpha-particle counting;
- beta-particle counting;
- liquid scintillation spectrometry;
- gamma-ray spectrometry;
- radon emanation;
- high-resolution alpha-particle spectrometry, without a tracer isotope, directly on the sample; and
- high-resolution alpha-particle spectrometry, using a tracer isotope, and involving chemical separation procedures.

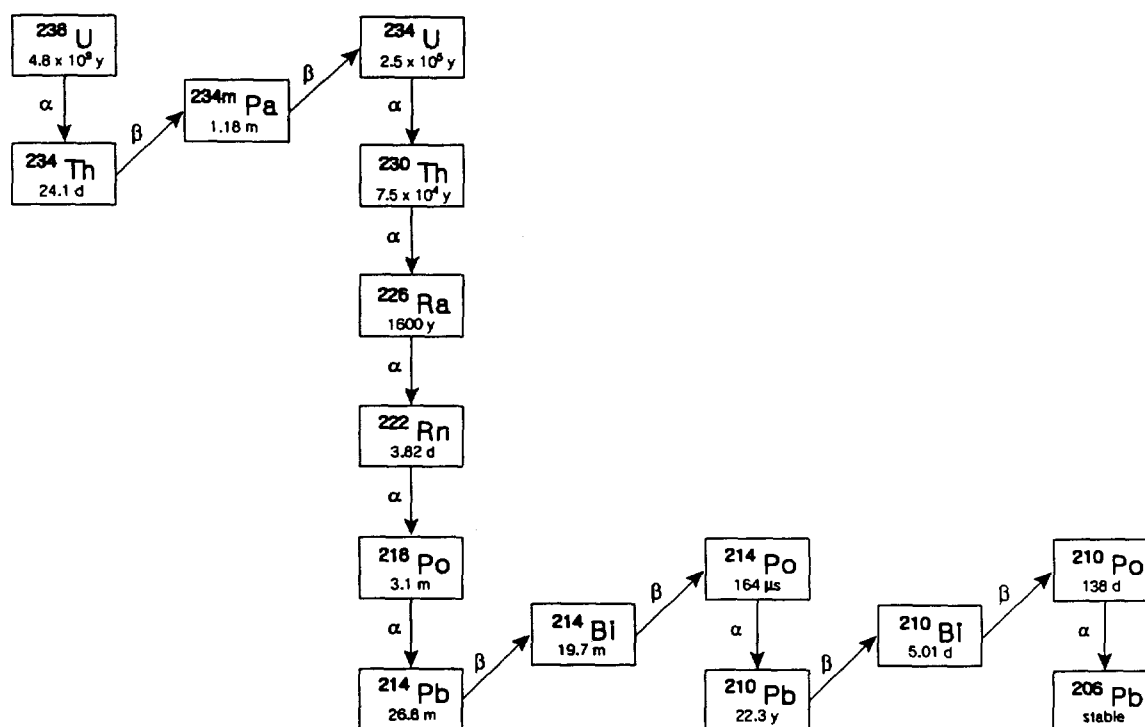


Figure 1. Uranium series ( $4n + 2$  series)

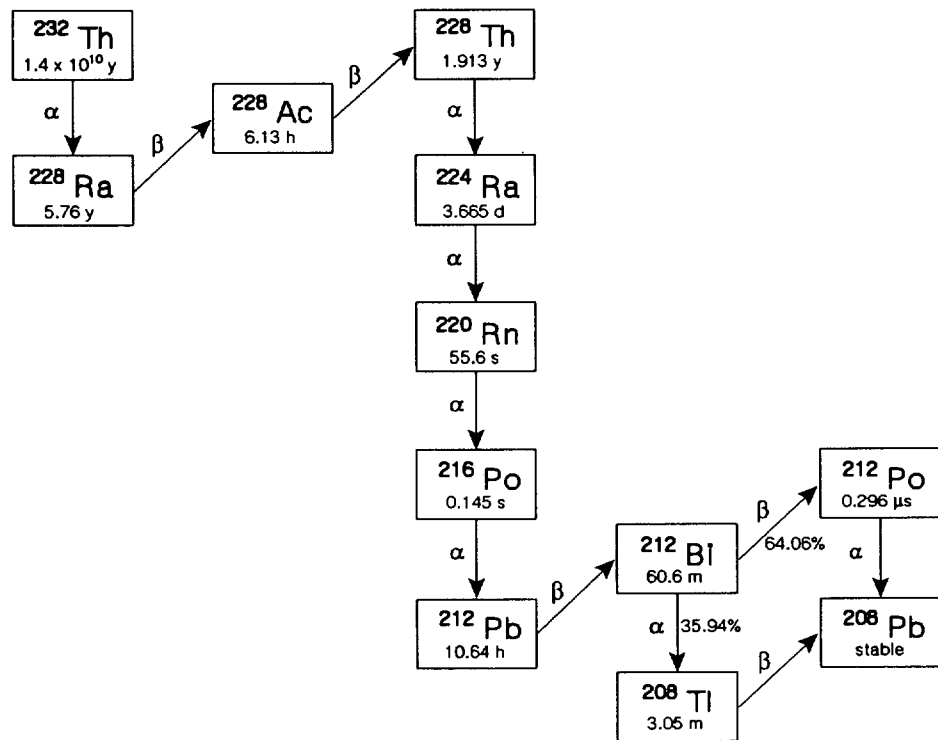


Figure 2. Thorium series (4n series)

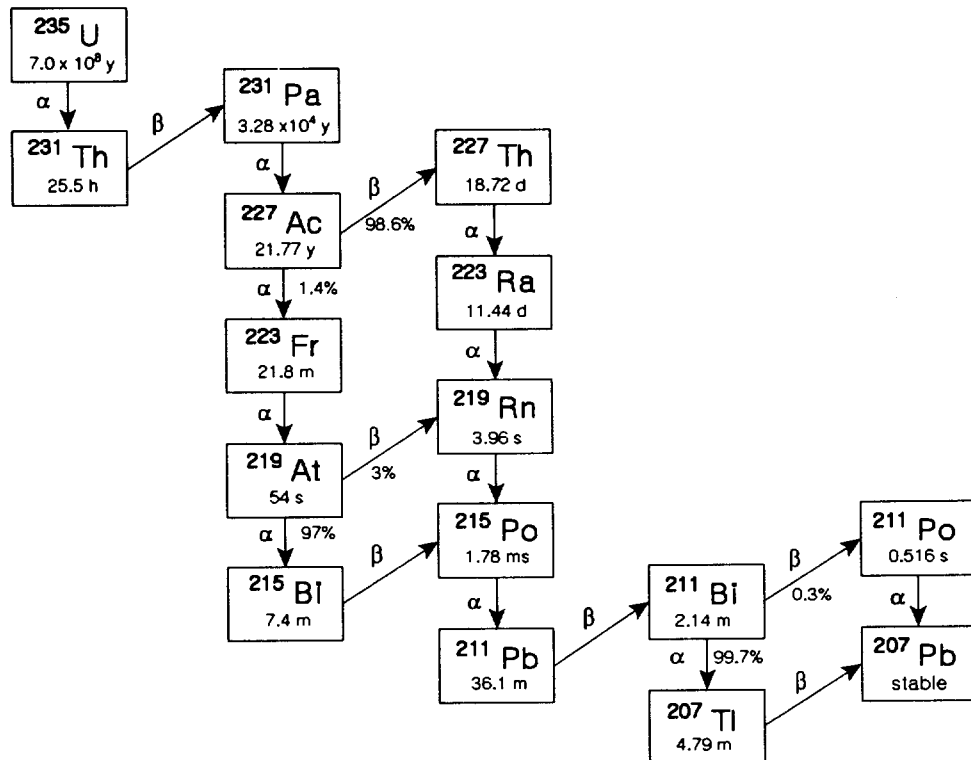


Figure 3. Actinium series (4n + 3 series)

This latter method has a number of advantages over other techniques of measurement of low-level activities, including:

- high sensitivity resulting from the observation of the high-yield alpha decay process, low intrinsic detector backgrounds and the elimination of competing radiation by chemical processing;
- the ability to use an alpha-emitting isotope as a tracer makes the technique reliable, provided no losses of either sample or tracer occur before the two isotopes have chemically equilibrated. The analytical error is dependent only on counting statistics, the accuracy of the tracer calibration, and weighing errors when measuring tracer solution and sample. As the result is obtained from the ratio of sample to tracer peaks, it is not affected by errors in the knowledge of counting efficiency;
- the range of radionuclides which can be determined. Those of interest to us here include:

$^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{234}\text{U}$   
 $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{228}\text{Th}$   
 $^{228}\text{Ra}$ ,  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$   
 $^{210}\text{Pb}$   
 $^{210}\text{Po}$   
 $^{227}\text{Ac}$

- the ability to measure concentrations of  $^{226}\text{Ra}$  without an ingrowth period for  $^{222}\text{Rn}$  and daughters; and
- the range of applicable sample types. Virtually any sample which can be chemically digested can be analysed using this technique.

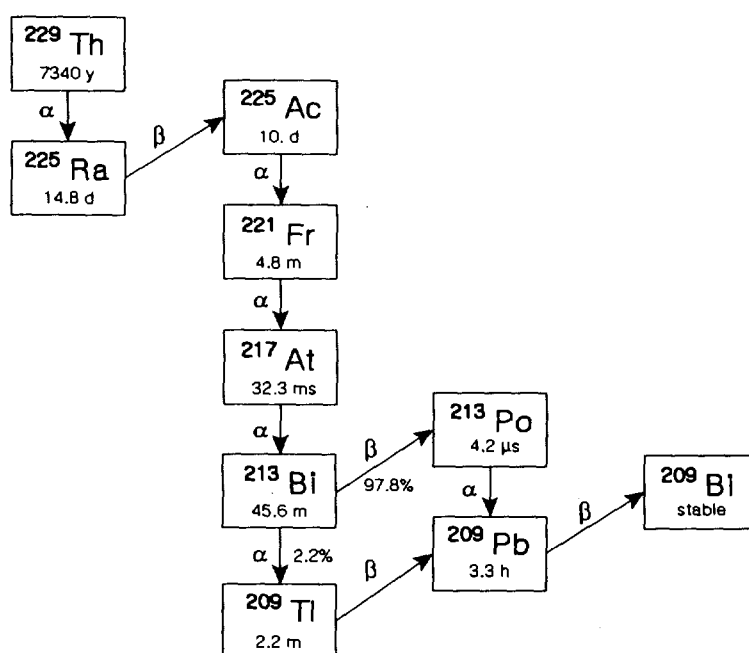


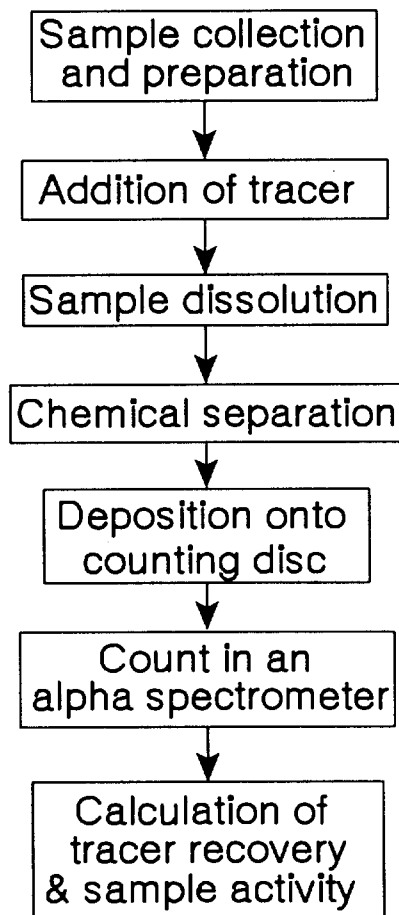
Figure 4.  $4n + 1$  series

Disadvantages of the technique include:

- the necessity of obtaining and calibrating a tracer isotope solution; and
- the lengthy chemical separation techniques required. These must separate the element of interest from other alpha-particle emitting radionuclides which would interfere with the spectrum. They must also remove metal ions which would deposit onto the source, resulting in a thick deposit and hence degraded spectral resolution.

Radiochemical techniques for the measurement of the nuclides listed above have been developed with the aim of utilising the advantages of alpha-particle spectrometry while minimising analysis time.

Figure 5 summarises the steps involved in analysis by alpha-particle spectrometry. The most time-consuming of these are generally those of sample dissolution and chemical separation. Hence, emphasis has been given to reducing to a minimum the number of chemical manipulations involved. This has been accomplished by the development of a chemical separation scheme which allows analysis of all 6 elements of interest on a single sample digest. Although the techniques are based primarily on alpha-particle spectrometry, a method for analysis of  $^{210}\text{Pb}$  by beta counting has been incorporated as part of the analysis scheme.



**Figure 5. Steps involved in analysis by alpha-particle spectrometry**

## 2. SAMPLE COLLECTION AND PREPARATION

### 2.1 Time constraints

Analysis of isotopes with relatively short half-lives can place constraints on sample collection and analysis timetables. For example, analysis for  $^{224}\text{Ra}$  ( $t_{1/2} = 3.7$  days) and  $^{223}\text{Ra}$  ( $t_{1/2} = 11.4$  days) should be performed as soon as possible after sample collection to minimise decay, and ingrowth from the parents.

Analysis of  $^{210}\text{Po}$  ( $t_{1/2} = 138$  days) should normally be completed within a week of sample collection. For samples for which the  $^{210}\text{Pb}$  and  $^{210}\text{Bi}$  parent activities are much higher than the  $^{210}\text{Po}$  activity (e.g. rainwaters), the maximum time advisable is 2 – 3 days or less.

### 2.2 Drying procedures

Polonium, despite its high boiling point, shares with other group VI elements the tendency to be volatilised when samples are dried at elevated temperatures (Bock 1979). This is probably due to the presence of volatile organic complexes, or polonium halides (volatile above  $150^\circ\text{C}$ ). Volatility varies widely with chemical form, and polonium has been shown to be partly volatilised from some samples at all temperatures above  $100^\circ\text{C}$  (Martin & Blanchard 1969).

It seems prudent, therefore, to keep drying temperatures as low as is practicable. At the Alligator Rivers Region Research Institute, samples are dried to a constant weight at  $80^\circ\text{C}$ .

### 2.3 Treatment of water samples

The elements of interest here are almost invariably present in water samples in extremely low concentrations. For example, a  $^{226}\text{Ra}$  concentration of 1 Bq/L represents a molarity of only  $1.2 \times 10^{-13} \text{ M Ra}$ . Even for the longer-lived  $^{232}\text{Th}$ , 1 Bq/L represents  $1.1 \times 10^{-6} \text{ M Th}$ .

At such low concentrations, it is imperative to avoid any loss of the element onto phase boundaries (e.g. adsorption onto suspended particles, colloids or the walls of the container). Samples should be collected into acid-washed plastic containers. Samples for analysis for total activity concentration should be acidified (usually 1%  $\text{HNO}_3$ ) immediately on collection. Samples to be filtered should be processed as soon as possible after collection and the filtered portion acidified. Immediately before any sub-sampling for analysis, samples (including filtered portions) must be shaken vigorously in order to resuspend any particulates and/or colloids.

Polonium is a particular problem in this respect. This element hydrolyses to a considerable extent in dilute ( $<0.01 \text{ N}$ ) acid solutions and is readily adsorbed onto colloids, suspended particles and glass surfaces. Desorption of such hydrolysed species can be difficult to achieve even with strong acid solutions. For further discussion of this problem see Bagnall (1957, pp. 29-32) and Beneš & Majer (1980).

### 3. SELECTION AND USE OF TRACERS

Tracers must be kept in air-tight plastic bottles, and dispensed with all reasonable care to prevent contamination of the solution. Checks must be made a number of times through the life of the tracer to ensure that neither contamination nor change in tracer strength has occurred.

Choice of tracer depends on a number of factors, including alpha-particle energy, half-life, detector contamination, purity, price and availability of supply. Details of alpha-particle energy and half-life for the nuclides of interest are summarised in Appendix 1.

#### 3.1 Polonium

The two tracers commonly used for  $^{210}\text{Po}$  determination are  $^{208}\text{Po}$  and  $^{209}\text{Po}$ .

$^{209}\text{Po}$  has a clear advantage over  $^{208}\text{Po}$  in energy separation from the  $^{210}\text{Po}$  peak and is the preferred tracer, if available. In addition, its longer half-life means that, should the solution have a  $^{210}\text{Po}$  load either from production or contamination, the solution may be set aside to allow decay of the  $^{210}\text{Po}$  with negligible loss of tracer strength.

Unfortunately, long half-life has a disadvantage in relation to detector contamination. Due to its volatility, atoms of polonium readily leave the counting planchet in the vacuum of the counting chamber. There, a significant fraction can drift to the detector, where they become firmly attached to the metal surfaces of the detector, causing a gradual increase in detector background with use. Given that contamination of detectors occurs at a more-or-less constant rate with use, contamination will increase until a steady state condition is reached where decay of contaminant atoms equals rate of contamination. The value of this contamination activity is proportional to the isotope half-life; hence, use of  $^{209}\text{Po}$  will eventually result in a much higher tracer activity on the detector than  $^{208}\text{Po}$ .

#### 3.2 Lead

For determination of  $^{210}\text{Pb}$ , stable lead is used as both carrier and tracer. Exact calibration of the tracer solution is not strictly necessary, since recovery is measured using a set of standards prepared from the same tracer solution used to spike the sample.

Most commercial lead salts contain significant concentrations of  $^{210}\text{Pb}$  and its grand-daughter  $^{210}\text{Po}$ , and will cause blank problems for both  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  measurements if used for preparation of the tracer solution. Hence, where possible a source of lead old enough to have allowed decay of most of the  $^{210}\text{Pb}$  activity should be used ( $^{210}\text{Pb}$   $t_{1/2} = 22.3$  years).

Most samples will contain some stable lead. The amount of lead tracer added must be known to be greatly in excess of the lead in the sample; otherwise a correction must be applied.

#### 3.3 Uranium

The three tracers commonly used for uranium determination are  $^{232}\text{U}$ ,  $^{233}\text{U}$  and  $^{236}\text{U}$ .

$^{233}\text{U}$  has the disadvantage that its energy (4.78 + 4.82 MeV) lies within the energy region of the  $^{234}\text{U}$  peak at 4.77 MeV.

$^{236}\text{U}$  (4.44 + 4.49 MeV) overlaps the  $^{235}\text{U}$  spectrum. For most environmental samples this may be allowed for by assuming the normal  $^{235}\text{U}/^{238}\text{U}$  activity ratio of 0.04604.

$^{232}\text{U}$  has the advantage that its energy is well separated from those of  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{234}\text{U}$ , allowing all three to be measured. The daughter and grand-daughter of  $^{232}\text{U}$  are  $^{228}\text{Th}$  and  $^{224}\text{Ra}$  respectively; their presence in the tracer solution is a disadvantage if a measure of  $^{228}\text{Th}$  and/or  $^{224}\text{Ra}$  on the same sample digest is desired. However,  $^{228}\text{Th}$  may be used as a tracer for measurement of  $^{230}\text{Th}$  and  $^{232}\text{Th}$  (see Section 3.4), and  $^{224}\text{Ra}$  may be used as a tracer for  $^{223}\text{Ra}$ ,  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  (Section 3.5). In addition, measurement of the  $^{228}\text{Th}$  peak on the uranium spectrum gives a check of the efficiency of removal of thorium from the uranium fraction.

### 3.4 Thorium

The three tracers commonly used for thorium determination are  $^{228}\text{Th}$ ,  $^{229}\text{Th}$  and  $^{234}\text{Th}$ .

$^{228}\text{Th}$  may be used as a tracer for determination of  $^{230}\text{Th}$  and  $^{232}\text{Th}$ , but naturally precludes determination of  $^{228}\text{Th}$  in the sample. In many cases (e.g. sediments, mussels) where the  $^{228}\text{Th}$  activity in the sample itself is high and known from a separate determination, it may be used as the tracer. For example,  $^{228}\text{Th}$  may be measured by gamma-ray spectrometry and alpha-particle spectrometry used to determine the  $^{230}\text{Th}$  and  $^{232}\text{Th}$  activity concentrations.

Where  $^{228}\text{Th}$  is added as a tracer solution (a  $^{232}\text{U}$  tracer solution is the most usual source) and the  $^{228}\text{Th}$  contribution from the sample is not negligibly small compared with the added tracer activity, the sample  $^{228}\text{Th}$  contribution must be allowed for. This requires a separate measurement, unless  $^{228}\text{Th}$  is known to be in secular equilibrium with  $^{232}\text{Th}$  (see discussion of program THORE in Appendix 2).

Note that, where an aged  $^{232}\text{U}$  solution is used as a source of  $^{228}\text{Th}/^{224}\text{Ra}$  tracer, at secular equilibrium the  $^{228}\text{Th}$  and  $^{224}\text{Ra}$  activity concentrations equal 1.027 times the  $^{232}\text{U}$  concentration, due to the relative half-lives of  $^{232}\text{U}$  and  $^{228}\text{Th}$ .

$^{229}\text{Th}$  allows measurement of all three isotopes of interest; it also has the advantage of being an artificial isotope not normally present in environmental samples. Some contribution of the  $^{229}\text{Th}$  peak to the  $^{230}\text{Th}$  peak is inevitable due to their proximity in the spectrum and to some minor  $^{229}\text{Th}$  peaks directly under  $^{230}\text{Th}$ . Hence, the tracer activity may need to be limited for samples with low  $^{230}\text{Th}$  activity concentration.

$^{229}\text{Th}$  may also interfere with the  $^{228}\text{Th}$  peak measurement for two reasons. Firstly,  $^{229}\text{Th}$  solutions usually contain some  $^{228}\text{Th}$  activity. This problem is best avoided by using  $^{229}\text{Th}$  tracer solutions which have been aged so that the tracer  $^{228}\text{Th}$  activity is negligible in comparison with that of the sample; otherwise, a correction must be applied. Secondly, tailing from the  $^{229}\text{Th}$  daughter  $^{225}\text{Ac}$  (Figure 4) will also contribute to the  $^{228}\text{Th}$  peak due to their proximity in the spectrum (Section 8.6). This effect may be minimised by counting the disc as soon as possible after deposition.

$^{234}\text{Th}$  is a beta emitter, and recovery must be determined by either beta counting or gamma-ray spectrometry. This requires accurate calibration of both alpha and beta/gamma detectors.  $^{234}\text{Th}$  is also naturally-occurring (daughter of  $^{238}\text{U}$ ), and hence can only be used where the  $^{234}\text{Th}$  activity in the sample is known or is known to be small compared with the added tracer activity. A description of the use of this tracer is not included in this report.



### 3.5 Radium

The three tracers commonly used for radium determination are  $^{223}\text{Ra}$ ,  $^{224}\text{Ra}$  and  $^{225}\text{Ra}$ .  $^{225}\text{Ra}$  is ideal because it does not occur naturally and is, therefore, not present in environmental samples. Alternatively,  $^{223}\text{Ra}$  or  $^{224}\text{Ra}$  can be used if one accepts a limitation on the range of isotopes analysed and provided the tracer activity used is large compared with that present naturally in the sample.

With use of  $^{225}\text{Ra}$  as a yield tracer,  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ , and  $^{223}\text{Ra}$  are determined from an initial counting immediately after deposition, and from the calculated  $^{225}\text{Ra}$  recovery determined after a suitable ingrowth period for  $^{225}\text{Ac}$  and daughters (Fig. 4).  $^{228}\text{Ra}$  is determined after an ingrowth period for  $^{228}\text{Th}$  and  $^{224}\text{Ra}$ .

The chemical recovery of  $^{225}\text{Ra}$  is determined from the  $^{217}\text{At}$  peak (7.07 MeV).  $^{225}\text{Ra}$  ( $t_{1/2}=14.8\text{d}$ ) is a beta emitter and decays to  $^{225}\text{Ac}$ , which in turn decays to a series of short-lived alpha-emitting daughters, of which only  $^{217}\text{At}$  is conveniently measured. The  $^{225}\text{Ac}$  activity reaches a maximum after 17 days (Fig. 6). However, if the activity of the added  $^{225}\text{Ra}$  is high enough, counting can begin any time after deposition.

If  $^{226}\text{Ra}$  only is to be measured, the quantity of added  $^{225}\text{Ra}$  will depend on the statistical error required, remembering that  $^{225}\text{Ac}$  (and hence  $^{217}\text{At}$ ) will grow in to a maximum of only ~44% of the initial  $^{225}\text{Ra}$  spike. If  $^{223}\text{Ra}$  and/or  $^{224}\text{Ra}$  are to be determined, the  $^{225}\text{Ra}$  spike should be limited, as  $^{225}\text{Ac}$  will slowly grow into the  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  energy region, and must be stripped from this area before they can be determined (see Section 8.4).

Where both thorium and radium analyses are required on a sample, it is convenient to add as tracer a  $^{229}\text{Th}$  solution in equilibrium with its  $^{225}\text{Ra}$  daughter (Fig. 4), or a  $^{228}\text{Th}$  solution in equilibrium with its  $^{224}\text{Ra}$  daughter (Fig. 2). The radium tracer activity is then calculated back to the first point in the separation procedure at which thorium/radium separation occurs (see Section 5.5).

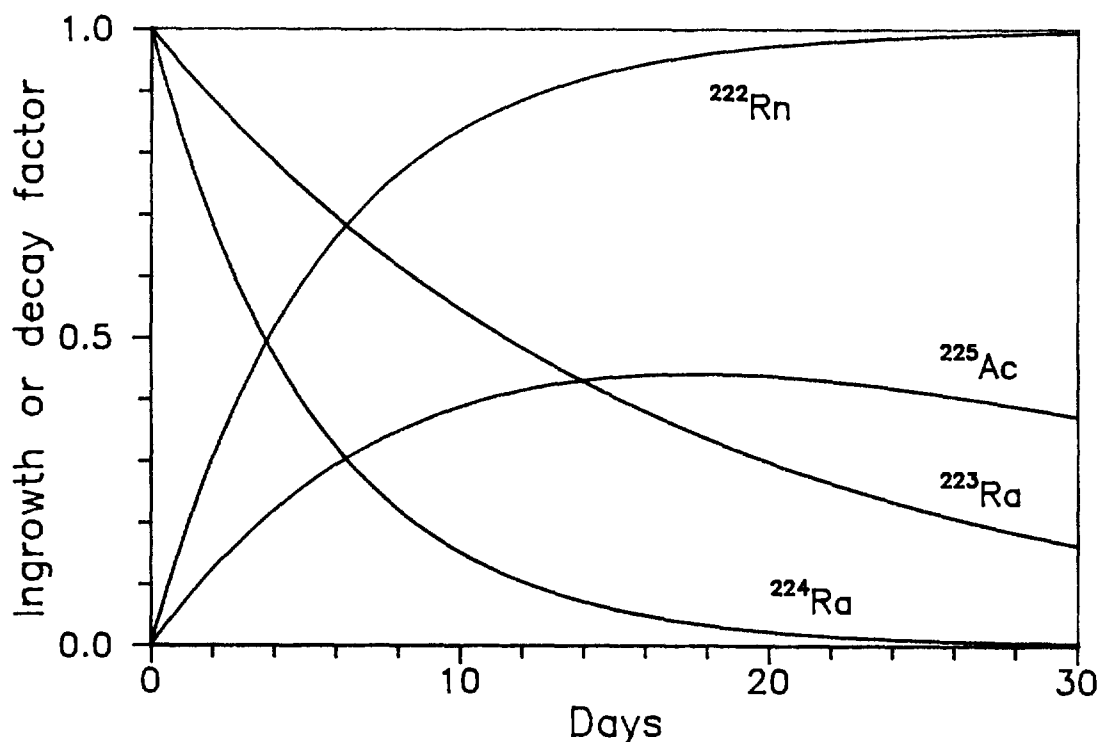


Figure 6.  $^{225}\text{Ac}$  ingrowth from  $^{225}\text{Ra}$ ,  $^{222}\text{Rn}$  ingrowth from  $^{226}\text{Ra}$ , and  $^{223}\text{Ra}$  &  $^{224}\text{Ra}$  decay on an initially pure radium source

This method assumes that no thorium/radium separation occurs before this point, and that the separation is quantitative. The first assumption may only be made where the analyst is confident that all material is in solution when the separation procedure is begun. The second assumption of 100% removal of thorium cannot, in practice, be attained in a single chemical separation step. However, the procedures described in Sections 5.4 and 5.5 involve at least two separate separation steps, where the first step should remove thorium to less than 1-2% of its original activity; provided the second thorium separation step is performed within 2-3 hours of the first, the error resulting will then be negligible.

Alternatively, a radium tracer solution free of the thorium parent may be prepared before addition to the sample. Some procedures for the preparation of  $^{224}\text{Ra}$  solutions are given by Bojanowski *et al.* (1983) and Sebesta and Sary (1974). The following method utilises the preparation of a radium isotope generator by adsorption of the thorium parent onto Dowex 1-X8 resin from 8 M  $\text{HNO}_3$  solution. After an ingrowth period, the radium daughter is milked from the generator with 8 M  $\text{HNO}_3$ . A second anion exchange step is then used to ensure complete removal of the thorium parent from the radium tracer solution.

1. Evaporate the thorium solution to dryness, and take up in 2-3 mL 8 M  $\text{HNO}_3$ .  
Fill a column (8 cm height, 0.7 cm internal diameter) with Dowex 1-X8 resin. Convert the column to the  $\text{NO}_3$  form by washing with 20 mL 8 M  $\text{HNO}_3$ .  
Add the thorium solution.  
Wash with 8 M  $\text{HNO}_3$  in two 5 mL aliquots and discard the eluate.\*  
Cap the column at both ends and allow an ingrowth period for the radium isotope daughter. The resin bed must not be allowed to go dry during this period.

\* If a  $^{232}\text{U}/^{228}\text{Th}/^{224}\text{Ra}$  tracer solution is used, 80 mL 8 M  $\text{HNO}_3$  must be passed through the column at this point to remove  $^{232}\text{U}$ .

2. Elute radium from the column by washing with 8 M  $\text{HNO}_3$  in two 10 mL aliquots.  
Recap the column and store as above.
3. Evaporate the radium solution to dryness at low heat, and take up in 2-3 mL 8 M  $\text{HNO}_3$ .  
Fill a column (4 cm height, 0.7 cm internal diameter) with Dowex 1-X8 resin. Convert the column to the  $\text{NO}_3$  form by washing with 10 mL 8 M  $\text{HNO}_3$ .  
Add the radium solution, collecting the eluate.  
Elute the remainder of the radium with 8 M  $\text{HNO}_3$  in two 10 mL aliquots.
4. Dilute the radium tracer solution to the required activity concentration.  
Calibrate against a standard  $^{226}\text{Ra}$  solution using the methods detailed in Sections 5.5 and 8.4.  
A thorium analysis should also be carried out on the solution to ensure that complete removal of the thorium isotope parent has been achieved.

As noted above (Section 3.4)  $^{229}\text{Th}$  solutions usually contain some  $^{228}\text{Th}$  activity, and hence some  $^{224}\text{Ra}$  activity will also be present. For measurement of a low  $^{224}\text{Ra}$  activity a correction may need to be applied. However, if a  $^{225}\text{Ra}$  tracer solution is prepared by separation from the  $^{229}\text{Th}$  parent, as described above, any  $^{224}\text{Ra}$  activity present will decay to a negligible amount within 2 weeks of the separation.

### 3.6 Actinium

For the determination of  $^{227}\text{Ac}$ ,  $^{225}\text{Ac}$  ( $t_{1/2} = 10.0\text{d}$ ) is the preferred tracer as it does not occur naturally and is conveniently measured via its grand-daughter  $^{217}\text{At}$ . It can be added as part of the  $^{229}\text{Th}/^{225}\text{Ra}/^{225}\text{Ac}$  decay series (Fig. 4), allowing analysis of thorium, radium and actinium on the same sample digest. The chemical recovery is determined from an initial count as soon as possible after deposition.  $^{227}\text{Ac}$  is determined from a second count after the decay of  $^{225}\text{Ac}$ , and ingrowth of the  $^{227}\text{Ac}$  progeny  $^{227}\text{Th}$  and  $^{223}\text{Ra}$ . The quantity of  $^{225}\text{Ac}$  tracer added will depend largely on how soon the  $^{227}\text{Ac}$  determination is required. Figure 7 shows the relative ingrowth and decay curves for  $^{227}\text{Th} + ^{223}\text{Ra}$ , and  $^{225}\text{Ac}$ . If a determination of  $^{227}\text{Ac}$  within 2 months is required, the quantity of  $^{225}\text{Ac}$  added should be limited so that the  $^{225}\text{Ac}$  activity present in the final count is small compared to the integrated  $^{227}\text{Th}$  and  $^{223}\text{Ra}$  activity.

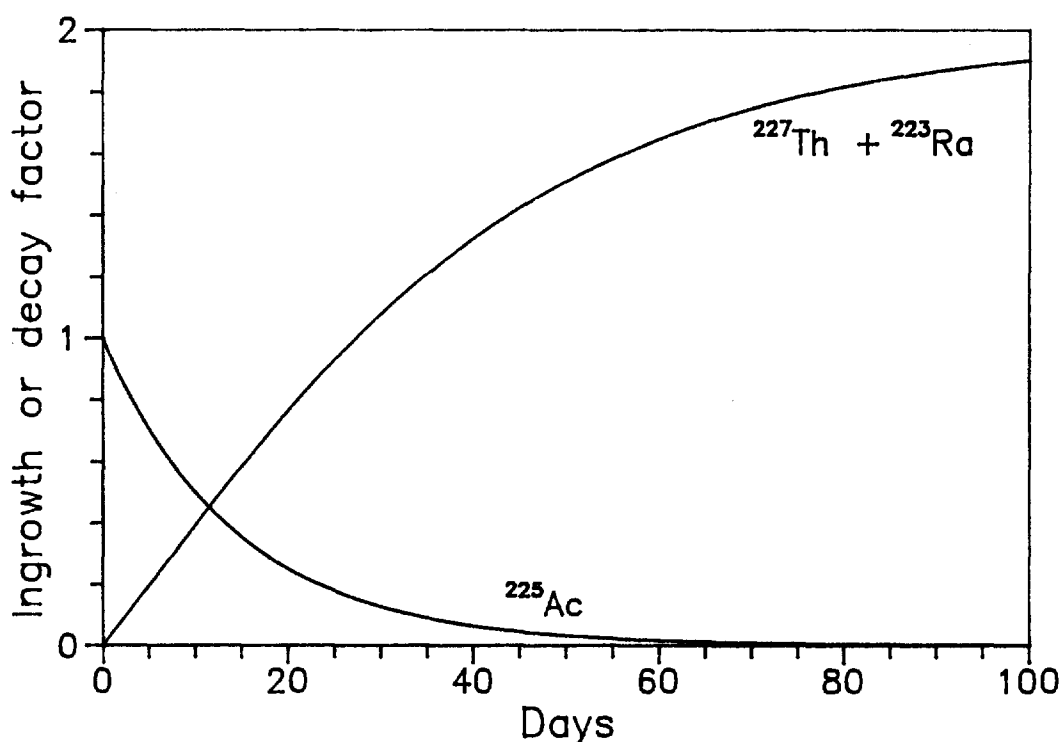


Figure 7.  $^{227}\text{Th} + ^{223}\text{Ra}$  ingrowth from  $^{227}\text{Ac}$  (beta emitter) and  $^{225}\text{Ac}$  decay on an initially pure actinium source

Although not described in detail here,  $^{228}\text{Ac}$  ( $t_{1/2} = 6\text{h}$ ) is an alternative tracer. This isotope is a beta emitter, and recovery must be determined by beta counting immediately after deposition. This requires accurate calibration of both alpha and beta detectors.  $^{228}\text{Ac}$  is also naturally-occurring (daughter of  $^{228}\text{Ra}$ ), and hence can only be used as a tracer where the  $^{228}\text{Ac}$  activity in the sample is known or is known to be small compared with the added tracer activity.

#### 4. SAMPLE DIGESTION AND DISSOLUTION

Sample digestion and dissolution procedures vary from sample to sample, and have been well documented elsewhere (e.g. Bock 1979). At the ARRRI, sample dissolution for radiochemical analysis most commonly employs wet acid digestion, utilising nitric acid to oxidise any organic material present, and hydrofluoric acid to attack silicates. Perchloric acid is used where necessary, but for safety reasons never where substantial amounts (>0.1 g) of organic matter are present. For mineral samples resistant to acid attack, a fusion method may be necessary (e.g. Sill 1983).

Whichever technique is used, the sample must be brought completely into solution to allow chemical equilibration of the tracer isotope and the isotope to be measured to occur before element separation is carried out. The use of a tracer isotope in alpha-particle spectrometry is only valid if a known quantity of tracer isotope is chemically equilibrated with a known quantity of sample. If loss of either tracer solution or sample occurs before equilibration of tracer and sample isotopes, then unquantifiable errors will result.

When analysing for  $^{210}\text{Po}$ , it is important that the dry sample not be heated above  $150^\circ\text{C}$ , as over-heating of a dry deposit may result in loss of polonium and low recovery. High-temperature wet digestions, such as heating to fumes with perchloric acid, do not result in significant polonium losses. Fusion techniques generally result in substantial polonium loss and should not be used when analysing for  $^{210}\text{Po}$  (Akber, Hutton & Prescott 1985; Lowson & Short 1986).

##### 4.1 Manganese dioxide precipitation

This method is useful for concentrating radionuclides from large volumes of water where the nuclides are considered to be in solution (e.g. filtered groundwater).

The method given here is that of Bojanowski *et al.* (1983), and is designed for a 10 L sample. For a 1 L sample, only 2 mL each of 0.2 M  $\text{KMnO}_4$  and 0.3 M  $\text{MnCl}_2$  solutions are required.

1. After acidification of the sample and addition of the tracer, bubble the solution for 2 hours with nitrogen to ensure tracer equilibration, and to expel any dissolved  $\text{CO}_2$  which may inhibit precipitation of uranium.
2. Add 10 mL of 0.2 M  $\text{KMnO}_4$  and adjust the pH to 8-9 with  $\text{NH}_3$ .  
Add 10 mL of 0.3 M  $\text{MnCl}_2$ , and bubble the solution for one hour.  
Allow the precipitate to settle.
3. Remove the majority of supernatant by suction or decantation.  
Collect the precipitate by filtration and wash with 0.2%  $\text{NH}_4\text{Cl}$  (pH 8 to 9).  
Discard the wash solution.  
Dissolve the precipitate with 1 %  $\text{H}_2\text{O}_2$  in 1.2 M  $\text{HCl}$ .  
Evaporate to dryness, redissolve with a few mL of 5 M  $\text{HCl}$  and evaporate again to ensure complete decomposition of peroxides.

## 5. CHEMICAL SEPARATION PROCEDURES

The radionuclide separation scheme described here was developed to satisfy the following objectives:

- determination of the long-lived alpha-emitting isotopes of uranium, thorium, radium and polonium, and the beta-emitters  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{227}\text{Ac}$ ;
- the scheme should be applicable to a wide range of sample types;
- consistently high recoveries and element separation efficiencies need to be achieved in order to take advantage of the high potential sensitivity of radiochemical techniques;
- the analysis scheme should involve the minimum possible number of steps to minimise analysis time, contamination, and losses of the radionuclide being determined.

The separation scheme that has been developed at the ARRI is shown in Figure 8. Use of the full procedure as shown allows analysis of isotopes of all 6 elements of interest to be accomplished on a single sample digest, saving considerable analysis time. Sample types to which the procedure has been successfully applied include surface and ground waters, dried animal and plant material, air filters, and soils and sediments. A qualitative description of the separation procedures follows.

After sample digestion and/or pre-concentration steps (e.g. precipitation of radionuclides from water samples using manganese dioxide), the residue is brought into solution in 5 M HCl and polonium extracted using 0.1% diethylammonium diethyldithiocarbamate (DDTC) in chloroform.

The aqueous layer from the polonium extraction may now be diluted to 1.5 M HCl and lead extracted by 1% DDTC in chloroform for determination of  $^{210}\text{Pb}$ . If a  $^{210}\text{Po}$  determination is not required, and  $^{210}\text{Pb}$  is to be determined by the beta-counting method, the previous extraction of  $^{210}\text{Po}$  is not necessary.

The aqueous layer from the polonium and/or lead extractions are taken to dryness and the residue brought into solution in 8 M  $\text{HNO}_3$ ; if no  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  determinations are required, separations may be started directly on the sample residue from this point. Thorium and uranium are now extracted into tri-butyl phosphate from 8 M  $\text{HNO}_3$ . After dilution of the organic layer with xylene, thorium is back-extracted into 5 M HCl. Uranium is then back-extracted into water. The thorium and uranium extracts are further purified using an anion exchange resin before electrodeposition onto the counting disc.

The aqueous layer from the previous solvent extractions are taken to dryness and the residue brought into solution in 0.1 M HCl or  $\text{HNO}_3$ ; if no  $^{210}\text{Po}$ ,  $^{210}\text{Pb}$  and uranium determinations are required, separations may be started directly on the solubilised sample residue from this point.

Radium, actinium and thorium (if not previously extracted) are now co-precipitated with lead sulphate (Hancock & Martin 1991). The precipitate is dissolved in 0.1 M EDTA at pH 10. An anion exchange step is used to remove the sulphate ion, and separate radium (which passes through the column) from actinium and thorium (which are adsorbed). A cation exchange step is then used to separate radium from other interfering elements, particularly barium.

Actinium is removed from the anion exchange column with 0.005 M EDTA/0.1 M ammonium acetate at pH 5, and a final cation exchange step used to remove interfering elements, particularly trace thorium and radium, before electrodeposition. Thorium, if not previously extracted, may be removed from the anion exchange column with 9 M HCl, after first washing with 8 M  $\text{HNO}_3$ .

An alternative method of  $^{210}\text{Pb}$  determination utilises two successive determinations on the sample of the daughter  $^{210}\text{Po}$  separated by a delay (usually of at least 6 months).  $^{210}\text{Pb}$  is then calculated from the two determinations using ingrowth/decay equations for  $^{210}\text{Po}$  (see section on program POLON in Appendix 2). However, this method is only recommended where the activity concentration of  $^{226}\text{Ra}$  is known to be less than that of  $^{210}\text{Pb}$ .

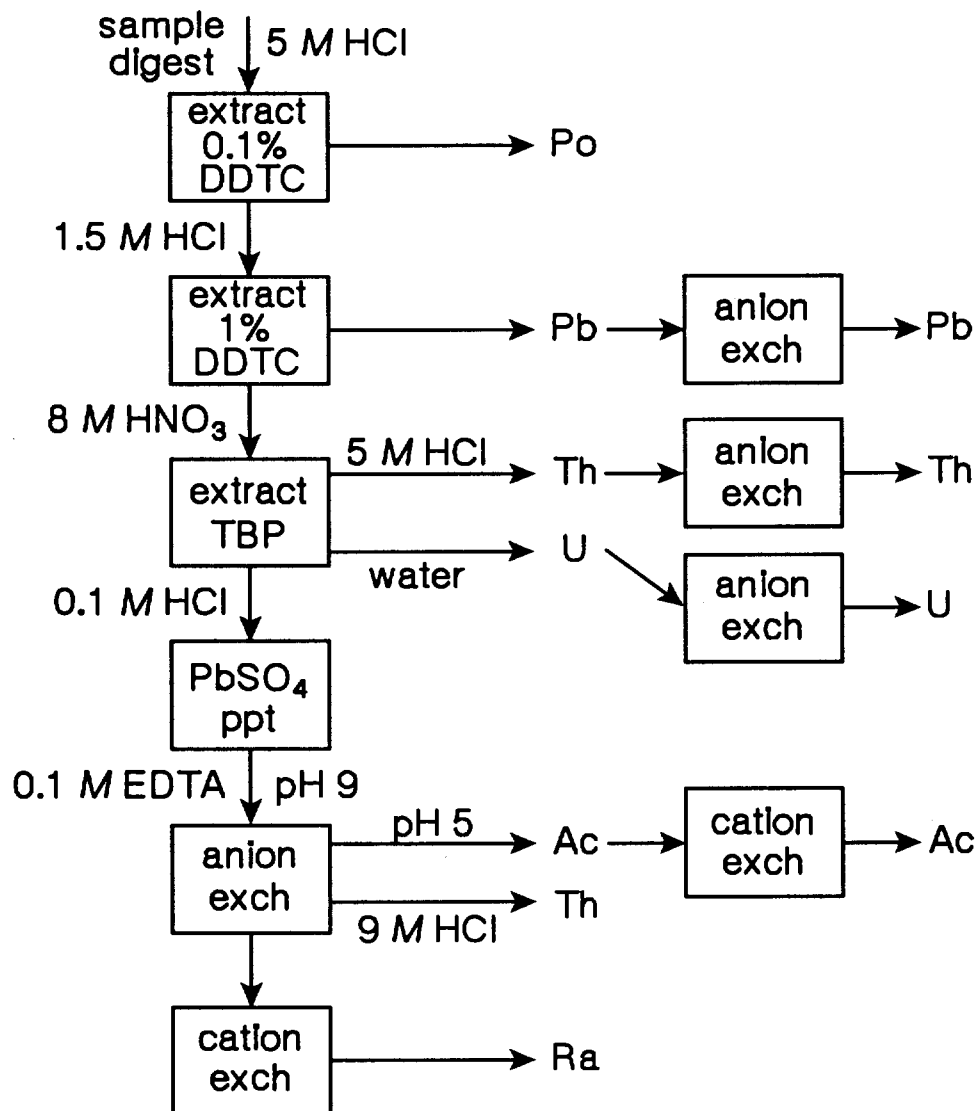


Figure 8. Chemical separation scheme

**Table 1. Properties of elements of interest.**

Element	Electronic Configuration	Group	Common Oxidation State	Ionic Radius (Å)
U	[Rn]5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>	actinides	U (IV) U (VI)	0.93
Th	[Rn]6d <sup>2</sup> 7s <sup>2</sup>	actinides	Th (IV)	0.99
Ac	[Rn]6d <sup>1</sup> 7s <sup>2</sup>	actinides	Ac (III)	1.077
Ra	[Rn]7s <sup>2</sup>	II	Ra (II)	1.57
Pb	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>	IV	Pb (II)	1.21
Bi	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>3</sup>	V	Bi (III)	1.08
Po	[Xe]4f(14)5d(10)6s(2)6p(4)	VI	Po (IV)	

Source: Cotton & Wilkinson (1980).

### 5.1 Polonium

Oxidation states which would be expected from polonium's electronic configuration include -2, +2, +4 and +6, and there is evidence for the formation of all of these states; however, +4 is considered to be the most stable state in solution (Figgins 1961).

The chemistry of the group VI elements (oxygen, sulphur, selenium, tellurium and polonium) varies in a more-or-less regular manner down the series. Due to increased atomic radius, electronegativities decrease down the group. Hence, while O, S and Se are non-metals and exhibit covalent bonding, tellurium shows some metallic character and cationic properties, and polonium should be regarded as a metallic element. While the maximum co-ordination number of oxygen is 4, the S to Po elements have *d* orbitals available for use in bonding, and hexacoordinate compounds are most common for Te and Po.

Halide complexes of the form  $\text{PoX}_5^-$  or  $\text{PoX}_5(\text{H}_2\text{O})^-$  are formed in dilute halogen acid solution, while  $\text{PoX}_6^{2-}$  is formed in more concentrated acid solutions ( $\text{X}=\text{Cl}, \text{Br}$  or  $\text{I}$ ) (Bagnall 1983). In the absence of more strongly complexing organic agents, halide complexes can be extracted into some organic solvents.

Polonium can be extracted into tri-butyl phosphate from strong (c. 7 to 9 *M*) HCl solutions (Figgins 1961). The complex involved is probably  $\text{PoCl}_4 \cdot 2\text{TBP}$  (Bagnall 1957). Polonium is not extracted into TBP from  $\text{HNO}_3$  solution. Other organic agents forming polonium complexes include EDTA and DDTC.

Diethylammonium diethyldithiocarbamate (DDTC) can be used to extract polonium into chloroform from HCl solution over a wide range of acid strengths. This is particularly useful for the separation of  $^{210}\text{Po}$  from  $^{210}\text{Bi}$  and  $^{210}\text{Pb}$ , as polonium will extract from HCl solutions of higher acid strength than either bismuth or lead (Smithson *et al.* 1979). The extraction also separates polonium from radium, thorium, uranium, actinium and iron. Extraction times should be kept short, as DDTC is unstable in acid solution (Cheng *et al.* 1982).

1. Take the sample digest to dryness by evaporation at low heat.  
Dissolve in 5 mL 5 M HCl and warm on a hot plate.  
Add ~50 mg ascorbic acid to reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , indicated by the disappearance of the characteristic yellow  $\text{Fe}^{3+}$  colour.  
Pour into a separating funnel and wash in with 3 x 5 mL 5 M HCl to give a total of 20 mL.
2. Extract Po with 10 mL 0.1% DDTC in chloroform. (Shake for 30 seconds.)  
Extract with 2 more 5 mL aliquots of 0.1% DDTC in  $\text{CHCl}_3$ . If the organic phase is coloured, extract with further aliquots until it is colourless.  
Combine the DDTC/ $\text{CHCl}_3$  portions.  
Evaporate to dryness over water bath or hot plate at low heat.  
Date of extraction is date of separation of Po from Bi and Pb.  
Pb, Ra, Th, U and Ac may be determined on the remaining aqueous phase.
3. To the dried DDTC/ $\text{CHCl}_3$  extract, carefully add 5 mL concentrated  $\text{HNO}_3$ .  
Heat (covered) for ~15 minutes on a hot plate.  
Remove the cover, take to incipient dryness, and autodeposit the polonium onto a silver disc as described in Section 6.1.

If  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  are to be determined on the same sample digest, extract the polonium first from 15 mL of 5 M HCl into 0.1% DDTC, then dilute the aqueous phase with 35 mL water to make it 1.5 M HCl and extract the lead using 1% DDTC (see Section 5.2).

## 5.2 Lead

The dominant oxidation state of lead in aqueous solution is +2.

Most lead salts are sparingly soluble or insoluble in water, and lead separations usually involve one or more precipitation steps, the most common being those of lead sulphate, carbonate, chromate, dichromate and sulphide. Lead nitrate may also be precipitated from fuming nitric acid solutions. In HCl solution, complexes of the form  $\text{PbCl}_n^{(n-2)-}$  are formed, with  $n$  dependent on HCl concentration. Complexes are also formed with a number of organic reagents, including EDTA, DDTC, dithizone, cupferron, oxine, TTA and acetylacetone. For a comprehensive discussion of the radiochemistry of lead, see Gibson (1961).

Two methods are presented here for the determination of  $^{210}\text{Pb}$ . The first involves separation of lead from other beta-emitters, and beta-counting of a lead chromate precipitate for the  $^{210}\text{Bi}$  daughter. The second method utilises determination of the grand-daughter  $^{210}\text{Po}$  after an ingrowth period.

### 5.2.1 Beta-counting method for $^{210}\text{Pb}$

The following method is based upon Waters and Powell (1985) and Lowson and Short (1986). Stable lead is used as both tracer and carrier for  $^{210}\text{Pb}$ . Lead is separated from other beta-emitters (except bismuth) by extraction with DDTC into chloroform. Where a final clean-up step is deemed advisable, an anion exchange step is used; lead is adsorbed onto Dowex 1-X8 from 1.5 M HCl, and may be eluted with either 9 M HCl or with water. Finally, lead chromate is precipitated,  $^{210}\text{Bi}$  allowed to grow in (if necessary) and the  $^{210}\text{Bi}$  activity in the precipitate determined by beta counting. After counting, the precipitate is redissolved and recovery determined using atomic absorption spectrometry.



1. Add the stable lead carrier/tracer solution, equivalent to approximately 3 - 4 mg lead. Dissolve the sample using an appropriate technique, and take to dryness. Take the sample digest up into 5 mL 1.5 M HCl and warm on a hot plate. Add ~50 mg ascorbic acid to reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , indicated by the disappearance of the characteristic yellow  $\text{Fe}^{3+}$  colour. Pour into a separating funnel and wash in with 3 x 5 mL 1.5 M HCl to give a total of 20 mL.
2. Extract Pb and Bi with 10 mL 1% DDTC in chloroform. (Shake for 30 seconds.) Extract with 2 more 5 mL aliquots of 1% DDTC in  $\text{CHCl}_3$ . Combine the DDTC/ $\text{CHCl}_3$  portions. Evaporate to dryness over a water bath or hot plate at low heat. Date of extraction is date of separation of Pb from Ra. Ra, Th, U and Ac may be determined on the remaining aqueous phase.
3. To the dried DDTC/ $\text{CHCl}_3$  extract, carefully add 5 mL concentrated  $\text{HNO}_3$ . Heat (covered) for ~15 minutes on hot plate. Remove the cover and take to incipient dryness.
4. Add approximately 10 mL concentrated  $\text{HNO}_3$  and a few drops concentrated  $\text{HClO}_4$  and take to white fumes. Add approximately 20 mL of a 0.5 M acetic acid/1 M ammonium acetate solution and swirl to dissolve the lead precipitate. Precipitate lead chromate with 2 mL of 20% wt/vol sodium chromate added dropwise while swirling the beaker. Set the solution aside for 30 - 60 minutes and then filter using a 25 mm diameter 0.45  $\mu\text{m}$  membrane filter. Wash the precipitate with a few mL of deionized water. Mount the filter for beta counting, covering with mylar film to prevent contamination of the detector and the detection of  $^{210}\text{Po}$  alpha particles.
5. After beta counting, dissolve the filter and precipitate by heating in concentrated  $\text{HNO}_3$ . Take to incipient dryness and redissolve in 0.5%  $\text{HNO}_3$ . Make to 250 mL in a volumetric flask with 0.5%  $\text{HNO}_3$ . Determine lead concentration by flame atomic absorption spectrometry (FAAS) using the 283.3 nm line.

For the determination of  $^{210}\text{Pb}$  by beta counting, separation of lead from all beta-decay radionuclides must be guaranteed, since counts from interfering isotopes cannot be distinguished from the  $^{210}\text{Bi}$  counts used to measure  $^{210}\text{Pb}$ . For most samples, the DDTC extraction described above is adequate; however, a final clean-up step is advisable in cases where the  $^{226}\text{Ra}$  activity is greatly in excess of the  $^{210}\text{Pb}$  activity (e.g. mussels, process waters).

Take the Pb extract after Step 3. above to dryness, and take up in 5 mL 1.5 M HCl. Fill a column (5 cm height, 0.7 cm i.d.) with Dowex 1-X8 resin, Cl form. Equilibrate the column by washing with 10 mL 1.5 M HCl. Add the sample solution. Wash with 2 x 5 mL 1.5 M HCl to elute radium and other interfering ions. Elute lead with 20 mL 9 M HCl. Take to dryness and continue with Step 4 above.

Bismuth remains on the column. Time of elution is time of separation of  $^{210}\text{Pb}$  from  $^{210}\text{Bi}$ . U(VI) also remains on the column. Most other elements, including radium, actinium, and thorium are eluted with the 1.5 M HCl wash.

### *Beta-counting of lead chromate precipitate*

Since the beta-particles emitted by  $^{210}\text{Pb}$  are of low energy (0.061 MeV, 19%; 0.015 MeV, 81%), they are absorbed by the window of the beta-particle detector. However, a measure of  $^{210}\text{Pb}$  may be obtained using the higher-energy beta particles of its daughter  $^{210}\text{Bi}$  (4.69 MeV, 40%; 4.65 MeV, 60%;  $t_{1/2} = 5$  days).

Care must be taken to exclude recording of counts from alpha-particles of the  $^{210}\text{Bi}$  daughter  $^{210}\text{Po}$  which will slowly grow in on the precipitate ( $^{210}\text{Po}$   $t_{1/2} = 138$  days). The exclusion of these counts should be confirmed by a series of tests utilising a silver disc on which  $^{210}\text{Po}$  has been autodeposited (Section 6.1). Increasing numbers of layers of mylar film are placed over the disc before counting with the beta-counter. The number of layers at which there is no further decrease in count rate is the number of layers used to cover the lead chromate precipitate.

Calibration of the beta-counter is performed using standard filters prepared as detailed above using a standard  $^{210}\text{Pb}$  solution. After counting, the filter is consumed in the determination of lead recovery as detailed in Step 5 above.

### *Standards*

A set of standards for determination of lead by FAAS is prepared in a similar matrix to the samples. Aliquots of a suitable dilution of the spike solution are taken which will yield a set of standards in the range 0 - 20 mg Pb/L when finally diluted to 250 mL. The aliquots are taken to dryness, redissolved using acetic acid/ammonium acetate solution, and lead chromate precipitated and filtered as described above. The precipitate and filter paper are dissolved with nitric acid, taking care to recover any precipitate on the filtration funnel. The solution is taken to incipient dryness, taken up again in 0.5%  $\text{HNO}_3$  and diluted to 250 mL using 0.5%  $\text{HNO}_3$ .

#### **5.2.2 $^{210}\text{Po}$ ingrowth method for $^{210}\text{Pb}$**

$^{210}\text{Pb}$  may be determined via two successive determinations on the sample of its daughter  $^{210}\text{Po}$ , separated by a delay (usually of at least 6 months).  $^{210}\text{Pb}$  is then calculated from the two determinations using ingrowth/decay equations for  $^{210}\text{Po}$  (see section on program POLON in Appendix B). However, this method is only recommended where the activity concentration of  $^{226}\text{Ra}$  is known to be less than that of  $^{210}\text{Pb}$ . Where this is not the case, the contribution of ingrowth from  $^{226}\text{Ra}$  to the  $^{210}\text{Pb}$  determination may be significant. This contribution is usually difficult to quantify since the  $^{222}\text{Rn}$  retention in the sample is seldom known accurately. This problem may be avoided by chemically isolating lead soon after sample collection;  $^{210}\text{Pb}$  may then be determined via a  $^{210}\text{Po}$  determination on this isolate after an ingrowth period.

In the following method, stable lead is used as both tracer and carrier for  $^{210}\text{Pb}$ . Polonium is removed by extraction into 0.1% DDTC in chloroform from 5 M HCl. Lead is then separated from radium by extraction into 1% DDTC in chloroform from 1.5 M HCl. Bismuth and residual polonium are removed on an anion exchange column, and lead recovery determined by atomic absorption spectroscopy. After an ingrowth period (usually of at least 6 months)  $^{210}\text{Po}$  is determined by alpha-particle spectrometry on the separated lead (Section 5.1), and the  $^{210}\text{Pb}$  activity calculated to date of sample collection (see discussion of program LEDPO in Appendix 2).

1. Add the stable lead carrier/tracer solution, equivalent to approximately 3 - 4 mg lead. Dissolve the sample using an appropriate technique, and take to dryness. Take the sample digest up into 5 mL 5 M HCl and warm on a hot plate. Add ~50 mg ascorbic acid to reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , indicated by the disappearance of the characteristic yellow  $\text{Fe}^{3+}$  colour. Pour into a separating funnel and wash in with 2 x 5 mL 5 M HCl to give a total of 15 mL.
2. Extract Po with 10 mL 0.1% DDTC in chloroform. (Shake for 30 seconds). Extract with 2 more 5 mL aliquots of 0.1% DDTC in  $\text{CHCl}_3$ . If the organic phase is coloured, extract with further aliquots until it is colourless.
3. Dilute the aqueous phase with 35 mL water to make it 1.5 M HCl. Extract Pb with 10 mL 1% DDTC in chloroform. (Shake for 30 seconds.). Extract with 2 more 5 mL aliquots of 1% DDTC in  $\text{CHCl}_3$ . Combine the 1% DDTC/ $\text{CHCl}_3$  portions. Evaporate to dryness over a water bath or hot plate at low heat. Date of extraction is date of separation of Pb from Ra and Po. Ra, Th, U and Ac may be determined on the remaining aqueous phase.
4. To the dried DDTC/ $\text{CHCl}_3$  extract, carefully add 5 mL concentrated  $\text{HNO}_3$ . Heat (covered) for ~15 minutes on a hot plate. Remove the cover and take to incipient dryness.
5. Dissolve the residue in 5 mL 9 M HCl. Fill a column (5 cm height, 0.7 cm i.d.) with Dowex 1-X8 resin,  $\text{Cl}^-$  form. Equilibrate the column by washing with 10 mL 9 M HCl. Add the sample solution and collect the eluate. Elute with a further 2 x 10 mL 9 M HCl.
6. Pour the eluate from step 5 into a tared plastic bottle. Add a known activity of  $^{208}\text{Po}$  or  $^{209}\text{Po}$  tracer (in HCl solution). Add distilled water so that the HCl concentration is 5 M (approximately 50 mL total volume). Weigh the solution. Shake the solution to mix. Remove the required amount (~1-2 mL) for determination of lead by atomic absorption spectroscopy. Store the solution for  $^{210}\text{Po}$  analysis after a suitable ingrowth period.

### 5.3 Uranium

Uranium is a highly reactive metallic element, combining with a large number of elements to form an extensive series of compounds. The oxidation states known in aqueous solution are +3, +4, +5 and +6, the most important of these being +4 and +6.

Methods of separation for measurement by alpha spectrometry commonly employ extraction of the uranyl ( $\text{UO}_2^{2+}$ ) ion, complexed by nitrate or chloride, into one of a large number of possible organic solvents. One of the most commonly-used extractants is tri-butyl phosphate (TBP).

The following method is based upon Holm (1984). Uranium is extracted (along with thorium) into concentrated TBP from 8 M  $\text{HNO}_3$ . At this molarity uranium extraction efficiency is at a maximum. Radium and actinium remain in the aqueous phase and may be subsequently determined on this. Most other metals, including polonium, lead, bismuth and iron, also remain in the 8 M  $\text{HNO}_3$  solution.

Extraction efficiency decreases with increased temperature (Gindler 1962); hence, after dissolution of the sample, the solution should be allowed to cool to room temperature before proceeding with extraction. Phosphate, sulphate and fluoride reduce extraction efficiency by complexing uranium (Gindler 1962). For some samples it may be advantageous to include a salting-out agent in the initial 8 M  $\text{NO}_3^-$  phase to mask these anions (e.g. nitrate salts of Fe(III) or aluminium for phosphate; Fe(III) for sulphate; aluminium or calcium for fluoride).

After dilution of the TBP with xylenes, the organic phase is washed a number of times with 5 M HCl to remove thorium. This wash also removes nitrate ions, considerable amounts of which dissolve in the TBP layer and which would, if not removed, interfere with the back-extraction of uranium into water.

After digestion of the sample, dissolve in 20 mL 8 M  $\text{HNO}_3$ .

Shake with 5 mL of TBP for 3 minutes.

After settling, run the 8 M  $\text{HNO}_3$  layer into a beaker. If this fraction is to be used for further analysis, it should be run through a pre-wetted filter paper to remove any traces of TBP.

Wash the TBP portion twice by shaking with 10 mL 8 M  $\text{HNO}_3$  for 1 minute.

Combine the aqueous portions to give the radium/actinium fraction. If radium and/or actinium are to be determined, note the date and time of extraction as the Th/Ra separation time.

Add 20 mL of xylene to the TBP layer.

Wash 4 times with 10 mL 5 M HCl to remove thorium, shaking for 1 minute.

Wash 3 times with 15 mL distilled water to back-extract uranium, shaking for 1 minute. Combine the three extracts in a 50 mL beaker.

This procedure results in a uranium fraction which for many samples is pure enough to electrodeposit. However, in order to ensure complete removal of thorium, which would interfere in the alpha-particle spectrum, and to remove traces of resolution-degrading elements which might be present, a final clean-up step using an anion-exchange resin is recommended. The following method removes thorium and most other elements (an exception being iron; Marhol 1982).

Evaporate the uranium extract solution to dryness, and take up in 5 mL 9 M HCl.

Prepare a column (4 cm height, 0.7 cm i.d.) with Dowex 1-X8 resin, Cl form.

Equilibrate the column by washing with 10 mL 9 M HCl.

Add the sample solution.

Wash with 20 mL 9 M HCl to elute thorium and other interfering ions.

Elute uranium with 40 mL 8 M  $\text{HNO}_3$  in two 20 mL aliquots.

Deposit using the sulphate electrodeposition technique (Section 6.2).

#### 5.4 Thorium

The only oxidation state known for thorium in solution is +4. Being a small, highly charged cation, Th(IV) forms complexes with a number of anions in aqueous solution. It also forms insoluble salts with many anions, including hydroxide, phosphate, fluoride, dichromate and oxalate. Although solubility products may not be exceeded, the tendency of such species to adsorb onto solid phases (such as the walls of glass beakers) is high and can lead to low recovery and cross-contamination problems. The insolubility of many thorium salts also highlights the importance of completely digesting the sample before proceeding with element separation.

Thorium is unusual in that it forms a negatively-charged ion in nitric acid solutions, and is strongly adsorbed onto anion exchange resins with maximum adsorption at approximately 8 M HNO<sub>3</sub> (Marhol 1982). Uranium is also adsorbed, but to a lesser extent.

The following method is based upon Holm (1984). Thorium is extracted (along with uranium) into concentrated TBP from 8 M HNO<sub>3</sub> solution. Radium and actinium remain in the aqueous phase and may be subsequently determined on this. Most other metals, including polonium, lead, bismuth and iron, also remain in the 8 M HNO<sub>3</sub> solution. Hyde (1960, pp.14-20) states that thorium extraction efficiency is improved when most of the nitric acid in the aqueous phase is replaced with a nitrate salt such as sodium, calcium or aluminium nitrate; the reason given was the lower solubilities of these salts in TBP relative to that of HNO<sub>3</sub>. 1 M Al(NO<sub>3</sub>)<sub>3</sub>/5 M HNO<sub>3</sub> has been successfully used in this laboratory as a replacement for the initial 8 M HNO<sub>3</sub> extraction solution. This practice is probably best avoided, however, where the aqueous phase is to be analysed for radium and/or actinium.

After dilution of the TBP with xylenes, thorium is back-extracted by washing four times with 5 M HCl. Uranium remains in the organic phase and may be subsequently back-extracted (Section 5.3). For a final clean-up of the thorium fraction after TBP extraction, an anion exchange technique is employed; this ensures the removal of traces of uranium and other major metal ions.

1. After digestion of the sample, dissolve in 20 mL 8 M HNO<sub>3</sub>.  
Shake with 5 mL of TBP for 3 minutes.  
After settling, run the 8 M HNO<sub>3</sub> layer into a beaker. If this fraction is to be used for further analysis, it should be run through a pre-wetted filter paper to remove any traces of TBP.  
Wash the TBP portion twice by shaking with 10 mL 8 M HNO<sub>3</sub> for 1 minute.  
Combine the aqueous portions to give the radium/actinium fraction. If radium and/or actinium are to be determined, note the date and time of extraction as the Th/Ra separation time.  
Add 20 mL of xylene to the TBP layer.  
Wash 4 times with 10 mL 5 M HCl to back-extract thorium, shaking for 1 minute.  
Combine each extract by running it into a 50 mL beaker.
2. Evaporate the thorium extract to dryness, and take up in 5 mL 8 M HNO<sub>3</sub>.  
Fill a column (4 cm height, 0.7 cm i.d.) with Dowex 1-X8 resin. Convert the column to the NO<sub>3</sub> form by washing with 10 mL 8 M HNO<sub>3</sub>.  
Add the sample solution.  
Wash with a further 40 mL 8 M HNO<sub>3</sub> to elute uranium and other interfering ions.  
Elute thorium with 30 mL 9 M HCl.  
Deposit using the sulphate electrodeposition technique (Section 6.2).

An alternative procedure is described below in which thorium is separated from the sample matrix by precipitation with lead sulphate in the presence of potassium. This allows for the determination of thorium in conjunction with radium and actinium without the need for a solvent extraction step. The lead sulphate precipitate is dissolved using an alkaline EDTA solution and passed through an anion exchange column. Thorium and actinium are adsorbed on the column; radium passes through in the EDTA solution and may be determined on this fraction (Section 5.5). If desired, actinium may now be removed for analysis using an EDTA solution at pH 5 (Section 5.6). The anion exchange column is then washed with 8 M HNO<sub>3</sub> to remove interfering elements, including actinium, polonium and lead. Finally, thorium is eluted with 9 M HCl.

1. Add the required tracer, and dissolve the sample using an appropriate technique. Evaporate to dryness and bring the residue into solution in 100 mL 0.1 M HCl or HNO<sub>3</sub>.
2. Add 1 mL of 98% H<sub>2</sub>SO<sub>4</sub>, 2 g K<sub>2</sub>SO<sub>4</sub> and dissolve.  
Add 1 mL 0.24 M Pb(NO<sub>3</sub>)<sub>2</sub> solution drop-wise whilst stirring.  
Heat, allow the precipitate to settle, and decant the supernatant when cool.  
Wash with 20 mL 0.1 M K<sub>2</sub>SO<sub>4</sub>/0.2 M H<sub>2</sub>SO<sub>4</sub> solution and decant again.
3. Add 5 mL 0.1 M ammoniacal EDTA solution (pH 10), and 2 drops ammonia to the PbSO<sub>4</sub> precipitate, and warm the beaker to aid dissolution. If necessary add further 1 mL portions of EDTA solution until the precipitate has dissolved.  
Pass the solution through an anion exchange column (Bio-Rad AG1-X8, 100-200 mesh, Cl form, 8 cm height, 0.7 cm i.d.), and wash with 13 mL 0.005 M EDTA/0.1 M ammonium acetate at pH 8. Thorium and actinium are retained on the column; radium is eluted at this stage.
4. Elute actinium with 25 mL 0.005 M EDTA/0.1 M ammonium acetate at pH 5 in five 5 mL aliquots. This step is not necessary if an actinium analysis is not required.
5. Wash the column with three 20 mL aliquots 8 M HNO<sub>3</sub> to remove interfering elements.  
Elute thorium with 30 mL 9 M HCl.  
Deposit using the sulphate electrodeposition technique (Section 6.2).

## 5.5 Radium

Within group II, calcium, strontium, barium, and radium form a series of closely related elements. All are highly electropositive metals existing in the +2 oxidation state in solution. Problems inherent in chemically isolating radium from other Group II elements in alpha-particle spectrometry methods often result in erratic chemical yields, a poorly resolved spectrum, and/or the use of lengthy labour-intensive analytical techniques.

The method described here can measure all alpha-emitting radium isotopes ( $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ ,  $^{223}\text{Ra}$ ) and, after a suitable ingrowth period,  $^{228}\text{Ra}$  on a single source (Hancock & Martin 1991). The separation and electrodeposition of radium can be comfortably completed in 1 day (8 hours) on a digested sample, with an operator time of approximately 1 hour per sample for a batch of 4 samples. With use of  $^{226}\text{Ra}$  as a yield tracer,  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ , and  $^{223}\text{Ra}$  are determined from an initial counting immediately after deposition, and from the calculated  $^{226}\text{Ra}$  recovery determined after a suitable ingrowth period for  $^{226}\text{Ac}$  and daughters.  $^{228}\text{Ra}$  is determined after an ingrowth period for  $^{228}\text{Th}$  and  $^{224}\text{Ra}$ . The resolution obtained is typically ~40 keV, and chemical recoveries are typically in the range 75-85%.

Radium is separated from the sample matrix by precipitation with lead sulphate. Thorium and actinium are also precipitated. Uranium remains in solution. The precipitate is then dissolved in an ammoniacal EDTA solution and passed through an anion exchange column. Radium passes through the column and is collected in the eluant. Sulphate, thorium and actinium are adsorbed. The pH of the eluant is adjusted to 4.5, and the solution passed through a cation exchange column. The lead carrier is eluted in an ammonium acetate wash (Khopkar & De 1960), along with any remaining thorium, actinium, polonium, and uranium. The alkaline earths (calcium, strontium, barium) are eluted sequentially in the 1.5 M ammonium acetate and 2.5 M HCl washes. The decontamination factor for thorium, actinium, polonium, uranium and lead is  $>10^4$ , and is  $>200$  for barium.

1. Add the required tracer, and dissolve the sample using an appropriate technique. Evaporate to dryness and bring the residue into solution in 100 mL 0.1 M HCl or  $\text{HNO}_3$ . Filtered water samples in which the radium is considered to be in solution may be simply acidified, evaporated to a volume of 1 litre or less, and step 2 proceeded with. The final acid concentration should not, however, exceed 0.1 M.
2. Add 1 mL of 98%  $\text{H}_2\text{SO}_4$ , 2 g  $\text{K}_2\text{SO}_4$  and dissolve. Add 1 mL 0.24 M  $\text{Pb}(\text{NO}_3)_2$  solution drop-wise whilst stirring. For a sample volume of 1 litre add 10 mL  $\text{H}_2\text{SO}_4$ , 10 g  $\text{K}_2\text{SO}_4$  and 2 mL 0.24 M  $\text{Pb}(\text{NO}_3)_2$ . Heat, allow the precipitate to settle, and decant the supernatant when cool. Wash with 20 mL 0.1 M  $\text{K}_2\text{SO}_4$ /0.2 M  $\text{H}_2\text{SO}_4$  solution and decant again.
3. Add 5 mL 0.1 M ammoniacal EDTA solution (pH 10), and 2 drops ammonia to the  $\text{Pb}(\text{Ra})\text{SO}_4$  precipitate, and warm the beaker to aid dissolution. If necessary add further 1 mL portions of EDTA solution until the precipitate has dissolved. Pass the solution through an anion exchange column (Bio-Rad AG1-X8, 100-200 mesh, Cl form, 8 cm height, 0.7 cm i.d.) to remove sulphate, and wash with 13 mL 0.005 M EDTA/0.1 M ammonium acetate at pH 8. Thorium\* and actinium are also retained on the column. Collect the eluate in a beaker containing 1 mL 0.5 M ammoniacal EDTA and 0.5 mL 5 M ammonium acetate. Adjust the pH to 4.5 with 6 M  $\text{HNO}_3$  using bromocresol green as an indicator. The final volume should be about 20 mL.

\* If  $^{229}\text{Th}(^{225}\text{Ra})$  or  $^{228}\text{Th}(^{224}\text{Ra})$  are used as tracers, record the time of thorium/radium separation.

4. Prepare a cation exchange column (Bio-Rad AG50W-X12, 200-400 mesh, 8 cm height, 0.7 cm i.d.) in the ammonium form, by washing with 15 mL 1.5 M ammonium acetate, followed by 15 mL 0.2 M ammonium acetate solution previously adjusted to pH 4.5 with  $\text{HNO}_3$ .

The flow rate is 0.8-1.0 mL/min., and can be obtained by fitting a Luer tubing adapter, and raising the column to the required height.

Transfer the solution from 3. onto the column and wash with 50 mL 1.5 M ammonium acetate in 0.1 M  $\text{HNO}_3$  to elute lead. Residual thorium and actinium are also eluted.

Add 2.5 M  $\text{HCl}$ (\*\*) in three 18 mL aliquots to wash the ammonium acetate out of the column, and elute barium.

Radium is then eluted with 25 mL 6 M  $\text{HNO}_3$ .

\*\* If  $^{225}\text{Ra}$  is used as a tracer, record the time  $^{225}\text{Ac}$  starts to build in.

5. Evaporate the solution to a low volume, and bring to dryness at low heat. Deposit using the aqueous/alcohol electrodeposition technique (Section 6.3).

If the radium tracer is added as a daughter product in equilibrium with its parent (i.e.  $^{229}\text{Th}/^{225}\text{Ra}$ ,  $^{232}\text{U}/^{228}\text{Th}/^{224}\text{Ra}$ ), then preferential losses of thorium or radium during sample dissolution and/or pre-treatment prior to Step 2 must be avoided. The thorium/radium separation should be quantitative, and the time of separation known.

When using  $^{225}\text{Ra}$  tracer, the time  $^{225}\text{Ac}$  starts to build in from the decay of  $^{225}\text{Ra}$  must also be known. The complete removal of  $^{225}\text{Ac}$  is essential, otherwise the fraction remaining on the cation exchange column will be eluted and electrodeposited along with  $^{225}\text{Ra}$ . This will result in an erroneously high recovery figure, the magnitude of which will depend on how soon after deposition the disc is counted (Johnston & Martin 1988).  $^{225}\text{Ac}$  commences to build in immediately the cation exchange column is converted to the acid form by the  $\text{HCl}$  wash, and is eluted with 8 M  $\text{HNO}_3$  along with radium. Electrodeposition efficiency is >90% for both radium and actinium, nevertheless it should be performed without delay (i.e. on the same day) to minimize the effect of any differences in deposition efficiencies between them.

#### *Ba-Ra Separation*

Barium is chemically very similar to radium, and will accompany radium in the lead sulphate lattice during precipitation. Unless removed prior to electrodeposition, it will cause incomplete radium plating, and a poorly resolved alpha spectrum.

Both barium and radium are strongly adsorbed in a narrow band at the top of the cation exchange column from 0.05 M EDTA solution at pH 4.5, and are separated by elution with 1.5 M ammonium acetate and 2.5 M  $\text{HCl}$ . The distribution coefficient for barium is approximately equal in the latter two solutions. Barium-radium separation with  $\text{HCl}$  as described in Step 4 gives a final radium fraction virtually free from visual residue for samples containing up to 2 mg barium. Figure 9 shows the results obtained for the separation of  $^{133}\text{Ba}$  and  $^{226}\text{Ra}$  in a trial which followed the procedure outlined in Step 4 above. The barium decontamination factor is >200 (>99.5% removal of barium). Approximately 5% of the radium is sacrificed in the 2.5 M  $\text{HCl}$  wash. Since the exchange capacity of the resin may vary slightly between batches, the elution volumes should be checked with a standard  $^{226}\text{Ra}$  solution.

For samples with a low barium concentration, a shorter cation exchange column can be used than that specified in step 4 above. The volume of the wash solutions are then reduced proportionally. For example, with a column of 6 cm height, 0.7 cm i.d., the wash volumes are 35 mL 1.5 M ammonium acetate in 0.1 M  $\text{HNO}_3$ , followed by 42 mL 2.5 M  $\text{HCl}$  in three 14 mL aliquots. Radium is then eluted with 20 mL 6 M  $\text{HNO}_3$ . This procedure reduces considerably the time required for this step.



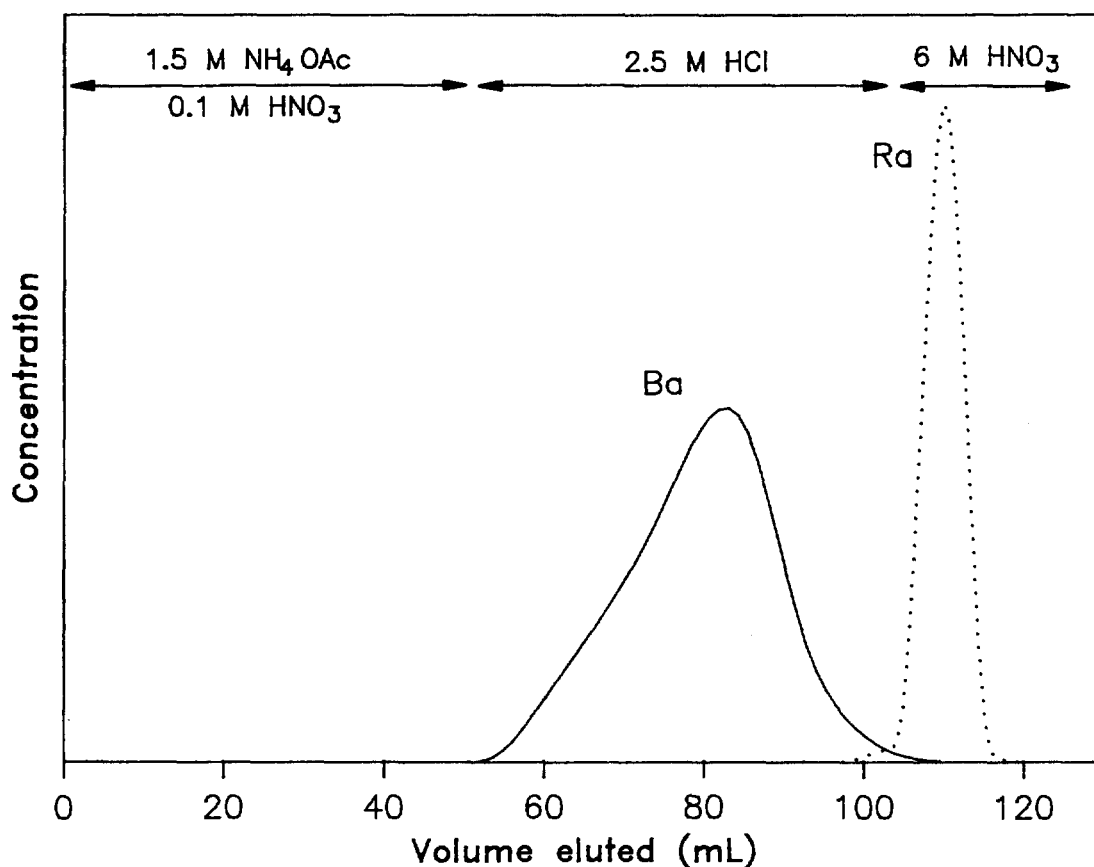


Figure 9. Separation of  $^{133}\text{Ba}$  and  $^{226}\text{Ra}$  using a 50W-X12 cation exchange column

#### *Size of sample*

The quantity of barium present is the major limiting factor in most environmental samples. If the above cation exchange step is carried out properly, a sample containing 2 mg Ba will have less than 10  $\mu\text{g}$  Ba remaining in the final solution for electrodeposition. A resolution of 50 keV FWHM is attainable under these conditions with little or no decrease in the deposition efficiency of radium.

Sediments and soils generally contain less than 1 mg/g barium, and a 0.5 g sample is adequate to give a  $^{226}\text{Ra}$  determination with a counting error of less than 5% at the 1 sigma level (100 ksec count). Samples with a high barium content, e.g. uranium mill tailings, should be limited to contain less than 2 mg barium, or else a second cation exchange step employed with AG50W-X12 resin, using HCl only as the eluant. Thirty-nine column volumes of 2.5 M HCl will elute most of the remaining barium. Radium is eluted as in Step 4.

## 5.6 Actinium

The chemistry of actinium is discussed by Bagnall (1957). It is highly electropositive, with a stable oxidation state of +3. It is chemically similar to trivalent transuranic and rare-earth elements, particularly lanthanum.

Actinium-227 ( $t_{1/2} = 21.8\text{y}$ ) is a member of the  $^{235}\text{U}$  series. This series is present in nature as only 4.6% of the activity of the  $^{238}\text{U}$  series. Hence the activity of  $^{227}\text{Ac}$  in most environmental samples is extremely low.

In the method described here, actinium is separated from the sample matrix by precipitation with lead sulphate in the presence of potassium, dissolved in an alkaline EDTA solution, and adsorbed onto an anion exchange column. Radium passes through the column and actinium is then eluted with 0.005 M EDTA/0.1 M ammonium acetate at pH 5. A cation exchange step is then employed (Bojanowski *et al.* 1987), and interfering elements such as rare-earths, lead, and residual radium, polonium, and uranium are eluted prior to elution of the final actinium fraction. Residual thorium is retained on the column.

1. Add the required tracer, and dissolve the sample using an appropriate technique. Evaporate to dryness and bring the residue into solution in 100 mL 0.1 M HCl or  $\text{HNO}_3$ .
2. Add 1 mL of 98%  $\text{H}_2\text{SO}_4$ , 2 g  $\text{K}_2\text{SO}_4$  and dissolve.  
Add 1 mL 0.24 M  $\text{Pb}(\text{NO}_3)_2$  solution drop-wise whilst stirring.  
Heat, allow the precipitate to settle, and decant the supernatant when cool.  
Wash with 20 mL 0.1 M  $\text{K}_2\text{SO}_4$ /0.2 M  $\text{H}_2\text{SO}_4$  solution and decant again.
3. Add 5 mL 0.1 M ammoniacal EDTA solution (pH 10), and 2 drops ammonia to the  $\text{PbSO}_4$  precipitate, and warm the beaker to aid dissolution. If necessary add further 1 mL portions of EDTA solution until the precipitate has dissolved.  
Pass the solution through an anion exchange column (Bio-Rad AG1-X8, 100-200 mesh, Cl form, 8 cm height, 0.7 cm i.d.), and wash with 13 mL 0.005 M EDTA/0.1 M ammonium acetate at pH 8. Thorium and actinium are retained on the column; radium is eluted at this stage.\*  
Elute actinium with 25 mL 0.005 M EDTA/0.1 M ammonium acetate at pH 5 in five 5 mL aliquots.  
Collect the eluate and evaporate to dryness.  
Add 5 mL concentrated  $\text{HNO}_3$ .  
Heat (covered) for ~15 minutes on a hot plate.  
Remove the cover and take to dryness.  
Dissolve the residue in a minimum volume (3-5 mL) of 3 M  $\text{HNO}_3$ .  
\* Note the time ( $t_0$ ) of separation of radium and actinium.
4. Prepare a cation exchange column (Bio-Rad AG50W-X8, 200-400 mesh, H form, 8 cm height, 0.7 cm i.d.), and wash with 15 mL 3 M  $\text{HNO}_3$ .  
Pour the solution containing the actinium fraction onto the column, and wash with further 2 mL aliquots of 3 M  $\text{HNO}_3$  until a total of 10 mL has been added.  
Wash the column with a further 25 mL 3 M  $\text{HNO}_3$  to elute lead and residual radium and polonium.  
Add a further 35 mL 3 M  $\text{HNO}_3$  and collect the eluate.
5. Evaporate the solution to a low volume, and bring to dryness at low heat.  
Deposit using the aqueous/alcohol electrodeposition technique (Section 6.3).

If the tracer is added as a  $^{229}\text{Th}/^{225}\text{Ra}/^{225}\text{Ac}$  solution, Steps 2 and 3 above should be performed as soon as possible after each other (i.e. within a few hours). This will minimize the effect of any differences in the efficiency with which thorium, radium and actinium are carried in the lead sulphate lattice.

## 6. DEPOSITION METHODS

### 6.1 Auto-deposition of polonium

In 1905 Marckwald found that polonium deposited readily on silver from dilute  $\text{HNO}_3$  or  $\text{HCl}$  solution (Figgins 1961). Since that time numerous procedures have been published for auto-deposition of polonium onto silver, nickel, copper and other metals.

Many polonium methods rely solely upon polonium autodeposition on silver or nickel discs to give separation from radionuclides and resolution-degrading elements (e.g. Flynn 1968). However, if some  $^{210}\text{Bi}$  and/or  $^{210}\text{Pb}$  deposit along with the polonium and there is a delay between deposition and counting, an incorrect result for  $^{210}\text{Po}$  will be obtained. Ehinger *et al.* (1986) studied auto-deposition of a  $^{210}\text{Pb}$ - $^{210}\text{Bi}$ - $^{210}\text{Po}$  solution onto various metals. Their results may be summarised as follows:

Nickel:	$^{210}\text{Po}$ and $^{210}\text{Bi}$ deposited. $^{210}\text{Pb}$ remained in solution.
Copper:	$^{210}\text{Po}$ deposited. $^{210}\text{Bi}$ deposited, but not quantitatively. Some $^{210}\text{Pb}$ deposited, but most remained in solution.
Silver:	$^{210}\text{Po}$ deposited. There was evidence of some deposition of $^{210}\text{Pb}$ and $^{210}\text{Bi}$ .

Flynn (1968) found that  $^{212}\text{Bi}$  deposited onto silver, though not its parent  $^{212}\text{Pb}$ . He recommended addition of 10 mg of bismuth carrier to prevent  $^{210}\text{Bi}$  deposition. He also used hydroxylamine hydrochloride to reduce  $\text{Fe}^{3+}$  and  $\text{Cr}^{6+}$ , and sodium citrate to complex tellurium. Some methods (e.g. Smith & Hamilton 1984) use ascorbic acid in preference to hydroxylamine hydrochloride.

If the DDTC extraction procedure described in Section 5.1 is carried out before deposition, separation of  $^{210}\text{Po}$  from both  $^{210}\text{Pb}$  and  $^{210}\text{Bi}$  is assured. This extraction also removes polonium from most other interfering elements. The following method may then be used to reliably deposit the separated polonium:

- Evaporate the digest solution to incipient dryness.
- Add 2 mL of 5 M  $\text{HCl}$ . Warm on a hot plate.
- Add ascorbic acid to the disappearance of the yellow  $\text{Fe(III)}$  colour (generally 100-200 mg).
- Transfer to a deposition vial containing a silver disc.
- Wash the sample in with 10 mL of water.
- Place the vial in a water bath at 70 - 80°C for 2 hours. Mix using an air bubbler or mechanical stirrer.
- Remove the disc, wash with propanol and dry.
- Count on an alpha counter to check that a reasonable recovery has been attained.

The silver disc is polished before use by rubbing with a small quantity of an aqueous slurry of high-purity aluminium oxide (elementary particle size about 0.3  $\mu\text{m}$ ), then rinsing with water followed by alcohol. The deposition cell consists of a plastic scintillation vial with the bottom cut off and the disc placed inside the lid with a stainless steel disc placed underneath for support. Leakage is checked for by filling the vial with demineralised water and standing it on some absorbant paper for half an hour or so. Advantages of this system are that the vials are cheap and readily available, they may be disposed of after use, minimising cross-contamination problems, and a good seal can be obtained between vial lip and disc which requires no rubber O-ring.

To avoid contamination of the surface-barrier detector, polonium discs should not be counted until at least two days have elapsed after auto-deposition. The fraction of polonium atoms volatilized in the vacuum of the counting chamber is reduced by a period of exposure to air before counting, possibly due to the formation of a surface oxide film on the silver (Bagnall 1957, p. 16; 1966, p. 17).

## 6.2 Sulphate electrolyte

The following electrodeposition technique was published by Hallstadius (1984). He states that this method deposits U, Th, Po, Pb, Cm, Am, Pu, and Np onto electropolished stainless steel discs, with a yield of 90% or greater. Radium deposition is less than 1%. The cell is a disposable polyethylene scintillation vial as described by Talvitie (1972). The distance between cathode and anode is 8 mm.

Evaporate the solution to a few mL in a small (e.g. 50 mL) beaker.

Add 1 mL 0.3 M NaSO<sub>4</sub>.

Evaporate to total dryness.

Add 0.3 mL concentrated H<sub>2</sub>SO<sub>4</sub>.

Warm and swirl the beaker to dissolve the residue. (Do not heat more than necessary; no significant amount of H<sub>2</sub>SO<sub>4</sub> should evaporate in the process.)

Add 4 mL distilled water and 2 drops 0.2% thymol blue.

Add drops of concentrated NH<sub>3</sub> to a yellow-yellow/orange colour.

Pour the solution into the electrodeposition cell and wash in with approximately 5 mL 1% H<sub>2</sub>SO<sub>4</sub>.

Adjust the pH to 2.1-2.4 with concentrated NH<sub>3</sub> using Merck pH paper 9540.

(If the end-point is over-stepped, adjust with 20% H<sub>2</sub>SO<sub>4</sub>.)

Deposit at 1.2 A for 1 hour.

Add 1 mL of concentrated NH<sub>3</sub> about 1 minute before switching off the current.

Wash the disc with 1% NH<sub>3</sub> solution, followed by acetone, and dry by heating it slightly.

Tome and Sanchez (1991) studied this deposition technique in detail for uranium. They found that improved peak resolution with a minimal loss of yield could be obtained by a reduction in the deposition time (Table 2). Consequently, a deposition time for uranium of 40 minutes is recommended.

**Table 2.** Effect of deposition time on energy resolution and yield for uranium deposition by the Hallstadius method. Taken from Table 1 of Tome and Sanchez (1991). Current was 2 A with a 3.8 cm<sup>2</sup> disc area.

Time (min)	Yield* (%)	FWHM (keV)
10	70	16.7
20	91	18.2
30	96	19.4
40	99	19.7
50	97	20.4
60	98	24.9

\* Uncertainty is 3% (1 $\sigma$ ).

### 6.3 Aqueous/alcohol electrolyte

Deposition of radium from various aqueous/alcohol electrolytes has been described by Koide and Bruland (1975), Smith and Mercer (1970), Harada and Tsunogai (1985) and Bojanowski *et al.* (1983), and for actinium by Bojanowski *et al.* (1987). The following method (H. Pettersson, personal communication) is used at the ARRRI for the electrodeposition of both radium and actinium. Ethanol may be successfully used as an alternative to propanol. The cell is a disposable polyethylene scintillation vial as described by Talvitie (1972). The distance between cathode and anode is 5 mm.

Dissolve the residue in 1.0 mL 0.1 M HNO<sub>3</sub> and transfer to a deposition cell with 9 mL propanol.

Electrodeposit onto a stainless steel disc at 120 mA for 30 minutes.

Add 2 drops of ammonia 1 minute before stopping.

Remove the disc and allow to air-dry.

Store the disc in a container containing a dessicating agent (e.g. silica gel).

The surface of the source should not be touched.

### 6.4 Ammonium acetate/nitric acid electrolyte

A procedure for the electrodeposition of radium from an aqueous medium has been developed by Roman (1984). This technique produces a high resolution source, and has the added advantage that all radon isotopes and daughters are retained in a thin film on the disc, eventually growing into secular equilibrium with the parent radium isotope. This enables a direct determination of <sup>223</sup>Ra and <sup>224</sup>Ra by measurement of their daughter products.

As reported earlier (Martin & Hancock 1987), the deposition efficiency of this technique is adversely affected by even a few micrograms of impurities, and it is generally unsuitable for environmental samples. It is, however, useful for the calibration of relatively pure standard solutions. The method is as follows:

Transfer the sample into an electrodeposition cell with 10 mL 0.35 M ammonium acetate/0.1 M HNO<sub>3</sub> solution.

Electrodeposit onto a stainless steel disc at 600 mA for 3 hours. Add small volumes of water periodically to compensate for evaporative losses.

Remove the disc and wash with propanol. Dry by warming on a hot plate.

### 6.5 Deposition by adsorption of hydroxides

Wyllie & Lowenthal (1984) described a method for the deposition of isotopes of Am, Cm and Co onto mylar or platinum substrates using adsorption of the insoluble hydroxides. They found that this method produced extremely thin deposits with internal energy losses of 2 keV or less.

This technique has been adapted to the deposition of thorium onto stainless steel discs. The method is as follows:

Evaporate the solution to a few mL and transfer to a small (5 mL or 10 mL) beaker. Remove any  $\text{HNO}_3$  by repeated evaporation to near dryness and addition of HCl.

Evaporate to incipient dryness, and add 0.3 mL 0.1 M HCl.

Warm on the hot plate, and pour onto the stainless steel disc in an auto-deposition vial (Section 6.1).

Wash in with a further 0.3 mL 0.1 M HCl. There should now be enough solution in the vial to just cover the disc.

Add 0.5 mL 1 M KOH, and agitate the vial to mix.

To prevent evaporation of the solution, place the vial inside a beaker containing a few mL of 1 M KOH and cover (see Fig. 10).

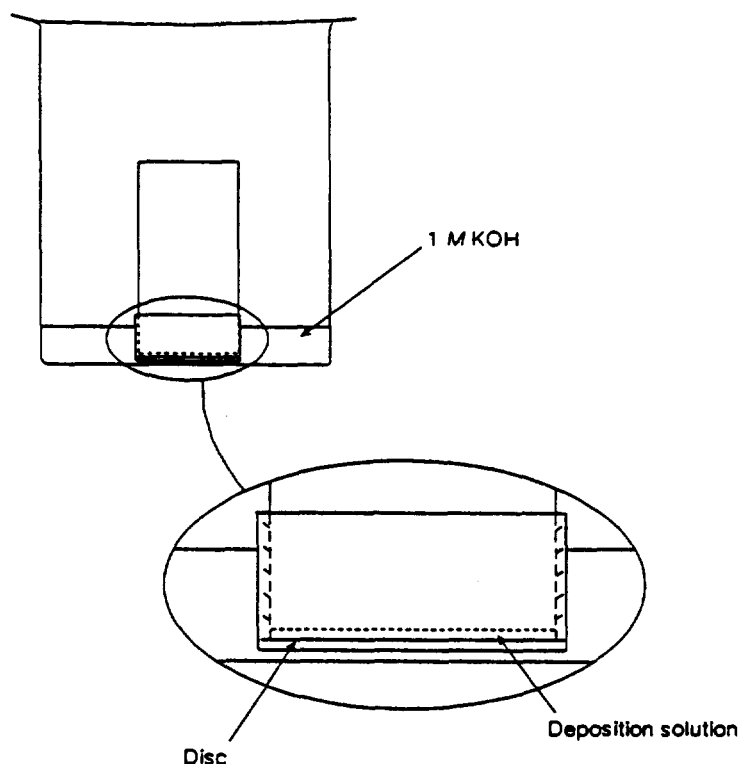
Leave for approximately 8 hours at room temperature.

Pour off the solution, and wash the disc with distilled water followed by propanol.

Dry by warming on the edge of a hot plate.

Since the deposition is carried out using small volumes, care must be taken with transferring of solutions and washing of the beaker if good recoveries are to be obtained.

This method is suitable for the production of thin test sources. Its application to samples is possible, but recoveries are generally too low (<20%).



**Figure 10. Arrangement for deposition by adsorption of hydroxides**

## 7. DETECTION SYSTEM

Most systems for alpha-particle spectrometry utilise silicon surface-barrier detectors, due to their high resolution performance, compact size and ready availability from commercial suppliers, although ionisation chamber detectors of comparable energy resolution have also been developed, particularly for large-source applications (e.g. Murray and Marten 1985).

A typical spectrometry system based upon a surface barrier detector is shown in Figure 11. Detector and source are housed in a vacuum chamber. This allows both the regulation of the operating gas pressure, and the exclusion of visible light which would produce a high noise level.

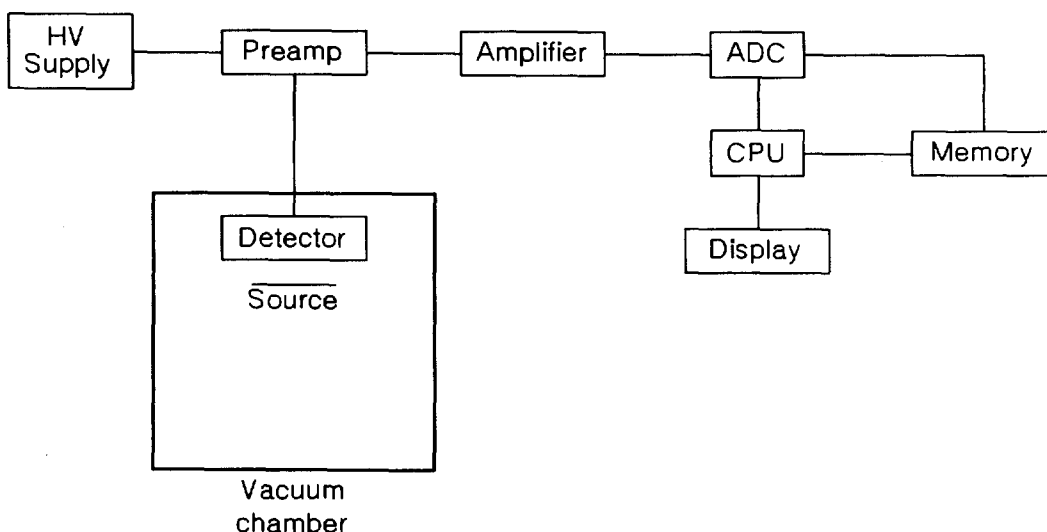


Figure 11. Typical alpha-particle spectrometry assembly

### 7.1 Source/detector counting geometry

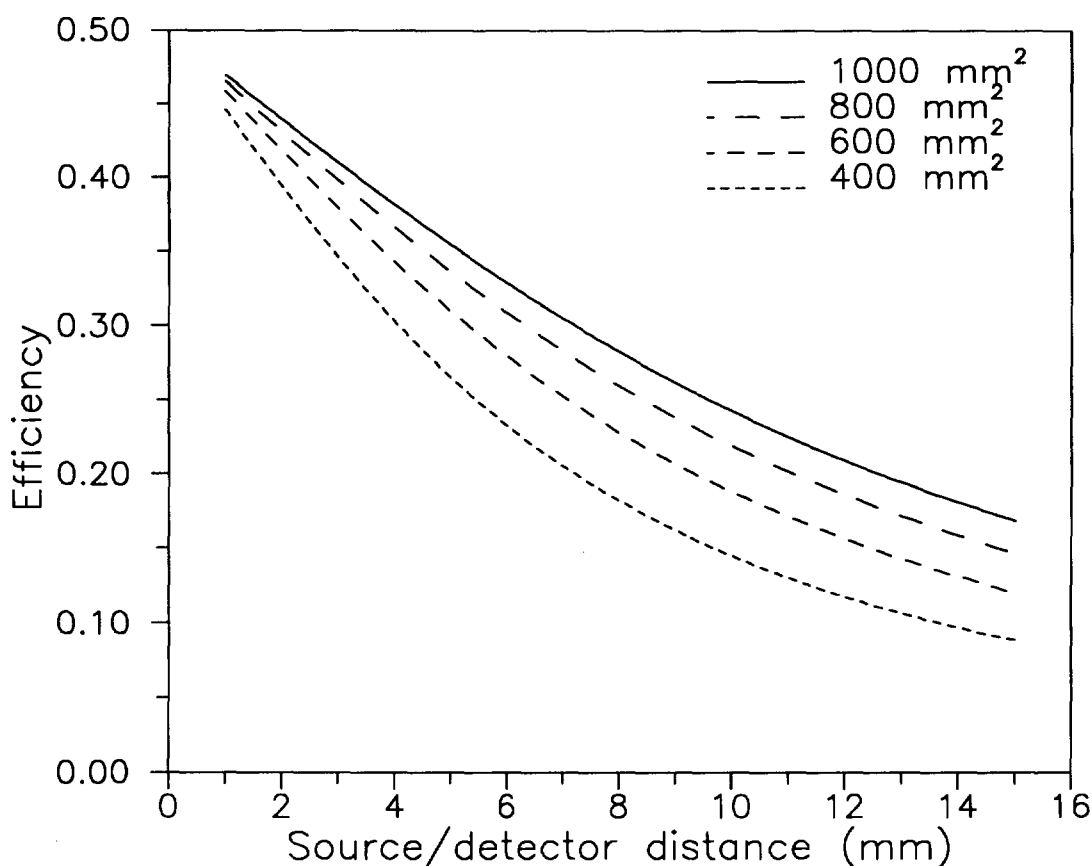
For most environmental samples, measured activities are low, and counting efficiency is a major consideration. For a disc source of radius  $a$  counted at a distance  $h$  from a detector of radius  $r$ , the counting efficiency is given by (Hendee 1984):

$$E = 0.5 \left( 1 - \frac{h}{\sqrt{h^2 + r^2}} \right) - \frac{3}{16} \left( \frac{ar}{h^2} \right)^2 \left( \frac{h}{\sqrt{h^2 + r^2}} \right)^5$$

The efficiency may be increased by increasing detector area (Section 7.2), by decreasing source/detector distance (Section 7.3) and/or by decreasing source area.

### 7.2 Detector area

Figure 12 shows counting efficiency vs. source/detector distance for a number of commonly-available detector sizes, for the source diameter usually used at the ARRRI (17.5 mm). Increasing detector area will increase counting efficiency at any particular source/detector distance. However, increasing area also adversely affects resolution due to an increase in detector capacitance. Detectors in use at the ARRRI are mostly around 600 mm<sup>2</sup> area, which gives an efficiency of approximately 25% (source diameter 17.5 mm, source/detector distance approximately 7 mm).



**Figure 12. Counting efficiency vs source/detector distance for 4 common detector sizes**  
Source diameter is 17.5 mm

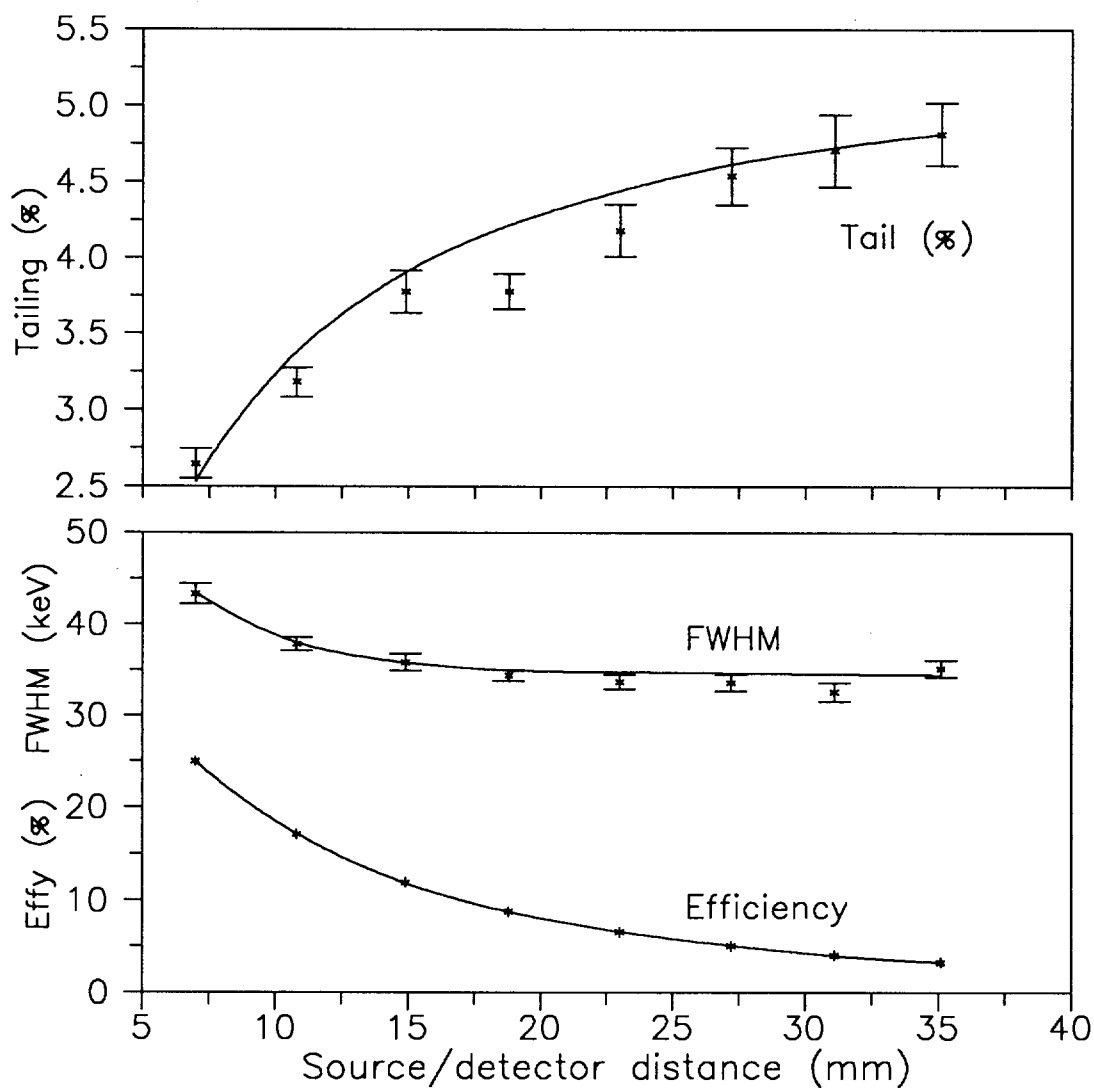
### 7.3 Source/detector distance

Increasing source/detector distance will reduce the number of alpha particles detected which have left the source at low escape angles. This will reduce energy straggling caused by loss of energy in the dead layer of the detector, and hence improve resolution as measured by full-width-at-half-maximum (FWHM) of a singlet peak.

The low activities present in most environmental samples require the use of a high counting efficiency, and source/detector distances used at the ARRRI are generally around 5-8 mm. This results in peak resolutions poorer than those quoted in detector specifications. However, this is not necessarily a major disadvantage, as peak FWHM is of less importance than peak tailing.

Figure 13 shows the results of a trial in which a <sup>230</sup>Th source, prepared by adsorption of the hydroxide (Section 6.5), was counted at varying distances from a detector (active area 600 mm<sup>2</sup>). Tailing was measured as the number of counts recorded in the region 4.12-4.42 MeV expressed as a percentage of the number of counts recorded in the <sup>230</sup>Th area (4.43-4.73 MeV). Although increasing source/detector distance resulted in improved peak FWHM, peak tailing actually increased. This behaviour arises when tailing is dominated by counts recorded at the detector edge. As source/detector distance increases, the proportion of counts produced near the edge of the detector also increases. The solid line in the diagram (Fig. 13(a)) shows the calculated variation in tailing, assuming that tailing is entirely due to counts produced in the outside 1 mm of the detector (calculated relative to the tailing observed at 35.1 mm distance).

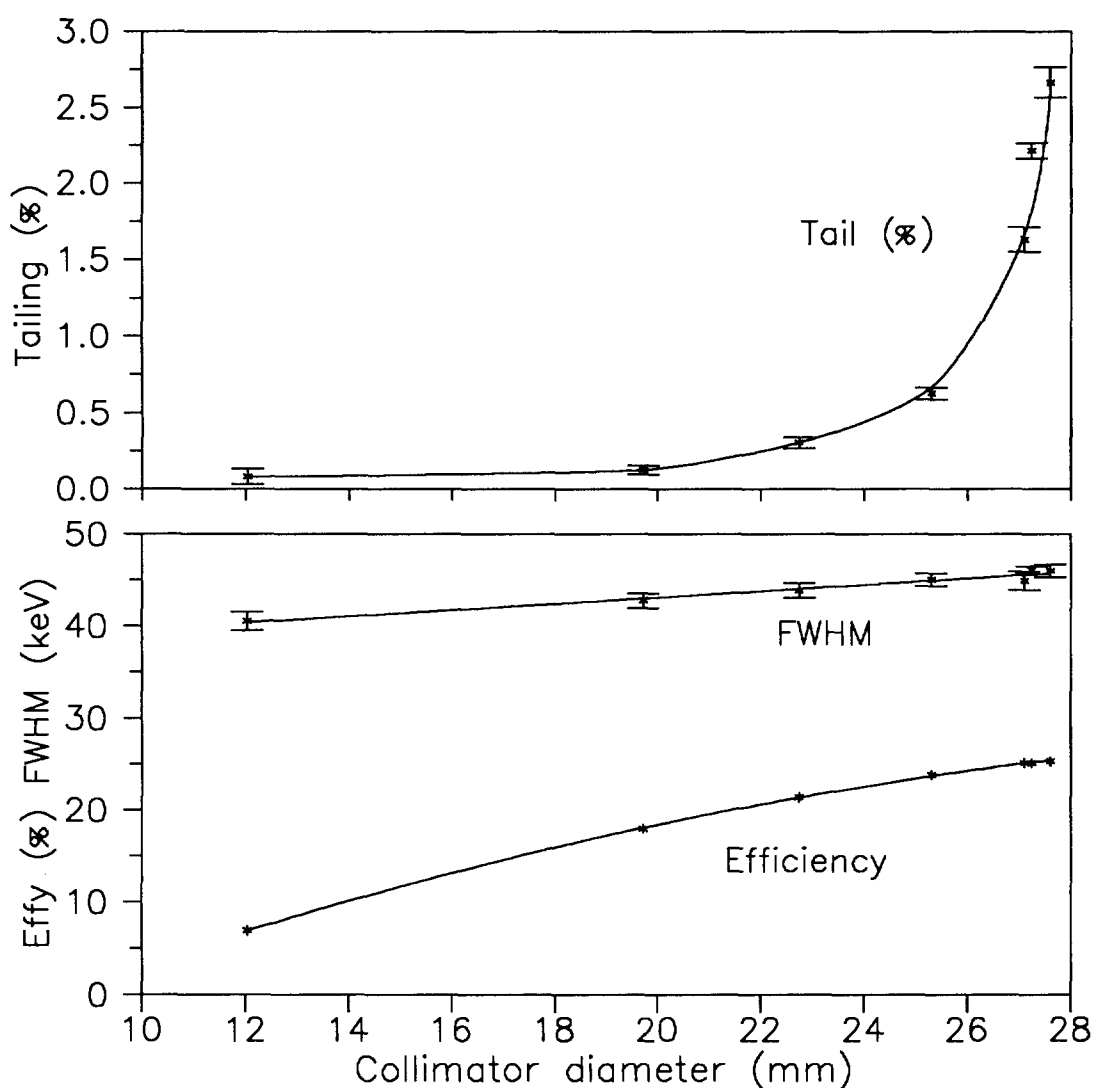




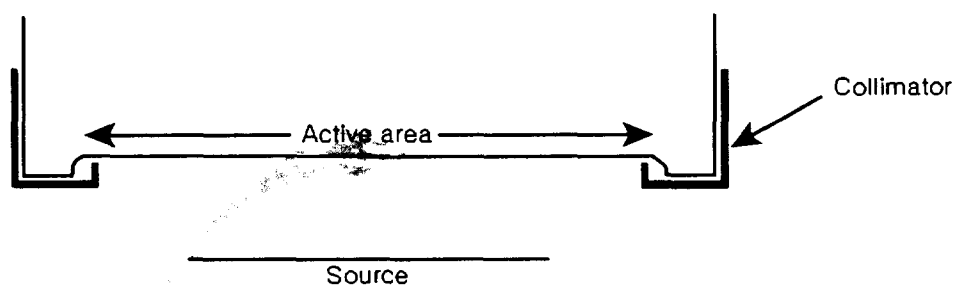
**Figure 13. Effect of source/detector distance, measured with 600 mm<sup>2</sup> detector**  
 Source: <sup>230</sup>Th prepared by hydroxide precipitation (Section 6.5)  
 (a) Peak tailing  
 (b) Full-width-at-half-maximum (FWHM) and counting efficiency

#### 7.4 Detector collimation

Collimation of the detector may be used to decrease peak tailing by reducing edge effects. Figure 14 shows the results of a collimation trial with the same detector and source used for the source/detector distance investigations above. Subsequent use of a collimator of 26 mm diameter resulted in substantial reduction in tailing with a minimal loss of efficiency. Figure 15 shows a typical arrangement using a circular plastic collimator slipped over the detector body.



**Figure 14. Effect of detector collimation, measured with a 600 mm<sup>2</sup> detector**  
 Source: <sup>230</sup>Th prepared by hydroxide precipitation (Section 6.5)  
 (a) Peak tailing  
 (b) Full-width-at-half-maximum (FWHM) and counting efficiency



**Figure 15. Arrangement for collimation of a detector**

### 7.5 Recoil protection

Sill and Olson (1970) described a technique by which recoil contamination of solid-state alpha detectors can be minimised. By adjusting the chamber pressure to allow at least 12  $\mu\text{g}/\text{cm}^2$  of air absorber between the source and detector, the recoiling atoms from the source will be prevented from hitting the detector surface. The application of a small negative potential (-5.6V) to the source will then attract these atoms back to the source. The chamber pressure  $P$  (torr) required is given by

$$P = 0.63 * a / h$$

at 20°C, where  $a$  is the amount of air absorber ( $\mu\text{g}/\text{cm}^2$ ) and  $h$  is the source-detector distance (cm). Thus for a source-detector distance of 0.5 cm, a pressure of 15 torr is required to give 12  $\mu\text{g}/\text{cm}^2$  air absorber.

Application of this technique does not protect the detector from contamination by polonium, since  $^{208}\text{Po}$ ,  $^{209}\text{Po}$  and  $^{210}\text{Po}$  do not move to the detector by an alpha-recoil mechanism.

## 8. SPECTRAL ANALYSIS

Techniques for mathematical stripping of alpha particle spectra have been described which are adaptable to computer analysis (e.g. Westmeier 1984). Such techniques are, however, of limited use for the low-activity spectra obtained from most environmental samples.

Energy intervals are best determined by preparing and counting standard discs with an appropriate mix of the nuclides of interest. Alpha-particle spectrometry detectors are generally stable enough to necessitate the counting of such discs only every month or so.

### 8.1 Polonium

Figure 16 shows a polonium spectrum with  $^{209}\text{Po}$  used as the tracer. The spectrum is a simple one, consisting essentially of two singlet peaks. The spectrum obtained using  $^{208}\text{Po}$  as tracer is similar, but with a smaller separation between the tracer and  $^{210}\text{Po}$  peaks.

As the two peaks will be the same shape, the simplest method of spectral analysis is to take windows of equal energy intervals around each peak and record the number of counts in each window.  $^{209}\text{Po}$  has a minor (0.57%) peak at 4.62 MeV; the analysis window should be chosen to either exclude or include this peak, and the  $^{209}\text{Po}$  tracer solution calibrated accordingly.

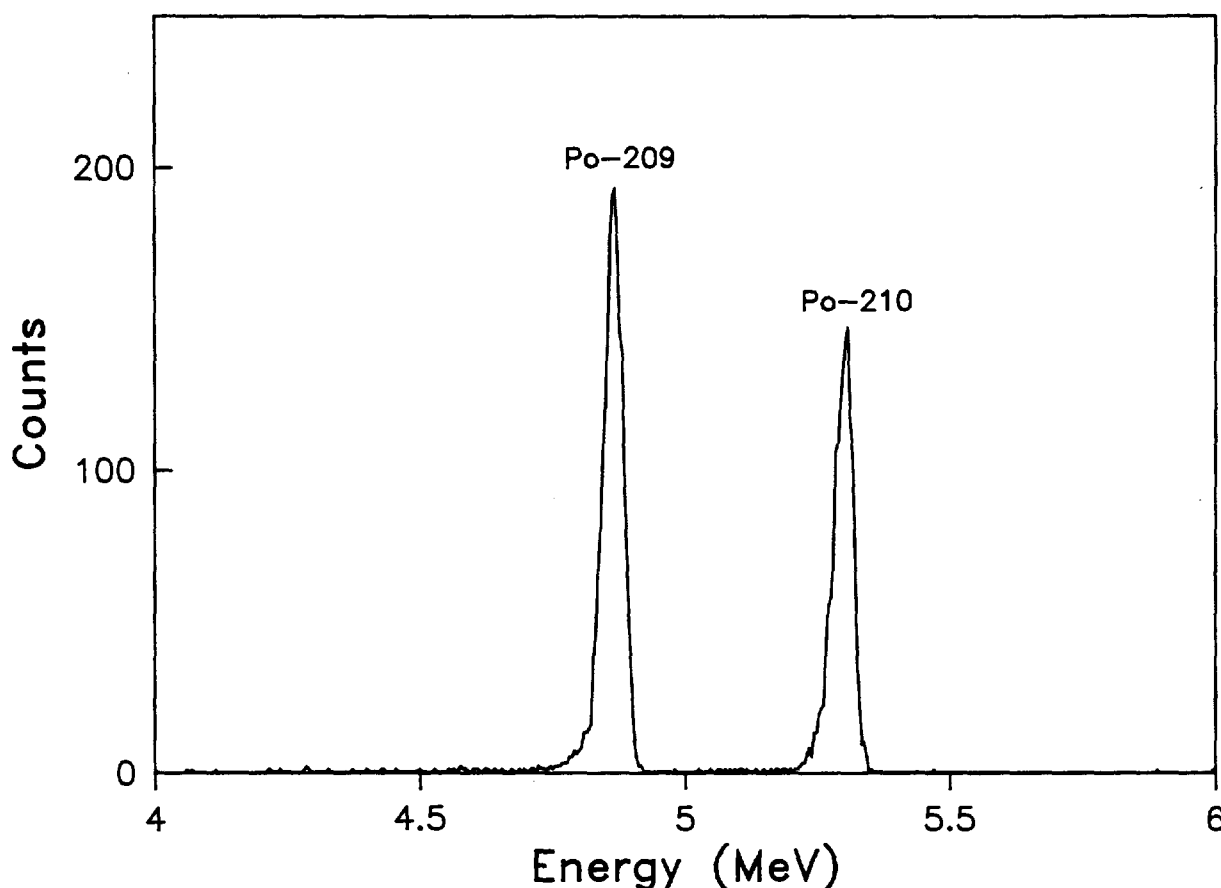
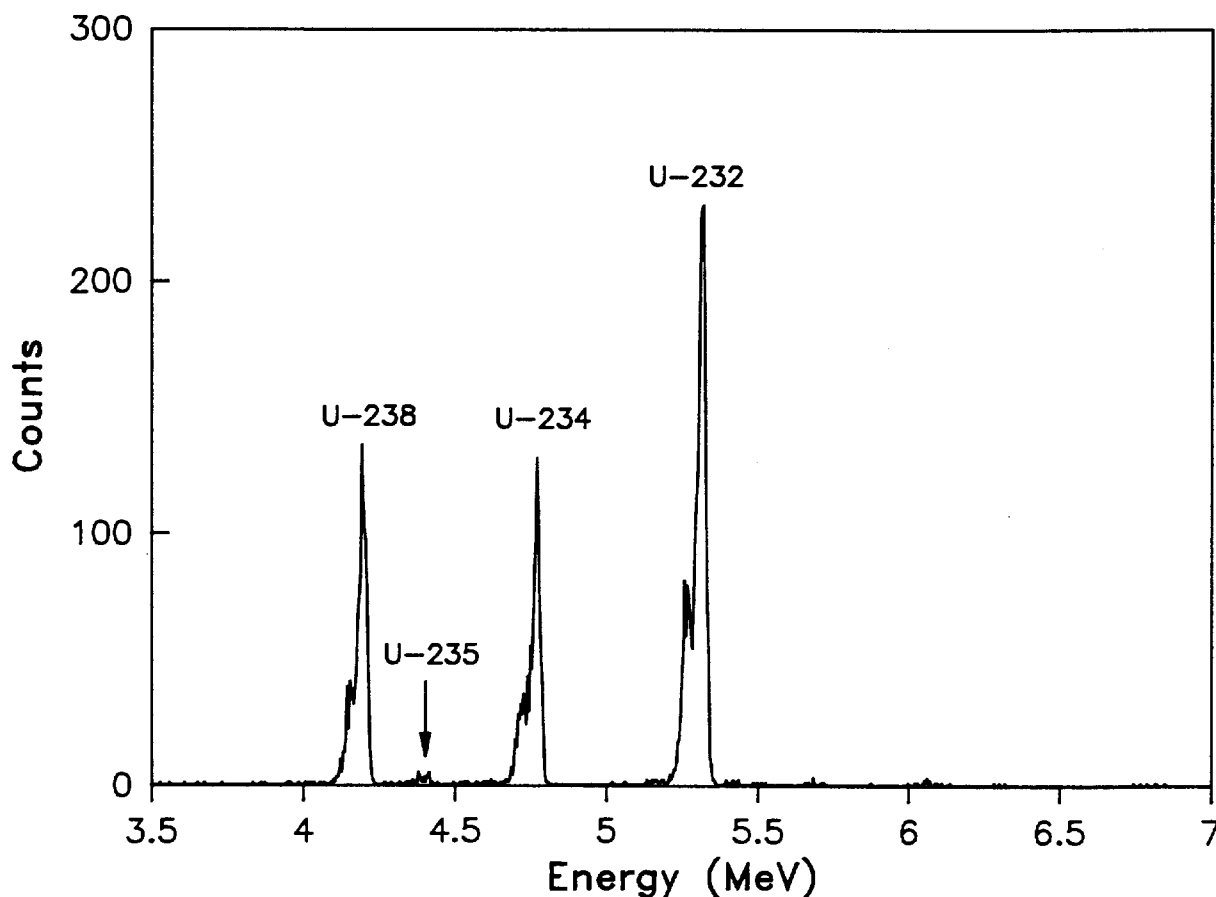


Figure 16. Typical polonium spectrum  
Tracer isotope:  $^{209}\text{Po}$

## 8.2 Uranium

Figure 17 shows a uranium spectrum with  $^{232}\text{U}$  used as the tracer. As  $^{238}\text{U}$ ,  $^{234}\text{U}$  and  $^{232}\text{U}$  have similar shapes, the same size window should be used for each.



**Figure 17. Typical uranium spectrum**  
Tracer isotope:  $^{232}\text{U}$

$^{228}\text{Th}$ , which grows in on the disc from  $^{232}\text{U}$ , overlaps with its parent's peak. Either  $^{224}\text{Ra}$  or the upper-energy peak of  $^{228}\text{Th}$  must be measured to allow for this. Prior to counting, the disc should not be stored so that its surface is in contact with any other solid surface, else recoil losses of  $^{228}\text{Th}$  and  $^{224}\text{Ra}$  may occur.

The  $^{235}\text{U}$  spectrum overlaps with both  $^{238}\text{U}$  and  $^{234}\text{U}$ . 82% of its decays can be measured in the 4.24–4.45 MeV region. For environmental samples the normal  $^{235}\text{U}/^{238}\text{U}$  activity ratio of 0.04604 should apply; hence, in calculating  $^{234}\text{U}$  and  $^{238}\text{U}$ , the overlap with  $^{235}\text{U}$  can be allowed for using a figure based on the  $^{238}\text{U}$  activity.

### 8.3 Thorium

Figure 18 shows a thorium spectrum with  $^{229}\text{Th}$  used as the tracer. The  $^{232}\text{Th}$  and  $^{230}\text{Th}$  spectra have similar shapes, and the same size window should be used for each.

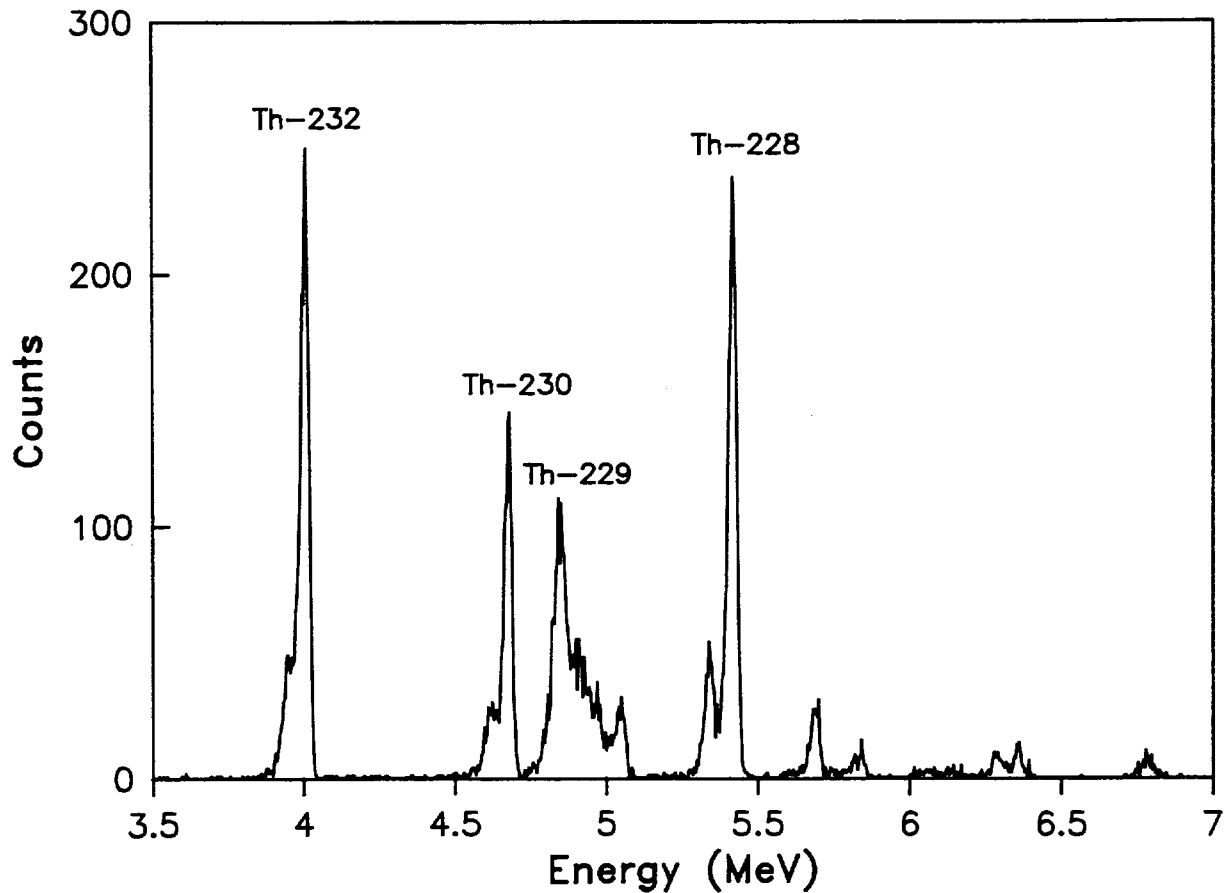


Figure 18. Typical thorium spectrum  
Tracer isotope:  $^{229}\text{Th}$

Some overlap of the  $^{229}\text{Th}$  and  $^{230}\text{Th}$  spectra is inevitable, and hence the placement of the upper-energy boundary for  $^{230}\text{Th}$  must be chosen carefully.

The 5.44 MeV, 5%  $^{224}\text{Ra}$  peak lies under the  $^{228}\text{Th}$  spectrum, and this must be allowed for later in the  $^{228}\text{Th}$  calculation. Prior to counting, the disc should not be stored so that its surface is in contact with any other solid surface, else recoil losses of  $^{224}\text{Ra}$  may occur.

#### 8.4 Radium

Figure 19 shows typical radium spectra obtained for a groundwater sample. The same disc was counted immediately after deposition and then again after 20 days, illustrating peak positions and changes in the spectrum due to isotope ingrowth and decay. Resolution of the  $^{226}\text{Ra}$  line is 38 keV FWHM.

The  $^{226}\text{Ra}$  activity is measured directly from its peaks at 4.60 and 4.78 MeV. The chemical recovery of  $^{226}\text{Ra}$  is determined from the  $^{217}\text{At}$  peak (7.07 MeV).  $^{226}\text{Ra}$  ( $t_{1/2}=14.8\text{d}$ ) is a beta emitter and decays to  $^{226}\text{Ac}$ , which in turn decays to a series of short-lived alpha-emitting daughters; of these,  $^{217}\text{At}$  is the most convenient measure, although  $^{213}\text{Po}$  (8.38 MeV) may also be used. The  $^{226}\text{Ac}$  activity reaches a maximum after 17 days (Fig. 6). However, if the activity of the added  $^{226}\text{Ra}$  is high enough, counting can begin any time after deposition.

If  $^{224}\text{Ra}$  ( $t_{1/2}=3.7\text{d}$ ) or  $^{223}\text{Ra}$  ( $t_{1/2}=11.4\text{d}$ ) are to be determined, counting should be commenced immediately after plating in order to minimize decay of  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  and ingrowth of both  $^{222}\text{Rn}$  ( $t_{1/2}=3.8\text{d}$ ) and  $^{225}\text{Ac}$  ( $t_{1/2}=10.0\text{d}$ ). However, prior to counting the disc should be stored under counting conditions for at least 1 hour to ensure that  $^{214}\text{Po}$  and  $^{211}\text{Bi}$  are in equilibrium with their parents  $^{222}\text{Rn}$  and  $^{219}\text{Rn}$  respectively.

If a measure of  $^{228}\text{Ra}$  is required, the disc should be stored for at least six months to allow ingrowth of  $^{228}\text{Th}$ , and re-counted (Fig. 19c). A measure of the ingrown  $^{228}\text{Th}$  is obtained by analysis of the  $^{224}\text{Ra}$  peak (5.69 MeV, 95%), (Koide & Bruland 1975). During storage, the surface of the source should not be in contact with any other solid surface, else recoil losses of  $^{224}\text{Ra}$  will occur. Abrasive contact with other surfaces would also remove some of the deposit from the disc. Flaming of the disc to volatilize  $^{222}\text{Rn}$  is not recommended, as the resolution of the source may be seriously degraded. If the  $^{226}\text{Ra}/^{228}\text{Ra}$  ratio is high, the  $^{224}\text{Ra}$  peak may be difficult to resolve from the surrounding  $^{222}\text{Rn}$  and  $^{218}\text{Po}$  peaks. In this case the deposit can be transferred from the disc, and a  $^{228}\text{Th}$  determination carried out (Bojanowski *et al.* 1983).

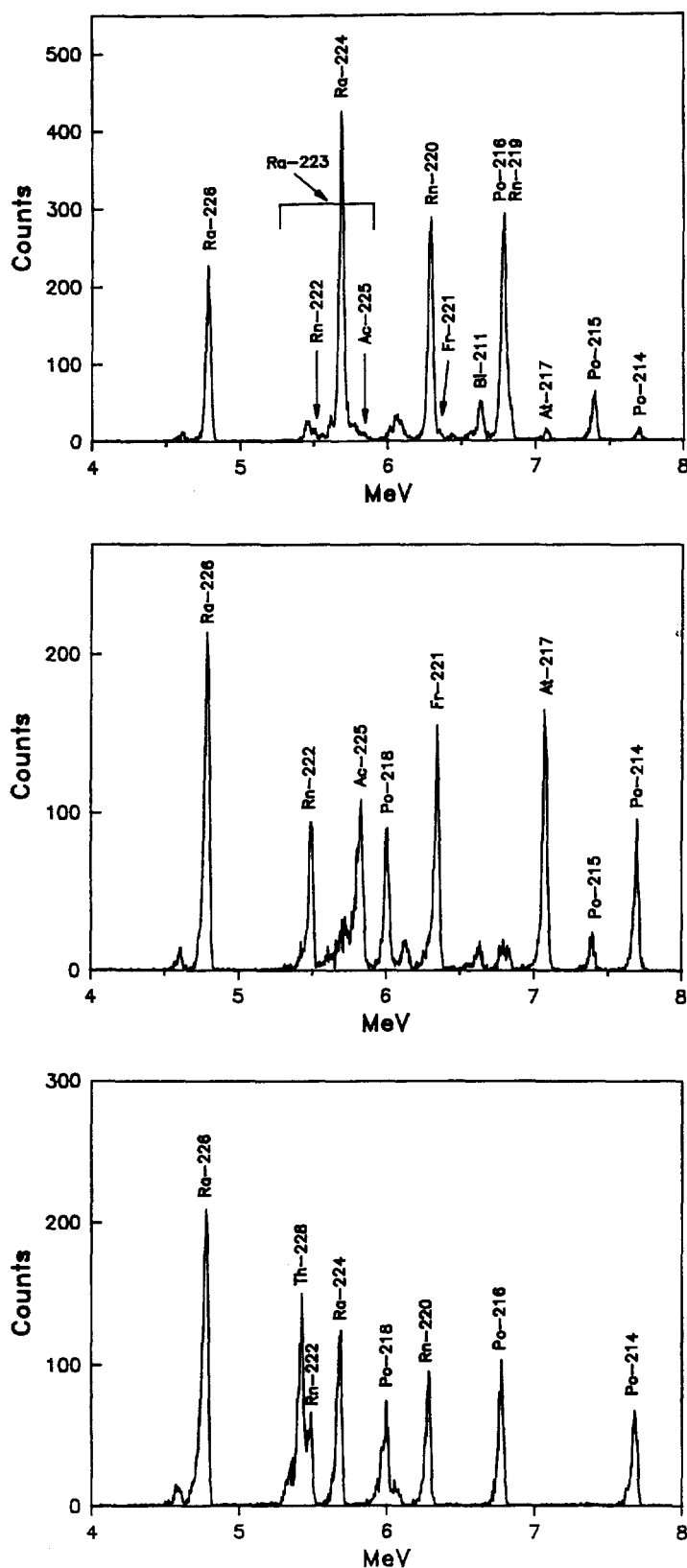
##### *Determination of $^{223}\text{Ra}$ and $^{224}\text{Ra}$*

Determination of the activities of  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  is not straightforward, because their direct decay lines overlap in the alpha-particle spectrum. Although their activities can be determined from the observed activities of their daughter products, the analysis procedure must take into account the finite and variable loss of their immediate daughters ( $^{219}\text{Rn}$  and  $^{220}\text{Rn}$  respectively) by emanation from the electrodeposited sample.

The procedure developed here involves the following steps:

- establishment of the value of  $\epsilon$ , the ratio of the retention of  $^{220}\text{Rn}$  to that of  $^{219}\text{Rn}$ , by a separate calibration measurement; this need only be carried out once.
- measurement of the total activity of  $^{223}\text{Ra}$  plus  $^{224}\text{Ra}$ ,  
 $A_{\text{Ra}} = [^{223}\text{Ra}] + [^{224}\text{Ra}]$
- measurement of the ratio  $[^{224}\text{Ra}]/[^{223}\text{Ra}]$  for the sample being analysed by measurement of the radon activity ratio,  $[^{220}\text{Rn}]/[^{219}\text{Rn}]$ , and correcting for differential radon loss using  $\epsilon$ .
- calculation of the  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  activities from the radium activity ratio and the measured value of the total radium activity,  $A_{\text{Ra}}$ .

These steps are described in the paragraphs following on page 40.



**Figure 19. Typical radium spectra**

Tracer isotope:  $^{226}\text{Ra}$ . See Figure 6 for ingrowth and decay curves

(a) Counted immediately after deposition

(b) The same disc counted 20 days after deposition

(c) The same disc counted after 6 months



The 5.2-5.9 MeV region includes the  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  activities as well as in-growing  $^{222}\text{Rn}$  (5.49 MeV), and  $^{225}\text{Ac}$  plus 2%  $^{213}\text{Bi}$  (5.5-5.9 MeV) resulting from the decay of  $^{226}\text{Ra}$  and  $^{225}\text{Ra}$  respectively (Fig. 19b). As all radon isotopes will be in secular equilibrium with their daughters, the  $^{222}\text{Rn}$  contribution can be stripped from this region by subtraction of the  $^{214}\text{Po}$  activity at 7.69 MeV. Similarly,  $^{225}\text{Ac}$  and  $^{213}\text{Bi}$  can be stripped by measurement of the  $^{217}\text{At}$  activity. The remaining activity in this region,  $A_{\text{Ra}}$ , is due to  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$ .

If both  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  are present in significant quantities, e.g. in groundwaters (Fig. 19a), then their daughter products must be used to derive their activities. Since both isotopes decay to short-lived gaseous radon isotopes, ( $^{219}\text{Rn}$   $t_{1/2}=4$  sec,  $^{220}\text{Rn}$   $t_{1/2}=56$  sec), losses by diffusion would be expected to occur from a thin source electrodeposited from an aqueous/ethanol solution as described in Section 6.3.

To obtain a measure of these losses, 7 sources were prepared as described above containing both  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$ . The  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  solutions used were separately calibrated against a  $^{226}\text{Ra}$  solution, giving a percentage standard error due to counting statistics on the  $^{224}\text{Ra}/^{223}\text{Ra}$  activity ratio on the sources of 0.71%.

The measured  $^{220}\text{Rn}/^{219}\text{Rn}$  activity ratio was divided by the calculated  $^{224}\text{Ra}/^{223}\text{Ra}$  activity ratio for each source to give the radon retention ratio,  $\epsilon$  (see Table 3). A mean value for  $\epsilon$  of 0.957 was obtained with a standard error of 0.006. Taking into account the  $^{224}\text{Ra}/^{223}\text{Ra}$  calibration error gives an overall uncertainty on this value of  $\epsilon$  of 0.009 at the one sigma confidence level.

This measure of  $\epsilon$  is used to correct for the proportionally higher losses of  $^{220}\text{Rn}$  from the source compared to that of  $^{219}\text{Rn}$  (see below). For each individual source the value of  $\epsilon$  was independent of the actual retentions of  $^{220}\text{Rn}$  and  $^{219}\text{Rn}$ , even though these retentions were observed to vary from 0.55 to 0.8 between sources (Table 3).

**Table 3.  $^{220}\text{Rn}/^{219}\text{Rn}$  retention ratio ( $\epsilon^*$ ) and  $^{220}\text{Rn}$  retentions for 7 standard sources. Counting errors correspond to 1 standard deviation**

Source	$^{220}\text{Rn}$ Retention	Retention Ratio $\epsilon^*$
ZS776	$0.569 \pm 0.002$	$0.961 \pm 0.010$
ZS773	$0.623 \pm 0.002$	$0.951 \pm 0.010$
ZS766	$0.635 \pm 0.002$	$0.956 \pm 0.012$
ZS767	$0.656 \pm 0.003$	$0.950 \pm 0.015$
ZS772	$0.692 \pm 0.003$	$0.928 \pm 0.010$
ZS764	$0.698 \pm 0.002$	$0.980 \pm 0.008$
ZS765	$0.771 \pm 0.003$	$0.973 \pm 0.011$
		mean = 0.957
		standard deviation = 0.016
		standard error = 0.006

\*  $\epsilon = (^{220}\text{Rn}/^{224}\text{Ra})/(^{219}\text{Rn}/^{223}\text{Ra})$ . Errors for  $\epsilon$  include counting and calibration error.

As stated above the calculation of the  $^{224}\text{Ra}/^{223}\text{Ra}$  activity ratio for a particular sample requires the determination of the observed  $^{220}\text{Rn}/^{219}\text{Rn}$  activity ratio. A measure of  $^{219}\text{Rn}$  can be obtained from the well separated peak at 7.39 MeV due to the decay of its daughter,  $^{215}\text{Po}$ . The  $^{220}\text{Rn}$  activity can be obtained by integrating the count rate observed in the energy region 6.15-6.86 MeV. After subtraction of a small contribution due to  $^{221}\text{Fr}$  at 6.24 and 6.34 MeV (which is given by 85% of the  $^{217}\text{At}$  activity at 7.07 MeV), the activity observed in this region is twice the  $(^{220}\text{Rn} + ^{219}\text{Rn})$  activity; that is, the activity arises from the decay of  $^{220}\text{Rn}$ ,  $^{216}\text{Po}$ ,  $^{219}\text{Rn}$  and  $^{211}\text{Bi}$ . The  $^{220}\text{Rn}$  activity is then half the remaining activity after deducting twice the  $^{219}\text{Rn}$  activity.

Correcting for differential radon loss, the  $^{224}\text{Ra}/^{223}\text{Ra}$  activity ratio is given by

$$R_{\text{Ra}} = (1/\epsilon) [^{220}\text{Rn}]/[^{219}\text{Rn}]$$

and the individual  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  concentrations obtained from

$$[^{223}\text{Ra}] = A_{\text{Ra}}/(R_{\text{Ra}} + 1)$$

and 
$$[^{224}\text{Ra}] = A_{\text{Ra}}R_{\text{Ra}}/(R_{\text{Ra}} + 1)$$

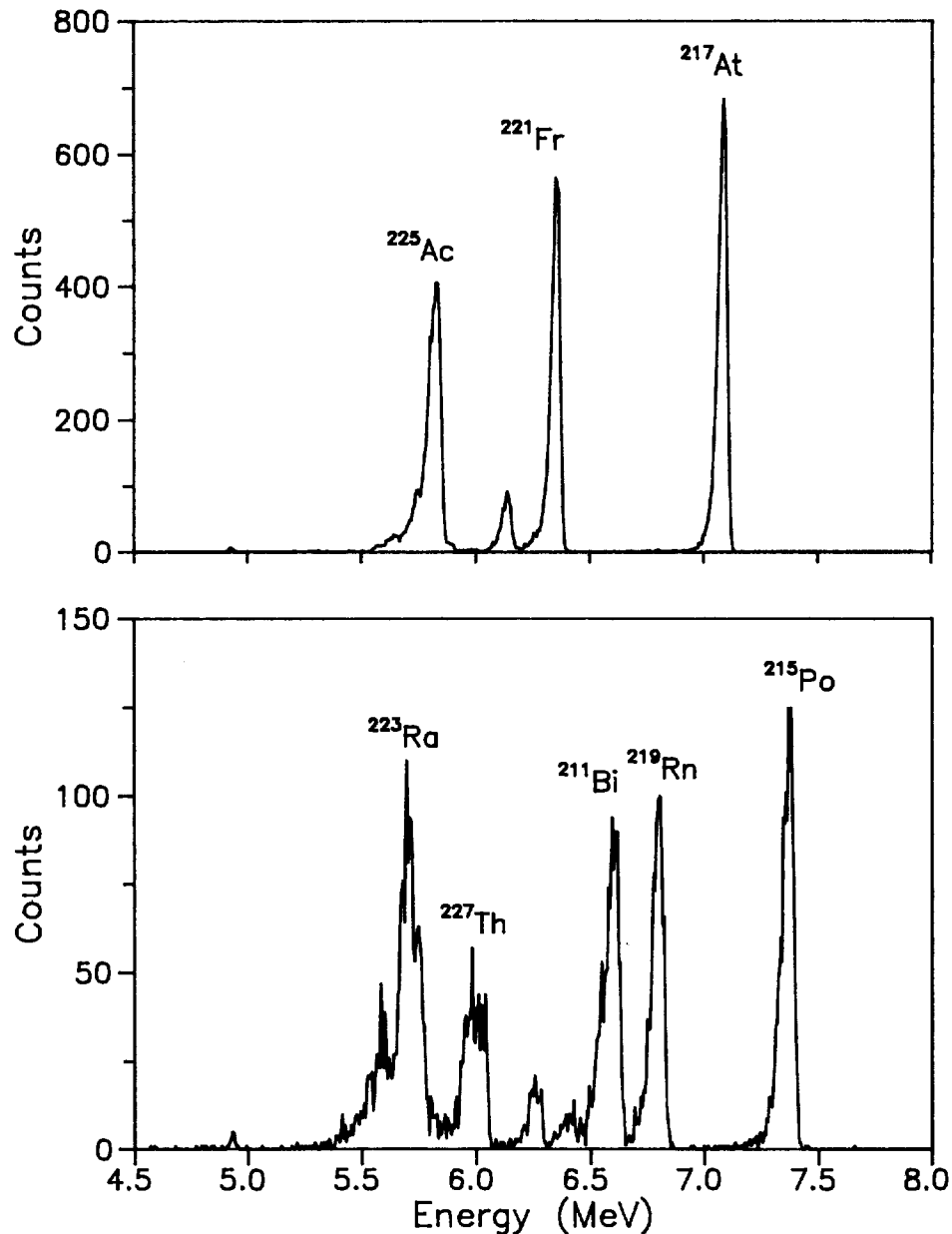
It should be noted that although this spectral stripping technique will yield a  $^{223}\text{Ra}$  determination with a high degree of sensitivity, the statistical accuracy of the  $^{224}\text{Ra}$  determination will suffer in the presence of substantial  $^{223}\text{Ra}$  activity. In this case, the sensitivity of the  $^{224}\text{Ra}$  determination can be improved by obtaining an estimate of the  $^{220}\text{Rn}$  activity from  $^{212}\text{Po}$  at 8.78 MeV, the activity of which is dependent on ingrowth of its  $^{212}\text{Pb}$  grandparent ( $t_{1/2} = 10.6\text{h}$ ) and parent  $^{212}\text{Bi}$  ( $t_{1/2} = 61\text{m}$ ). Care should be taken to allow  $^{212}\text{Po}$  to grow in under counting conditions, as the  $^{220}\text{Rn}$  retention of the source is inversely related to air pressure (Hancock & Martin, in press). Failure to do this will result in an over-estimate of the  $^{224}\text{Ra}$  activity and subsequently an under-estimate of the  $^{223}\text{Ra}$  activity.

Contamination of the detector by recoiling  $^{222}\text{Rn}$  atoms from the source will, unless prevented, result in increased background levels in the  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  energy region. Furthermore,  $^{222}\text{Rn}$  on the detector surface is not necessarily in secular equilibrium with its daughters due to recoil losses. This may lead to a serious under-estimate of the  $^{222}\text{Rn}$  activity to be stripped from the  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  energy region via measurement of  $^{214}\text{Po}$ . Both of these problems are effectively eliminated by application of the recoil protection technique described in Section 7.5.

## 8.5 Actinium

The recovery of the  $^{225}\text{Ac}$  tracer ( $t_{1/2} = 10.0\text{d}$ ) is obtained via measurement of the  $^{217}\text{At}$  peak at 7.07 MeV, from an initial count as soon as possible after deposition (Fig. 20a). The disc is then stored for approximately 3 months, and recounted. The  $^{227}\text{Ac}$  activity is obtained by analysis of the 5.25-6.08 MeV region, which includes ingrown  $^{227}\text{Th}$  and  $^{223}\text{Ra}$ , plus  $^{223}\text{Fr}$  (Fig. 20b). During storage, the surface of the source should not be in contact with any other solid surface, else recoil losses of  $^{223}\text{Ra}$  may occur. Abrasive contact with other surfaces may also remove some of the deposit from the disc.

Potential interfering radionuclides in the  $^{227}\text{Th} + ^{223}\text{Ra}$  energy region are  $^{225}\text{Ac}$ ,  $^{222}\text{Rn} + ^{218}\text{Po}$  (progeny of  $^{226}\text{Ra}$ ),  $^{210}\text{Po}$  and  $^{228}\text{Th}$ . Any  $^{225}\text{Ac}$  still present on the second count can be stripped via measurement of the  $^{217}\text{At}$  peak. Although radium, polonium and thorium should have been completely removed during the chemical separation procedures, a check should be made for their presence. Any  $^{222}\text{Rn}$  (5.49 MeV) and  $^{218}\text{Po}$  (6.00 MeV) which may be present due to the decay of  $^{226}\text{Ra}$  can be stripped by deducting twice the activity of the  $^{214}\text{Po}$  peak at 7.68 MeV. Potential interference from  $^{210}\text{Po}$  (5.30 MeV) may



**Figure 20. Typical actinium spectra**

Tracer isotope:  $^{225}\text{Ac}$ . See Figure 7 for ingrowth and decay curves

(a) Counted immediately after deposition

(b) The same disc counted 3 months after deposition

be avoided by choosing 5.38 MeV as the lower energy limit for  $^{227}\text{Th}$  and  $^{223}\text{Ra}$  measurement. The resultant loss of measurable activity in the 5.25–5.38 MeV region due to  $^{223}\text{Fr}$  at 5.34 MeV and  $^{223}\text{Ra}$  (0.6%), is less than 1% of the total  $^{227}\text{Th}$  and  $^{223}\text{Ra}$  activity.

$^{228}\text{Th}$  and its daughters  $^{224}\text{Ra}$  and  $^{212}\text{Bi}$  are the major potential interferences, and their contribution to the  $^{227}\text{Th}$  and  $^{223}\text{Ra}$  area cannot be measured quantitatively. However, their presence can be detected via measurement of the  $^{212}\text{Po}$  peak at 8.78 MeV.

## 8.6 Tailing

Due to the nature of low-energy tailing of alpha spectra, some contribution from a higher-energy peak to the count rate in the analysis window of a lower-energy peak is inevitable, though in most cases small (i.e. <0.5%). However, where the activity of a higher-energy peak is much greater than that of a lower-energy peak, this tailing may be significant.

Tailing will depend on a number of factors, including:

- energy difference between the two peaks
- detector performance
- disc/detector distance (Section 7.3)
- detector collimation (Section 7.4)
- chamber gas pressure
- analysis window size
- disc deposit thickness

Tailing is best measured by preparing a strong source of the higher-energy nuclide. This is counted on the detector using the same conditions as sample discs, and the contribution of the higher-energy peak to the lower-energy analysis window measured.

Provided the chemical separation techniques used are adequate, tailing due to sample disc deposit thickness should be negligible in comparison to detector effects. Exceptions to this rule can occur, however, for discs with high  $^{238}\text{U}$  and  $^{232}\text{Th}$  activities, due to the long half-lives of these two isotopes. Disc deposits up to 30-35  $\mu\text{g}/\text{cm}^2$  can be tolerated in most cases. For the 1.75 cm diameter (2.41  $\text{cm}^2$  area) discs used at the ARRI, this means a limit on the activity of  $^{238}\text{U}$  of approximately 1 Bq (representing 80.9  $\mu\text{g}$  of natural uranium, or 34  $\mu\text{g}/\text{cm}^2$ ) and a limit for  $^{232}\text{Th}$  of approximately 0.3 Bq (73.7  $\mu\text{g}$  of thorium or 31  $\mu\text{g}/\text{cm}^2$ ).

### *Polonium*

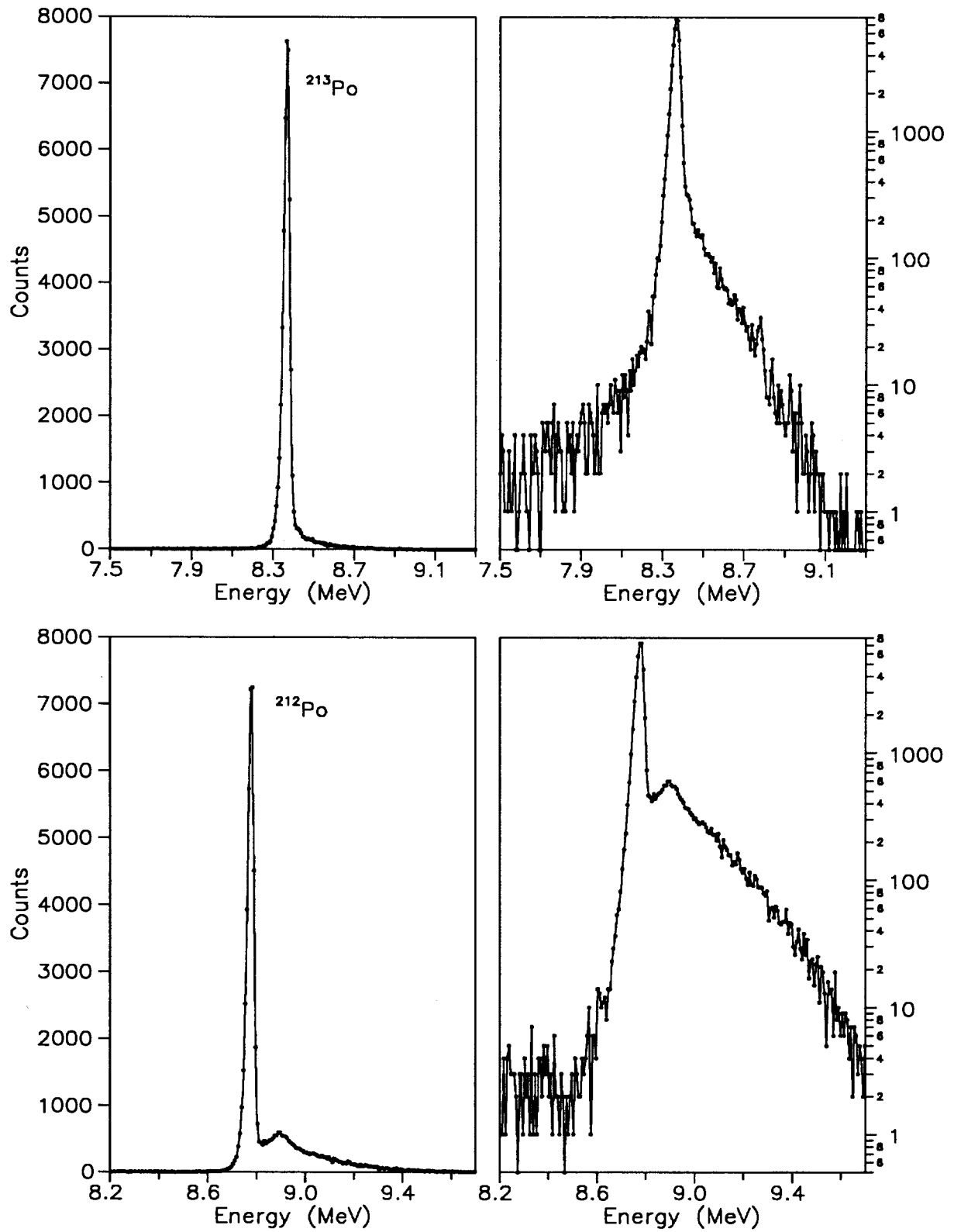
A  $^{210}\text{Po}$  source should be prepared and tailing into the tracer peak area measured. For  $^{209}\text{Po}$ , an alternative procedure is to use a  $^{209}\text{Po}$  source and assume identical tailing to the  $^{210}\text{Po}$  peak. For  $^{208}\text{Po}$ , however, a  $^{210}\text{Po}$  source must be used;  $^{209}\text{Po}$  sources are unsuitable due to a minor (0.6%) peak 0.3 MeV below the primary peak, while  $^{208}\text{Po}$  sources are unsuitable since some  $^{209}\text{Po}$  is usually present on the source.

### *Uranium*

A strong  $^{232}\text{U}$  source is used to measure tailing into the  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{234}\text{U}$  areas. The  $^{232}\text{U}$  and  $^{234}\text{U}$  peaks have a similar shape, and the same source may be used to estimate tailing of  $^{234}\text{U}$  into  $^{238}\text{U}$  and  $^{235}\text{U}$ . The source should not be used for more than a few weeks after preparation due to  $^{228}\text{Th}$  ingrowth on the disc.

### *Thorium*

$^{228}\text{Th}$ ,  $^{229}\text{Th}$  and  $^{230}\text{Th}$  sources must be separately prepared and measured. Tailing of  $^{225}\text{Ac}$  into the  $^{228}\text{Th}$  area is best measured relative to the  $^{217}\text{At}$  peak for a  $^{229}\text{Th}$  source in equilibrium with its daughters. The source should be prepared from an aged  $^{229}\text{Th}$  solution so that the  $^{228}\text{Th}$  activity present is negligible. If the tracer  $^{229}\text{Th}$  solution contains substantial  $^{228}\text{Th}$  this will need to be corrected for separately.



**Figure 21. Examples of upper-energy tailing**

On the log scale, 0 counts has been represented by 0.5

(a)  $^{213}\text{Po}$  spectrum

(b)  $^{212}\text{Po}$  spectrum

### *Radium*

Tailing of  $^{223}\text{Ra}$ ,  $^{224}\text{Ra}$  and  $^{225}\text{Ac}$  into the  $^{226}\text{Ra}$  energy region should be measured. Tailing of  $^{214}\text{Po}$  into  $^{215}\text{Po}$  may be significant if the  $^{226}\text{Ra}/^{223}\text{Ra}$  ratio is high. Similarly, if  $^{228}\text{Ra}$  is to be determined via measurement of ingrown  $^{224}\text{Ra}$ , tailing from the  $^{218}\text{Po}$  peak into the  $^{224}\text{Ra}$  energy region may also be significant if the  $^{226}\text{Ra}/^{228}\text{Ra}$  ratio is high. A measure of this tailing can be obtained from the same source by analysis of the corresponding energy interval below the  $^{214}\text{Po}$  peak.

### *Upper-energy tailing of $^{212}\text{Po}$ , $^{213}\text{Po}$ and $^{214}\text{Po}$*

These three peaks may show an upper-energy 'tail', most markedly for  $^{212}\text{Po}$  (Fig. 21b), less so for  $^{213}\text{Po}$  (Fig. 21a) and barely noticeable for  $^{214}\text{Po}$ . The effect is due to summation of pulses from the bismuth parent beta-particle decay and polonium daughter alpha-particle decay where the daughter decays within the signal processing time of the detection system. If desired, the degree of this type of tailing may be reduced by decreasing counting efficiency (e.g. by increasing source/detector distance).

Pulses within the upper-energy tail represent decays due to the polonium isotope being measured and should be included in the peak measurement. Otherwise a correction must be applied.

## 9. LOWER LIMITS OF DETECTION

The lower limit of detection (LLD) for any nuclide is critically dependent on detector background; however, an attempt has been made here to give typical limits assuming low background detectors (see Table 4). Limits have been calculated using the formula derived by Lochamy (1981):

$$LLD = \frac{k^2}{t} + 2\sqrt{2} \cdot k \cdot \sigma_b$$

where  $t$  = count time for both background and sample (assumed equal)  
 $\sigma_b$  = standard deviation in the background count rate  
 $k$  = one-sided confidence factor  
= 1.65 if  $k$  is chosen so that 95% of measurements give a count rate above the minimum detectable activity

Calculations have been based on an 85 kilosecond (approximately 1 day) count, a counting efficiency of 25% for alpha spectrometers and 30% for a beta counter, and typical recoveries and ingrowth/decay factors listed in the table.

The detection limit given for  $^{210}\text{Pb}$  is that obtained with the beta counting method. If analysis can be delayed for a suitable period,  $^{210}\text{Pb}$  may be determined by analysis for ingrown  $^{210}\text{Po}$  using alpha-particle spectrometry (Section 5.2.2). The detection limit then depends on the length of the delay period.

The detection limit given for  $^{224}\text{Ra}$  assumes use of the  $^{212}\text{Po}$  peak, which is the most sensitive measurement technique in the presence of significant  $^{223}\text{Ra}$  (Section 8.4). In samples with relatively low  $^{223}\text{Ra}$  activities, the  $^{220}\text{Rn}$  and  $^{216}\text{Po}$  peaks may be used, improving the  $^{224}\text{Ra}$  detection limit.

**Table 4. Lower limits of detection, calculated using the formula in Section 9 and assuming an 85 kilosecond count and typical detection efficiencies, recoveries and ingrowth/decay factors.**

Nuclide	Background (c.p.ksec)	Detection * Efficiency (%)	Recovery (%)	Ingrowth/ Decay	Detection limit (mBq)
<sup>210</sup> Po	0.05	25	95		0.6
<sup>210</sup> Pb	4.	30	95		3.5
<sup>238</sup> U	0.01	25	90		0.4
<sup>235</sup> U	0.005	21	90		0.4
<sup>234</sup> U	0.01	25	90		0.4
<sup>232</sup> Th	0.01	25	85		0.4
<sup>230</sup> Th	0.01	25	85		0.4
<sup>228</sup> Th	0.05	25	85		0.7
<sup>226</sup> Ra	0.01	25	80		0.4
<sup>223</sup> Ra **	0.01	19	80	0.96	0.6
<sup>224</sup> Ra ***	0.005	12	80	0.72	1.0
<sup>228</sup> Ra ****	0.01	24	80	0.45	1.0
<sup>227</sup> Ac	0.05	50	75	1.0	0.4

\* Detection efficiency is a product of the counting efficiency of the detector (here assumed 25% for alpha spectrometry and 30% for beta counting) and the proportion of decays resulting in particles in the energy region being measured.

\*\* Detection efficiency for <sup>223</sup>Ra is reduced from 25% due to loss of <sup>219</sup>Rn from the source, assumed here to be 25%. Decay factor is for a 24-hour count begun 3 hours after Th/Ra separation.

\*\*\* <sup>224</sup>Ra is assumed measured using the <sup>212</sup>Po peak. 25% <sup>220</sup>Rn loss is assumed. <sup>212</sup>Po is a member of a 64% decay branch, further affecting detection efficiency. Ingrowth/decay factor is for a 24-hour count begun 24 hours after Th/Ra separation.

\*\*\*\* Ingrowth factor for <sup>228</sup>Ra (ingrowth of <sup>228</sup>Th) is that reached after 2 years. Maximum ingrowth is 0.578, reached after 4.5 years.





## **APPENDIX 1**

### **RADIONUCLIDE DECAY DATA**

## APPENDIX 1

### RADIONUCLIDE DECAY DATA

Intensities are given as % of all decays of the isotope. Transformations with intensities of less than 0.01% have not been included in this table.

#### References

Lederer, C.M. & Shirley, V.S. (1978). Table of isotopes, 7th ed. John Wiley & Sons, New York.

Westmeier, W. & Merklin, A. (1985). Catalog of alpha particles from radioactive decay. Report No. 29-1, Fachinformationszentrum GmbH, Karlsruhe, Germany.

#### *Polonium tracer isotopes*

Isotope	Half-life	Decay Mode	Energies (MeV)	Intensities %	Daughter
Po-208	2.898 years	alpha	5.114	100.	Pb-204
Po-209	102. years	alpha	4.882 4.617	99.43 0.57	Pb-205

#### *Thorium series (4n series)*

Isotope	Half-life	Decay Mode	Energies (MeV)	Intensities %	Daughter
U-236	2.34 x 10 <sup>7</sup> years	alpha	4.494 4.445 4.331	74. 26. 0.26	Th-232
U-232	71.7 years	alpha	5.321 5.264 5.137	68.6 31.2 0.28	Th-228
Th-232	1.41 x 10 <sup>10</sup> years	alpha	4.016 3.957 3.834	77. 23. 0.2	Ra-228
Ra-228	5.76 years	beta	0.039 0.014	60. 40.	Ac-228

*Thorium series (4n series) cont...*

Isotope	Half-life	Decay Mode	Energies (MeV)	Intensities %	Daughter
Ac-228	6.13 hours	beta	2.18 1.85 1.70 1.11 0.64 0.45	10.1 9.6 6.7 53. 7.6 13.	Th-228
Th-228	1.9131 years	alpha	5.423 5.341 5.209 5.172 5.137	72.7 26.7 0.36 0.18 0.05	Ra-224
Ra-224	3.665 days	alpha	5.686 5.445 5.152 5.040	94.98 5.0 0.01 0.01	Rn-220
Rn-220	55.61 sec	alpha	6.288 5.747	99.93 0.07	Po-216
Po-216	0.145 sec	alpha	6.778	100.	Pb-212
Pb-212	10.64 hours	beta	0.569 0.331	12. 88.	Bi-212
Bi-212	60.60 mins	beta 64.06 %	2.27 1.55 0.93 0.67 0.45 0.085	40.5 6.5 4.5 4. 5.5 3.	Po-212
		alpha 35.94 %	6.090 6.051 5.769 5.626 5.607 5.486	9.78 25.12 0.60 0.05 0.39 0.01	Tl-208
Po-212	0.296 microsec	alpha	8.785	100.	Pb-208
Tl-208	3.053 mins	beta	2.38 1.80 1.52 1.29 1.04	0.03 48.8 22.7 23.9 4.6	Pb-208

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*4n+1 series*

Isotope	Half-life	Decay Mode	Energies (MeV)	Intensities %	Daughter
U-233	1.59 x 10 <sup>5</sup> years	alpha	4.824	84.4	Th-229
			4.804	0.05	
			4.796	0.28	
			4.783	13.23	
			4.758	0.02	
			4.754	0.16	
			4.751	0.01	
			4.729	1.61	
			4.701	0.06	
			4.681	0.01	
			4.664	0.04	
			4.634	0.01	
			4.611	0.01	
			4.513	0.02	
			4.507	0.01	
Th-229	7340 years	alpha	5.078	0.01	Ra-225
			5.053	1.6	
			5.051	5.2	
			5.034	0.24	
			4.978	3.2	
			4.968	6.4	
			4.929	0.11	
			4.901	10.8	
			4.879	0.03	
			4.866	0.03	
			4.862	0.18	
			4.853	0.03	
			4.845	56.2	
			4.838	4.8	
			4.834	0.29	
			4.815	8.45	
			4.810	0.22	
			4.798	1.27	
			4.762	0.63	
			4.755	0.05	
			4.738	0.01	
			4.693	0.08	
			4.689	0.15	
			4.599	0.01	
			4.485	0.01	
Ra-225	14.8 days	beta	0.32	100.	Ac-225

*4n+1 series* cont...

Isotope	Half-life	Decay Mode	Energies (MeV)	Intensities %	Daughter
Ac-225	10.0 days	alpha	5.830	50.6	Fr-221
			5.805	0.30	
			5.794	24.30	
			5.792	2.50	
			5.732	10.1	
			5.724	3.4	
			5.682	1.25	
			5.637	4.35	
			5.609	1.2	
			5.598	0.04	
			5.580	1.2	
			5.563	0.03	
			5.554	0.1	
			5.545	0.03	
			5.540	0.02	
			5.442	0.15	
			5.434	0.07	
			5.319	0.08	
			5.286	0.3	
			5.268	0.02	
			5.210	0.02	
			5.206	0.01	
Fr-221	4.8 mins	alpha	6.341	83.4	At-217
			6.243	1.34	
			6.126	15.1	
			6.076	0.15	
			5.980	0.49	
			5.966	0.08	
			5.939	0.17	
			5.925	0.03	
			5.776	0.06	
At-217	32.3 millisec	alpha	7.067	99.9	Bi-213
			6.813	0.06	
			6.610	0.01	
			6.484	0.02	
Bi-213	45.59 mins	alpha	5.869	2.0	Tl-209
		2.16 %	5.549	0.16	
		beta	1.40	65.	Po-213
		97.84 %	1.00	33.	
Tl-209	2.20 mins	beta	1.9	100.	Pb-209
Po-213	4.2 microsec	alpha	8.375	100.	Pb-209
Pb-209	3.3 hours	beta	0.64	100.	Bi-209

*Uranium series (4n+2 series)*

Isotope	Half-life	Decay Mode	Energies (MeV)	Intensities %	Daughter
U-238	4.47 x 10 <sup>9</sup> years	alpha	4.196 4.149 4.041	77. 23. 0.23	Th-234
Th-234	24.10 days	beta	0.19 0.10	65. 35.	Pa-234m
Pa-234m	1.18 mins	beta 99.87 %	2.29 1.53 1.25	98.	U-234
		Isomeric transition 0.13 %			Pa-234
Pa-234	6.75 hours	beta	1.51 1.19 0.68 0.51 0.28	1. 5. 19. 63. 12.	U-234
U-234	2.45 x 10 <sup>5</sup> years	alpha	4.775 4.723 4.604	71.4 28.4 0.21	Th-230
Th-230	7.52 x 10 <sup>4</sup> years	alpha	4.688 4.621 4.480 4.438	76.3 23.4 0.15 0.02	Ra-226
Ra-226	1600 years	alpha	4.785 4.602 4.344	94.45 5.55 0.01	Rn-222
Rn-222	3.824 days	alpha	5.490 4.987	99.9 0.08	Po-218
Po-218	3.1 mins	alpha	6.002	100.	Pb-214
Pb-214	26.8 mins	beta			Bi-214
Bi-214	19.7 mins	beta 99+ %	3.26 1.88 1.51 1.02 0.42	19. 9. 40. 23. 9.	Po-214
		alpha 0.021 %	5.512 5.448 5.268	0.0082 0.0113 0.0012	Tl-210
Po-214	164 microsec	alpha	7.687 6.904	99.99 0.01	Pb-210

*Uranium series (4n+2 series) cont...*

Isotope	Half-life	Decay Mode	Energies (MeV)	Intensities %	Daughter
Tl-210	1.30 mins	beta	2.34	19.	Pb-210
			1.87	56.	
			1.32	25.	
Pb-210	22.26 years	beta	0.061	19.	Bi-210
			0.015	81.	
Bi-210	5.013 days	beta	4.687	40.	Po-210
			4.650	60.	
Po-210	138.378 days	alpha	5.304	100.	Pb-206

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*Actinium series (4n+3 series)*

Isotope	Half-life	Decay Mode	Energies (MeV)	Intensities %	Daughter
U-235	7.04 x 10 <sup>8</sup> years	alpha	4.598	4.6	Th-231
			4.557	3.7	
			4.503	1.2	
			4.446	0.6	
			4.416	4.	
			4.397	57.	
			4.367	18.	
			4.345	1.5	
			4.324	3.	
			4.267	0.6	
			4.217	5.7	
			4.158	0.5	
Th-231	25.52 hours	beta	0.30	52.	Pa-231
			0.22	20.	
			0.14	22.	
			0.09	6.	
Pa-231	3.276 x 10 <sup>4</sup> years	alpha	5.058	11.0	Ac-227
			5.031	2.5	
			5.028	20.0	
			5.011	25.4	
			4.984	1.4	
			4.974	0.4	
			4.950	22.8	
			4.933	3.0	
			4.851	1.4	
			4.794	0.04	
			4.736	8.4	
			4.712	1.	
			4.680	1.5	
			4.642	0.1	
			4.631	0.1	
			4.598	0.02	
			4.565	0.01	



*Actinium series (4n+3 series) cont...*

Isotope	Half-life	Decay Mode	Energies (MeV)	Intensities %	Daughter
Ac-227	21.773 years	beta 98.62 %	0.0455	98.62	Th-227
			4.36 - 4.74	0.01	Fr-223
			4.765	0.02	
			4.793	0.01	
			4.853	0.06	
			4.872	0.09	
			4.938	0.52	
			4.947	0.65	
Fr-223	21.8 mins	alpha	5.340	100.	At-219
At-219	54 sec	alpha 97 %	6.275	97.	Bi-215
		beta 3 %			Rn-219
Bi-215	7.4 mins	beta 100 %			Po-215
Th-227	18.718 days	alpha	6.038	24.5	Ra-223
			6.009	2.90	
			5.978	23.4	
			5.960	3.00	
			5.916	0.78	
			5.910	0.17	
			5.867	2.42	
			5.808	1.27	
			5.796	0.31	
			5.762	0.23	
			5.757	20.3	
			5.728	0.03	
			5.713	4.89	
			5.709	8.2	
			5.701	3.63	
			5.693	1.50	
			5.674	0.06	
			5.668	2.06	
			5.640	0.02	
			5.613	0.22	
			5.601	0.17	
			5.586	0.18	
			5.532	0.02	
			5.510	0.02	

*Actinium series (4n+3 series) cont...*

Isotope	Half-life	Decay Mode	Energies (MeV)	Intensities %	Daughter
Ra-223	11.435 days	alpha	5.872	0.87	Rn-219
			5.858	0.32	
			5.748	9.1	
			5.716	53.7	
			5.608	26.0	
			5.540	9.1	
			5.502	0.80	
			5.482	0.01	
			5.434	2.30	
			5.366	0.11	
			5.339	0.10	
			5.288	0.13	
			5.283	0.10	
			5.259	0.04	
			5.237	0.04	
			5.212	0.01	
			5.173	0.03	
			5.152	0.02	
			5.135	0.02	
Rn-219	3.96 sec	alpha	6.819	80.9	Po-215
			6.553	11.5	
			6.529	0.12	
			6.425	7.5	
			6.312	0.05	
			6.158	0.02	
Po-215	1.780 millisec	alpha	7.386	99.95	Pb-211
			6.957	0.03	
			6.950	0.02	
Pb-211	36.1 mins	beta	1.355	92.4	Bi-211
			0.951	1.4	
			0.525	5.5	
			0.251	0.7	
Bi-211	2.14 mins	alpha	6.623	83.8	Tl-207
		99+ %	6.279	16.0	
		beta 0.274 %			Po-211
Tl-207	4.79 mins	beta	1.44	100.	Pb-207
Po-211	0.516 sec	alpha	7.450	98.9	Pb-207
			6.893	0.55	
			6.570	0.55	

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## **APPENDIX 2**

### **DESCRIPTION OF COMPUTER PROGRAMS**

### LIST OF COMPUTER PROGRAMS

Program	Tracer	Application
ACT	Ac-225	Determination of Ac-227 by alpha spectrometry.
ACTB		Calculation of background count rate in the Ra-223 + Th-227 count area for use by program ACT.
BETAB		Background count rate calculation.
CRATE		Background count rate calculation.
EFFY		Calculation of detection efficiency and source/detector distance.
LEAD	stable lead	Determination of Pb-210 by beta counting Equilibrium between Pb-210 and Bi-210 assumed.
LEADSEP	stable lead	Determination of Po-210 by beta counting. Complete separation of Bi-210 at a known time assumed.
LEDPO		Calculation of Po-210 and Pb-210 activities in a sample at date of collection, using two Po-210 determinations, one of Po-210 activity concentration in the sample, the other of Po-210 activity (after an ingrowth period) in a separated Pb-210 portion.
NUCLIDE2		Calculation of activity of 2nd nuclide in a decay series using measurements of its parent and daughter.
POLCOR		Correction of Po-210 activity to date of collection, given Pb-210 activity in the sample at date of collection.
POLLY	Po-209	Determination of Po-210 by alpha spectrometry.
POL208	Po-208	Determination of Po-210 by alpha spectrometry.
POLON		Calculation of Po-210 and Pb-210 activities in a sample at date of collection, using two separate Po-210 activity determinations.
RADB		Calculation of background count rate in the Ra-224 + Ra-223 and Rn-220 count areas for use by programs RAD224, RAD226, RAD346 and RADPO.
RAD225	Ra-225	Determination of Ra-226 by alpha spectrometry.
RAD226	Ra-226	Determination of Ra-223 and Ra-224 by alpha spectrometry.
RAD346		Determination of Ra-223, Ra-224 and Ra-226 by alpha spectrometry. Generally used where radium recovery is determined via a later count for Ra-225 daughters and Ra-226 activity is low.

RAD68	Ra-226	Determination of Ra-228 by alpha spectrometry.
RADPO	Ra-226	Determination of Ra-223 and Ra-224 by alpha spectrometry. Po-212 used as a measure of Rn-220.
RATH228		Determination of Ra-228 by alpha spectrometry utilising a Th-228 determination on a redissolved radium disc deposit.
TAIL		Calculation of tailing of a higher-energy peak into a lower-energy peak area.
THOR	Th-229	Determination of Th-232, Th-230 and Th-228 by alpha spectrometry.
THORE	Th-229	Determination of Th-232 and Th-230 by alpha spectrometry. Th-228 assumed in secular equilibrium with Th-232 in the sample.
THORN	Th-228	Determination of Th-232 and Th-230 by alpha spectrometry. Th-228 concentration in the sample known.
URAN	U-232	Determination of U-238, U-235 and U-234 by alpha spectrometry. Ra-224 used as a measure of Th-228.
URANTH	U-232	Determination of U-238, U-235 and U-234 by alpha spectrometry. Th-228 measured using upper-energy peak.

## DESCRIPTION OF COMPUTER PROGRAMS

In order to simplify the calculation of results after spectral analysis, a number of computer programs have been written in FORTRAN77 to perform the most commonly required calculations. Most of these programs require the data to be entered into an input file before running the program; the following notes apply in such cases:

### Units:

Count time should be in kiloseconds  
Backgrounds should be in counts per kilosecond  
Energy boundaries should be in MeV

Tracer mass/volume and Tracer activity concentration must be in compatible units  
e.g. grams and mBq/gram respectively **OR** millilitres and mBq/millilitre respectively

Units chosen for Tracer activity concentration and  
Sample mass/volume will determine the result units  
e.g. where Tracer activity concentration is in mBq/gram  
Tracer mass is in grams  
Sample volume is in Litres  
then the result will be in mBq/Litre

### Formats:

Dates are input as DD.MM.YYYY e.g. 25.03.89 or 25.03.1989  
Dates with time : DD.MM.YY.HHMM e.g. 25.03.89.1355

All other input, including number of counts, are read as real numbers and require a decimal point.

Format for number of counts is F12.2  
Format for other input is F12.6

Other information generally present in the input file such as tracer solution number, detector code, analyst's initials, input file name, etc. is ignored by the program.

### Errors:

Errors both for input (e.g. background error) and output are one standard deviation due to counting statistics only. Tracer calibration errors, weighing errors and detector efficiency errors are not taken into account by the program.

### Ratios:

Isotope ratios are calculated using the ratio of counts in the peaks seen in the spectrum. Hence the error indicated for the ratio will generally be lower than one calculated from the activity concentration results, since the ratio error does not need to take the tracer peak counting error into account.

**Background count rates:**

In most cases, for the following peaks no background count rate is required: At-217, Po-214 and Po-213. This is also the case for Ra-224 in programs THORE and THORN. In these cases, the isotope is being measured in order to calculate the contribution from itself or a parent or daughter to a separate peak (e.g. Po-214 is measured to calculate the contribution of its parent Rn-222 to the Ra-224 + Ra-223 area). This contribution must be subtracted whether the observed counts originate from the disc or from contamination of the detector (e.g. due to recoil). The assumption has been made that the counts seen in the analysis window are all due to the isotope being measured. Caution should therefore be exercised if a detector has been exposed to sources with other isotopes emitting alpha particles in the regions of interest; background count rates should be checked in such cases to ensure that detector contamination has not occurred.

**Tailing corrections:**

Factors are required for the most important of the tailing corrections. For example:

$$\% \text{ Tailing (Th-232:Th-230)}$$

is the count rate observed in the Th-232 area as a percentage of the count rate observed in the Th-230 area when only Th-230 is present on the source. This is usually measured by counting a high-activity source of the second isotope (Th-230). Where this isotope or its daughters are short-lived (e.g. Po-215), tailing is measured using a source with the relevant isotope series in secular equilibrium.



## ACT

*Application:* Determination of Ac-227 by alpha spectrometry.

*Tracer isotope:* Ac-225 (Th-229/Ra-225/Ac-225)

### *Spectra*

Determination of Ac-227 requires a first count to determine Ac-225 recovery (via the daughter At-217), followed by a second count for the Ac-227 daughters Th-227 and Ra-223 after waiting a time interval to allow decay of Ac-225 and build-up of Th-227/Ra-223.

#### 1st count

At-217: a singlet peak (7.07 MeV, 99.9%).

#### 2nd count

Th-227 + Ra-223:

There is also a peak in this area from Fr-223 (5.34 MeV, 100% of Fr-223) which is a daughter of Ac-227, resulting from its 1.38% alpha decay process.

Although a decay period has been left to allow decay of Ac-225, counting after any finite time may still see a significant activity present (depending on the decay period and original activity present). Ac-225 and its daughters Fr-221 and Bi-213 all contribute to this area. This is allowed for using the At-217 daughter peak.

A lower energy boundary in MeV is required to calculate the decay yields for Ac-225, Ra-223 and Fr-223 in the area measured. An upper energy boundary in MeV is also required to calculate the decay yield for Fr-221 in the area measured.

If any Po-210 is present, interference should be avoided by raising the lower energy boundary to 5.38 MeV.

If any Rn-222 background is present, this will also contribute to this region (Rn-222 5.49 MeV, 99.9%; plus Po-218 6.00 MeV, 100%; plus Bi-214 5.45 + 5.51 MeV, 0.02%). This is allowed for via the Po-214 peak.

The presence of thorium isotopes on the disc should be checked for on either of the two counts, as Th-228 and its daughter Ra-224 would contribute to this area if present. This interference cannot be corrected for.

At-217: a singlet peak (7.07 MeV, 99.9%).

Po-215: a singlet peak (7.39 MeV, 99.95%).

Po-214: a singlet peak (7.69 MeV, 99.99%).

### *Discussion*

ACT assumes that separation of actinium from both radium and thorium is quantitative and occurs at the time input as "Ra/Ac separation date".

The background count rate input for the (Ra-224 + Ra-223) area on the second count must have had contributions from Rn-222, Ac-225 and Fr-221 subtracted using program ACTB.

ACT assumes that errors in the knowledge of detector efficiency for the two counts are negligible.

ACT example input file and example output

16.02.89.1130 Ra/Ac separation date  
17.02.89.1145 1st count date start  
18.02.89.1430 1st count date finish  
95.973 1st count time (ksecs)  
5.3899 Sample mass/volume  
2.0761 Tracer mass/volume  
175.5 Tracer activity conc  
0.2212 Detector efficiency  
0.004 At-217 bgd  
0.002 At-217 bgd error  
5385. At-217 counts  
S Detector 1  
13 Th-229 Tracer  
07.08.89 2nd count date (midpoint)  
82.697 2nd count time (ksecs)  
0.2212 Detector efficiency  
0.066 Th-227 + Ra-223 bgd  
0.012 Th-227 + Ra-223 bgd error  
3184. Th-227 + Ra-223 counts  
4. At-217 counts  
1181. Po-215 counts  
2. Po-214 counts  
5.25 Th-227/Ra-223 lower energy boundary (MeV)  
6.08 Th-227/Ra-223 upper energy boundary (MeV)  
0.253 % Tailing (At-217:Po-215)  
0.034 Error in tailing ratio  
S Detector 2  
PM Analyst  
OA059S.01 1st count code  
OA059S.02 2nd count code

Ac-225 recovery = 77.7 +/- 1.1 %

Ac-227	
Activity	Error
21.189	.476

- Note: 1) 1st count started 1.01 days after separation  
2) 2nd count midpoint 172.0 days after separation  
3) Ac-227 calculated to separation date  
1st count decay factor Ac-225 : .8973  
2nd count decay factors Ac-225 : .0000  
Ac-227 : .9851  
2nd count ingrowth factors Th-227 : .9857  
Ra-223 : .9845  
4) Rn-219 retention = 75.0 +/- 2.6 %  
5) Errors are one std deviation due to counting statistics only  
6) Calculated using program ACT

## ACTB

*Application:* Calculation of background count rate in the Ra-223 + Th-227 count area for use by program ACT.

### *Discussion*

ACTB subtracts the contributions of Rn-222 and Ac-225 from the (Ra-223 + Th-223) area background actinium spectrum. The Po-214 peak area is used as a measure of Rn-222, and the At-217 peak area is used as a measure of Ac-225 and Fr-221.

## BETAB

*Application:* Background count rate calculation.

### *Discussion*

Counts observed in a series of up to 1000 counting periods are input. Count time refers to the time for each counting period. This program was originally written for use with a beta counter.

BETAB example input file and example output

```
YL013B1.03   Disc/count code
PM           Analyst
30.09.87      Count date start
28.8          Count time
140.
147.
120.
116.
130.
128.
121.
```

Background count rate = 4.474 +/- .149

Note: 1) No. counting periods = 7  
2) Total no. counts = 902  
3) Mean no. counts  
per count interval = 128.86  
with std deviation = 10.43  
4) Calculated using program BETAB

## CRATE

*Application:* Background count rate calculation.

### *Discussion*

Count time and number of counts are input. CRATE calculates count rate and an error based on the square root of the number of counts.

## EFFY

*Application:* Calculation of efficiency of detector given source diameter, detector diameter and source/detector distance

or

calculation of source/detector distance given source diameter, detector diameter and counting efficiency.

### Discussion

EFFY can be used for the case of a uniform circular planar source and circular planar detector, where the source and detector are parallel with aligned centres. Hence, it is particularly useful for alpha-particle spectrometry utilising a silicon surface barrier detector.

Source diameter and detector diameter must be input. Where source/detector distance is input, EFFY calculates counting efficiency. Where counting efficiency is input, EFFY calculates source/detector distance. Source diameter, detector diameter and source/detector distance must all be in identical units.

The relation used is:

$$E = 0.5 \left( 1 - \frac{h}{\sqrt{h^2 + r^2}} \right) - \frac{3}{16} \left( \frac{ar}{h^2} \right)^2 \left( \frac{h}{\sqrt{h^2 + r^2}} \right)^5$$

where  $a$  is the radius of the source  
 $h$  is the source/detector distance  
 $r$  is the detector radius  
 $E$  is the counting efficiency

### EFFY example input file and example output

17.5	Source diameter
27.64	Detector diameter
5.1	Source/Detector distance
0.	Detector efficiency

Efficiency = .30674

## LEAD

*Application:* Determination of Pb-210 by beta counting.  
Equilibrium between Pb-210 and Bi-210 assumed.

*Tracer isotope:* stable lead

### *Discussion*

Pb-210 is measured by beta counting its daughter Bi-210. LEAD assumes that Bi-210 is in secular equilibrium with its parent. This may be assured by leaving the preparation for at least one month after separation before counting (Bi-210 half-life = 5.01 days).

Counts observed in a series of up to 1000 counting periods are input. Count time refers to the time for each counting period.

LEAD example input file and example output

```
HL011B1.01  Disc/count code
1           Pb tracer no.
PM          Analyst
20.06.86    Ra/Pb separation date
26.08.86    Count date start
27.6        Count time (ksecs) per count period
86.35       Pb tracer recovery (%)
0.84        Pb tracer recovery error
4.1664      Pb tracer mass (g)
0.380       Pb tracer Pb-210 blank (mBq/g)
0.05836     Sample mass/volume
0.2974      Detector efficiency
3.998       Background
0.115       Background error
614.        Bi-210 counts
631.
588.
579.
592.
```

Pb-210	
Activity	Error
1165.267	32.172

- Note: 1) No. counting periods = 5  
2) Total no. counts = 3004.  
3) Mean no. counts  
per count interval = 600.80  
with std deviation = 18.99  
4) Calculated using program LEAD

## LEADSEP

*Application:* Determination of Pb-210 by beta counting.  
Complete separation of Bi-210 at a known time assumed.

*Tracer isotope:* stable lead

### Discussion

Pb-210 is measured by beta counting its daughter Bi-210. LEADSEP assumes that Bi-210 is completely removed from the Pb-210 preparation on the separation date, and grows in towards secular equilibrium from this point (Bi-210 half-life = 5.01 days).

Counts observed in a series of up to 1000 counting periods are input. Count time refers to the time for each counting period.

### LEADSEP example input file and example output

```
HL031B1.01    Disc/count code
1             Pb tracer no.
PM           Analyst
23.07.87.1100 Pb/Bi separation date
27.07.87.1430 Count date start
27.6          Count time (ksecs) per count period
95.45         Pb tracer recovery (%)
1.05          Pb tracer recovery error
3.9855        Pb tracer mass (g)
0.380         Pb tracer Pb-210 blank (mBq/g)
0.1437        Sample mass/volume
0.2974        Detector efficiency
3.944         Background
0.098         Background error
780.          Bi-210 counts
795.
897.
876.
897.
974.
```

Ct no.	% ingrowth	No. cts	Pb-210	error
1	42.4	780.	1396.447	59.882 *
2	44.9	795.	1348.100	57.031 *
3	47.3	897.	1471.376	57.108 *
4	49.6	876.	1365.584	53.914 *
5	51.7	897.	1343.675	52.185 *
6	53.8	974.	1418.342	52.034 *
Total	48.3	5219.	1390.447	22.933 *
				28.542 **

- Note: 1) Pb-210 calculated to date of Pb/Bi sepn  
2) Errors marked \* are due to counting statistics only  
3) Errors marked \*\* are due to counting statistics plus recovery error  
4) Calculated using program LEADSEP

## **LEDPO**

*Application:* Calculation of Po-210 and Pb-210 activities in a sample at date of collection, using two Po-210 determinations, one of Po-210 activity concentration in the sample, the other of Po-210 activity (after an ingrowth period) in a separated Pb-210 portion.

### *Discussion*

LEDPO makes the following assumptions:

- (1) Po-210 activity concentration is determined in the sample on some date after sample collection. This result must be corrected to make allowance for decay of Po-210 and ingrowth from its parents.
- (2) Pb-210 is separated from Ra-226, Bi-210 and Po-210 on an aliquot of the sample on a date after sample collection. A known activity of Po-208 or Po-209 tracer is then added to the Pb-210 extract. A portion of the resulting solution is removed to determine lead recovery in the separation procedure (usually using a stable lead tracer/carrier).
- (3) After an ingrowth period, the Po-210 activity in the lead solution is determined. As the polonium tracer was added prior to removal of the aliquot for determination of lead recovery (step 2), the measured Po-210 activity relates to the Pb-210 activity in the solution before removal of this aliquot.

Estimates of the Ra-226 activity and Rn-222 retention in the sample are required. Ra-226 is assumed to be unsupported.

If only a Pb-210 determination is required, the sample Po-210 activity concentration determination need not be carried out. If the Po-210 sample activity concentration is to be determined, knowledge of the position of equilibrium between Pb-210 and Bi-210 is required; this is input as the activity ratio Bi-210/Pb-210 at the date of sample collection.

LEDPO example input file and example output

```

06.08.90    Date sample collection
3.772      Ra-226 activity concentration
0.041      Ra-226 activity conc error
50.        Rn-222 retention (%)
10.        Rn-222 retention error
1.0        Bi-210/Pb-210 ratio at collection date
0.05       Bi-210/Pb-210 ratio error
08.08.90   Date 1st Po-210 determination
55.723     Sample Po-210 activity conc at 1st determination
0.626      Error
09.08.90   Date Pb separation
1.0866     Sample mass/volume
86.11      Pb tracer recovery (%)
0.75       Pb tracer recovery error
4.8156     Pb tracer mass (g)
0.081      Pb tracer Pb-210 blank (mBq/g)
23.07.91   Date 2nd Po-210 determination
146.282    Solution Po-210 activity at 2nd determination
24.565     Error
HP043V.01  Code for 1st Po-210 determination
HP116V.01  Code for 2nd Po-210 determination
HR013R.01  Code for Ra-226 determination

```

Po-210		Pb-210	
Activity	Error	Activity	Error
54.328	.718	194.258	32.726

- Note: 1) Po-210 and Pb-210 calculated to date sample collected  
 2) 1st Po determination 2. days after sample collected  
 3) Pb separation 3. days after sample collected  
 4) 2nd Po determination 348. days after Pb separation  
 5) Relative contributions to the Po-210 activities observed at the two determinations are:

	Ra-226	Pb-210	Bi-210	Po-210	Tracer
Det 1	.0000	.0044	.0304	.9653	
Det 2	.0000	.9982			.0018

- 6) Calculated using program LEDPO



## NUCLIDE2

*Application:* Calculation of activity of 2nd nuclide in a decay series using measurements of its parent and daughter.

### *Discussion*

3 nuclides decay in series:

1 ----> 2 ----> 3 ---->

Nuclide 1 is assumed to be unsupported.

We measure the activities of nuclides 1 and 3 at time  $t = 0$ . We then measure the activity of nuclide 3 at time  $t = T$  (generally,  $T$  will be of the order of or greater than the half-life of nuclide 3). NUCLIDE2 is used to subsequently calculate the activity of nuclide 2 at time  $t = 0$ .

Note: in the case of Ac-227/Th-227/Ra-223, input only 98.62% of total Ac-227 activity, as 1.38% of Ac-227 decays via a side-branch to Po-215.

## POLCOR

*Application:* Correction of Po-210 activity to date of collection, given Pb-210 activity in the sample at date of collection.

### *Discussion*

POLCOR is used where Po-210 activity has been determined in a sample with a delay between sample collection and Po-210 determination (see POLLY and POL208). Pb-210 activity in the sample is determined by a suitable method (e.g. gamma spectrometry or beta counting methods) and calculated to date of collection; this information is used by POLCOR to correct the Po-210 activity back to collection date.

Pb-210 is assumed to be unsupported in the sample.

Knowledge of the position of equilibrium between Pb-210 and Bi-210 is required; this is input as the activity ratio Bi-210/Pb-210 at the date of sample collection.

Po-210 and Pb-210 activity units must be identical in the input.

### POLCOR example input file and example output

```
20.08.89    Date sample collection
196.22      Pb-210 activity
18.86       Standard error on Pb-210
1.0         Bi-210/Pb-210 ratio at collection date
0.05        Bi-210/Pb-210 ratio error
22.08.89    Date Po-210 determination
235.36      Po-210 activity
15.22       Standard error on Po-210
BL022Bl.01  Code for Pb-210 determination
BP533V.01   Code for Po-210 determination
```

```
          Po-210
Activity  Error
235.754   15.375
```

- Note: 1) Po-210 calculated to date sample collected  
2) Po-210 separated 2. days after sample collected  
3) Relative contributions to the Po-210 activity observed are:
- | Pb-210 | Bi-210 | Po-210 |
|--------|--------|--------|
| .0011  | .0073  | .9917  |
- 4) Calculated using program POLCOR

## POLLY

*Application:* Determination of Po-210 by alpha spectrometry.

*Tracer isotope:* Po-209

### *Spectrum*

Po-209: essentially a singlet peak (4.88 MeV, 99.43%; 4.62 MeV, 0.57%).

Po-210: a singlet peak (5.30 MeV, 100%).

### *Discussion*

POLLY assumes complete separation of Po-210 from both Pb-210 and Bi-210 on the separation date. Po-210 is consequently calculated back to separation date assuming that it is unsupported on the disc.

POLLY assumes that the tracer activity concentration is that on the calibration date, and allows for decay of Po-209 between calibration date and count date.

Where separation date is later than sample collection date, a measure of Pb-210/Bi-210 support in the sample is necessary to correct the results back to collection date (see LEDPO, POLON and POLCOR).

### POLLY example input file and example output

polly	Program
05.07.89	Separation date (Pb-Bi/Po)
09.07.89	Count date
112.048	Count time (ksecs)
10.	Tracer mass/vol
5.154	Tracer activity conc
2.365	Sample mass/volume
0.2157	Detector efficiency
0.109	Po-209 bgd
0.015	Po-209 bgd error
0.066	Po-210 bgd
0.010	Po-210 bgd error
1221.	Po-209 counts
3989.	Po-210 counts
0.098	% Tailing (Po-209:Po-210)
0.012	Error in tailing ratio
05.07.88	Calibration date (Po-209)
GH 12 V	Analyst; Po-209 Tracer no.; Detector

Po-209 recovery = 97.4 +/- 2.8 %

Po-210	
Activity	Error
72.970	2.427

- Note: 1) Disc counted 4. days after separation  
Po-210 calculated to date of separation  
2) Errors are one std deviation due to counting statistics only  
3) Calculated using program POLLY

## POL208

*Application:* Determination of Po-210 by alpha spectrometry.

*Tracer isotope:* Po-208

### *Spectrum*

Po-208: a singlet peak (5.11 MeV, 100%).

Po-210: a singlet peak (5.30 MeV, 100%).

### *Discussion*

POL208 assumes complete separation of Po-210 from both Pb-210 and Bi-210 on the separation date. Po-210 is consequently calculated back to separation date assuming that it is unsupported.

POL208 assumes that the tracer activity concentration is that on the calibration date, and allows for decay of Po-208 between calibration date and count date.

Where separation date is later than sample collection date, a measure of Pb-210/Bi-210 support in the sample is necessary to correct the results back to collection date (see LEDPO, POLON and POLCOR).

### POL208 example input file and example output

pol208	Program
27.04.88	Separation date (Pb-Bi/Po)
09.05.88	Count date
148.250	Count time (ksecs)
10.	Tracer mass/volume
8.146	Tracer activity conc
7.4231	Sample mass/volume
0.2157	Detector efficiency
0.073	Po-208 bgd
0.006	Po-208 bgd error
0.045	Po-210 bgd
0.008	Po-210 bgd error
1910.	Po-208 counts
2204.	Po-210 counts
0.207	% Tailing (Po-208:Po-210)
0.018	Error in tailing ratio
13.03.87	Calibration date (Po-208)
GH 2 V	Analyst; Po-208 Tracer no.; Detector

Po-208 recovery = 95.9 +/- 2.2 %

Po-210	
Activity	Error
10.245	.323

- Note: 1) Disc counted 12. days after separation  
Po-210 calculated to date of separation  
2) Errors are one std deviation due to counting statistics only  
3) Calculated using program POL208

## POLON

*Application:* Calculation of Po-210 and Pb-210 activities in a sample at date of collection, using two separate Po-210 activity determinations.

### *Discussion*

POLON is used where Po-210 activity has been determined in a sample on two separate occasions after sample collection (see POLLY and POL208).

Estimates of the Ra-226 activity and Rn-222 retention in the sample are required. Ra-226 is assumed to be unsupported.

Knowledge of the position of equilibrium between Pb-210 and Bi-210 is required; this is input as the activity ratio Bi-210/Pb-210 at the date of sample collection.

Activity units for the Ra-226 and two Po-210 determinations must be identical in the input.

### POLON example input file and example output

```
06.02.87    Date sample collection
12.353      Ra-226 activity
0.859       Ra-226 activity error
50.         Rn-222 retention (%)
10.         Rn-222 retention error
1.00        Bi-210/Pb-210 ratio at collection date
0.05        Bi-210/Pb-210 ratio error
08.02.87    Date 1st Po-210 determination
3487.584    Po-210 activity at 1st determination
105.296     Standard error on 1st determination
23.07.89    Date 2nd Po-210 determination
4155.053    Po-210 activity at 2nd determination
118.403     Standard error on 2nd determination
DP054V.01   Code for 1st Po-210 determination
DP116V.01   Code for 2nd Po-210 determination
DR027Y.01   Code for Ra-226 determination
```

Po-210		Pb-210	
Activity	Error	Activity	Error
3478.219	106.393	4417.768	127.108

- Note: 1) Po-210 and Pb-210 calculated to date sample collected  
2) 1st Po determination 2. days after sample collected  
3) 2nd Po determination 898. days after sample collected  
4) Relative contributions to the Po-210 activities observed at the two determinations are:

	Ra-226	Pb-210	Bi-210	Po-210
Det 1	.0000	.0016	.0110	.9874
Det 2	.0001	.9902	.0004	.0093

- 5) Calculated using program POLON

## **RADB**

*Application:* Calculation of background count rate in the Ra-224 + Ra-223 and Rn-220 count areas for use by programs RAD224, RAD226, RAD346 and RADPO.

### *Discussion*

RADB subtracts the contributions of Rn-222 and Ac-225 from the (Ra-224 + Ra-223) area and Fr-221 from the Rn-220 area in a background radium spectrum. The Po-214 peak area is used as a measure of Rn-222, and the At-217 peak area is used as a measure of Ac-225 and Fr-221.

## **RAD224**

*Application:* determination of Ra-226 and Ra-223 by alpha spectrometry

*Tracer isotope:* Ra-224 (U-232/Th-228/Ra-224)

### *Spectrum*

This spectrum is a complex one, especially if Ra-225 daughters are present.

Ra-226: a doublet (4.78 MeV, 94.4%; 4.60 MeV, 5.6%).

Ra-224 + Ra-223 + Rn-222 + Ac-225:

this area is used to calculate total (Ra-224 + Ra-223) activity after subtracting Rn-222 (measured using Po-214) and Ac-225 (measured using At-217 and/or Po-213). An upper energy boundary in MeV is required to calculate the decay yields for Ra-223 and Ac-225 in the area measured. If Ac-225 is present, this boundary should be greater than 5.83 MeV.

Rn-220 + Bi-211:

this area is used in conjunction with the Po-215 and the (Ra-224 + Ra-223) areas to give the Rn-220 retention value and consequently Ra-224 activity. The contribution of Rn-219 daughters to this area is low (16.07%) relative to that in the (Po-216 + Rn-219 + Bi-211) area; hence this area is particularly useful when the Ra-223/Ra-224 ratio is high. The Ra-225 daughter Fr-221 has a high-yield (84.74%) peak in this area, however; hence its use should be avoided when there is substantial Ra-225 daughter activity present.

Po-216 + Rn-219 + Bi-211:

this area is used in conjunction with the Po-215 and the (Ra-224 + Ra-223) areas to give the Rn-220 retention value and consequently Ra-224 activity. A lower energy boundary in MeV is required to calculate the decay yield for Rn-219 in the area measured, as there is a minor peak (7.5%) at 6.425 MeV. If the energy boundary is given as less than 6.43 MeV, this peak is included in the calculations.

At-217: a singlet peak (7.07 MeV, 99.9%).

Po-215: a singlet peak (7.39 MeV, 99.95%).

Po-214: a singlet peak (7.69 MeV, 99.99%).

Po-213: a singlet peak (8.38 MeV, 100%).

### *Discussion*

RAD224 assumes that the tracer is a Th-228 solution with Ra-224 in secular equilibrium.

The tracer activity concentration given should be that at the time of radium/thorium separation. RAD224 assumes this separation is quantitative. The Ra-224 tracer activity remaining at time of counting, integrated over the counting period, is given in the output.

Two areas (Rn-220 + Bi-211) and (Po-216 + Rn-219 + Bi-211) may be used as a measure of Rn-220 retention. If either of these areas are not used, input the number of counts as 0.

If the At-217 and/or Po-213 peaks are not used, input the number of counts as 0.

Po-213 is the daughter of Bi-213 via a 98% decay branch. This peak usually has a pronounced upper-energy tail, the magnitude of which is detection efficiency dependent. Inclusion of the full tail in the analysis window is not always possible due to the Po-212 (daughter of Ra-224) peak at 8.78 MeV. The decay yield for this peak is therefore measured experimentally using a high-activity source of Th-229 in secular equilibrium with its daughters and input as the ratio of counts observed for Po-213 to counts observed for At-217.

The background count rates input for the Ra-224 + Ra-223 and Rn-220 areas must have had contributions from Rn-222, Ac-225 and Fr-221 subtracted using program RADB.

RAD224 example input file and example output

```

05.02.88.1330 Ra/Th separation date (first)
05.02.88.1430 Ra/Ac separation date (last)
06.02.88.1500 Count date start
07.02.88.1330 Count date finish
80.98          Count time (ksecs)
20.8629        Tracer mass/volume
13.723         Tracer activity conc
0.12307        Sample mass/volume
0.3077         Detector efficiency
0.957          Rn-220/Rn-219 retention ratio
0.109          Ra-226 bgd
0.007          Ra-226 bgd error
0.421          Ra-224 bgd
0.017          Ra-224 bgd error
0.047          Rn-220 bgd
0.010          Rn-220 bgd error
0.047          Po-216 bgd
0.010          Po-216 bgd error
0.013          Po-215 bgd
0.008          Po-215 bgd error
Input counts observed in each region. Input = 0. if region not used.
8066.          Ra-226.....measure of Ra-226
4842.          Ra-224 + Rn-222 + Ra-223 + Ac-225...measure of Ra-224 + Ra-223
0.             Rn-220 + Bi-211.....measure of Rn-220
3179.          Po-216 + Rn-219 + Bi-211.....measure of Rn-220
0.             At-217.....use if Ac-225 present
230.          Po-215.....measure of Rn-219
355.          Po-214.....measure of Rn-222
0.             Po-213.....use if Ac-225 present
5.25          Lower energy boundary for Ra-224 area (MeV)
5.72          Upper energy boundary for Ra-224 area (MeV)
6.39          Lower energy boundary for Po-216 area (MeV)
0.121         % Tailing (Ra-226:Ra-224)
0.021         Tailing error
0.270         % Tailing (Po-215:Po-214)
0.042         Tailing error
0.9416        Ratio observed Po-213:At-217
5 Q           U-232 tracer soln. no.; detector

```

Using Po-216 peak as measure of radon retention,  
Ra-224 recovery = 77.2 +/- 1.9 %  
Rn-220 retention = 66.7 +/- 1.7 %

	Ra-226		Ra-223	
	Activity	Error	Activity	Error
	3399.114	89.931	151.519	11.448
	Ra-223/Ra-226		Ra-226/Ra-223	
Ratio	.04458		22.434	
Error	.00323		1.627	

- Note: 1) Disc count started 1.06 days after separation  
2) Ra-223 value adjusted to date of separation  
3) Tracer activity at counting = 214.594  
4) Ra-226 activity on disc = 323.120 +/- 3.608  
5) Errors are one std deviation due to counting statistics only  
6) Calculated using program RAD224



## **RAD225**

*Application:* Determination of Ra-226 by alpha spectrometry.

*Tracer isotope:* Ra-225 (Th-229/Ra-225)

### *Spectrum*

Ra-226: a doublet (4.78 MeV, 94.4%; 4.60 MeV, 5.6%).

Ra-224 + Ra-223 + Rn-222 + Ac-225:

    this region (5.25 - 5.90 MeV) may be measured to apply a tailing correction for the Ra-226 area (see discussion below).

At-217: a singlet peak (7.07 MeV, 99.9%).

Po-215: a singlet peak (7.39 MeV, 99.95%).

Po-214: a singlet peak (7.69 MeV, 99.99%).

Po-213: a singlet peak (8.38 MeV, 100%).

### *Discussion*

RAD225 assumes that the tracer is a Th-229 solution with Ra-225 in secular equilibrium.

The tracer activity concentration given should be that at the time of radium/thorium separation. RAD225 assumes that this separation is quantitative.

Radium/actinium separation time given should be the last point where Ra/Ac separation occurs. RAD225 assumes that at this time there is no actinium present.

Ac-225 ingrowth factor is the calculated Ac-225 ingrown activity, integrated over the count period, as a proportion of the original tracer activity at time of Ra/Th separation.

Both At-217 and Po-213 may be used as tracer peaks, or either may be used alone. If one of these peaks is not used, input the number of counts as 0.

A correction for the tailing due to counts in the 5.25 - 5.90 MeV energy region (Ra-224 + Ra-223 + Rn-222 + Ac-225) into the Ra-226 energy region may be applied. If a default value of 0. counts is input, the program calculates the tailing due to Ac-225, Ra-223 and Rn-222 only via the input At-217, Po-215 and Po-214 counts.

Po-213 is the daughter of Bi-213 via a 98% decay branch. This peak usually has a pronounced upper-energy tail, the magnitude of which is detection efficiency dependent. Inclusion of the full tail in the analysis window is not always possible due to the Po-212 (daughter of Ra-224) peak at 8.78 MeV. The decay yield for this peak is therefore measured experimentally using a high-activity source of Th-229 in secular equilibrium with its daughters and input as the ratio of counts observed for Po-213 to counts observed for At-217.

RAD225 example input file and example output

04.08.89.1515 Ra/Th separation date (first)  
04.08.89.1540 Ra/Ac separation date (last)  
22.08.89.1700 Count date start  
24.08.89.1545 Count date finish  
168.168 Count time (ksecs)  
7.2563 Tracer mass/volume  
14.084 Tracer activity conc  
0.9904 Sample mass/volume  
0.2809 Detector efficiency  
0.016 Ra-226 bgd  
0.007 Ra-226 bgd error  
0.009 At-217 bgd  
0.004 At-217 bgd error  
0.003 Po-213 bgd  
0.003 Po-213 bgd error  
7679. Ra-226 counts  
0. Counts Ra-224 + Ra-223 + Rn-222 + Ac-225 area  
1705. At-217 counts  
62. Po-215 counts  
1702. Po-214 counts  
0. Po-213 counts  
0.058 % Tailing (Ra-226:Ac-225)  
0.015 Error in tailing ratio  
0.095 % Tailing (At-217:Po-214)  
0.023 Error in tailing ratio  
0.105 % Tailing (At-217:Po-215)  
0.048 Error in tailing ratio  
0.9429 Ratio observed Po-213:At-217  
15 R Th-229 Tracer; Detector

Ra-225 recovery (from At-217 peak) = 80.2 +/- 1.9 %

Ra-226	
Activity	Error
204.488	5.489

- Note: 1) Ra/Ac separation .02 days after Ra/Th separation  
2) Count start 18.06 days after Ra/Ac separation  
3) Ac-225 ingrowth factor = .4399  
Po-213 ingrowth factor = .4400  
4) Ra-226 activity on disc = 162.459 +/- 1.856  
5) Errors are one std deviation due to counting statistics only  
6) Calculated using program RAD225

## **RAD226**

*Application:* Determination of Ra-223 and Ra-224 by alpha spectrometry.  
Used in the following situations:

- Ra-226 is determined separately (or by a later count of the same disc with Ra-225 as a tracer). In this case the Ra-226 peak acts essentially as a tracer peak for the Ra-224 and Ra-223 determinations.
- Ra-226 is added as a tracer isotope.
- Radium isotope ratios only are required; no tracer is necessary in this case.

### *Spectrum*

This spectrum is a complex one, especially if Ra-225 daughters are present.

Ra-226: a doublet (4.78 MeV, 94.4%; 4.60 MeV, 5.6%).

Ra-224 + Ra-223 + Rn-222 + Ac-225:

this area is used to calculate total (Ra-224 + Ra-223) activity after subtracting Rn-222 (measured using Po-214) and Ac-225 (measured using At-217 and/or Po-213). An upper energy boundary in MeV is required to calculate the decay yields for Ra-223 and Ac-225 in the area measured. If Ac-225 is present, this boundary should be greater than 5.83 MeV.

Rn-220 + Bi-211:

this area is used in conjunction with the Po-215 and the (Ra-224 + Ra-223) areas to give the Rn-220 retention value and consequently Ra-224 activity. The contribution of Rn-219 daughters to this area is low (16.07%) relative to that in the (Po-216 + Rn-219 + Bi-211) area; hence this area is particularly useful when the Ra-223/Ra-224 ratio is high. The Ra-225 daughter Fr-221 has a high-yield (84.74%) peak in this area, however; hence its use should be avoided when there is substantial Ra-225 daughter activity present.

Po-216 + Rn-219 + Bi-211:

this area is used in conjunction with the Po-215 and the (Ra-224 + Ra-223) areas to give the Rn-220 retention value and consequently Ra-224 activity. A lower energy boundary in MeV is required to calculate the decay yield for Rn-219 in the area measured, as there is a minor peak (7.5%) at 6.425 MeV. If the energy boundary is given as less than 6.43, this peak is included in the calculations.

At-217: a singlet peak (7.07 MeV, 99.9%).

Po-215: a singlet peak (7.39 MeV, 99.95%).

Po-214: a singlet peak (7.69 MeV, 99.99%).

Po-213: a singlet peak (8.38 MeV, 100%).

### *Discussion*

Two areas (Rn-220 + Bi-211) and (Po-216 + Rn-219 + Bi-211) may be used as a measure of Rn-220 retention. If either of these areas is not used, input the number of counts as 0.

If the At-217 and/or Po-213 peaks are not used, input the number of counts as 0.

RAD226 example input file and example output

```

18.07.89.1015 Th/Ra separation date (first)
18.07.89.1125 Th/Ra separation date (last)
18.07.89.1620 Count date start
20.07.89.0915 Count date finish
147.295      Count time (ksecs)
10.713      Sample Ra-226 activity conc
0.688      Error in sample Ra-226 conc
4.9077      Sample mass/volume
0.          Mass/volume of added tracer
0.          Tracer Ra-226 activity conc.
0.3077      Detector efficiency
0.957      Rn-220/Rn-219 retention ratio
0.107      Ra-226 bgd
0.007      Ra-226 bgd error
0.435      Ra-224 bgd
0.014      Ra-224 bgd error
0.040      Rn-220 bgd
0.009      Rn-220 bgd error
0.053      Po-216 bgd
0.006      Po-216 bgd error
0.003      Po-215 bgd
0.002      Po-215 bgd error
Input counts observed in each region. Input = 0. if region not used.
1950.      Ra-226.....measure of Ra-226
2425.      Ra-224 + Rn-222 + Ra-223 + Ac-225...measure of Ra-224 + Ra-223
1216.      Rn-220 + Bi-211(16%).....measure of Rn-220 retn.
1931.      Po-216 + Rn-219 + Bi-211.....measure of Rn-220 retn.
42.        At-217.....use if Ac-225 present
439.      Po-215.....measure of Ra-223
110.      Po-214.....measure of Rn-222
0.         Po-213.....use if Ac-225 present
5.25      Lower energy boundary for Ra-224 area (MeV)
5.88      Upper energy boundary for Ra-224 area (MeV)
6.40      Lower energy boundary for Po-216 area (MeV)
0.121     % Tailing (Ra-226:Ra-224)
0.021     Error
0.270     % Tailing (Po-215:Po-214)
0.042     Error
0.9374    Ratio observed Po-213:At-217
Q         Detector

```

Ra-226 recovery = 81.1 +/- 5.5 %

Rn-220	Rn-220 ret		Ra-224		Ra-223	
Peak	%		Activity	Error	Activity	Error
Rn-220	69.0	2.4	10.913	.809	3.607	.304
Po-216	69.5	2.8	10.945	.835	3.579	.308
Both	69.2	2.1	10.913	.816	3.587	.319

	Ra-224/Ra-226	Ra-223/Ra-226	Ra-224/Ra-223	Ra-223/Ra-224
Ratio	1.019	.335	3.042	.329
Error	.039	.021	.217	.023

- Note: 1) Disc count started .25 days after Th/Ra separation  
 2) Ra-223 & Ra-224 values adjusted to Th/Ra separation date  
     Decay factors: Ra-224 .8148  
                   Ra-223 .9356  
 3) Ra-226 activity on disc = 42.614 +/- .979  
 4) Errors are one std deviation due to counting statistics only  
 5) Calculated using program RAD226

Po-213 is the daughter of Bi-213 via a 98% decay branch. This peak usually has a pronounced upper-energy tail, the magnitude of which is detection efficiency dependent. Inclusion of the full tail in the analysis window is not always possible due to the Po-212 (daughter of Ra-224) peak at 8.78 MeV. The decay yield for this peak is therefore measured experimentally using a high-activity source of Th-229 in secular equilibrium with its daughters and input as the ratio of counts observed for Po-213 to counts observed for At-217.

The background count rates input for the Ra-224 + Ra-223 and Rn-220 areas must have had contributions from Rn-222, Ac-225 and Fr-221 subtracted using program RADB.

There are four tracer options in RAD226:

No Ra-226 in sample Ra-226 tracer added	Input sample Ra-226 concentration as 0.
Ra-226 sample conc. known Ra-226 tracer added	RAD226 sums Ra-226 activity from sample and tracer
Ra-226 sample conc. known No Ra-226 tracer added	Input tracer activity concentration as 0.
Ra-226 sample conc. not known No Ra-226 tracer added	RAD226 calculates radium isotope ratios only

## **RAD346**

*Application:* Determination of Ra-223, Ra-224 and Ra-226 by alpha spectrometry.  
Generally used where radium recovery is determined via a later count for Ra-225 daughters, and Ra-226 activity is low.

*Tracer isotope:* Radium recovery known.

### *Spectrum*

This spectrum is a complex one, especially as Ra-225 daughters are usually present.

Ra-226: a doublet (4.78 MeV, 94.4%; 4.60 MeV, 5.6%).

Ra-224 + Ra-223 + Rn-222 + Ac-225:

this area is used to calculate total (Ra-224 + Ra-223) activity after subtracting Rn-222 (measured using Po-214) and Ac-225 (measured using At-217 and/or Po-213). An upper energy boundary in MeV is required to calculate the decay yields for Ra-223 and Ac-225 in the area measured. If Ac-225 is present, this boundary should be greater than 5.83 MeV.

Rn-220 + Bi-211:

this area is used in conjunction with the Po-215 and the (Ra-224 + Ra-223) areas to give the Rn-220 retention value and consequently Ra-224 activity. The contribution of Rn-219 daughters to this area is low (16.07%) relative to that in the (Po-216 + Rn-219 + Bi-211) area; hence this area is particularly useful when the Ra-223/Ra-224 ratio is high. The Ra-225 daughter Fr-221 has a high-yield (84.74%) peak in this area, however; hence its use should be avoided when there is substantial Ra-225 daughter activity present.

Po-216 + Rn-219 + Bi-211:

this area is used in conjunction with the Po-215 and the (Ra-224 + Ra-223) areas to give the Rn-220 retention value and consequently Ra-224 activity. A lower energy boundary in MeV is required to calculate the decay yield for Rn-219 in the area measured, as there is a minor peak (7.5%) at 6.425 MeV. If the energy boundary is given as less than 6.43, this peak is included in the calculations.

Po-215: a singlet peak (7.39 MeV, 99.95%).

Po-214: a singlet peak (7.69 MeV, 99.99%).

At-217: a singlet peak (7.07 MeV, 99.9%).

Po-213: a singlet peak (8.38 MeV, 100%).

### *Discussion*

Two areas (Rn-220 + Bi-211) and (Po-216 + Rn-219 + Bi-211) may be used as a measure of Rn-220 retention. If either of these areas is not used, input the number of counts as 0.

If the At-217 and/or Po-213 peaks are not used, input the number of counts as 0.

Po-213 is the daughter of Bi-213 via a 98% decay branch. This peak usually has a pronounced upper-energy tail, the magnitude of which is detection efficiency dependent. Inclusion of the full tail in the analysis window is not always possible due to the Po-212 (daughter of Ra-224) peak at 8.78 MeV. The decay yield for this peak is therefore measured

experimentally using a high-activity source of Th-229 in secular equilibrium with its daughters and input as the ratio of counts observed for Po-213 to counts observed for At-217.

The background count rates input for the Ra-224 + Ra-223 and Rn-220 areas must have had contributions from Rn-222, Ac-225 and Fr-221 subtracted using program RADB.

RAD346 assumes that errors in the knowledge of detector efficiency are negligible.

#### RAD346 example input file

```

07.02.90.0930 Th/Ra separation date (first)
07.02.90.1055 Ra/Ac separation date (last)
07.02.90.1730 Count date start
09.02.90.1345 Count date finish
159.205      Count time (ksecs)
82.77       Radium recovery (%)
2.13        Radium recovery error
0.79811     Sample mass/volume
0.3077      Detector efficiency
0.957       Rn-220/Rn-219 retention ratio
0.112       Ra-226 bgd
0.006       Ra-226 bgd error
0.335       Ra-224 bgd
0.024       Ra-224 bgd error
0.035       Rn-220 bgd
0.009       Rn-220 bgd error
0.044       Po-216 bgd
0.007       Po-216 bgd error
0.004       Po-215 bgd
0.002       Po-215 bgd error
Input counts observed in each region. Input = 0. if region not used.
5218.       Ra-226.....measure of Ra-226
1557.       Ra-224 + Rn-222 + Ra-223 + Ac-225...measure of Ra-224 + Ra-223
502.        Rn-220 + Bi-211(16%).....measure of Rn-220 retn.
726.        Po-216 + Rn-219 + Bi-211.....measure of Rn-220 retn.
8.          At-217.....use if Ac-225 present
157.        Po-215.....measure of Ra-223
687.        Po-214.....measure of Rn-222
0.          Po-213.....use if Ac-225 present
5.25        Lower energy boundary for Ra-224 area (MeV)
5.88        Upper energy boundary for Ra-224 area (MeV)
6.40        Lower energy boundary for Po-216 area (MeV)
0.121       % Tailing (Ra-226:Ra-224)
0.021       Error
0.270       % Tailing (Po-215:Po-214)
0.042       Error
0.9374      Ratio observed Po-213:At-217
HS836Q.01   Recovery count code

```

RAD346 example output

Ra-226						
Activity			Error			
160.637			4.700			
Rn-220	Rn-220 ret		Ra-224		Ra-223	
Peak	%		Activity	Error	Activity	Error
Rn-220	75.74	5.70	23.960	1.762	6.509	.743
Po-216	71.96	5.86	23.563	2.599	6.851	.810
	73.85	5.12	23.767	1.799	6.676	.736
	Ra-224/Ra-226		Ra-223/Ra-226		Ra-224/Ra-223	
Ratio	.148		.042		3.560	
Error	.011		.004		.458	

- Note: 1) Disc count started .33 days after Ra/Th separation  
 2) Ra-223 & Ra-224 values adjusted to Ra/Th separation date  
     Decay factors: Ra-224 .7927  
                     Ra-223 .9272  
 3) Ra-226 activity on disc = 106.116 +/- 1.477  
 4) Errors are one std deviation due to counting statistics only  
 5) Calculated using program RAD346



## **RAD68**

*Application:* Determination of Ra-228 by alpha spectrometry.

*Tracer isotope:* known sample Ra-226 activity concentration

### *Spectrum*

Ra-226: a doublet (4.78 MeV, 94.4%; 4.60 MeV, 5.6%).

Ra-224: the upper-energy Ra-224 peak (5.686 MeV, 94.98%) is used as a measure of Ra-224 and consequently its parent Th-228. The Rn-222 peak (5.49 MeV, 99.9%) and Po-210 peak (5.30 MeV, 100%, ingrown on the disc from Ra-226 via Rn-222 and Pb-210) prevent use of the 5% Ra-224 peak at 5.44 MeV.

Po-214: a singlet peak (7.69 MeV, 99.99%). This peak is used as a measure of Rn-222 daughters for calculation of tailing (primarily from the Po-218 peak) into Ra-224.

### *Discussion*

RAD68 is used for analysis for Ra-228 using a radium disc after a period (usually at least 6 months) for ingrowth of Th-228 and Ra-224.

Due to the proximity of the Rn-222 peak, only a relatively small energy interval (approximately 0.15-0.17 MeV) can be used for measurement of the Ra-224 peak at 5.686 MeV. Although this peak theoretically represents 94.98% of Ra-224 decays, the high lower-energy cutoff for this region can mean loss of counts, particularly for poor-resolution discs. Consequently, RAD68 requires that an estimate of the ratio of observed Ra-224 counts to total Ra-224 decays be input. This estimate can be obtained from an analysis of the Ra-226 peaks in the same spectrum. The Ra-226 peak at 4.78 MeV (94.4%) is measured using an energy interval of the same size as that used for the Ra-224 measurement. The required ratio for Ra-224 (measured at 5.69 MeV:total) is then obtained from the ratio for Ra-226 (measured at 4.78 MeV:total) multiplied by  $(0.9498/0.944) = 1.006$ .

RAD68 example input file and example output

```

06.08.87    Th/Ra separation date
29.06.89    Count date
82.438      Count time (ksecs)
69.14       Sample Ra-226 activity conc
3.76        Error in sample Ra-226 conc
0.9842      Sample mass/volume
0.2809      Detector efficiency
0.014       Ra-226 bgd
0.008       Ra-226 bgd error
0.005       Ra-224 bgd
0.005       Ra-224 bgd error
1284.       Ra-226 counts
860.        Ra-224 counts (upper peak)
548.        Po-214 counts
0.197       % Tailing (Ra-224:Po-214)
0.049       Tailing error
0.9440      Ratio observed Ra-224 : total Ra-224
R           Detector

```

Ra-226 recovery = 81.4 +/- 5.0 %

	Ra-228	
	Activity	Error
	112.205	7.861
	Ra-228/Ra-226	Ra-226/Ra-228
Ratio	1.623	.616
Error	.072	.027

- Note: 1) Disc counted 693. days after separation  
 2) Ra-228 calculated to date of separation  
 3) Ra-224 build-up factor = .4368  
 4) Ra-226 activity on disc = 55.398 +/- 1.548  
 5) Errors are one std deviation due to counting statistics only  
 6) Calculated using program RAD68

## **RADPO**

*Application:* Determination of Ra-223 and Ra-224 by alpha spectrometry.

Po-212 used as a measure of Rn-220.

Used in the following situations:

- Ra-226 is determined separately (or by a later count of the same disc with Ra-225 as a tracer). In this case the Ra-226 peak acts essentially as a tracer peak for the Ra-224 and Ra-223 determinations.
- Ra-226 is added as a tracer isotope.
- Radium isotope ratios only are required; no tracer is necessary in this case.

### *Spectrum*

This spectrum is a complex one, especially if Ra-225 daughters are present.

Ra-226: a doublet (4.78 MeV, 94.4%; 4.60 MeV, 5.6%).

Ra-224 + Ra-223 + Rn-222 + Ac-225:

this area is used to calculate total (Ra-224 + Ra-223) activity after subtracting Rn-222 (measured using Po-214) and Ac-225 (measured using At-217 and/or Po-213). An upper energy boundary in MeV is required to calculate the decay yields for Ra-223 and Ac-225 in the area measured. If Ac-225 is present, this boundary should be greater than 5.83 MeV.

At-217: a singlet peak (7.07 MeV, 99.9%).

Po-215: a singlet peak (7.39 MeV, 99.95%).

Po-214: a singlet peak (7.69 MeV, 99.99%).

Po-213: a singlet peak (8.38 MeV, 100%).

Po-212: a singlet peak (8.78 MeV, 100% of Po-212). This area is used in conjunction with the Po-215 and the (Ra-224 + Ra-223) areas to give the Rn-220 retention value and consequently Ra-224 activity.

### *Discussion*

RADPO is used in preference to program RAD226 when the Ra-223/Ra-224 ratio is high. In this case, interference from Rn-219 and daughters to the Rn-220 and Po-216 peak areas used by RAD226 would adversely affect the sensitivity of the Ra-224 determination. Program RADPO avoids this problem by using the Po-212 peak as a measure of Rn-220 and hence Ra-224. The disadvantage of using the Po-212 peak is the low count rate due to two factors:

- the slow ingrowth of the parents Pb-212 ( $t_{1/2} = 10.64$  h) and Bi-212 ( $t_{1/2} = 60.60$  m); and
- Po-212 is produced by a 64.06% branch decay of Bi-212.

RADPO assumes quantitative separation of radium from thorium on the Th/Ra separation date. Quantitative separation of radium from lead and bismuth on the Ra/Pb-Bi separation date is assumed. It is then assumed that the Pb-212 ( $t_{1/2} = 10.64$  h) and Bi-212 ( $t_{1/2} = 60.60$  m) parents of Po-212 grow in on the preparation at a constant rate, i.e. that the Rn-220 retention remains constant from the time of Ra/Pb-Bi separation. Although this last condition cannot be achieved in practice using current source preparation techniques, if the time between the last Ra/Pb-Bi separation and electrodeposition steps is kept short (less than

RADPO example input file and example output

```

07.08.90.1115 Th/Ra separation date
07.08.90.1310 Ra/Pb separation date
08.08.90.1515 Count date start
10.08.90.0910 Count date finish
150.948      Count time (ksecs)
9.188        Sample Ra-226 activity conc
0.435        Error in sample Ra-226 conc
6.6918       Sample mass/volume
0.           Mass/volume of added tracer
0.           Tracer Ra-226 activity conc
0.2357       Detector efficiency
0.957        Rn-220/Rn-219 retention ratio
0.098        Ra-226 bgd
0.008        Ra-226 bgd error
0.363        Ra-224 bgd
0.014        Ra-224 bgd error
0.003        Po-215 bgd
0.002        Po-215 bgd error
0.003        Po-212 bgd
0.002        Po-212 bgd error
Input counts observed in each region. Input = 0. if region not used.
1803.        Ra-226.....measure of Ra-226
1795.        Ra-224 + Ra-223 + Rn-222 + Ac-225...measure of Ra-224 + Ra-223
45.          At-217.....use if Ac-225 present
790.         Po-215.....measure of Rn-219
80.          Po-214.....measure of Rn-222
40.          Po-213.....use if Ac-225 present
262.         Po-212.....measure of Rn-220
5.25         Lower energy boundary for Ra-224 area (MeV)
5.88         Upper energy boundary for Ra-224 area (MeV)
0.105        % Tailing (Ra-226:Ra-224)
0.020        Error
0.249        % Tailing (Po-215:Po-214)
0.030        Error
2.710        % Tailing (Po-212:Po-213)
0.075        Error
0.9374       Ratio observed Po-213:At-217
Q            Detector

```

Ra-226 recovery = 81.7 +/- 4.3 %  
 Rn-220 retention = 70.9 +/- 3.0 %

	Ra-224		Ra-223	
	Activity	Error	Activity	Error
	4.165	.318	6.204	.403
	Ra-224/Ra-226	Ra-223/Ra-226	Ra-224/Ra-223	Ra-223/Ra-224
Ratio	.453	.675	.671	1.490
Error	.027	.030	.048	.107

- Note: 1) Disc count started 1.167 days after Th/Ra separation  
 2) Disc count started 1.087 days after Ra/Pb-Bi separation  
 3) Ra-224 & Ra-223 values adjusted to Th/Ra separation date  
     Decay factors: Ra-224 .6830  
                     Ra-223 .8841  
     Po-212 ingrowth factor:1.0374  
 4) Ra-226 activity on disc = 50.210 +/- 1.199  
 5) Errors are one std deviation due to counting statistics only  
 6) Calculated using program RADPO

1 hour) and the disc is kept under counting conditions prior to counting, the resultant error should be small.

The Po-212 ingrowth factor given is the (time integrated) ratio of the activity of Po-212 to that of Rn-220 over the counting period, assuming constant Rn-220 retention between Ra/Pb-Bi separation date and the end of the counting period. It does not include the 0.6406 branch decay factor (this factor is allowed for by the program, however).

The % tailing factor (Po-212:Po-213) is the ratio of the count rate observed in the Po-212 analysis area to that in the Po-213 analysis area due to the upper-energy tail of the Po-213 peak. This factor varies with detection efficiency. The Po-213:At-217 observed ratio is dependent on a number of factors (analysis area chosen for Po-213; Po-213 upper-energy tailing; Po-213 is the daughter of Bi-213 via a 98% decay branch). Both the % tailing factor (Po-212:Po-213) and the Po-213:At-217 count rate ratio are measured experimentally using a high-activity source of Th-229 in secular equilibrium with its daughters.

RADPO assumes that the Ra/Pb-Bi separation date is also the last Ra/Ac separation date, and calculates the relative ingrowth of Po-213 and Ac-225 on the source (the half-life of Bi-213 is 46 minutes).

If the At-217 and/or Po-213 peaks are not used, input the number of counts as 0.

The background count rates input for the Ra-224 + Ra-223 area must have had contributions from Rn-222, Ac-225 and Fr-221 subtracted using program RADB.

There are four tracer options in RADPO:

No Ra-226 in sample Ra-226 tracer added	Input sample Ra-226 concentration as 0.
Ra-226 sample conc. known Ra-226 tracer added	RADPO sums Ra-226 activity from sample and tracer
Ra-226 sample conc. known No Ra-226 tracer added	Input tracer activity concentration as 0.
Ra-226 sample conc. not known No Ra-226 tracer added	RADPO calculates radium isotope ratios only

## **RATH228**

*Application:* Determination of Ra-228 by alpha spectrometry utilising a Th-228 determination on a redissolved radium disc deposit.

### *Discussion*

Program RATH228 is used where determination of Ra-228 by measurement of the ingrown Ra-224 peak on a radium disc is not possible e.g. due to interference from the Rn-222 and Po-218 peaks.

In this case, the deposit is washed from the disc, Th-229 tracer added to the solution and a thorium disc prepared and counted. Program THOR is used with the sample mass/volume given as 1.0. This gives the Th-228 activity on the radium disc.

Th-228 determination date is the deposition date used in THOR.

# RATH228 example input file and example output

## Details from radium disc:

04.11.88 Ra/Th separation date  
 59.601 Activity Ra-226 on disc  
 1.643 Error: Activity Ra-226 on disc  
 PM Analyst  
 OS066 Disc name

## Details from thorium disc:

19.07.89 Th-228 determination date  
 16.186 Activity Th-228 on radium disc  
 0.966 Error: Activity Th-228 on radium disc  
 GH Analyst  
 14 Th-229 tracer soln. no.  
 OS154J.01 Disc name

	Ra-228/Ra-226	Ra-226/Ra-228
Ratio	1.261	.793
Error	.083	.052

- Note: 1) Th-228 determined 257. days after separation  
 Ra-228 calculated to date of separation  
 2) Th-228 build-up factor =.2154  
 3) Calculated using program RATH228

## TAIL

*Application:* Calculation of tailing of a higher-energy peak into a lower-energy peak area.

## TAIL example input file and example output

2 No. of tailing peak areas (up to 9)  
 148.692 Count time  
 0.014 Peak #1 bgd  
 0.007 Peak #1 bgd error  
 0.004 Peak #2 bgd  
 0.003 Peak #2 bgd error  
 0.006 Peak #3 bgd  
 0.004 Peak #3 bgd error  
 95328. Peak #1 counts  
 223. Peak #2 counts  
 248. Peak #3 counts

Peak no.	Tail(%)	error	Count rate	error
1			641.096	2.076
2	.233	.016	1.496	.101
3	.259	.017	1.662	.106

- Note: 1) Tailing represents the no. of counts observed in the lower-energy peak area as a percentage of the no. of counts observed in the high-energy peak area (peak no.1).  
 2) Errors are one std deviation due to counting statistics only  
 3) Calculated using program TAIL

## THOR

*Application:* Determination of Th-232, Th-230 and Th-228 by alpha spectrometry.

*Tracer isotope:* Th-229

### *Spectrum*

Th-232: essentially a doublet (4.02 MeV, 77%; 3.96 MeV, 23%; 3.83 MeV, 0.2%).

Th-230: essentially a doublet (4.69 MeV, 76.3%; 4.62 MeV, 23.4%; 4.48 MeV, 0.15%; 4.44 MeV, 0.02%) situated just below the broad Th-229 peak band; in addition, some minor (0.25% total) Th-229 peaks lie under the Th-230 upper-energy peak and cannot be separated from it. Hence, the accuracy of the tailing correction is critical for spectra where the Th-229/Th-230 ratio is high.

Th-229: this is a complex spectrum. THOR assumes that the 99.75% of counts above the Th-230 peaks are measured.

Th-228: essentially a doublet (5.42 MeV, 72.7%; 5.34 MeV, 26.7%; 5.21 MeV, 0.36%; 5.17 MeV, 0.18%; 5.14 MeV, 0.05%). The lower-energy Ra-224 peak (5.44 MeV, 5%) lies under the upper-energy Th-228 peak (5.42 MeV) and cannot be separated from it. This must be allowed for as Ra-224 is the daughter of Th-228 and will inevitably be present in the spectrum.

Ac-225 can also show significant tailing into Th-228; it is the grand-daughter of Th-229 and will therefore be present in the spectrum. It may be conveniently measured using one of its progeny, At-217, which has a singlet peak free of interferences at 7.07 MeV.

### *Discussion*

THOR assumes complete separation of thorium from radium on the deposition date.

Ra-224 cannot be measured directly from the spectrum due to interference from the Ac-225 peak. In addition, its daughters cannot be used as an indirect measure due to diffusion losses of Rn-220 from the source. Hence, THOR calculates Ra-224 ingrowth between deposition date and count date and subsequently the Ra-224 contribution to the Th-228 peak.

Th-228 activity is corrected to deposition date, allowing for Th-228 decay, and ingrowth from Th-232 via Ra-228.

As explained above, At-217 may be used as a measure of Ac-225. Alternatively, if the At-217 counts are input as 0., THOR will calculate ingrowth of Ac-225 using the Th-229 peak and assuming complete separation of Th-229 from both Ra-225 and Ac-225 on the deposition date.

THOR example input file and example output

```

18.05.89.1115 Deposition date
21.05.89.1020 Count date (start)
23.05.89.1305 Count date (finish)
182.370      Count time (ksecs)
4.5751      Tracer mass/volume
18.070      Tracer activity concentration
2.1421      Sample mass/volume
0.2711      Detector efficiency
0.007       Th-232 bgd
0.003       Th-232 bgd error
0.014       Th-230 bgd
0.003       Th-230 bgd error
0.014       Th-229 bgd
0.005       Th-229 bgd error
0.060       Th-228 bgd
0.019       Th-228 bgd error
76.         Th-232 counts
106.        Th-230 counts
3650.       Th-229 counts
315.        Th-228 counts
93.         At-217 counts
4.51        Left cursor position for Th-230 area (MeV)
5.23        Left cursor position for Th-228 area (MeV)
0.963       % Tailing (Th-228:At-217)
0.052       Tailing error
0.525       % Tailing (Th-229:Th-228)
0.034       Tailing error
0.263       % Tailing (Th-230:Th-228)
0.022       Tailing error
0.157       % Tailing (Th-232:Th-228)
0.020       Tailing error
0.692       % Tailing (Th-230:Th-229)
0.049       Tailing error
0.292       % Tailing (Th-232:Th-229)
0.035       Tailing error
0.180       % Tailing (Th-232:Th-230)
0.032       Tailing error
GH 14 J     Analyst; Th-229 tracer no.; detector

```

Th-229 recovery = 89.4 +/- 1.5 %

	Th-232		Th-230		Th-228	
	Activity	Error	Activity	Error	Activity	Error
	.670	.101	.819	.125	3.150	.198

	Th-228/Th-232	Th-230/Th-232	Th-228/Th-230
Ratio	4.700	1.222	3.846
Error	.760	.261	.629

- Note: 1) Th-228 calculated to date of deposition  
2) Count midpoint = 4.0 days after deposition  
3) Theoretical ingrowth factors:  
Ra-224 : .5298  
At-217 : .0225  
Observed ratio At-217/Th-229:  
.0255 +/- .0027  
4) Errors are one std deviation due to counting statistics only  
5) Calculated using program THOR



## THORE

*Application:* Determination of Th-232 and Th-230 by alpha spectrometry.

Th-228 assumed in secular equilibrium with Th-232 in the sample.

*Tracer isotope:* Th-228

### *Spectrum*

Th-232: essentially a doublet (4.02 MeV, 77%; 3.96 MeV, 23%; 3.83 MeV, 0.2%).

Th-230: essentially a doublet (4.69 MeV, 76.3%; 4.62 MeV, 23.4%; 4.48 MeV, 0.15%; 4.44 MeV, 0.02%)

Th-228: essentially a doublet (5.42 MeV, 72.7%; 5.34 MeV, 26.7%; 5.21 MeV, 0.36%; 5.17 MeV, 0.18%; 5.14 MeV, 0.05%). The lower-energy Ra-224 peak lies under the upper-energy Th-228 peak and cannot be separated from it. This must be allowed for as Ra-224 is the daughter of Th-228 and will inevitably be present in the spectrum.

Ra-224: essentially a doublet (5.69 MeV, 95.0%; 5.44 MeV, 5.0%; 5.15 MeV, 0.01%; 5.04 MeV, 0.01%). Only the upper-energy (5.69 MeV) peak is measured.

### *Discussion*

THORE assumes complete separation of thorium from radium on both separation and deposition dates. The Th-228 activity is then corrected to separation date, allowing for Th-228 decay, and ingrowth from Th-232 via Ra-228.

Th-228 is assumed in secular equilibrium with Th-232 in the sample. Consequently, the Th-232 peak is used as a measure of the sample contribution to the Th-228 tracer peak.

The contribution of the Ra-224 lower-energy peak to the Th-228 area may be allowed for by either:

- (a) measuring the upper-energy Ra-224 peak, or
- (b) giving the number of Ra-224 counts as 0. THORE then calculates the theoretical Ra-224 ingrowth.

In either case, the Ra-224 contribution to the Th-228 area is calculated using the tailing factor given in the input file (% Tailing Th-228:Ra-224). This is the count rate due to Ra-224 observed in the Th-228 area as a percentage of the upper-energy (5.69 MeV) Ra-224 peak only.

Note that use of the Ra-224 5.69 MeV peak assumes that all of the counts observed in this region are due to Ra-224. This peak should not be used where there is a background in this region due to another nuclide. The nuclide most likely to interfere in this case is Ac-225, the daughter of Ra-225 which may be present on the detector if sources have previously been counted with Th-229 as tracer. Hence, the presence of Ac-225 MUST be checked for using the At-217 peak at 7.07 MeV before the 5.69 MeV Ra-224 peak can be used.

A second complication in the use of the Ra-224 5.69 MeV peak appears in the calculation of Th-228 background count rate. Where there is significant Ra-224 present in the background spectrum, its contribution to the Th-228 area must be subtracted from the Th-228 background spectrum count rate given to THORE if the Ra-224 5.69 MeV peak is to be used. This situation is most likely to arise where the counting of a high-activity Th-228 source has resulted in significant Ra-224 on the detector due to recoil.

THORE example input file and example output

```

01.03.89.1200 Separation date
02.03.89.1430 Deposition date
06.03.89.1000 Count date (start)
08.03.89.0945 Count date (finish)
171.860      Count time (ksecs)
6.9472      Tracer mass/volume
13.585      Tracer activity conc
1.5217      Sample mass/volume
0.2612      Detector efficiency
0.011       Th-232 bgd
0.004       Th-232 bgd error
0.032       Th-230 bgd
0.005       Th-230 bgd error
0.115       Th-228 bgd
0.023       Th-228 bgd error
237.        Th-232 counts
295.        Th-230 counts
4035.       Th-228 counts
2129.       Ra-224 counts
4.51        Left cursor position for Th-230 area (MeV)
5.23        Left cursor position for Th-228 area (MeV)
0.278       % Tailing (Th-230:Th-228)
0.030       Tailing error
0.153       % Tailing (Th-232:Th-228)
0.018       Tailing error
0.231       % Tailing (Th-232:Th-230)
0.032       Tailing error
5.26        % Tailing (Th-228:Ra-224)
0.05        Tailing error
GH 6 Z      Analyst; U-232 tracer no.; detector

```

Th-228 recovery = 87.8 +/- 1.6 %

	Th-232		Th-230	
	Activity	Error	Activity	Error
	3.805	.271	4.647	.308
	Th-230/Th-232		Th-232/Th-230	
Ratio	1.221		.819	
Error	.114		.077	

- Note: 1) Count midpoint = 4.8 days after deposition  
 2) Ra-224 ingrowth factor.  
     Calculated: .5953  
     Observed: .5741 +/- .0202  
 3) Sample Th-228 assumed in equilibrium with Th-232  
 4) Errors are one std deviation due to counting statistics only  
 5) Calculated using program THORE

## THORN

*Application:* Determination of Th-232 and Th-230 by alpha spectrometry.  
Th-228 concentration in the sample known.

*Tracer isotope:* Th-228

### *Spectrum*

Th-232: essentially a doublet (4.02 MeV, 77%; 3.96 MeV, 23%; 3.83 MeV, 0.2%).

Th-230: essentially a doublet (4.69 MeV, 76.3%; 4.62 MeV, 23.4%; 4.48 MeV, 0.15%; 4.44 MeV, 0.02%)

Th-228: essentially a doublet (5.42 MeV, 72.7%; 5.34 MeV, 26.7%; 5.21 MeV, 0.36%; 5.17 MeV, 0.18%; 5.14 MeV, 0.05%). The lower-energy Ra-224 peak lies under the upper-energy Th-228 peak and cannot be separated from it. This must be allowed for as Ra-224 is the daughter of Th-228 and will inevitably be present in the spectrum.

Ra-224: essentially a doublet (5.69 MeV, 95.0%; 5.44 MeV, 5.0%; 5.15 MeV, 0.01%; 5.04 MeV, 0.01%). Only the upper-energy (5.69 MeV) peak is measured.

### *Discussion*

THORN assumes complete separation of thorium from radium on both separation and deposition dates. The measured Th-228 activity is then corrected to separation date, allowing for Th-228 decay, and ingrowth from Th-232 via Ra-228.

A measure of the Th-228 activity concentration in the sample is required. The sample Th-228 activity is added to the Th-228 tracer activity figure to give the total activity present before separation.

The contribution of the Ra-224 lower-energy peak to the Th-228 area may be allowed for by either:

- (a) measuring the upper-energy Ra-224 peak, or
- (b) giving the number of Ra-224 counts as 0. THORN then calculates the theoretical Ra-224 ingrowth.

In either case, the Ra-224 contribution to the Th-228 area is calculated using the tailing factor given in the input file (% Tailing Th-228:Ra-224). This is the count rate due to Ra-224 observed in the Th-228 area as a percentage of the upper-energy (5.69 MeV) Ra-224 peak only.

Note that use of the Ra-224 5.69 MeV peak assumes that all of the counts observed in this region are due to Ra-224. This peak should not be used where there is a background in this region due to another nuclide. The nuclide most likely to interfere in this case is Ac-225, the daughter of Ra-225 which may be present on the detector if sources have previously been counted with Th-229 as tracer. Hence, the presence of Ac-225 MUST be checked for using the At-217 peak at 7.07 MeV before the 5.69 MeV Ra-224 peak can be used.

A second complication in the use of the Ra-224 5.69 MeV peak appears in the calculation of Th-228 background count rate. Where there is significant Ra-224 present in the background spectrum, its contribution to the Th-228 area must be subtracted from the Th-228 background count rate given to THORN if the Ra-224 5.69 MeV peak is to be used. This situation is most likely to arise where the counting of a high-activity Th-228 source has resulted in significant Ra-224 on the detector due to recoil.

THORN example input file and example output

```

03.03.89.1200 U/Th separation date
04.03.89.1430 Deposition date
08.03.89.1000 Count date (start)
10.03.89.0930 Count date (finish)
171.085      Count time (ksecs)
9.4286      Tracer mass/vol (added Th-228)
13.585      Tracer activity conc (added Th-228)
2.085       Th-228 activity conc in sample
0.062       Error in Th-228 sample act. conc.
8.8296      Sample mass/volume
0.2612      Detector efficiency
0.011       Th-232 bgd
0.004       Th-232 bgd error
0.032       Th-230 bgd
0.005       Th-230 bgd error
0.115       Th-228 bgd
0.023       Th-228 bgd error
178.        Th-232 counts
399.        Th-230 counts
6207.       Th-228 counts
3417.       Ra-224 counts
4.51        Left cursor position for Th-230 area (MeV)
5.23        Left cursor position for Th-228 area (MeV)
0.278       % Tailing (Th-230:Th-228)
0.030       Tailing error
0.153       % Tailing (Th-232:Th-228)
0.018       Tailing error
0.231       % Tailing (Th-232:Th-230)
0.032       Tailing error
5.26        % Tailing (Th-228:Ra-224)
0.05        Tailing error
GH 6 Z      Analyst; U-232 tracer no.; detector

```

Th-228 recovery = 92.9 +/- 1.3 %

	Th-232		Th-230	
	Activity	Error	Activity	Error
	.452	.038	1.029	.058

	Th-230/Th-232	Th-232/Th-230	Th-228/Th-232	Th-228/Th-230
Ratio	2.274	.440	4.608	2.026
Error	.227	.044	.413	.129

- Note: 1) Deposition 1.1 days after separation  
2) Count midpoint 4.8 days after deposition  
3) Ra-224 ingrowth factor.  
Calculated: .5949  
Observed: .5987 +/- .0154  
4) Sample Th-228 concentration input by user  
5) Errors are one std deviation due to counting statistics only  
6) Calculated using program THORN

## URAN

*Application:* Determination of U-238, U-235 and U-234 by alpha spectrometry.  
Ra-224 used as a measure of Th-228.

*Tracer isotope:* U-232

### *Spectrum*

U-238: essentially a doublet (4.2 MeV, 77%; 4.15 MeV, 23%; 4.04 MeV, 0.23%). Two minor U-235 peaks (6.2% total U-235) overlap this area.

U-235: this is a complex spectrum, with inevitable overlap with U-238 and U-234. URAN assumes that the peaks between 4.25 and 4.45 MeV (total 84.7%) are measured.

U-234: essentially a doublet (4.78 MeV, 71.4%; 4.72 MeV, 28.4%; 4.60 MeV, 0.21%). Three minor U-235 peaks (9.5% total U-235) overlap this area.

U-232: essentially a doublet (5.32 MeV, 68.6%; 5.26 MeV, 31.2%; 5.14 MeV, 0.28%). A number of Th-228 peaks (27.3% total Th-228) overlap this area.

Ra-224: the upper-energy Ra-224 peak (5.686 MeV, 94.98%) is used as a measure of Th-228 activity on the disc, and therefore of Th-228 contribution to the U-232 peak.

### *Discussion*

URAN determines a calculated U-235 figure based upon 0.04604 times the observed U-238 activity. This is then used to determine the U-235 contribution to the U-238 and U-234 peaks. Note that this procedure assumes the natural U-235/U-238 ratio; the calculation may, therefore, not be correct if applied to a source prepared from U-235-enriched or -depleted uranium.

The Th-228 activity calculated from the Ra-224 peak is used to give a thorium break-through figure. URAN assumes that Th-228 is in secular equilibrium with U-232 in the tracer solution (at equilibrium, the Th-228 activity is 1.027 times the U-232 activity, due to the relative half-lives of the two isotopes). The program then calculates Th break-through from the excess of observed thorium activity over the calculated ingrown activity. The Th-228 activity in the sample is assumed to be negligible compared to the tracer activity.

URAN assumes that the tracer activity concentration is calibrated to the input calibration date, and allows for decay of U-232 between calibration date and count date.

URAN example input file and example output

```

15.07.85    Separation date
16.07.85    Deposition date
22.07.85    Count date
179.22     Count time (ksecs)
9.5418     Tracer mass/volume
6.893      Tracer activity concentration
0.1159     Sample mass/volume
0.278      Detector efficiency
0.055      U-238 bgd
0.011      U-238 bgd error
0.012      U-235 bgd
0.005      U-235 bgd error
0.082      U-234 bgd
0.013      U-234 bgd error
0.104      U-232 bgd
0.014      U-232 bgd error
0.123      Ra-224 bgd
0.016      Ra-224 bgd error
1609.      U-238 counts
74.        U-235 counts
1639.      U-234 counts
3203.      U-232 counts
41.        Ra-224 counts
0.267      % Tailing (U-234:U-232)
0.066      Tailing error
0.020      % Tailing (U-235:U-232)
0.018      Tailing error
0.030      % Tailing (U-238:U-232)
0.028      Tailing error
0.411      % Tailing (U-235:U-234)
0.088      Tailing error
0.275      % Tailing (U-238:U-234)
0.065      Tailing error
15.07.85   Calibration date (U-232)
4 PM T     U-232 Tracer soln no.; Analyst; Detector

```

U-232 recovery = 96.9 +/- 1.7 %

U-238		U-234		U-235(meas)		U-235(calc)	
Activity	Error	Activity	Error	Activity	Error	Activity	Error
283.876	8.809	287.385	8.938	13.6178	1.9778	13.0696	.4056

	U-234/U-238	U-235/U-238
Ratio	1.012	.0480
Error	.036	.0070

- Note: 1) Disc counted 7. days after separation  
6. days after deposition
- 2) Th-228 ingrowth factors: Calculated: .0069  
Observed : .0093 +/- .0041  
Th-228 breakthrough = .21 +/- .40 % assuming no Th-228 in sample
- 3) Errors are one std deviation due to counting statistics only
- 4) Calculated using program URAN

## URANTH

*Application:* Determination of U-238, U-235 and U-234 by alpha spectrometry.  
Th-228 measured using upper-energy peak.

*Tracer isotope:* U-232

### *Spectrum*

U-238: essentially a doublet (4.2 MeV, 77%; 4.15 MeV, 23%; 4.04 MeV, 0.23%). Two minor U-235 peaks (6.2% total U-235) overlap this area.

U-235: this is a complex spectrum, with inevitable overlap with U-238 and U-234. URANTH assumes that the peaks between 4.25 and 4.45 MeV (total 84.7%) are measured.

U-234: essentially a doublet (4.78 MeV, 71.4%; 4.72 MeV, 28.4%; 4.60 MeV, 0.21%). Three minor U-235 peaks (9.5% total U-235) overlap this area.

U-232: essentially a doublet (5.32 MeV, 68.6%; 5.26 MeV, 31.2%; 5.14 MeV, 0.28%). A number of Th-228 peaks (27.3% total Th-228) overlap this area.

Th-228: the upper-energy Th-228 peak (5.423 MeV, 72.7%) is used as a measure of Th-228 activity on the disc, and therefore of Th-228 contribution to the U-232 peak.

### *Discussion*

URANTH determines a calculated U-235 figure based upon 0.04604 times the observed U-238 activity. This is then used to determine the U-235 contribution to the U-238 and U-234 peaks. Note that this procedure assumes the natural U-235/U-238 ratio; the calculation may, therefore, not be correct if applied to a source prepared from U-235-enriched or -depleted uranium.

The Th-228 activity is used to give a thorium break-through figure. URANTH assumes that Th-228 is in secular equilibrium with U-232 in the tracer solution (at equilibrium, the Th-228 activity is 1.027 times the U-232 activity, due to the relative half-lives of the two isotopes). The program then calculates Th break-through from the excess of observed thorium activity over the calculated ingrown activity. The Th-228 activity in the sample is assumed to be negligible compared to the tracer activity.

URANTH assumes that the tracer activity concentration is calibrated to the input calibration date, and allows for decay of U-232 between calibration date and count date.

URANTH example input file and example output

```

15.07.85    U/Th Separation date
16.07.85    Deposition date
22.07.85    Count date
179.22      Count time (ksecs)
9.5418      Tracer mass/volume
6.893       Tracer activity concentration
0.1159      Sample mass/volume
0.278       Detector efficiency
0.055       U-238 bgd
0.011       U-238 bgd error
0.012       U-235 bgd
0.005       U-235 bgd error
0.082       U-234 bgd
0.013       U-234 bgd error
0.104       U-232 bgd
0.014       U-232 bgd error
0.095       Th-228 bgd
0.013       Th-228 bgd error
1609.       U-238 counts
74.         U-235 counts
1639.       U-234 counts
3203.       U-232 counts
32.         Th-228 counts
0.267       % Tailing (U-234:U-232)
0.066       Tailing error
0.020       % Tailing (U-235:U-232)
0.018       Tailing error
0.030       % Tailing (U-238:U-232)
0.028       Tailing error
0.411       % Tailing (U-235:U-234)
0.088       Tailing error
0.275       % Tailing (U-238:U-234)
0.065       Tailing error
33.05       % Tailing (U-232:Th-228)
1.71        Tailing error
15.07.85    Calibration date (U-232)
4 PM T      U-232 Tracer soln no.; Analyst; Detector

```

U-232 recovery = 97.0 +/- 1.7 %

U-238		U-234		U-235(meas)		U-235(calc)	
Activity	Error	Activity	Error	Activity	Error	Activity	Error
283.725	8.802	287.232	8.930	13.6105	1.9767	13.0627	.4052

	U-234/U-238	U-235/U-238
Ratio	1.012	.0480
Error	.036	.0070

Note: 1) Disc counted 7. days after separation  
6. days after deposition

2) Th-228 ingrowth factors: Calculated: .0069

Observed : .0073 +/- .0036

Th-228 breakthrough = .02 +/- .35 % assuming no Th-228 in sample

3) Errors are one std deviation due to counting statistics only

4) Calculated using program URANTH





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## SUPERVISING SCIENTIST FOR THE ALLIGATOR RIVERS REGION RESEARCH PUBLICATIONS

Alligator Rivers Region Research Institute Research Report 1983-84  
Alligator Rivers Region Research Institute Annual Research Summary 1984-85  
Alligator Rivers Region Research Institute Annual Research Summary 1985-86  
Alligator Rivers Region Research Institute Annual Research Summary 1986-87  
Alligator Rivers Region Research Institute Annual Research Summary 1987-88  
Alligator Rivers Region Research Institute Annual Research Summary 1988-90  
Alligator Rivers Region Research Institute Annual Research Summary 1989-90  
Alligator Rivers Region Research Institute Annual Research Summary 1990-91 (in press)

### *Research Reports (RR) and Technical Memoranda (TM)*

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|-----|---|--|
| RR1 | The macroinvertebrates of Magela Creek, Northern Territory. April 1982 (pb, mf-46pp.)   | R. Marchant  |
| RR2 | Water quality characteristics of eight billabongs in the Magela Creek catchment. December 1982 (pb, mf-60 pp.)  | B.T. Hart &<br>R.J. McGregor   |
| RR3 | A limnological survey of the Alligator Rivers Region. I. Diatoms (Bacillariophyceae) of the Region. August 1983 (pb, mf-160 pp.)<br><br>A limnological survey of the Alligator Rivers Region. II. Freshwater algae, exclusive of diatoms. (pb, mf-176 pp.)  | D.P. Thomas<br><br>H.U. Ling &<br>P.A. Tyler   |
| RR4 | Ecological studies on the freshwater fishes of the Alligator Rivers Region, Northern Territory. Volume I. Outline of the study, summary, conclusions and recommendations. 1986 (pb, mf-63 pp.)<br><br>Ecological studies on the freshwater fishes of the Alligator Rivers Region, Northern Territory. Volume II. Synecology. 1990 (pb - 155pp.)<br><br>Ecological studies on the freshwater fishes of the Alligator Rivers Region, Northern Territory. Volume III. Autecology. (in press) | K.A. Bishop,<br>S.A. Allen,<br>D.A. Pollard &<br>M.G. Cook<br><br>K.A. Bishop,<br>S.A. Allen,<br>D.A. Pollard &<br>M.G. Cook<br><br>K.A. Bishop,<br>S.A. Allen,<br>D.A. Pollard &<br>M.G. Cook |
| RR5 | Macrophyte vegetation of the Magela Creek flood plain, Alligator Rivers Region, Northern Territory. March 1989 (pb - 41pp.)   | C.M. Finlayson,<br>B.J. Bailey &<br>I.D. Cowie   |
| RR6 | Modern sedimentation and late Quaternary evolution of the Magela Creek plain. (in press)  | R.J. Wasson  |
| RR7 | Routine analysis of naturally occurring radionuclides in environmental samples by alpha-particle spectrometry. (in press)   | P. Martin &<br>G. Hancock  |
| RR8 | Transport of naturally occurring radionuclides in the surface waters of the Magela Creek and flood plain, northern Australia. (in press)  | A.S. Murray,<br>A. Johnston,<br>P. Martin,<br>G. Hancock,<br>R. Marten &<br>J. Pfitzner  |
| RR9 | Fish communities in sandy pools of Magela Creek, Alligator Rivers Region. (in press)  | D.J. Woodland &<br>P.J. Ward   |
| TM1 | Transport of trace metals in the Magela Creek system, Northern Territory. I. Concentrations and loads of iron, manganese, cadmium, copper, lead and zinc during flood periods in the 1978-1979 Wet season. December 1981 (pb, mf-23 pp.)  | B.T. Hart,<br>S.H.R. Davies<br>& P.A. Thomas   |
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