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Routine analysis of

naturally occurring

radionuclides in

environmental samples

by alpha-particle

spectrometry



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Australian Government

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Abstract

The high sensitivity and wide range of applicable sample types make α -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 α -emitting radionuclides:

- ²³⁴U, ²³⁵U and ²³⁸U
- ²²⁸Th, ²³⁰Th and ²³²Th
- 223 Ra, 224 Ra and 226 Ra, and
- ²¹⁰Po

together with a method for the determination of ²¹⁰Pb by β counting. In addition, the β -emitters ²²⁸Ra, ²¹⁰Pb and ²²⁷Ac can be determined within a few months of their separation from the sample digest by measurement of their α -emitting progeny.

After addition of a suitable tracer and dissolution of the sample, a chemical separation scheme is used which allows the sequential separation and analysis of radioisotopes of U, Th, Ra, Pb, Po and Ac 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 spectrum 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.

This report updates and replaces an earlier report on this topic (Martin & Hancock 1992).

Keywords

alpha particle spectrometry, environmental samples, uranium, thorium, radium, lead, polonium, actinium, radionuclide

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1 Introduction

The aim of this publication is to provide a description of procedures for radiochemical analysis of environmental samples developed and used at the Environmental Research Institute of the Supervising Scientist (*eriss*). This report updates and replaces an earlier report on this topic (Martin & Hancock 1992).

eriss conducts research into the environmental effects, including the radiological impact on humans, of uranium mining in the Alligator Rivers Region. Consequently, the procedures described here are primarily for measurement of members of the uranium, thorium and actinium decay chains with half-lives of the order of a few days or longer. Figures 1.1 - 1.3 show the dominant pathway members of these decay chains, together with their half-lives and modes of decay (Firestone 1996). A fourth decay chain (the neptunium series), whose members are often used as isotopic tracers, is shown in Figure 1.4.

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

- α -particle counting;
- β -particle counting;
- etched track detectors,
- liquid scintillation counting and/or spectrometry;
- scintillation detectors for low-resolution γ -ray spectrometry, most commonly NaI(Tl) crystal/photomultipler tube systems,
- semiconductor diode detectors for high-resolution γ -ray spectrometry, most commonly high-purity germanium (HPGe) systems,
- α -particle spectrometry performed directly on the sample (e.g. Murray & Marten 1985), and
- high-resolution α -particle spectrometry using a tracer isotope and involving chemical separation procedures.

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

- The high sensitivity of the technique, resulting from the observation of the highyield α decay process, low intrinsic detector backgrounds and the elimination of competing radiation by chemical processing.
- The ability to use an α -emitting isotope as a tracer makes the technique reliable, provided no losses of either sample or tracer occur before the tracer and sample isotopes have chemically equilibrated.
- As the result is obtained from the ratio of sample to tracer peaks, it is not affected by errors in the knowledge of detector counting efficiency.
- The range of radionuclides which can be determined. Those of interest here are 234,235,238 U, 227,228,230,232 Th, 227 Ac, 223,224,226,228 Ra, 210 Po and 210 Pb.



Figure 1.1 The uranium decay series (4n + 2 series)



Figure 1.2 The thorium decay series (4n series)

- The ability to measure concentrations of 226 Ra without an ingrowth period for 222 Rn and progeny.
- The range of applicable sample types. Virtually any sample which can be chemically digested can be analysed using this technique.

Disadvantages of the technique include:

- The necessity of obtaining and calibrating a tracer isotope solution.
- The time-consuming chemical separation techniques required. These separations are required for the following reasons: to remove elements which would interfere with the final source preparation step in such a way as to reduce recovery of the element of interest; to remove elements which would deposit on the final source, resulting in a thick deposit and consequently degraded spectral resolution; and to separate the element of interest from other α -emitting radionuclides.



Figure 1.3 The actinium decay series (4n + 3 series)



Figure 1.4 The neptunium decay series (4n + 1 series)



Figure 1.5 Steps involved in analysis by α -particle spectrometry.

The radiochemical techniques described in this report have been developed with the aim of utilising the advantages of α -particle spectrometry while minimising analysis time. Figure 1.5 summarises the steps involved in a typical analysis by α -particle spectrometry. The most demanding of these in terms of operator time 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 α -particle spectrometry, a method for analysis of ²¹⁰Pb by beta counting has been incorporated as part of the analysis scheme.

2 Sample collection and preparation

2.1 Time constraints

Analysis of radionuclides with relatively short half-lives can place constraints on sample collection and analysis timetables. For example, analysis for 224 Ra ($t_{1/2} = 3.7$ days) and 223 Ra ($t_{1/2} = 11.4$ days) should be performed as soon as possible after sample collection to minimise the importance of decay and of ingrowth from the parents. Even for radionuclides with half-lives of the order of months or years, ingrowth can be significant over the course of several days when the activity concentration is substantially less than that of the parent. Some examples are:

- The activity concentration of 210 Po in rainwater is usually one to two orders of magnitude lower than that of its 210 Pb progenitor, and so the maximum analysis delay time advisable is 2-3 days.
- The activity concentration of ²²⁸Th in groundwater is usually one to two orders of magnitude lower than that of ²²⁸Ra; the maximum analysis delay time advisable is about 1 week.
- The activity concentration of 210 Pb in uranium mine waters is usually substantially lower than that of 226 Ra; the maximum analysis delay time advisable is about 1 2 weeks.

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° C). Volatility varies widely with chemical form, and polonium has been shown to be partly volatilised from some samples above 100° C (Martin & Blanchard 1969).

It seems prudent, therefore, to keep drying temperatures as low as is practicable. At eriss, samples are dried to a constant weight at 80° 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 ²²⁶Ra concentration of 1 Bq L⁻¹ represents a molarity of only 1.2×10^{-13} *M* Ra. Even for the longer-lived ²³²Th 1 Bq L⁻¹ represents 1.1×10^{-6} *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 concentrations should be acidified (usually 1 % 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 must be shaken vigorously in order to resuspend any particulate matter. Polonium is a particular problem in this respect. This element hydrolyses to a considerable extent in dilute (<0.01 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 a further discussion of this problem see Bagnall (1957, pp. 29–32) and Beneš & Majer (1980).

3 Element separations and source preparation

3.1 Use of tracer isotopes

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 at regular intervals throughout the life of the tracer solution to ensure that neither contamination nor change in tracer strength has occurred.

Choice of tracer depends on a number of factors, including α -particle energy, half-life, progeny, purity, price and availability of supply. Tracers used at **eriss** for Po, Pb, U, Th, Ra and Ac are discussed in sections 5 to 10. Details of half-life and α -particle energy for the radionuclides of interest are summarised in Appendix B.

3.2 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 *eriss*, 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 when organic matter is present. For mineral samples resistant to acid attack, a fusion method may be necessary (e.g. Sill 1987).

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

When analysing for 210 Po, it is important that the dry sample not be heated above 150° 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, have not been found to result in significant polonium losses. Fusion techniques generally result in substantial polonium loss and should not be used when analysing for 210 Po (Akber *et al.* 1985; Lowson & Short 1986).

3.2.1 Manganese dioxide precipitation

This method is useful for concentrating radionuclides from large volumes of water where the radionuclides are considered to be in solution. 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.

Procedure

After acidification of the sample and addition of the tracer, bubble the solution for 2 hours with N_2 to ensure tracer equilibration and to expel any dissolved CO_2 which may inhibit precipitation of uranium.

Add 10 mL of 0.2 M KMnO₄ and adjust the pH to 8–9 with NH₃.

Add 10 mL of 0.3 M MnCl₂ and bubble the solution for one hour.

Allow the precipitate to settle.

Remove the majority of supernatant by suction or decantation.

Collect the precipitate by filtration and wash with 0.2% NH₄Cl (pH 8 to 9).

Discard the wash solution.

Dissolve the precipitate with $1\% H_2O_2$ in 1.2 *M* HCl.

Evaporate to dryness, redissolve with a few mL of 5 M HCl and evaporate again to ensure complete decomposition of peroxides.

3.2.2 Iron oxide precipitation

This method is also useful for concentrating radionuclides from large volumes of water where the radionuclides are considered to be in solution. It has the advantage over the manganese dioxide precipitation method that the precipitate may be dissolved directly in the acid solution needed for the start of the separation procedure (e.g. 8 M HNO₃ where the procedure begins with a TBP extraction for U or Th).

Procedure

Acidify the sample, add the required amount of tracer, and bubble the solution for 2 hours with N_2 to ensure tracer equilibration and to expel any dissolved CO_2 which may inhibit precipitation of uranium.

Add an aqueous solution of 20 mg/mL ferric chloride, sufficient to ensure successful precipitation of hydrous iron oxides in step 3. In general, a minimum of 20 mg of ferric chloride per litre of sample should be added, but the mass of ferric chloride added should not be less than 40 mg or greater than 1000 mg.

Add sufficient concentrated NH_3 solution while stirring to bring the pH above 8. Allow the precipitate to settle, decant the supernate and filter the precipitate through a Whatman No. 1 filter paper. Wash with a few mL of a 4% NH_3 solution.

Bring the residue into solution in acid solution as required for the following element separation step.

3.3 Chemical separation procedures

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

- determination of α -emitting isotopes of uranium, thorium, radium and polonium, and the β -emitters ²²⁸Ra, ²¹⁰Pb and ²²⁷Ac;
- 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; and
- the analysis scheme should involve the minimum possible number of steps in order to minimise analysis time, contamination, and losses of the radionuclide being determined.



Figure 3.1 Chemical separation scheme

The separation scheme that has been developed at *eriss* is shown in Figure 3.1. Depending upon which analytes are required, after sample digestion the separation procedure can be started from points (1), (2), (3) or (4).

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 groundwaters, dried animal and plant material, air filters, and soils and sediments. The chemical separation procedures are detailed in Sections 5 to 10; a short summary follows here.

If analysis for 210 Po is required, then the sample is brought into solution in 5 *M* HCl, Fe³⁺ reduced to Fe²⁺ with ascorbic acid, and Po extracted with 0.1% diethylammonium diethyldithiocarbamate (DDTC) in 1,1,1-trichloroethane (CH₃CCl₃). Under these conditions, Po is extracted into the organic phase, while Pb and Bi remain in the aqueous phase (Smithson *et al.* 1979). U, Th, Ra, Ac and most of the Fe also remain in the aqueous phase. After evaporating the organic phase to dryness, Po is brought into solution in 12 mL 0.8 *M* HCl and autodeposited onto a silver disc at 70–80 °C for 2 hours in the presence of ascorbic acid (Flynn 1968; Smith & Hamilton 1984).

If analysis for ²¹⁰Pb is required, then the acid phase from the first DDTC extraction is diluted to 1.5 M HCl, and Pb extracted with 1% DDTC in CH₃CCl₃, followed by purification using anion exchange chromatography with Dowex 1-X8 resin. ²¹⁰Pb may then be determined after a suitable ingrowth period either by a determination on the extract of the ²¹⁰Bi daughter by β counting or of the ²¹⁰Po grand-daughter by α -particle spectrometry. If a ²¹⁰Po determination on the sample is not required and if ²¹⁰Pb is to be determined by the β counting method, then the previous extraction of ²¹⁰Po is not required, i.e. the procedure can begin from point (2) after bringing the sample digest up into 1.5 *M* HCl.

If determination of isotopes of U and/or Th are required, then an extraction/backextraction procedure with tri-butyl phosphate (TBP) is used (Holm 1984). The residue is dissolved in 8 M HNO₃ and U and Th extracted into TBP; Ra and Ac remain in the 8 M HNO₃ phase. After washing the organic phase with 8 M HNO₃ and diluting the TBP with xylenes, Th is back-extracted with 5 M HCl. If required, U is then back-extracted with distilled water. The extracts are then purified using anion exchange chromatography with Dowex 1-X8 resin, and U and/or Th electrodeposited onto stainless steel discs using the method of Hallstadius (1984).

If determinations of Ra and/or Ac isotopes are required, then the 8 M HNO₃ solution remaining from the TBP extraction is taken to dryness on a hot plate, and the residue brought into solution in 0.1 M HCl or HNO₃. Ra, Ac and residual Th are then coprecipitated with PbSO₄; residual Po and U remain in the supernate. The precipitate is dissolved in 0.1 M EDTA at pH 10. An anion exchange step is used to separate Ra and Pb (which pass through the column) from Ac and Th (which are adsorbed). Ac is then eluted with 0.005 M EDTA at pH 4.2. If Th was not previously extracted by the TBP procedure, it remains on the column and can be removed for analysis. In this case, after elution of Ac the column is first washed with three 20 mL aliquots of 8 M HNO₃. Any residual traces of Po remaining after the PbSO₄ precipitation step are eluted with the 8 M HNO₃. Th is then eluted with 30 mL 9 M HCl; the extract can then proceed to the electrodeposition step. After the above procedure, the Ra and Ac extracts are purified further by cation exchange chromatography, prior to electrodeposition using a mixed acid/alcohol electrolyte solution.

One of the advantages of this scheme is its flexibility. If a ²¹⁰Po determination is not required, then the procedure can be started from point (2) in Figure 3.1. If only U, Ra, Ac and/or Th determinations are required, then the procedure can begin at points (3) (with U) or (4) (without U).

An alternative method of ²¹⁰Pb determination utilises two successive determinations on the sample of the daughter ²¹⁰Po separated by a delay (usually of at least 6 months). ²¹⁰Pb is then calculated from the two determinations using ingrowth/decay equations for ²¹⁰Po (see section on program POLON in Appendix A). However, this procedure is not recommended when the sample ²²⁶Ra/²¹⁰Pb ratio is expected to be high. In this case, an extraction of the sample ²¹⁰Pb should be performed soon after sample collection.

3.4 Source preparation

Once element separations are completed, various methods are available for final source preparation. These include:

- evaporation of a solution onto a source backing surface (such as a metal disc),
- precipitation and filtration,
- autodeposition onto a metal surface,
- electrodeposition onto a metal surface, and



Figure 3.2 Electrodeposition rig.

• deposition by adsorption of hydroxides.

Evaporation methods for source preparation are not used at *eriss*. A lead chromate precipitation is used for source preparation for determination of ²¹⁰Pb by the β counting method (Section 6). Autodeposition is the method used for polonium analyses, and is discussed in detail in Section 5.

3.4.1 Electrodeposition

Figure 3.2 shows the electrodeposition rig used at $eriss^1$. The anode is a platinum wire coiled at the end, while the stainless steel disc acts as the cathode. The cell is a disposable polyethylene vial with the bottom cut off, as described by Talvitie (1972). The vial cap has its inside base milled flat, with a hole drilled through the middle to allow electrical contact between the stainless steel disc and the power supply. The seal between the vial lip and the disc should be watertight; this should be checked before use by filling the vial with demineralised water and standing it on some absorbant paper for about half an hour.

Electrodeposition conditions are determined by the following variables:

- solution composition,
- solution temperature,
- anode/cathode distance,
- current (I),
- voltage (V), and
- deposition time.

¹These units were supplied by the University of Lund, Sweden.

The first five of these are related by Ohm's Law:

$$V = IR \tag{3.1}$$

where the resistance R is a function of solution composition, solution temperature, and anode/cathode distance. A power supply is used which automatically varies the voltage (up to a maximum of 55 V) in order to supply a preset current. Stirring of the solution is effected by bubbling produced by the passage of the current through the solution. This also causes the formation of some aerosol above the solution, and so after the Pt electrode has been lowered into place a plastic cap is placed over the top of the vial to minimise loss of solution. Nevertheless, the deposition should be carried out in a fume cupboard to prevent inhalation of any aerosol.

A sulfate electrolyte is used for preparation of sources for U and Th (Hallstadius, 1984), while an aqueous/alcohol electrolyte is used for Ra and Ac. The methods are described in detail in the individual sections on U, Th, Ra and Ac.

Cleaning the Pt electrode

If a solution containing 210 Po has been deposited (e.g. where a standard activity of 226 Ra has been deposited for calibration purposes, without prior chemical separations), then the Pt electrode should be cleaned to remove 210 Po. The electrode is heated using a bunsen burner to red hot for a few seconds, then soaked for a few minutes in concentrated HNO₃ and washed with demineralised water.

3.4.2 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. It is suitable for the production of thin test sources, but recoveries have been found to be too low ($\langle 20\% \rangle$) for it to be generally useful for samples. Since the deposition is carried out using small volumes, care must be taken with transferring of solutions and washing of the beaker if useful recoveries are to be obtained. 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 HNO₃ 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 a deposition vial similar to that used for Po auto-deposition (Section 5.1.2).

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 Figure 3.3).

Leave for approximately 8 hours at room temperature.



Figure 3.3 Arrangement for deposition by adsorption of hydroxides.

Pour off the solution, and wash the disc with distilled water followed by propanol. Dry by warming on the edge of a hot plate.

4 Detection system and spectrum analysis

Most systems for α -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 & Marten 1985).

A typical spectrometry system using a surface barrier detector is illustrated in Figure 4.1. 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 4.1 Typical α -particle spectrometry assembly

4.1 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 with an active area with radius r, the counting efficiency may be approximated by the following formula (Hendee 1984):

$$E = 0.5 \left(1 - \frac{h}{\sqrt{h^2 + r^2}} \right) - \frac{3}{16} \left(\frac{ar}{h^2} \right)^2 \left(\frac{h}{\sqrt{h^2 + r^2}} \right)^5$$
(4.1)

The efficiency may be increased by increasing the detector active surface area, by decreasing the source/detector distance and/or by decreasing the source area.

4.1.1 Detector area

Figure 4.2 shows counting efficiency vs. source/detector distance for a number of commonly-available detector sizes, for the source diameter usually used at *eriss* (17.5 mm). Increasing detector area will increase counting efficiency at any particular source/detector distance. However, increasing area also adversely affects resolution



Figure 4.2 Counting efficiency vs. source/detector distance for 4 common detector sizes. Source diameter is 17.5 mm.

due to an increase in detector capacitance. The most common detector area in use at *eriss* is 600 mm², which gives an efficiency of approximately 25-30% (source diameter 17.5 mm, source/detector distance approximately 5-7 mm).

4.1.2 Source/detector distance

Increasing source/detector distance will reduce the proportion of α 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 *eriss* are generally around 5 – 7 mm. This results in a peak FWHM poorer than that quoted in detector specifications. However, this is not necessarily a major disadvantage, as peak FWHM is of less importance than peak tailing.

Figure 4.3 shows the results of a trial in which a ²³⁰Th source, prepared by adsorption of the hydroxide (Section 3.4.2), was counted at varying distances from a dectector (active area 600 mm²). 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 main ²³⁰Th energy window (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 (Figure 4.3a) shows the calculated variation in tailing, assuming that the 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 4.3 Effect of source/detector distance, measured with a 600 mm² detector. Source: ²³⁰Th prepared by hydroxide precipitation. (a) Peak tailing. (b) Full-width-at-half-maximum (FWHM) and counting efficiency.

4.1.3 Detector collimation

Collimation of the detector may be used to decrease peak tailing by reducing edge effects (Holm 1984). Figure 4.4 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 4.5 shows a typical arrangement using a circular plastic collimator slipped over the detector body.

4.2 Peak tailing

Due to the nature of low-energy tailing of α spectra, some contribution from a higherenergy peak to the count rate in the analysis window of a lower-energy peak is inevitable. In most cases, the tailing contribution to a lower-energy peak is only a small fraction of the count rate in the higher-energy peak. However, where the count rate for the higher-energy peak is much greater than that of the lower-energy peak, this tailing may be significant and must be allowed for. In the case of tracer isotope peaks, tailing corrections can be minimised by choice of appropriate tracer activity and sample mass



Figure 4.4 Effect of detector collimation, measured with a 600 mm² detector. Source: ²³⁰Th prepared by hydroxide precipitation. (a) Peak tailing. (b) Full-width-at-half-maximum (FWHM) and counting efficiency.

(provided the analyst can reasonably estimate the activity concentration of the analyte radionuclide in the sample). However, in the case of analyte radionuclides (for example, 238 U, 235 U and 234 U in a uranium analysis), the relative activity concentrations are characteristic of the sample and cannot be varied by the analyst.

Tailing will depend on a number of factors, including:

- detector performance
- energy difference between the two peaks
- spectrum analysis window size
- source/detector distance (Section 4.1.2)
- detector collimation (Section 4.1.3)
- chamber gas pressure (Section 4.3)
- source deposit thickness (Section 4.4)

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.



Figure 4.5 Arrangement for collimation of a detector



Figure 4.6 Examples of upper-energy tailing. On the log scale, 0 counts has been represented by 0.5 (a) 212 Po spectrum. (b) 213 Po spectrum.



Figure 4.7 Effect of N₂ pressure on 230 Th peak FWHM and tailing.

4.2.1 Upper-energy tailing of 212 Po, 213 Po and 214 Po

These three peaks may show an upper-energy 'tail', most markedly for ²¹²Po (Figure 4.6a), less so for ²¹³Po (Figure 4.6b) and barely noticeable for ²¹⁴Po. The effect appears to be due to summation of pulses from the bismuth parent β -particle decay and polonium daughter α -particle decay where the two decays occur within the signal processing time of the detection system, and where both particles interact with the active volume of the detector. 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.

4.3 Recoil protection

Sill & Olson (1970) described a technique by which recoil contamination of solid-state α detectors can be minimised. By adjusting the chamber pressure to allow at least 12 μ g cm⁻² of gas absorber between the source and detector, the recoiling atoms from the source are prevented from hitting the detector surface. The application of a small negative potential (a few volts) to the source will attract these atoms back to the source. For N₂ gas the chamber pressure P (torr) required is given by

$$P = 0.65 \frac{a}{h} \tag{4.2}$$

at 20°C, where *a* is the amount of N₂ absorber ($\mu g \text{ cm}^{-2}$) and *h* is the source-detector distance (cm). Thus for a source-detector distance of 0.4 cm, a pressure of 20 torr is required to give 12 $\mu g \text{ cm}^{-2}$ of N₂ absorber.

In passing through the gas absorber, α particles lose energy through interactions with electrons. This results in peaks having lower apparent energies than when no gas is

present. In addition, statistical variation in the amount of energy lost by individual α particles leads to peak broadening.

Figure 4.7 shows the results of a test of the effects of changing chamber pressure on peak FWHM and tailing for a thin ²³⁰Th source. The results for FWHM were similar to those reported by Sill & Olson (1970), i.e. FWHM increased linearly with chamber pressure. Peak position measured both at the peak maximum and the upper energy boundary were affected by increasing pressure, with the positions at 40 μ g cm⁻² being lower than at 0.1 μ g cm⁻² by about 29 keV. Each spectrum was therefore shifted to bring the peak maximum for the main ²³⁰Th peak to 4.688 MeV before calculation of tailing. Tailing in the region 4.28–4.50 MeV was not significantly affected up to 40 μ g cm⁻² (Figure 4.7). However, this result will be dependent on the energy difference between the peak and the tailing area. In the region 4.38–4.55 MeV, tailing began to increase above about 25 μ g cm⁻²; above this pressure the ²³⁰Th peaks became so broad that the main body of the 4.62 MeV peak entered the tailing area.

For the majority of α -particle spectra, measured peaks are separated by at least 0.2 MeV. In such cases, based on the above test, for a thin source use of the recommended 12 μ g cm⁻² gas absorber should have a negligible effect on tailing. Although the results obtained here imply that peaks separated by only 0.1 MeV can be resolved, at this level the thickness of the source deposit would be critical (see Section 4.4).

Polonium sources

Application of the recoil protection system described above does not protect the detector from contamination by 208 Po, 209 Po or 210 Po from a source used for 210 Po determination, as these do not move to the detector by an α -recoil mechanism. In this case, the detector must be protected by ageing of the source in air before counting (see Section 5.1.2).

4.4 Source deposit thickness

Chemical separation techniques should curtail sample source thickness such that peak resolution is optimised. However, long-lived nuclides such as ²³⁸U and ²³²Th can provide problems if their deposit mass per unit area is not controlled. Ideally, the analyst should take sufficient sample mass to give a low counting statistic uncertainty, but not so much as to result in an unacceptably thick source. However, this requires prior knowledge of the sample radionuclide activity concentration, something which is not always available.

Figure 4.8 shows the results of a set of trials where varying amounts of uranium were deposited using the deposition method described by Hallstadius (1984). Two sets of sources were prepared using different deposition times (20 and 60 minutes). All sources were counted with a 450 mm² silicon surface barrier detector, and the source density (μ g cm⁻²) calculated from the count rate of the ²³⁸U peaks. To simulate normal counting conditions, the recoil protection system utilising 12 μ g cm⁻² N₂ gas absorber was also applied. Source–detector distance was 7 mm.

Tailing was measured below the 238 U peak using energy windows chosen to mimic the tailing of 234 U into the 235 U measurement window. FWHM was measured for the 238 U peak at 4.20 MeV. The peak maxima for the higher mass per unit area spectra were at lower energies due to peak broadening. However, unlike the effect of gas absorber discussed above, the peak upper energy boundaries were not lower. This is logical, as the given mass per unit area is only an average. α particles originating from near the



Figure 4.8 Effect of deposit thickness for uranium sources. (a) FWHM vs. source density (^{238}U) . (b) Tailing below the ^{238}U peak vs. FWHM.

surface of the source lose less energy than those originating from the base. As a result, spectra were not energy-shifted prior to analysis.

There was a strong positive correlation between source density and peak FWHM (Figure 4.8a). The slope of the linear regression line for the combined dataset was 0.63 keV per (μ g cm⁻²), which is almost double that of 0.33 keV per (μ g cm⁻²) obtained for the effect of N₂ gas (Figure 4.7) indicating a greater deleterious effect on spectral resolution by source mass. This is almost certainly due in part to the effect of α particles originating from different depths in the source deposit (as discussed above). Uneven deposition of uranium over the surface of the disc may also contribute (Benedik *et al.* 2002).

Figure 4.8b shows that tailing was reasonably constant up to a FWHM of about 100 keV, corresponding to a source density of about 100 $\mu \text{g cm}^{-2}$. For the 1.75 cm diameter (2.41 cm² area) discs used at *eriss*, this means a limit on the activity of ²³⁸U of approximately 3 Bq and a limit for ²³²Th of approximately 1 Bq.

Source deposit thickness may also be a problem when analyzing for Ra isotopes. Although the Ra separation technique detailed in Section 9 gives a high degree of separation of Ra from Ba, analysis of high-Ba samples may still result in some Ba in the final electrodeposition solution. In a study of the aqueous/alcohol electrodeposition technique described in Section 9.1.2, varying amounts of Ba were added to a standard ²²⁶Ra solution and the Ra deposited onto a stainless steel disc. Source deposit density was


Figure 4.9 Effect of barium for electrodeposited radium sources. (a) 226 Ra recovery and FWHM vs. source density. (b) Tailing of 214 Po into the 217 At peak area vs. source density. (c) Tailing of 214 Po into the 215 Po peak area vs. source density.

calculated assuming an identical deposition recovery for ²²⁶Ra and Ba.

The ²²⁶Ra recovery obtained at 38 μ g cm⁻² Ba was 92% (Figure 4.9a), illustrating the robustness of this electrodeposition technique in the presence of Ba. Peak FWHM increased linearly with source deposit density, with the effect being somewhat greater than that obtained for the uranium deposition trials described above.

Measured tailing of the ²¹⁴Po peak into the ²¹⁷At (6.86–7.12 MeV) and ²¹⁵Po (7.18–7.44 MeV) peak areas is shown in Figure 4.9b, c. No significant change in tailing into the ²¹⁷At area was observed up to 38 μ g cm⁻² Ba. The data for the ²¹⁵Po region are consistent with a relatively constant tailing up to 28 μ g cm⁻² Ba (FWHM 87 keV), but a higher tailing for 38 μ g cm⁻² FWHM 108 keV). Similar results were obtained for tailing of the ²¹⁸Po peak into the ²²⁴Ra 6.85 MeV peak area.

In summary, the trials discussed above indicate that tailing corrections obtained with thin standard sources can be used for calculations for sample sources up to a certain source thickness, and that peak FWHM can be used as an indicator of the acceptability of these standard corrections for a particular source. The maximum allowable FWHM will depend upon the energy difference between the peaks of interest. As a general rule, caution should be exercised when the FWHM is greater than about 80 keV. Beyond this limit, the use of a peak fitting routine (e.g. Westmeier 1984) would be advisable.

4.5 Background and blank subtraction

Following the recording of counts in the regions of interest of an α spectrum, those counts which are not due to the presence of the radionuclide of interest in the original sample must be allowed for. Such counts can arise for a number of reasons, including:

- peak tailing;
- interfering lines from other α -emitters present on the source (e.g. contribution to the (²²³Ra + ²²⁴Ra) measurement area from ²²²Rn and ²²⁵Ac on a radium source);
- α -emitters present on the detector, counting chamber, etc; and
- contamination of chemicals, tracer solution, glassware, etc.

Peak tailing is discussed in Section 4.2 above. Interfering lines are discussed in detail in Chapters 5 to 10, as well as in Appendix A.

For convenience, the third item in the list above will be referred to here as the "detector background", while the fourth item will be referred to as the "procedure blank". The detector background may be determined by counting an unprocessed source disc in the counting chamber. Its value can change with time if contamination of the chamber/detector system occurs, for example by recoil of daughter products (see Section 4.3).

Procedure blank count rate values can also change with time. For example a new batch of reagent used in the separation procedures may introduce contaminants, elevating blank readings. In addition, the true procedure blank count rate can vary from source to source, particularly if contamination of sample digests or laboratory equipment occurs or if chemical recoveries vary markedly between samples.

Background and blank count rates need to be controlled and monitored through a series of quality control and quality assurance procedures. It is particularly important that with every batch of samples processed, a separate procedure blank source is prepared. The full chemical digest and separation procedure is followed in an identical way to that for the samples, excepting that no sample or tracer are included. This blank source is counted on the same detector(s) as the sample sources. This gives a measure of the total (detector background + procedure blank) count rate which needs to be input into the analysis computer programs for subtraction from the sample source count rate (see Appendix A).

4.6 Lower limits of detection

The lower limit of detection (LLD) for any radionuclide is critically dependent on the detector background and procedure blank count rates. However, an attempt has been made here to give typical limits assuming low background detectors (see Table 4.1). Limits have been calculated using the formula derived by Lochamy (1981):

$$LLD = \frac{k^2}{t} + 2\sqrt{2k\sigma_b} \tag{4.3}$$

Radionuclide	Background	$Detection^a$	Recovery	lngrowth/	Detection
		Efficiency		Decay	Limit
	(c.p.ks)	(%)	(%)		(mBq)
²¹⁰ Po	0.05	25	95		0.6
^{210}Pb	4	30	95		3.5
238 U	0.01	25	90		0.4
235 U	0.005	21	90		0.4
234 U	0.01	25	90		0.4
232 Th	0.01	25	85		0.4
²³⁰ Th	0.01	25	85		0.4
^{228}Th	0.05	25	85		0.7
226 P 2	0.01	25	80		0.4
223 D - b	0.01	25	00	0.06	0.4
Ka-	0.01	19	80	0.90	0.0
²²⁴ Ra ^c	0.005	12	80	0.72	1.0
$^{228}Ra^d$	0.01	24	80	0.45	1.0
²²⁷ Ac	0.05	50	75	1.0	0.4

Table 4.1 Lower limits of detection, calculated using equation 4.3 and assuming an 85 kilosecond count and typical detection efficiencies, recoveries and ingrowth/decay factors.

^{*a*} Detection efficiency is a product of the counting efficiency of the detector (here assumed 25% for α -particle spectrometry and 30% for β counting) and the proportion of decays resulting in particles in the energy region being measured.

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

 $^{c\ 224} {\rm Ra}$ is assumed measured using the $^{212} {\rm Po}$ peak. 25% $^{220} {\rm Rn}$ loss is assumed. $^{212} {\rm Po}$ 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.

 d Ingrowth factor for 228 Ra (ingrowth of 228 Th) is that reached after 2 years. Maximum ingrowth is 0.578, reached after 4.5 years.

where t is the count time for both background and sample (assumed equal), σ_b is the standard deviation in the background count rate, and k is the 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 α detectors and 30% for a β counter, and typical recoveries and ingrowth/decay factors listed in the table.

The detection limit given for ²¹⁰Pb is that obtained with the β counting method. If analysis can be delayed for a suitable period, ²¹⁰Pb can be determined by analysis for ingrown ²¹⁰Po using α -particle spectrometry (Section 6.3). The detection limit then depends on the length of the delay period.

The detection limit given for 224 Ra assumes use of the 212 Po peak, which is the most sensitive measurement technique in the presence of significant 223 Ra (Section 9). In samples with relatively low 223 Ra activities, the 220 Rn and 216 Po peaks may be used, improving the 224 Ra detection limit.

5 Polonium

5.1 Introduction

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, sulfur, 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 oxygen, sulfur and selenium 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 sulfur to polonium elements have d orbitals available for use in bonding, and hexacoordinate compounds are most common for tellurium and polonium.

Halide complexes of the form PoX_5^- or $PoX_5(H_2O)^-$ are formed in dilute halogen acid solution, while PoX_6^{-2} is formed in more concentrated acid solutions (X = Cl, Br or 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 PoCl₄.2TBP (Bagnall 1957). Polonium is not extracted into TBP from HNO₃ solution. Other organic agents forming polonium complexes include EDTA and DDTC.

5.1.1 Extraction using DDTC

Diethylammonium diethyldithiocarbamate (DDTC) can be used to extract polonium into chlorinated hydrocarbons such as carbon tetrachloride, chloroform or 1,1,1-trichloroethane from HCl solution over a wide range of acid strengths. This is particularly useful for the separation of 210 Po from 210 Bi and 210 Pb, as polonium will extract from HCl solutions of higher acid concentration 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).

5.1.2 Auto-deposition of polonium onto metals

In 1905 Marckwald found that polonium deposited readily on silver from dilute HNO_3 or 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 ²¹⁰Po methods rely solely upon polonium auto-deposition on silver or nickel discs to give separation from radionuclides and resolution-degrading elements (e.g. Flynn 1968). However, if some ²¹⁰Bi and/or ²¹⁰Pb deposit along with the polonium and there is a delay between deposition and counting, an incorrect result for ²¹⁰Po activity concentration in the sample may be obtained. Ehinger *et al.* (1986) studied auto-deposition of a ²¹⁰Pb-²¹⁰Bi-²¹⁰Po solution onto various metals. Their results may be summarised as follows:

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

Flynn (1968) found that ²¹²Bi deposited onto silver, though not its parent ²¹²Pb. He recommended addition of 10 mg of bismuth carrier to prevent ²¹⁰Bi deposition. He also used hydroxylamine hydrochloride to reduce Fe^{3+} and 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 the previous section in carried out before deposition, separation of ²¹⁰Po from both ²¹⁰Pb and ²¹⁰Bi is assured. This extraction also removes polonium from most other interfering elements. The polonium may then be reliably deposited onto a silver disc using the procedure described below.

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 μ m), then rinsed 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 and a good seal can be obtained between vial lip and disc which requires no rubber O-ring.

The DDTC/chlorinated hydrocarbon solution from the polonium extraction step is taken to dryness on a low hot plate, and organics destroyed by heating with some concentrated HNO₃. After evaporating to dryness, the polonium is taken up in a few mL of dilute HCl, ascorbic acid used to reduced Fe^{3+} ion, and the solution transferred to the deposition vial. The vial is placed in a water bath at 70–80 °C for 2 hours to allow polonium to auto-deposit onto the disc.

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).

5.2 Tracers

The two tracers commonly used for ²¹⁰Po determination are ²⁰⁸Po and ²⁰⁹Po.

²⁰⁹Po has a clear advantage over ²⁰⁸Po in energy separation from the ²¹⁰Po peak and is the preferred tracer, if available. In addition, its longer half-life means that, should the solution have a ²¹⁰Po load either from production or contamination, the solution may be set aside to allow decay of the ²¹⁰Po 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 disc in the vacuum of the counting chamber. There, a significant fraction can drift to the detector, where they become firmly attached to the surface of the detector, causing a gradual increase in detector background with use. Given that contamination of detectors occurs at a moreor-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 ²⁰⁹Po will eventually result in a much higher tracer activity on the detector than ²⁰⁸Po.

Note that ²⁰⁸Po solutions normally contain trace activities of ²⁰⁹Po.

5.3 Separation and deposition procedure

DDTC extraction

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 as corbic acid to reduce $\rm Fe^{3+}$ to $\rm Fe^{2+},$ indicated by the disappearance of the characteristic yellow $\rm Fe^{3+}$ colour.

Pour into a separating funnel and wash in with 3 \times 5 mL 5 M HCl to give a total of 20 mL.

Extract Po with 10 mL 0.1% DDTC in CH₃CCl₃ (shake for 30 seconds).

Extract with 2 more 5 mL aliquots of 0.1% DDTC in CH₃CCl₃. If the organic phase is coloured, extract with further aliquots until it is colourless.

Combine the $DDTC/CH_3CCl_3$ portions.

Evaporate to dryness over a 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.

To the dried DDTC/CH₃CCl₃ extract, carefully add 5 mL concentrated HNO₃.

Heat (covered) for ~ 15 minutes on a hot plate.

Auto-deposition

Polish a silver disc by rubbing with a small quantity of an aqueous slurry of high-purity aluminium oxide (elementary particle size about 0.3 μ m).

Rinse the silver disc with water followed by alcohol.

Prepare a deposition cell and stainless steel disc by washing with 2% HNO₃ followed by water.

Place the disc in the deposition cell, with the stainless steel disc placed underneath for support.

Check that the cell is watertight.

Evaporate the Po solution to incipient dryness.

Add 2 mL of 5 M HCl. Warm on a hot plate.

Add as corbic acid to the disappearance of the yellow ${\rm Fe}^{3+}$ colour.

Transfer to a deposition vial containing a silver disc.

Wash the sample in with 10 mL of water.



Figure 5.1 Typical Po α -particle spectrum. Tracer isotope: ²⁰⁹Po.

Place the vial in a water bath at 70–80 $^{\circ}\mathrm{C}$ for 2 hours. Mix using an air bubbler or mechanical stirrer.

Remove the disc, wash with propanol and dry.

Leave the disc for at least 2 days before counting, in order to avoid contamination of the surface-barrier detector.

5.4 Spectrum analysis

Figure 5.1 shows a polonium spectrum with 209 Po used as the yield tracer. The spectrum is a simple one, consisting essentially of two singlet peaks. The spectrum obtained using 208 Po as a tracer is similar, but with a smaller separation between the tracer and 210 Po peaks.

As the two peaks will be essentially 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 Po has a minor (0.92%) peak at 4.62 MeV; the analysis window should be chosen to either exclude or include this peak, and the 209 Po tracer solution calibrated accordingly.

5.4.1 Tailing corrections

A ²¹⁰Po source should be prepared and tailing into the tracer peak energy window measured. If ²⁰⁹Po is the tracer being used, an alternative procedure is to use a ²⁰⁹Po source and assume identical tailing for the ²¹⁰Po peak. For ²⁰⁸Po, however, a ²¹⁰Po source must be used; ²⁰⁹Po sources are unsuitable due to the minor peak at 4.62 MeV, while ²⁰⁸Po sources are unsuitable since some ²⁰⁹Po is usually present on the source.

5.4.2 Calculations

Depending upon which tracer isotope was used, programs POLLY or POL208 may be used to calculate the ²¹⁰Po activity concentration in the sample. These programs correct the results to the date of separation of ²¹⁰Po from its parents ²¹⁰Pb and ²¹⁰Bi, this date being that of the DDTC extraction in the above procedure. If there was any delay between sample collection and ²¹⁰Po separation, then the results should be subsequently corrected back to the date of sample collection using either program POLCOR or program POLON. For this correction, data on the activity concentrations of the parents of ²¹⁰Po (²²⁶Ra, ²¹⁰Pb and ²¹⁰Bi) will be required.

6 Lead

6.1 Introduction

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 sulfate, carbonate, chromate, dichromate and sulfide. Lead nitrate may also be precipitated from fuming nitric acid solutions. In HCl solution, complexes of the form $PbCl_n^{(n-2)-}$ 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 ²¹⁰Pb. The first involves separation of lead from other β emitters, and β -counting of a lead chromate precipitate for the ²¹⁰Bi daughter. The second method utilises determination of the grand-daughter ²¹⁰Po after an ingrowth period.

6.2 Beta-counting method for ²¹⁰Pb

The following method is based upon Waters & Powell (1985) and Lowson & Short (1986). Stable lead is used as both tracer and carrier for ²¹⁰Pb. Lead is separated from other β emitters (except bismuth) by extraction with DDTC into CH₃CCl₃. 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, ²¹⁰Bi allowed to grow in (if necessary) and the ²¹⁰Bi activity in the precipitate determined by β counting. After counting, the precipitate is redissolved and recovery determined using atomic absorption spectrometry.

$DDTC\ extraction$

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 Fe^{3+} to Fe^{2+} , indicated by the disappearance of the characteristic yellow Fe^{3+} colour.

Pour into a separating funnel and wash in with 3 \times 5 mL 1.5 M HCl to give a total of 20 mL.

Extract Pb and Bi with 10 mL 1% DDTC in CH₃CCl₃. (Shake for 30 seconds).

Extract with 2 more 5 mL aliquots of 1% DDTC in CH₃CCl₃. If the organic phase is coloured, extract with further aliquots until it is colourless. Combine the 1% DDTC/CH₃CCl₃ portions.

Evaporate to dryness over a water bath or hot plate at low heat.

Carefully add 5 mL concentrated HNO₃.

Heat (covered) for ~15 minutes on a hot plate.

Remove the cover and take to incipient dryness.

Date of extraction is date of separation of Pb from Ra.

Ra, Th, U and Ac may be determined on the remaining aqueous phase.

Lead chromate precipitation

To the dried $DDTC/CH_3CCl_3$ extract, add approximately 10 mL concentrated HNO₃ and a few drops concentrated HClO₄ and heat 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 $\mu {\rm m}$ membrane filter.

Wash the precipitate with a few mL of deionized water.

Mount the filter for β counting, covering with mylar film to prevent contamination of the detector and the detection of α particles from ²¹⁰Po decay.

Recovery determination

After β counting, dissolve the filter and precipitate by heating in concentrated HNO₃.

Take to incipient dryness and redissolve in 0.5% HNO₃.

Make to 250 mL in a volumetric flask with 0.5% HNO₃.

Determine lead concentration (e.g. by flame atomic absorption spectrometry using the 283.3 nm line).

Anion exchange

For the determination of ²¹⁰Pb by β counting, separation of lead from all β -emitting radionuclides must be guaranteed, since counts from interfering radionuclides cannot be distinguished from the ²¹⁰Bi counts used to determine ²¹⁰Pb. For most samples, the DDTC extraction described above is adequate; however, the following final clean-up step is advisable in cases where the ²²⁶Ra activity is greatly in excess of the ²¹⁰Pb activity (e.g. mussels, process waters):

Take the Pb extract from the DDTC extraction step 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 \times 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 proceed with the lead chromate precipitation procedure above.

Bismuth remains on the column. Time of elution is time of separation of 210 Pb from 210 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.

6.2.1 β counting of lead chromate precipitate

Since the β particles emitted by ²¹⁰Pb are of low energy (0.061 MeV, 19%; 0.015 MeV, 81%), they are absorbed by the window of the β -particle detector. However, a measure of ²¹⁰Pb may be obtained using the higher-energy β particles of its daughter ²¹⁰Bi (4.69 MeV, 40%; 4.65 MeV, 60%; $t_{1/2} = 5.01$ d).

Care must be taken to exclude recording of counts from α particles of the ²¹⁰Bi daughter ²¹⁰Po which will slowly grow in on the precipitate (²¹⁰Po $t_{1/2} = 138$ d). The exclusion of these counts should be confirmed by a series of tests utilising a silver disc on which ²¹⁰Po has been auto-deposited (Section 5.1.2). Increasing numbers of layers of mylar film are placed over the disc before counting with the β 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.

6.2.2 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⁻¹ when finally diluted to 250 mL. The aliquots are taken to dryness, redissolved using acetic acid/ammonium acetate solution, and lead chromate precipitated 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% HNO₃ and diluted to 250 mL using 0.5% HNO₃.

6.3 ²¹⁰Po ingrowth method for ²¹⁰Pb

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

In the following method, stable lead is used as both tracer and carrier for 210 Pb. Polonium is removed by extraction into 0.1% DDTC in CH₃CCl₃ from 5 *M* HCl. Lead is then separated from radium by extraction into 1% DDTC in CH₃CCl₃ from 1.5 *M* HCl. Bismuth and residual polonium are removed on an anion exchange column, and lead recovery determined by methods such as atomic absorption spectroscopy or ICP-MS.

6.3.1 Separation and deposition procedure

DDTC extraction for Po removal

Add the stable lead carrier/tracer solution, equivalent to approximately 3-4 mg lead, if

this has not been added in a previous step.

If 210 Po is also being determined on the sample, add the required tracer.

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 as corbic acid to reduce $\rm Fe^{3+}$ to $\rm Fe^{2+},$ indicated by the disappearance of the characteristic yellow $\rm Fe^{3+}$ colour.

Pour into a separating funnel and wash in with 2 \times 5 mL 5 M HCl to give a total of 15 mL.

Prepare fresh solutions of 0.1% and 1% DDTC in CH₃CCl₃ for the Po and Pb extraction steps.

Extract Po with 10 mL 0.1% DDTC in CH₃CCl₃. (Shake for 30 seconds).

Extract with 2 more 5 mL aliquots of 0.1% DDTC in CH₃CCl₃. If the organic phase is coloured, extract with further aliquots until it is colourless.

DDTC extraction for Pb extraction

Dilute the aqueous phase with 35 mL of water to make it 1.5 M HCl.

Extract Pb with 10 mL 1% DDTC in CH₃CCl₃. (Shake for 30 seconds).

Extract with 2 more 5 mL aliquots of 1% DDTC in CH₃CCl₃.

Combine the 1% DDTC/CH₃CCl₃ 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.

Anion exchange

To the dried DDTC/CH₃CCl₃ extract, carefully add 5 ml concentrated HNO₃.

Heat (covered) for ${\sim}15$ minutes on a hot plate.

Remove the cover and take to incipient dryness.

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, 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 \times 10 mL 9 M HCl.

Storage for ingrowth

Pour the eluate from the anion exchange step into a tared plastic bottle.

Add a known quantity of ²⁰⁸Po or ²⁰⁹Po 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 $(\sim 10 \text{ mL})$ for determination of lead by ICP-MS.

Store the solution for ²¹⁰Po analysis after a suitable ingrowth period.

7 Uranium

7.1 Introduction

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.

7.1.1 Extraction using TBP

Methods of separation for measurement by α -particle spectrometry commonly employ extraction of the uranyl (UO₂²⁺) 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 extraction method described here is based on that of Holm (1984). Uranium is extracted (along with thorium) into concentrated TBP from 8 M HNO₃. At this molarity uranium extraction 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 HNO₃ 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, sulfate 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 NO₃⁻ phase to mask these anions (e.g. nitrate salts of Fe³⁺ or aluminium for phosphate; Fe³⁺ for sulfate; 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.

7.1.2 Anion-exchange

The TBP extraction 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 α -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 procedure described below removes thorium and most other elements (an exception being iron; Marhol 1982).

7.1.3 Electrodeposition

The electrodeposition procedure given here is based on that of Hallstadius (1984). He stated 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 for a deposition time of 1 hour. Radium deposition is less than 1%.

Tomé and Sanchez (1991) studied this deposition technique in detail for uranium. They reported that improved peak resolution with a minimal loss of yield could be obtained

Table 7.1 Effect of deposition time on energy resolution and yield for uranium deposition by the Hallstadius method. Taken from Table 1 of Tomé & Sanchez (1991). Current was 2 A with a 3.8 cm^2 disc area.

Time	$Yield^a$	FWHM
(min)	(%)	(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

 a Uncertainty is 3% (1 σ).

by a reduction in the deposition time (Table 7.1). Consequently, a deposition time for uranium of 40 minutes is recommended in the present procedure.

7.2 Tracers

The three tracers commonly used for uranium determination are ²³²U, ²³³U and ²³⁶U.

 233 U has the disadvantage that its α energy (4.78 + 4.82 MeV) lies within the energy region of the 234 U peak at 4.77 MeV.

 236 U (4.44 + 4.49 MeV) overlaps the 235 U spectrum. For most environmental samples this may be allowed for by assuming the normal 235 U/ 238 U activity ratio of 0.046.

²³²U has the advantage that its α energy is well separated from those of ²³⁸U, ²³⁵U and ²³⁴U, allowing all three to be measured. The daughter and grand-daughter of ²³²U are ²²⁸Th and ²²⁴Ra respectively; their presence in the tracer solution is a disadvantage if a measure of ²²⁸Th and/or ²²⁴Ra on the same sample digest is desired. However, ²²⁸Th may be used as a tracer for measurement of ²³⁰Th and ²³²Th (see Section 8.2), and ²²⁴Ra may be used as a tracer for ²²³Ra, ²²⁶Ra and ²²⁸Ra (Section 9.2). In addition, measurement of the ²²⁸Th peak on the uranium spectrum gives a check of the efficiency of removal of thorium from the uranium fraction.

7.3 Separation and deposition procedure

$TBP \ extraction$

After digestion of the sample, dissolve in 20 mL 8 M HNO₃.

Transfer to a separating funnel and shake with 5 mL TBP for 3 minutes.

After settling, run the 8 M HNO₃ 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 HNO₃ for 1 minute.

If Ra and/or Ac are to be determined, combine the aqueous portions to give the Ra/Ac fraction. Note the date and time of extraction as the Th/Ra separation time for use in

the Ra and Ac analyses¹.

Add 20 mL xylenes to the TBP layer.

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

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

Anion exchange

Evaporate the U 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 with 10 mL 9 M HCl.

Add the sample solution.

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

Elute U with 40 mL 8 M HNO₃ in two 20 mL aliquots.

Note the date of anion exchange as the date of U/Th separation for U analysis.

Take the solution to dryness on a hot plate.

Electrode position

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

Add 1 mL 0.3 M NaSO₄.

Evaporate to total dryness (at low heat to prevent spitting).

Add 0.3 mL concentrated H_2SO_4 .

Warm and swirl the beaker to dissolve the residue. (Do not heat more than necessary; no significant amount of H_2SO_4 should evaporate in the process.)

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

Add drops of concentrated NH₃ to a yellow-yellow/orange colour.

Pour the solution into the electrodeposition cell and wash in with approximately 5 mL 1% H₂SO₄.

Adjust the pH to 2.1–2.4 with concentrated NH_3 using Merck pH paper 9540. (If the enpoint is over-stepped, adjust with $20\% H_2SO_4$.

Buff the anode lightly with sandpaper to remove oxides from the surface.

Rinse the Pt cathode with 2% HNO₃ followed by water.

Deposit at 1.2 A for 40 minutes in a fume cupboard. The distance between cathode and anode is 8 mm; the cell is covered to minimise loss of solution from the cell.

Add 1 mL of concentrated NH_3 about 1 minute before switching off the current.

Wash the disc with 1% NH₃ solution, followed by iso-propanol, and dry by heating it slightly.

Note the date of electrodeposition as the date of final Th/Ra separation.

Rinse the Pt cathode with 2% HNO₃ followed by water.

¹The Ra analysis needs to proceed without delay from this point; see Section 9.



Figure 7.1 Typical U α -particle spectrum. Tracer isotope: ²³²U.

7.4 Spectrum analysis

Figure 7.1 shows a uranium spectrum with 232 U used as the yield tracer. As the 238 U, 234 U and 232 U peaks have similar shapes, the same size analysis window should be used for each.

 228 Th, which grows in on the disc from 232 U, overlaps with its parent's peak. Either of the upper-energy peaks of 224 Ra or 228 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 losses of 228 Th and 224 Ra may occur.

The ${}^{235}\text{U}$ spectrum overlaps with those of both ${}^{238}\text{U}$ and ${}^{234}\text{U}$. 81.7% 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 0.046 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 ${}^{238}\text{U}$ count rate.

7.4.1 Tailing corrections

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

7.4.2 Calculations

Depending upon whether the upper-energy peaks of 228 Th or 224 Ra are to be used as a measure of the 228 Th activity on the disc, either of programs URAN or URANTH may be used to calculate the 238 U, 235 U and 234 U activity concentrations in the sample.

8 Thorium

8.1 Introduction

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 an ion exchange resins with maximum adsorption at approximately 8 M HNO₃ (Marhol 1982). Uranium is also adsorbed, but to a lesser extent.

8.1.1 Extraction using TBP

The extraction method described here is based on that of Holm (1984). Thorium is extracted (along with uranium) into concentrated TBP from 8 M HNO₃. 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 HNO₃ 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 HNO₃. 1 M Al(NO₃)₃/5 M HNO₃ has been successfully used in the *eriss* laboratories as a replacement for the initial 8 M HNO₃ extraction solution. This practice is probably best avoided, however, where the aqueous phase is to be susequently used for analysis of 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 7).

8.1.2 Anion-exchange

For a final clean-up of the thorium fraction after the TBP extraction step, an anion exchange technique is employed; this ensures the removal of traces of uranium and other metal ions.

8.1.3 Electrodeposition

The electrodeposition procedure given here is based on that of Hallstadius (1984). He stated 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%.

8.2 Tracers

The two tracers commonly used for thorium determination are 228 Th and 229 Th.

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

Where 228 Th is added as a tracer solution (e.g. by addition of a 232 U tracer with 228 Th in secular equilibrium) and the 228 Th activity from the sample is not negligibly small compared with the added tracer activity, the sample 228 Th activity must be allowed for. This requires a separate measurement, unless 228 Th is known to be in secular equilibrium with 232 Th in the sample (see discussion of program THORE in Appendix A).

Note that, where an aged 232 U solution is used as a source of 228 Th/ 224 Ra tracer, at secular equilibrium the 228 Th and 224 Ra activity concentrations equal 1.029 times the 232 U concentration, due to the relative half-lives of 232 U and 228 Th.

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

²²⁹Th may also interfere with the ²²⁸Th measurement for two reasons. Firstly, ²²⁹Th solutions usually contain some ²²⁸Th activity. This problem is best avoided by using ²²⁹Th tracer solutions which have been aged so that the tracer ²²⁸Th activity is negligible in comparison with that of the sample; otherwise, a correction must be applied. Secondly, tailing from the ²²⁹Th daughter ²²⁵Ac (Figure 1.4) will also contribute to the ²²⁸Th analysis window due to their proximity in the spectrum. This interference may be minimised by counting the disc as soon as possible after deposition.

8.3 Separation and deposition procedure

$TBP \ extraction$

After digestion of the sample, dissolve in 20 mL 8 M HNO₃.

Transfer to a separating funnel and shake with 5 mL TBP for 3 minutes.

After settling, run the 8 M HNO₃ 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 HNO₃ for 1 minute.

If Ra and/or Ac are to be determined, combine the aqueous portions to give the Ra/Ac fraction. Note the date and time of extraction as the Th/Ra separation time for use in the Ra and Ac analyses.

Add 20 mL xylenes to the TBP layer.

Wash 4 times with 10 mL 5 M HCl to back-extract Th, shaking for 1 minute.

Combine the four extracts in a 50 mL beaker.

Anion exchange

Evaporate the Th extract solution to dryness, and take up in 5 mL 8 M HNO₃.

Prepare a column (4 cm height, 0.7 cm i.d.) with Dowex 1-X8 resin, Cl⁻ form. Convert the column to the NO_3^- form by washing with 10 mL 8 *M* HNO₃.

Add the sample solution.

Wash with 40 mL 8 M HNO₃ to elute U and other interfering ions.

Elute Th with 30 mL 9 M HCl.

${\it Electrode position}$

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

Add 1 mL 0.3 M NaSO₄.

Evaporate to total dryness (at low heat to prevent spitting).

Add 0.3 mL concentrated H_2SO_4 .

Warm and swirl the beaker to dissolve the residue. (Do not heat more than necessary; no significant amount of H_2SO_4 should evaporate in the process.)

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

Add drops of concentrated NH₃ to a yellow-yellow/orange colour.

Pour the solution into the electrode position cell and wash in with approximately 5 mL 1% $\rm H_2SO_4.$

Adjust the pH to 2.1–2.4 with concentrated NH_3 using Merck pH paper 9540. (If the enpoint is over-stepped, adjust with $20\% H_2SO_4$.

Buff the anode lightly with sandpaper to remove oxides from the surface.

Rinse the Pt cathode with 2% HNO₃ followed by water.

Deposit at 1.2 A for 1 hour in a fume cupboard. The distance between cathode and anode is 8 mm; the cell is covered to minimise loss of solution from the cell.

Add 1 mL of concentrated NH_3 about 1 minute before switching off the current.

Wash the disc with 1% $\rm NH_3$ solution, followed by iso-propanol, and dry by heating it slightly.

Note the date and time of electrodeposition (this is the point at which Ra begins to grow in on the disc).

Rinse the Pt cathode with 2% HNO₃ followed by water.

8.4 Spectrum analysis

Figure 8.1 shows a thorium spectrum with 229 Th used as the yield tracer. As the 232 Th and 230 Th peaks have similar shapes, the same size analysis window should be used for each.

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

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



Figure 8.1 Typical Th α -particle spectrum. Tracer isotope: ²²⁹Th.

8.4.1 Tailing corrections

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

8.4.2 Calculations

If 229 Th is used as the yield tracer, then program THOR may be used to calculate the 228 Th, 230 Th and 232 Th activity concentrations in the sample. This program calculates the 228 Th activity concentration back to the date and time of deposition. Subsequent correction to date of sample collection will require a measure of the 228 Ra activity concentration in the sample.

If the yield tracer is 228 Th, then one of the following programs may be used to calculate the 230 Th and 232 Th activity concentrations in the sample:

- THORE, if the $^{228}\mathrm{Th}$ in the sample can be assumed to be in secular equilibrium with $^{232}\mathrm{Th}.$
- THORN, if the ²²⁸Th activity concentration in the sample is known.

9 Radium

9.1 Introduction

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 α -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 be used to measure all α -emitting radium isotopes (²²⁶Ra, ²²⁴Ra, ²²³Ra) and, after a suitable ingrowth period, ²²⁸Ra 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 ²²⁵Ra as a yield tracer, ²²⁶Ra, ²²⁴Ra, ²²⁴Ra, and ²²³Ra are determined from an initial counting soon after deposition, and from the calculated ²²⁵Ra recovery determined after a suitable ingrowth period for ²²⁵Ac and daughters. ²²⁸Ra is determined after an ingrowth period for ²²⁸Th and ²²⁴Ra. Peak FWHM obtained is typically ~40 keV, and chemical recoveries are typically in the range 75–85%.

9.1.1 Element separations

Radium, thorium and actinium are coprecipitated from the sample matrix with lead sulfate. Uranium remains in solution. The sulfate ion is then removed by passage through an anion exchange resin. Thorium and actinium form anionic complexes with EDTA, and are also adsorbed. Radium and lead pass through the anion exchange column in the eluate. Lead (Khopkar & De 1960) and any remaining thorium, actinium, polonium or uranium in the eluate are eluted from the following cation exchange column in the ammonium acetate wash. The alkaline earths (calcium, strontium, barium) are eluted sequentially in the 1.5 M ammonium acetate and 2.5 M HCl washes. The decontamination factors for thorium, actinium, polonium, uranium and lead are greater than 10^4 .

Ba-Ra Separation

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

Gleason (1979) used DCYTA at pH 8.5 to separate barium and radium. However, the use of complexing agents to obtain separation on a cation exchange column often results in residual traces of the complexing agent contaminating the final radium fraction, adversely affecting electrodeposition. For this reason, in the present method 18 column volumes of 2.5 M HCl are used to wash the ammonium acetate and traces of EDTA from the column prior to the elution of radium.

Both barium and radium are strongly adsorbed in a narrow band at the top of the cation exchange column from 0.025 M EDTA solution at pH 4.5, and are separated by elution with 1.5 M ammonium acetate and 2.5 M HCl. The distribution coefficient for barium is approximately equal in the latter two solutions. Approximately 3–5% of the radium



Figure 9.1 133 Ba and 226 Ra separation on a 6 cm cation exchange column. The area under each histogram has been normalised to unity.

is sacrificed in the 2.5 M HCl wash.

The decontamination factor for barium is dependent on the column length. Figure 9.1 shows the results obtained for the separation of 133 Ba and 226 Ra in a trial with a column of 6 cm length. The decontamination factor obtained was 50 (98% removal of barium). For samples with a high barium concentration, a longer cation exchange column can be used. The volume of the wash solutions are then increased proportionally. For example, with a column of 8 cm height, 0.7 cm i.d., the wash volumes are 50 mL 1.5 *M* ammonium acetate in 0.1 *M* HNO₃, followed by 54 mL 2.5 *M* HCl in three 18 mL aliquots. Radium is then eluted with 25 mL 6 *M* HNO₃. This procedure increases the time required for this step, but also increases the barium decontamination factor to ~200.

9.1.2 Electrodeposition

Aqueous/alcohol electrolyte

The majority of radium electrodeposition techniques reported in the literature use an aqueous/alcohol electrolyte solution (Smith & Mercer 1970, Koide & Bruland 1975, Bojanowski *et al.* 1983, Harada & Tsunogai 1985, Hancock & Martin 1991). In the procedure described below, the radium is transferred to the deposition cell with 1.0 mL $0.1 \ M \ HNO_3$ and washed in with 9 mL propanol. Radium is then electrodeposited onto a stainless steel disc at 70 mA for 30 minutes. Ethanol may be used as an alternative to propanol.

During deposition, there should only be a very gentle bubbling action originating from the Pt electrode. Vigorous bubbling may be an indication that the electrolyte solution is boiling. If this is the case, then the current should be reduced slightly to prevent this occurring.

The deposit may be removed by physical abrasion, and so the surface of the source

should not be touched following electrodeposition. Absorption of moisture from the air can lead to degraded peak resolution, and so sources should be stored in a container containing a desiccating agent such as silica gel.

Ammonium acetate/nitric acid electrolyte ("Roman method")

Roman (1984) reported that radium could be electrodeposited onto stainless steel discs from an aqueous solution of ammonium acetate and nitric acid. This method will be referred to here as the "Roman method". The following procedure is that which has been used at *eriss*, and is essentially the same as that of Roman, excepting that he used a current of 400 mA.

Transfer the sample into an electrode position cell with 10 mL 0.35 M ammonium acetate /0.1 $M~{\rm HNO}_3$ 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

The Roman method offers a number of advantages over aqueous/alcohol electrolyte methods. Firstly, the deposit is surprisingly robust. Roman (1984) states that "not more than 10–15% of the activity could be removed from the stainless steel or platinum electrodes when wiped with wet tissue paper or after immersion in water (25°C) for 1 h under vigorous stirring." He gave evidence that the deposit was covered with a protective layer, possibly of platinum (presumably stripped from the anode).

Secondly, sources deposited using the Roman method are usually of high resolution (typically an improvement of 5–10 keV FWHM over a source prepared with an aqueous/alcohol electrolyte).

Finally, the sources have a very high radon retention factor, usually close to 100% even for the longer-lived 222 Rn. If complete retention of radon on the disc could be attained, or if the retention factor were consistent and known, radium isotopes could be determined using their daughter isotope activities. Unfortunately, experience at **eriss** has been that radon retention on sources prepared by the Roman method is variable, occasionally being as low as 80% for 222 Rn.

The most serious problem with the Roman method is the effect of traces of barium on the radium deposition efficiency. Table 9.1 shows the results of a trial in which varying amounts of barium were added to a ²²⁶Ra solution before evaporation and subsequent deposition. Even 1 μ g barium resulted in a significant reduction in deposition efficiency. Consequently, although the Roman method is useful for the production of test sources and for the calibration of relatively pure standard solutions, it is not used at **eriss** as the standard deposition method for radium from environmental samples.

9.2 Tracers

The three tracers commonly used for radium determination are 223 Ra, 224 Ra and 225 Ra. 225 Ra is ideal because it does not occur naturally and is, therefore, not present in environmental samples. Alternatively, 223 Ra or 224 Ra can be used if one accepts a limitation on

Barium	Ra recovery
(μg)	(%)
0	92.7
1	62.5
2	44.8
9	31.2
19	23.5
30	18.0
35	17.0
60	10.5
190	4.0
375	3.0
750	1.2

Table 9.1 Dependence of the efficiency of radium deposition on the quantity of barium present when using the Roman deposition method.

the range of isotopes determined and provided the tracer activity used is large compared with that present naturally in the sample.

 225 Ra ($t_{1/2} = 14.8$ d) is a β emitter and decays to 225 Ac, which in turn decays to a series of short-lived α -emitting progeny. The chemical recovery of 225 Ra is determined from the count rates recorded for the progeny 217 At and/or 213 Po. The activity of 225 Ac reaches a maximum after 17 days (Figure 9.2). However, if the activity of the added 225 Ra is high enough, the recovery can be determined from a count started on the same day as the electrodeposition.

If ²²⁶Ra and/or ²²⁸Ra only are to be measured, the quantity of added ²²⁵Ra will depend on the statistical error required, remembering that the ²²⁵Ac activity will grow to a maximum of only ~44% of the initial ²²⁵Ra spike. If ²²³Ra and/or ²²⁴Ra are to be determined, the added ²²⁵Ra activity should be limited, as ²²⁵Ac will slowly grow in on the disc and contribute to the ²²³Ra + ²²⁴Ra energy region on the spectrum, and this contribution must be subtracted before ²²³Ra and ²²⁴Ra can be determined (see Section 9.4).

Where both thorium and radium analyses are required on a sample, it is convenient to add as tracer a 229 Th solution in secular equilibrium with its 225 Ra daughter (Figure 1.4), or a 228 Th solution in secular equilibrium with its 224 Ra daughter (Figure 1.2). The radium tracer activity is then calculated back to the first point in the separation procedure at which thorium/radium separation occurs.

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 Ra solutions are given by Bojanowski *et al.* (1983) and Sebesta & Stary (1974).

 229 Th solutions usually contain some 228 Th activity, and hence some 224 Ra activity will also be present. For measurement of a low 224 Ra activity a correction may need to be applied.

9.3 Separation and deposition procedure

 $PbSO_4$ precipitation



Figure 9.2 225 Ac ingrowth from 225 Ra, 222 Rn ingrowth from 226 Ra, and 223 Ra & 224 Ra decay on an initially pure radium source.

After digestion of the sample, dissolve in 100 mL 0.1 M HCl or HNO₃.

Add 1 mL 98% H_2SO_4 and 2 g K_2SO_4 and dissolve.

Add 1 mL $0.24 M Pb(NO_3)_2$ solution drop-wise whilst stirring.

If necessary, add further 0.5 mL aliquots of 0.24 $M \operatorname{Pb}(\operatorname{NO}_3)_2$ solution drop-wise until an adequate precipitate has formed¹.

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.

Anion exchange

Add 2 drops ammonia and 5 mL 0.1 M EDTA solution adjusted to pH 10 with ammonia to the PbSO₄ 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, 80 mm height, 7 mm i.d.), and wash with 13 mL 0.005 M EDTA/0.1 M ammonium acetate at pH 8. The flow rate is 0.5–0.7 mL min⁻¹. If ²²⁹Th(²²⁵Ra) or ²²⁸Th(²²⁴Ra) are used as the tracer, record the time of Th/Ra separation.

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 HNO₃ using bromocresol green as an indicator.

The final volume should be about 20 mL.

Cation exchange

¹A good measure of the adequacy of the precipitate can be gained by comparison with the blank sample solution precipitate, which should readily form on addition of the first 1 mL 0.24 M Pb(NO₃)₂ solution

Prepare a cation exchange column (Bio-Rad AG50W-X12, 200-400 mesh, 60 mm height, 7 mm 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 HNO₃.

The flow rate is $0.8-1.0 \text{ mL min}^{-1}$, and can be obtained by fitting a Luer tubing adapter, and raising the column to the required height.

Transfer the solution from the anion exchange column step onto the column and wash with 35 mL 1.5 M ammonium acetate in 0.1 M HNO₃ to elute Pb. Residual Th and Ac are also eluted.

Add 2.5 M HCl in three 14 mL aliquots to wash the ammonium acetate out of the column, and elute Ba. If ²²⁵Ra is used as a tracer, record the time ²²⁵Ac starts to build in.

Ra is then eluted with 20 mL 6 M HNO₃.

Evaporate the solution to a low volume and bring to dryness at low heat.

Electrode position

Dissolve the residue in 1.0 mL 0.1 M HNO₃ and transfer to an electrodeposition cell with 9 mL propanol.

Electrode
posit onto a stainless steel disc at 50 mA for 30 minutes. The anode/cat
hode distance is 4 mm.

Add 2 drops of ammonia a few seconds before stopping the current.

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.

9.4 Spectrum analysis

Figure 9.3 shows typical radium spectra obtained for a groundwater sample. The same source was counted soon after deposition and then again after 20 days and after 6 months, illustrating peak positions and changes in the spectra due to isotope ingrowth and decay. Resolution of the main 226 Ra line is 38 keV FWHM.

The ²²⁶Ra count rate is measured directly from its peaks at 4.60 and 4.78 MeV. ²²⁵Ra $(t_{1/2} = 14.8 \text{ d})$ is a β emitter and decays to ²²⁵Ac, which in turn decays to a series of short-lived α -emitting progeny; of these, ²¹⁷At (7.07 MeV) is the most convenient measure, although ²¹³Po (8.38 MeV) may also be used. The ²²⁵Ac activity reaches a maximum after 17 days (Figure 9.2). However, if the activity of the added ²²⁵Ra is high enough, counting can begin any time after deposition.

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

If a measure of ²²⁸Ra is required, the disc should be stored for at least six months to



Figure 9.3 Typical Ra α -particle spectra. Tracer isotope: ²²⁵Ra. (a) Counted soon after deposition. (b) The same source counted 20 days after deposition. (c) The same source counted after 6 months.

allow ingrowth of ²²⁸Th, and re-counted (Figure 9.3c). A measure of the ingrown ²²⁸Th is obtained by analysis of the ²²⁴Ra peak (5.69 MeV, 95%). During storage, the surface of the source should not be in contact with any other solid surface, else recoil losses of ²²⁴Ra will occur. Abrasive contact with other surfaces would also remove some of the deposit from the disc. Flaming of the disc to volatilize ²²²Rn is not recommended, as the resolution of the source may be seriously degraded.

If the 226 Ra/ 228 Ra ratio is high, the 224 Ra peak may be difficult to resolve from the surrounding 222 Rn and 218 Po peaks. In this case, 228 Ra can be determined by washing the deposit from the disc (e.g. with dilute HNO₃) and subsequently determining 228 Th on the washings (Bojanowski *et al.* 1983). After drying, the washed disc must be counted to ensure that all of the 228 Th activity has been removed; otherwise, a correction for the activity remaining on the disc must be made.

Determination of ²²³Ra and ²²⁴Ra

Determination of the activities of 223 Ra and 224 Ra is not straightforward, because their direct decay lines overlap in the α -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 Rn and 220 Rn respectively) by emanation from the electrodeposited sample. The procedure developed here involves the following steps:

- establishment of the value of ϵ , the ratio of the retention of ²²⁰Rn to that of ²¹⁹Rn, by a separate calibration measurement; this need only be carried out once.
- measurement of the total activity of ²²³Ra plus ²²⁴Ra, $A_{Ra} = [^{223}Ra] + [^{224}Ra]$
- 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 ϵ .
- calculation of the 223 Ra and 224 Ra activities from the radium activity ratio and the measured value of the total radium activity, A_{Ra} .

These steps are described in the following paragraphs.

The 5.2–5.9 MeV region includes the ²²³Ra and ²²⁴Ra peaks, as well as ingrowing ²²²Rn (5.49 MeV) resulting from the decay of ²²⁶Ra and ingrowing ²²⁵Ac plus 2% ²¹³Bi (5.5–5.9 MeV) resulting from the decay of ²²⁵Ra. This ingrowth can be minimized by counting as soon as possible after deposition. The ²²²Rn contribution can be stripped from this region by subtraction of the ²¹⁴Po activity at 7.69 MeV. Similarly, ²²⁵Ac and ²¹³Bi can be stripped by measurement of the ²¹⁷At activity. The remaining activity in this region, A_{Ra} , is due to ²²³Ra and ²²⁴Ra.

As both ²²³Ra and ²²⁴Ra can be expected to be present in most environmental samples, their daughter products must be used to derive their activities. Since both isotopes decay to short-lived gaseous radon isotopes, (²¹⁹Rn $t_{1/2} = 4$ s, ²²⁰Rn $t_{1/2} = 56$ s), losses by diffusion would be expected to occur from a thin source. To obtain a measure of these losses, 7 sources were prepared as described above containing both ²²³Ra and ²²⁴Ra. The ²²³Ra and ²²⁴Ra solutions used were separately calibrated against a ²²⁶Ra solution, giving a percentage standard error due to counting statistics on the ²²⁴Ra/²²³Ra activity ratio of 0.71%. The measured ²²⁰Rn/²¹⁹Rn activity ratio was divided by the

Source	220 Rn retention	Retention ratio ϵ^a
ZS776	0.569 ± 0.002	0.961 ± 0.010
ZS773	0.623 ± 0.002	0.951 ± 0.010
ZS766	0.635 ± 0.002	0.956 ± 0.012
ZS767	0.656 ± 0.003	0.950 ± 0.015
ZS772	0.692 ± 0.003	0.928 ± 0.010
ZS764	0.698 ± 0.002	0.980 ± 0.008
ZS765	0.771 ± 0.003	0.973 ± 0.011
	mean:	0.957
	standard deviation:	0.016
	standard error:	0.006

Table 9.2 220 Rn/ 219 Rn retention ratio (ϵ) and 220 Rn retentions for 7 standard sources. Counting errors correspond to 1 standard deviation

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

calculated ²²⁴Ra/²²³Ra activity ratio for each source to give the radon retention ratio, ϵ (see Table 9.2). As expected, all values of ϵ were less than 1, indicating proportionally higher losses of the longer-lived ²²⁰Rn from the source compared to that of ²¹⁹Rn. For each individual source the value of ϵ appears to be independent, within experimental error, of the measured retention of ²²⁰Rn or ²¹⁹Rn, even though these retentions vary from 0.57 to 0.77 between sources. A mean value for ϵ of 0.957 was obtained with a standard error of 0.006, and this mean value is used in all sample analyses when determining ²²³Ra and ²²⁴Ra activities (see below).

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

Correcting for differential radon loss, the 224 Ra/ 223 Ra activity ratio is given by

$$R_{Ra} = \left(\frac{1}{\epsilon}\right) \left(\frac{^{220}Rn}{^{219}Rn}\right) \tag{9.1}$$

and the individual 223 Ra and 224 Ra concentrations obtained from

$$[^{223}Ra] = \frac{A_{Ra}}{(R_{Ra}+1)} \tag{9.2}$$

and

$$[^{224}Ra] = \frac{A_{Ra} \ R_{Ra}}{(R_{Ra}+1)} \tag{9.3}$$

It should be noted that although this spectral stripping technique will yield a 223 Ra determination with a high degree of sensitivity, the statistical accuracy of the 224 Ra determination will suffer in the presence of substantial 223 Ra activity. In this case, the

Table 9.3 ²²⁰Rn and ²²²Rn retention on the same electrodeposited source.

	$10 \ torr$	760 torr
$^{220} Rn^a / ^{224} Ra$	0.632 ± 0.014	0.488 ± 0.008
$^{222} { m Rn}^{b} / ^{226} { m Ra}$	0.412 ± 0.007	0.270 ± 0.007

 $^{a-220}\mathrm{Rn}$ activity determined from the $^{212}\mathrm{Po}$ peak after an ingrowth period of 60 hours at the specified pressure.

 $^{\hat{b}}$ ²²²Rn activity determined after an ingrowth period of 20 days at the specified pressure.

sensitivity of the ²²⁴Ra determination can be improved by obtaining an estimate of the ²²⁰Rn activity from ²¹²Po at 8.78 MeV, the activity of which is dependent on ingrowth of its ²¹²Pb grandparent ($t_{1/2} = 10.6$ h) and parent ²¹²Bi ($t_{1/2} = 61$ m). The ²²⁰Rn/²¹⁹Rn activity ratio is then given by [²¹²Po]/(0.64)[²¹⁵Po].

However, if there is a delay between electrodeposition and the commencement of counting, the disc should be stored under counting conditions, as the 220 Rn retention, and hence 212 Po ingrowth, are inversely related to air pressure. Table 9.3 shows that the 220 Rn retention of a source determined at 10 torr pressure is approximately 30% higher than that at 1 atmosphere. 222 Rn shows similar behaviour.

Contamination of the detector by recoiling ²²²Rn atoms from the source will, unless prevented, result in an increased background counting rate in the ²²³Ra and ²²⁴Ra energy region. Furthermore, ²²²Rn 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 ²²²Rn activity to be stripped from the ²²³Ra and ²²⁴Ra energy region via measurement of ²¹⁴Po. Both of these problems are effectively eliminated by application of the recoil protection technique described in Section 4.3.

9.4.1 Tailing corrections

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

9.4.2 Calculations

For determination of 226 Ra using 225 Ra as a yield tracer (i.e. for analysis of a spectrum such as that shown in Figure 9.3b), the calculations may be carried out using program RAD225. For 228 Ra determination from a count after an ingrowth period for 228 Th and 224 Ra (Figure 9.3c), program RAD68 may be used. In the case that 228 Ra is to be determined by a measurement of 228 Th after washing the deposit from a radium disc, program RATH228 may be used.

Analysis of an early count such as that shown in Figure 9.3a is more complex. The program used will depend on the circumstances:

• RAD226 is the most commonly used program when ²²³Ra and ²²⁴Ra are to be

determined. The ²²⁶Ra activity on the source disc acts essentially as a yield tracer.

- RAD346 is mainly used when the ²²⁶Ra activity on the disc is low. The radium recovery for the source must be known.
- RADPO is used when ²¹²Po is to be used as a measure of ²²⁰Rn. This approach is complex and is generally only used when the ²²³Ra/²²⁴Ra ratio is high.
- RAD224 is used when $^{224}\mathrm{Ra}$ is used as a tracer for determination of $^{223}\mathrm{Ra}$ and $^{226}\mathrm{Ra}.$

Note that, in the cases of programs RAD224, RAD226, RAD346 and RADPO, the background count rates input for the $(^{224}Ra + ^{223}Ra)$ and ^{220}Rn areas must have been adjusted for contributions from ^{222}Rn , ^{225}Ac and ^{221}Fr using program RADB.

Calculation of ²²⁵Ra recovery (program RAD225)

Let A_0 be the activity of ²²⁵Ra at the time t_0 of separation from ²²⁹Th. If t_1 is the latest time in the procedure at which radium and actinium are separated, then the activity of ²²⁵Ra at this point is given by:

$$A_1 = A_0 e^{-\lambda_1 (t_1 - t_0)} \tag{9.4}$$

where λ_1 is the decay probability of ²²⁵Ra. The subsequent activity of ²²⁵Ac at any time, A(t), is then given by:

$$A(t) = \frac{\lambda_2 A_1 \left[e^{-\lambda_1 (t-t_1)} - e^{-\lambda_2 (t-t_1)} \right]}{(\lambda_2 - \lambda_1)}$$
(9.5)

where λ_2 is the decay probability of ²²⁵Ac. Integrating over the counting period from t_2 to t_3 gives

$$A(t_{2}, t_{3}) = \frac{A_{1}\lambda_{2}}{(\lambda_{2} - \lambda_{1})(t_{3} - t_{2})} \left[\frac{\left[e^{-\lambda_{1}(t_{2} - t_{1})} - e^{-\lambda_{1}(t_{3} - t_{1})} \right]}{\lambda_{1}} - \frac{\left[e^{-\lambda_{2}(t_{2} - t_{1})} - e^{-\lambda_{2}(t_{3} - t_{1})} \right]}{\lambda_{2}} \right]$$
(9.6)

Hence the recovery of ²²⁵Ra is $A_m/A(t_2, t_3)$ where A_m is the measured activity of ²²⁷Ac. These calculations assume that:

- no thorium/radium separation occurs before time t_0
- separation of thorium and radium is quantitative at t_0
- separation of actinium and radium is quantitative at t_1
- no separation of actinium and radium occurs after t_1

In the separation procedures described above, thorium, actinium and radium should all be carried with the $PbSO_4$ precipitate, while radium should be separated from thorium and actinium at both the anion and cation exchange steps. Both radium and actinium should be deposited at the electrodeposition step. Although quantitative (100%) separations or recoveries cannot, in practice, be assured for complex chemical procedures, provided these four steps are carried out within a short period of time (a few hours), the error resulting should generally be negligible. However, in the case that the count occurs only a short time after deposition (say, the same day), then errors arising from inaccuracy in the knowledge of the true point of final actinium/radium separation t_1 could become significant (Johnston & Martin 1988).

10 Actinium

10.1 Introduction

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

 227 Ac is a member of the 235 U series, and is the parent of 227 Th and 223 Ra. This series is only naturally present as 4.6% of the activity of the 238 U series, and so the 227 Ac activity in most environmental samples is extremely low.

Although a β -emitter, ²²⁷Ac can be determined indirectly by measurement of its α emitting progeny, ²²⁷Th and ²²³Ra. Anderson and Fleer (1982) and Nozaki (1984) chemically isolated actinium, and then separated and measured ²²⁷Th after a suitable ingrowth period. Dickson (1985) determined ²²⁷Ac by measurement of the ²²³Ra activity in samples 5 months after collection. Bojanowski *et al.* (1987) electrodeposited actinium onto a stainless steel disc and measured the integrated ²²⁷Th and ²²³Ra activity after an ingrowth period of 2 to 3 months. This technique gave at least a twofold gain in sensitivity over the individual determination of ²²⁷Th or ²²³Ra. In their method, actinium was separated from the sample digest by preconcentration as oxalate and hydroxides, purified on ion-exchange columns and electrodeposited. ²²⁵Ac was used as a yield tracer.

The method described here uses lead sulfate to co-precipitate actinium, radium and thorium (Figure 3.1). Actinium is then separated from radium and thorium on an anion exchange column, purified on a cation exchange column and electrodeposited from an aqueous/ethanol solution. The chemical separation and electrodeposition of Ac can be completed in 5 hours on a digested sample, with an operator time of approximately 1/2 hour per sample for a batch of four samples. Chemical yields are typically 60 to 80%. The use of a ²²⁹Th/²²⁵Ra/²²⁵Ac tracer combined with separation on the anion exchange column enables the convenient determination of actinium, radium and thorium on the same sample digest. ²¹⁰Po, ²¹⁰Pb and isotopes of uranium can also be determined on the same digest by the use of suitable tracer isotopes and the incorporation of additional separation steps prior to the lead sulfate precipitation.

10.1.1 Lead sulfate precipitation

Actinium is separated from the sample matrix by co-precipitation with lead sulfate in the presence of potassium. Thorium and radium are also co-precipitated, whereas uranium and polonium remain in solution.

Actinium has similar chemistry to that of rare earth elements, especially lanthanum. To investigate whether rare earth elements could act as a hold-back carrier, reducing the fraction of Ac co-precipitated with lead sulfate, a series of precipitations was carried out in the presence of varying amounts of added lanthanum. Conditions were as described in Section 10.3. After decanting, the supernate was filtered through a 0.45 μ m filter before counting to remove any suspended precipitate. The results (Table 10.1) show that for up to 1 mg of added La over 90% of the Ac is recovered in the precipitate, but at 10 mg La this had fallen to 75%. It is likely that other rare earth elements will have a similar effect. Consequently, the rare earth element content of the sample should be considered when selecting sample size.

Table 10.1 Precipitation of ²²⁸Ac from 0.1 M HNO₃^{*a*} in the presence of lanthanum (Martin *et al.* 1995).

La	228 Ac in	228 Ac in
(mg)	precipitate (%)	supernate (%)
0.01	94 ± 3	4 ± 2
0.1	$100~\pm~5$	1 ± 1
1.0	$96~\pm~5$	5 ± 4
10	$75~\pm~2$	$25~\pm~4$

 a Note: solutions were 0.3 M in ammonium acetate due to the addition of the 228 Ac tracer solution.

10.1.2 Anion exchange column

Thorium and actinium form anionic EDTA complexes and are adsorbed onto the anion exchange column. Radium passes through the column and can be collected for analysis. Actinium is then eluted with 0.005 M EDTA/0.1 M ammonium acetate at pH 4.2. Thorium remains adsorbed on the column.

In trials with 228 Ac tracer it was found that significant quantities (up to 20%) of actinium pass through the anion exchange column in the 5 mL 0.1 M ammoniacal EDTA (pH 10) solution if this is loaded directly onto the column. This problem was solved by allowing the solution to equilibrate for at least 10 minutes with a small quantity of resin before addition to the column. The additional column height (about 5 mm) does not significantly affect the separation. Since a small amount of resin invariably remains in the beaker, all subsequent wash solutions must be used to wash the beaker before addition to the column.

Figure 10.1a shows a separation trial for a freshwater mussel sample. Only a small quantity (about 0.7%) of the ²²⁸Ac was eluted in the first 8 mL of 0.005 M EDTA/0.1 M ammonium acetate (pH 4.2). The reason is that a significant volume (about 5 to 10 mL) of this solution must pass through the column before a reduction in the pH of the eluate occurs. In order to reduce the volume of eluate collected, and hence the evaporation time and mass of residue remaining after evaporation, the pH of the eluate is monitored, and collection begun only after the pH has fallen to 7. With careful observation the pH change may be observed advancing through the column, as the resin takes on a slightly lighter hue after the pH has fallen. The fall in pH is rapid and so monitoring should be virtually continuous as the front approaches the column exit.

Figure 10.1a also shows the behaviour of 226 Ra and 210 Pb during the anion exchange procedure. These radionuclides were added to the sample and measured via their gamma lines at 186 and 46 keV respectively. More than 90% of both 226 Ra and 210 Pb passed through the column in the first 18 mL of eluate.

If a thorium isotope analysis is required, then after elution of actinium the column is washed with three 20 mL aliquots of 8 M HNO₃. Any residual traces of polonium remaining after the lead sulfate precipitation step are eluted with the 8 M HNO₃. Thorium is then eluted with 30 mL 9 M HCl and electrodeposited onto a stainless disc from a sulfate electrolyte (Hallstadius 1984).


Figure 10.1 (a) ²²⁸Ac, ²²⁶Ra and ²¹⁰Pb separation on an anion exchange column. The area under each histogram has been normalised to unity. (b) ²²⁸Ac behaviour on a cation exchange column. Eluate is 3 M HNO₃. (Martin *et al.* 1995)

10.1.3 Cation exchange column

A cation exchange column is used to purify the separated actinium fraction. The method used is that described by Bojanowski *et al.* (1987). This separation technique gives a final actinium fraction which, after evaporation to dryness, should be virtually free of visual residue. The first 25 mL wash with 3 M HNO₃ elutes rare earth elements and any residual radium, lead, uranium and polonium not removed by the precipitation and anion exchange steps. Actinium is eluted in the following 35 mL portion (Figure 10.1b). Any residual traces of thorium remaining after the anion exchange step are retained on the cation exchange column. Note that wash volumes have been given for a column of 80 mm length in water; after equilibration with 3 M HNO₃ the column will shrink by approximately 5 mm.

10.1.4 Electrodeposition

Actinium is electodeposited onto a stainless steel disc by the same method as that used for radium electodeposition (see Section 9.1.2, aqueous/alcohol electrolyte method). It



Figure 10.2 ^{227}Th + ^{223}Ra ingrowth from $^{227}\text{Ac},$ and ^{225}Ac decay, on an initially pure actinium source.

is important that the surface of the deposit not be touched following deposition, as the method relies on the assumption that no activity is lost from the source in the ingrowth/decay interval between the two counts.

10.2 Tracers

For the determination of ²²⁷Ac, ²²⁵Ac ($t_{1/2} = 10.0$ d) is the preferred tracer as it does not occur naturally and is conveniently measured via its grand-daughter ²¹⁷At. It can be added as a ²²⁹Th/²²⁵Ra/²²⁵Ac tracer solution at secular equilibrium (Figure 1.4), allowing analysis of thorium, radium and actinium on the same sample digest. If this is done then the anion and cation exchange steps in the chemical procedures should be performed as soon as possible after each other (ie within a few hours). This will minimise the effect of any differences in the efficiency with which thorium, radium and actinium are carried in the lead sulfate lattice.

The quantity of ²²⁵Ac tracer added will depend largely on how soon the ²²⁷Ac determination is required. Figure 10.2 shows the change in activity with time for ²²⁷Th + ²²³Ra and ²²⁵Ac, given initially equal activities of ²²⁷Ac and ²²⁵Ac. The quantity of ²²⁵Ac added should be limited so that the ²²⁵Ac activity present in the final count is small compared to the integrated ²²⁷Th and ²²³Ra activity, taking into account the time period within which the ²²⁷Ac determination must be completed.

10.3 Separation and deposition procedure

10.3.1 Standard Procedure

Lead sulfate precipitation

After digestion of the sample, dissolve in 100 mL 0.1 M HCl or HNO₃.

Add 1 mL 98% H_2SO_4 and 2 g K_2SO_4 and dissolve.

Add 1 mL 0.24 M Pb(NO₃)₂ solution drop-wise whilst stirring.

If necessary, add further 0.5 mL aliquots of 0.24 $M \operatorname{Pb}(NO_3)_2$ solution drop-wise until an adequate precipitate has formed¹.

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.

Anion exchange

Add 1 drop ammonia and 5 mL 0.1 M EDTA solution adjusted to pH 10 with ammonia to the PbSO₄ precipitate, and warm the beaker to aid dissolution. If necessary add further 1 mL portions of EDTA solution until the precipitate has dissolved. Add a few drops of an aqueous slurry of anion exchange resin (Bio-Rad AG1-X8) to the solution and allow to equilibrate for 10 min.

Add the solution plus resin onto an anion exchange column (Bio-Rad AG1-X8, 100-200 mesh, Cl^- form, 80 mm height, 7 mm i.d.). The flow rate is 0.5–0.7 mL min⁻¹. Note the time of Ra/Ac separation.

Wash with 13 mL 0.005 M EDTA/0.1 M ammonium acetate at pH 8.

Wash with a further 5 mL 0.005 M EDTA/0.1 M ammonium acetate at pH 8.

Wash with 2 mL 0.005 M EDTA/0.1 M ammonium acetate pH 4.2, then continue washing with 5 mL aliquots of this solution, monitoring the pH of the eluate with pH indicator strips. When the pH falls to 7, begin collecting the eluate and continue to a volume of 15 mL.

Evaporate the eluate to dryness and dissolve the residue in a minimum volume (2-3 mL) of 3 M HNO₃.

Cation exchange

Prepare a cation exchange column (Bio-Rad AG50W-X8, 200-400 mesh, H⁺ form, 80 mm height, 7 mm i.d.), and wash with 15 mL 3 M HNO₃. The flow rate is approximately 1 mL min⁻¹.

Transfer the solution from the anion exchange column step onto the column, and wash with 2 mL aliquots of 3 M HNO₃ until a total of 10 mL has been added.

Wash the column with a further 15 mL 3 M HNO₃.

Add a further 35 mL 3 M HNO₃ to elute Ac. Collect the eluate, evaporate to a low volume, and bring to dryness at low heat.

Electrode position

Dissolve the residue in 1.0 mL 0.1 M HNO₃ and transfer to an electrodeposition cell with 9 mL propanol.

Electrodeposit onto a stainless steel disc at 50 mA for 30 minutes. The anode/cathode distance is 4 mm.

¹A good measure of the adequacy of the precipitate can be gained by comparison with the blank sample solution precipitate, which should readily form on addition of the first 1 mL 0.24 M Pb(NO₃)₂ solution

Add 2 drops of ammonia a few seconds before stopping the current.

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.

10.3.2 PbSO₄ precipitation for large volume samples

For filtered water samples of up to 1 litre where the 227 Ac is considered to be in solution, the lead sulfate precipitation may be carried out directly on the sample. For larger volumes a ferric hydroxide precipitation preconcentration step is recommended in order to avoid the necessity of increasing the amount of lead sulfate precipitated (see Section 3.2.2).

Lead sulfate precipitation

Acidify the 1 litre sample to 0.1 M HCl or HNO₃, add the required amount of tracer, and allow at least one hour to equilibrate.

Add 10 mL 98% H₂SO₄ and 10 g K₂SO₄ and dissolve.

Add 2 mL 0.24 M Pb(NO₃)₂ solution drop-wise whilst stirring.

If necessary, add further 0.5 mL aliquots of 0.24 $M \operatorname{Pb}(NO_3)_2$ solution drop-wise until an adequate precipitate has formed.

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.

Proceed to the anion exchange step above.

10.4 Spectrum analysis

After electrodeposition the disc is stored for at least 15 to 20 minutes to allow ingrowth of the ²²⁵Ac daughter ²²¹Fr ($t_{1/2} = 4.8$ m). The recovery of the ²²⁵Ac tracer ($t_{1/2} = 10.0$ d) is then determined from a count for its grand-daughter ²¹⁷At at 7.06 MeV (Figure 10.3a). A measure of the ²²⁷Ac activity concentration may be obtained on this count from the 4.7–4.95 MeV region. However, since this region represents only 1.4% of ²²⁷Ac decays uncertainties will be large for all but high-activity samples.

A second count is obtained after storing the disc for 2 to 3 months to allow decay of 225 Ac and ingrowth of 227 Th and 223 Ra (Figure 10.3b). The activity in the 5.38–6.10 MeV energy region is due to 227 Th, 223 Ra (99.4%), plus any remaining 225 Ac activity to be deducted from this region.

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 Rn (5.49 MeV) and 218 Po (6.00 MeV) which may be present due to the decay of 226 Ra can be stripped by deducting twice the activity of the 214 Po peak at 7.68 MeV. Potential interference from 210 Po (5.30 MeV) may be avoided by routinely choosing 5.38 MeV as the lower energy limit for 227 Th and 223 Ra measurement. The resultant loss of measurable activity in the 5.25–5.38 MeV region due to 223 Fr at 5.34 MeV and 223 Ra (0.6%), is less than 1% of the total 227 Th and 223 Ra activity.

²²⁸Th and its daughters ²²⁴Ra and ²¹²Bi are the major potential interferences, and their



Figure 10.3 Typical Ac α -particle spectra. Tracer isotope: ²²⁵Ac. (a) Counted soon after deposition. (b) The same source counted 3 months after deposition.

contribution to the ²²⁷Th and ²²³Ra area cannot be measured quantitatively. However, their presence can be detected via measurement of the ²¹²Po peak at 8.78 MeV.

The method relies on the fact that no activity is lost from the source between the two counts. The source deposit is easily removed by mechanical abrasion, and so care should be taken that no solid surface comes into contact with this deposit. Absorption of moisture from the atmosphere can lead to a degradation in peak resolution, and so sources should be stored in a sealed container with a desiccating agent such as silica gel.

10.4.1 Tailing corrections

Tailing of the ²¹⁵Po peak into the ²¹⁷At analysis area on the second count should be allowed for. However, the correction arising from this will not be substantial, because if the activity ratio $(^{217}At)/(^{215}Po)$ is small, then the correction for the contribution of ²²⁵Ac to the (²²³Ra + ²²⁷Th) area must also be small.

10.4.2 Calculations

98.62% of the ²²⁷Ac activity decays by beta emission to ²²⁷Th, and 1.38% by α -particle emission to ²²³Fr (Figure 1.3). 100% of ²²⁷Th and 99.4% of ²²³Ra decays yield α -particle energies in the 5.38–6.10 MeV region. The ²²⁷Ac activity at the time of separation, for a disc counted at any time t after separation, is given by:

$$A_{Ac} = \frac{A_m(t)}{0.9862I_{Th}(t) + 0.994I_{Ra}(t)}$$
(10.1)

where $A_m(t)$ is the measured (²²⁷Th + ²²³Ra) activity; and $I_{Th}(t)$ and $I_{Ra}(t)$ are the calculated ingrowth fractions at time t for ²²⁷Th and ²²³Ra respectively.

Program ACT may be used to carry out the calculations. Note that the background count rate input for the $(^{224}Ra + ^{223}Ra)$ area on the second count must have had contributions from ^{222}Rn , ^{225}Ac and ^{221}Fr subtracted using program ACTB before input into program ACT.

ACT assumes that errors in the knowledge of detection efficiency for the two counts are negligible. Errors arising from this assumption may be avoided by using the same detector and source/detector geometry for the two counts.

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A Description of computer programs

In order to simplify the calculation of results after spectrum analysis, a number of computer programs have been written in the C language to perform the most commonly required calculations. A few of these (ACTB, CRATE, NUCLIDE2 and RADB) require no input apart from that supplied interactively by the user. The remainder require the basic data to be entered into an input file before running the program; the following notes apply to these programs:

Units

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

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

For programs outputting an activity concentration result, the result units will be interactively requested from the user. These units will be dependent on the units for the input tracer activity concentration, tracer mass and sample mass or volume. For example, where

Tracer activity concentration is in mBq/gram Tracer mass is in grams Sample volume is in litres then the activity concentration result will be in mBq/litre

Formats

The programs are "Y2K compliant". Dates may be input as DD.MM.YYYY or DD.MM.YY (e.g. 25.03.00 or 25.03.2000). Dates with time may be input as DD.MM.YY.HHMM or DD.MM.YYYY.HHMM (e.g. 25.03.00.1355 or 25.03.2000.1355). However, the format used must be consistent for all dates in the input file. The programs are "Y2K compliant", however if dates in the input are to span the Y2K point then the 4-digit format for years (YYYY) must be used.

Some programs expect certain information lines to be present in the input file, and these are shown in the example input files given in this appendix. Any other desired information (e.g. tracer solution number, detector code, analyst's initials, input file name) may be placed at the bottom of the input file for reference and will be ignored by the programs. Exceptions to this rule are programs BETAB, LEAD and LEADSEP; these were written for a beta counter output in which consecutive repeat counts are recorded at the bottom of the file.

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 programs.

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

"Background" count rates to be entered into the programs should be a measure of detector background plus procedure blank count rates. They should not include peak tailing corrections; these are allowed for separately. See Section 4.5 for a discussion of detector background and procedure blank measurement.

In most cases, for the following peaks no background count rate is required: 217 At, 214 Po and 213 Po. This is also the case for 224 Ra 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. 214 Po is measured to calculate the contribution of its parent 222 Rn to the 224 Ra + 223 Ra 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:

% Tailing (²³²Th:²³⁰Th)

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

Table A.1 List of computer programs.

Program	Tracer	Application
ACT	$^{225}\mathrm{Ac}$	Determination of 227 Ac by α spectrometry.
ACTB		Calculation of background count rate in the 223 Ra + 227 Th 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 ²¹⁰ Pb by beta counting. Equilibrium between ²¹⁰ Pb and ²¹⁰ Bi assumed.
LEADSEP	stable lead	Determination of 210 Pb by beta counting. Complete separation of 210 Bi at a known time assumed.
LEDPO	stable lead	Calculation of ²¹⁰ Po and ²¹⁰ Pb activity concentrations in a sample at date of collection, using two ²¹⁰ Po determinations, one of ²¹⁰ Po activity concentration in the sample, the other of ²¹⁰ Po activity (after an ingrowth period) in a separated ²¹⁰ Pb portion.
NUCLIDE2		Calculation of activity of 2nd nuclide in a decay series using measurements of its parent and daughter.
POLCOR		Correction of 210 Po activity to date of collection, given 210 Pb activity in the sample at date of collection.
POLLY	²⁰⁹ Po	Determination of ²¹⁰ Po by α spectrometry.
POL208	²⁰⁸ Po	Determination of 210 Po by α spectrometry.
POLON		Calculation of ²¹⁰ Po and ²¹⁰ Pb activity concentrations in a sample at date of collection, using two separate ²¹⁰ Po activity concentration determinations.
RADB		Calculation of background count rate in the 224 Ra + 223 Ra and 220 Rn count areas for use by programs RAD224, RAD226, RAD346 and RADPO.
RAD224	224 Ra	Determination of 223 Ra and 226 Ra by α spectrometry.
RAD225	225 Ra	Determination of 226 Ra by α spectrometry.

RAD226	226 Ra	Determination of 223 Ra and 224 Ra by α spectrometry.
RAD346		Determination of 223 Ra, 224 Ra and 226 Ra by α spectrometry. Generally used where radium recovery is determined by a later count for 225 Ra progeny and 226 Ra activity is low.
RAD68	226 Ra	Determination of 228 Ra by α spectrometry.
RADPO	226 Ra	Determination of 223 Ra and 224 Ra by α spectrometry. 212 Po used as a measure of 220 Rn.
RATH228		Determination of 228 Ra by α spectrometry utilising a 228 Th determination on a redissolved radium disc deposit.
TAILING		Calculation of tailing of a higher-energy peak into a lower-energy peak area.
THOR	$^{229}\mathrm{Th}$	Determination of 232 Th, 230 Th and 228 Th by α spectrometry.
THORE	$^{228}\mathrm{Th}$	Determination of 232 Th and 230 Th by α spectrometry. 228 Th assumed in secular equilibrium with 232 Th in the sample.
THORN	$^{228}\mathrm{Th}$	Determination of 232 Th and 230 Th by α spectrometry. 228 Th concentration in the sample known.
URAN	²³² U	Determination of 238 U, 235 U and 234 U by α spectrometry. 224 Ra used as a measure of 228 Th.
URANTH	$^{232}\mathrm{U}$	Determination of 238 U, 235 U and 234 U by α spectrometry. 228 Th measured using upper-energy peak.

ACT

Determination of ²²⁷Ac by α spectrometry. Tracer isotope: ²²⁵Ac (²²⁹Th/²²⁵Ra/²²⁵Ac)

Spectra

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

$\underline{1st \ count}$

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

2nd count

 227 Th + 223 Ra:

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

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

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

If any ²²²Rn background is present, this will also contribute to this region (²²²Rn 5.49 MeV, 99.92%; plus ²¹⁸Po 6.00 MeV, 100%; plus ²¹⁴Bi 5.45 + 5.52 MeV, 0.02%). This is allowed for via the ²¹⁴Po peak.

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

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

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

²¹⁴Po: 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 $(^{224}Ra + ^{223}Ra)$ area on the second count must have had contributions from ^{222}Rn , ^{225}Ac and ^{221}Fr subtracted using program ACTB.

ACT assumes that errors in the knowledge of detection efficiency for the two counts are negligible¹.

¹Errors arising from this assumption may be avoided by using the same detector and source/detector geometry for the two counts.

Example input file

16.08.1999.093	30 Th/Ra separation date
16.08.1999.100	00 Ra/Ac separation date
17.08.1999.114	45 1st count date start
18.08.1999.143	30 1st count date finish
95.973	1st count time (ks)
2.0761	Tracer mass or volume
175.5	Tracer activity concentration
5.3899	Sample mass or volume
0.2212	Detector efficiency
0.004	At-217 bgd
0.002	At-217 bgd error
5385.	At-217 counts
S	Detector 1
15	Th-229 Tracer
07.04.2000	2nd count date (midpoint)
82.697	2nd count time (ks)
0.2921	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
Т	Detector 2

Example output file

Ac-225 recovery = 78.0 +/- 1.1 % Ac-227 Act conc Error Units 16.022 0.360 mBq/g Note: 1) 1st count started 1.07 days after separation 2) 2nd count midpoint 235.1 days after separation 3) Ac-227 calculated to separation date 1st count decay factor Ac-225 : 0.8934 2nd count decay factors Ac-225 : 0.0000 Ac-227 : 0.9797 2nd count ingrowth factors Th-227 : 0.9819 Ra-223 : 0.9830 4) Rn-219 retention = 73.9 + - 2.5 %5) Errors are one std deviation due to counting statistics only 6) Calculated using program ACT v2.01i1

ACTB

Calculation of background count rate in the $^{223}\mathrm{Ra}+^{227}\mathrm{Th}$ count area for use by program ACT.

Discussion

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

BETAB

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.

Example input and output files

YP013B1.03	Source/count code
PM	Analyst
30.09.87	Count date start
28.8	Count time (ksecs)
140.	
147.	
120.	
116.	
130.	
128.	
121.	
Background	count rate = 4.474 + - 0.149
Note: 1) N	o. counting periods = 7
2) T	otal no. counts = 902
3) M	ean no. counts
р	er count interval = 128.86
w	ith std deviation = 10.43
4) C	alculated using program BETAB v2.00i1

CRATE

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.

\mathbf{EFFY}

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:

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

where a is the radius of the source, h is the source/detector distance, r is the detector radius, and E is the counting efficiency; this relation is an approximation only (Hendee 1984).

Example input and output files

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

```
Efficiency = 0.30674
```

LEAD

Determination of ²¹⁰Pb by beta counting. Equilibrium between ²¹⁰Pb and ²¹⁰Bi assumed. Tracer isotope: stable lead

Discussion

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

Example input file

HP011B1.01	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 weight/volume
0.2974	Detector efficiency
3.998	Background
0.115	Background error
614.	Bi-210 counts
631.	
588.	
579.	
592.	

Example output file

Pb-210 Act conc Error Units 1165.27 30.08 mBq/g Note: 1) No. counting periods = 5 2) Total no. counts = 3004 3) Mean no. counts per count interval = 600.80 with std deviation = 21.23 4) Calculated using program LEAD v2.01i1

LEADSEP

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

Tracer isotope: stable lead

Discussion

²¹⁰Pb is measured by beta counting its daughter ²¹⁰Bi. LEADSEP assumes that ²¹⁰Bi is completely removed from the ²¹⁰Pb preparation on the separation date, and grows in towards secular equilibrium from this point (²¹⁰Bi $t_{1/2} = 5.01$ days).

Counts observed in a series of up to 1000 counting periods are input. Count time refers to the time for each counting period. Count start date refers to the beginning date and time of the first counting period. Each counting period is assumed to begin immediately on the completion of the previous one.

Example input file

```
HL031B1.01
              Disc & count code
              Pb tracer no.
1
ΡМ
              Analyst
23.07.87.1100 Pb/Bi separation date
27.07.87.1430 Count start date
             Count time (ks) per count period
27.6
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 or volume
0.2974
             Detector efficiency
3.944
             Background
0.098
             Background error
780.
             Bi-210 counts
795.
897.
876.
```

Example output file

Ct no.	% ingrowth	No. cts	Pb-210	Error	Units
1	42.4	780	1397.228	56.159 *	mBq/g
2	44.8	795	1348.853	53.545 *	mBq/g
3	47.2	897	1472.244	53.981 *	mBq/g
4	49.5	876	1366.353	50.895 *	mBq/g
Total	48.3	3348	1327.971	25.832 * 30.800 **	mBq/g

Note: 1) Pb-210 calculated to date of Pb/Bi sepn

- 2) Errors marked * are due to counting statistics only3) Errors marked ** are due to
- counting statistics plus recovery error
- 4) Calculated using program LEADSEP v2.02i2

LEDPO

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

Discussion

LEDPO makes the following assumptions:

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

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

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

N.B. The input "Solution Po-210 activity at 2nd determination" refers to total activity of 210 Po in the separated Pb portion. This may be obtained using, for example, program POLLY with the sample mass/volume input as 1.0.

Example output file

			Pb-	210		Po-2	10		
		Act	conc	Erro	r Act	conc	Error	. Units	
		194	. 255	32.72	5 5	4.328	0.718	8 mBq/L	
Note:	1)	Pb-210	and	Po-210	calcul	ated to	date	sample col	lected
	2)	1st Po	dete	rminat	ion	2 days	after	sample col	lected
	3)	Pb sep	arati	on	3 days	after s	ample	collected	
	3)	2nd Po	dete	rminat	ion 34	8 days	after	Pb separat	ion
	4)	Relati	ve co	ntribu	tions t	o the P	o-210	activities	3
		observ	ed at	the t	wo dete	rminati	ons ar	re:	
			Ra-2	26	Pb-210	Bi	-210	Po-210	Tracer
		Det 1	0.00	00	0.0044	0.	0304	0.9652	
		Det 2	0.00	00	0.9982				0.0018
	5)	Calcul	ated	using	program	LEDPO	v2.00i	.1	

Example input file

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

NUCLIDE2

Calculation of activity of the 2nd nuclide in a decay series using measurements of its parent and daughter (e.g. determination of 227 Th using measurements of 227 Ac and 223 Ra).

Discussion

3 nuclides decay in series:

 $1 \longrightarrow 2 \longrightarrow 3 \longrightarrow$

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). This program is used to subsequently calculate the activity of nuclide 2 at time t = 0.

POLCOR

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

Discussion

POLCOR is used where ²¹⁰Po activity has been determined in a sample with a delay between sample collection and ²¹⁰Po determination (see POLLY and POL208). ²¹⁰Pb 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 ²¹⁰Po activity back to collection date.

²¹⁰Pb is assumed to be unsupported in the sample.

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

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

Example input file

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
BL022B1.01	Code for Pb-210 determination
BP533V.01	Code for Po-210 determination

Example output file

Po-210 Act conc Error Units 235.754 15.375 mBq/L

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 0.0011 0.0073 0.9917
4) Errors are one std deviation due to counting statistics only
5) Calculated using program POLCOR v2.0011

POLLY

Determination of $^{210}\mathrm{Po}$ by α spectrometry.

Tracer isotope: ²⁰⁹Po

Spectrum

 209 Po: essentially a singlet peak (4.88 MeV, 98.6%; 4.62 MeV, 0.92%).

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

Discussion

POLLY assumes complete separation of ²¹⁰Po from both ²¹⁰Pb and ²¹⁰Bi on the separation date. ²¹⁰Po 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 ²⁰⁹Po between calibration date and count date.

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

In order to allow the program to distinguish the input file from one designed for program POL208, the first line of the input file must begin with the string "polly".

Example input and output files

polly	Program				
05.07.93	Separation date (Pb-Bi/Po)				
09.08.93	Count date				
212.048	Count time (ks)				
10.	Tracer mass or volume				
7.325	Tracer activity conc				
2.365	Sample mass or volume				
0.2157	Detector efficiency				
0.109	Po-209 bgd				
0.015	Po-209 bgd error				
0.166	Po-210 bgd				
0.010	Po-210 bgd error				
3251.	Po-209 counts				
4989.	Po-210 counts				
0.098	% Tailing (Po-209:Po-210)				
0.012	Error in tailing ratio				
05.07.91	Calibration date (Po-209)				
Po-20	9 recovery = 97.6 +/- 1.7 %				
	Po-210				
	Act conc Error Units				
	55.923 1.273 mBq/g				
Note: 1)	Disc counted 35 days after separation				
100001 1)	Po-210 calculated to date of separation				
2)	Errors are one std deviation due to counting statistics only				
3)	Calculated using program POLLY v2.01i1				
υ,	Carcarator abino program rozzi (2)(0111				

POL208

Determination of ²¹⁰Po by α spectrometry.

Tracer isotope: ²⁰⁸Po

Spectrum

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

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

Discussion

POL208 assumes complete separation of ²¹⁰Po from both ²¹⁰Pb and ²¹⁰Bi on the separation date. ²¹⁰Po 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 208 Po between calibration date and count date.

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

In order to allow the program to distinguish the input file from one designed for program POLLY, the first line of the input file must begin with the string "pol208".

Example input and output files

pol208 I	Program					
	Separation date (Pb-Bi/Po)					
09.05.88 (Count date					
148.250 (Count time (ks)					
10.	Iracer mass or volume					
8.146	Iracer activity conc					
7.4231 \$	Sample mass or volume					
0.2157 I	Detector efficiency					
0.073 1	Po-208 bgd					
0.006 1	Po-208 bgd error					
0.045 1	Po-210 bgd					
0.008 1	Po-210 bgd error					
1910. I	Po-208 counts					
2204. I	Po-210 counts					
0.207	% Tailing (Po-208:Po-210)					
0.018 I	Error					
13.03.87 (Calibration date (Po-208)					
Po-208 1	recovery = 95.9 +/- 2.2 %					
	Po-210					
	Act conc Error Units					
	10.245 0.322 mBq/g					
Note: 1) Dis	sc counted 12 days after separation					
Po	-210 calculated to date of separation					
2) Er:	rors are one std deviation due to counting statistics only					
3) Ca	lculated using program POL208 v2.01i1					

POLON

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

Discussion

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

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

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

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

Example input file

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

Example output file

		Pb-210		Po-	210		
		Act conc	Error	Act conc	Error	Units	
		4417.77	127.11	3478.22	106.39	mBq/g	
Note:	1)	Pb-210 and	Po-210 ca	lculated t	o date s	ample coll	ected
	2)	1st Po dete	ermination	2 days	after s	ample coll	ected
	3)	2nd Po dete	ermination	. 898 days	after s	ample coll	ected
	4)	Relative co	ntributio	ns to the	Po-210 a	ctivities	
		observed at	t the two	determinat	ions are	e:	
		Ra-2	26 РЪ	-210 B	i-210	Po-210	
		Det 1 0.00	00 0.	0016 C	.0110	0.9874	
		Det 2 0.00	001 0.	9902 C	.0004	0.0093	
	г \	a 1 1 1 1					

5) Calculated using program POLON v2.00i1

RADB

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

Discussion

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

RAD224

Determination of 226 Ra and 223 Ra by α spectrometry

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

Spectrum

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

 226 Ra: a doublet (4.78 MeV, 94.45%; 4.60 MeV, 5.55%).

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

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

 220 Rn + 211 Bi:

this area is used in conjunction with the ²¹⁵Po and the (²²⁴Ra + ²²³Ra) areas to give the ²²⁰Rn retention value and consequently ²²⁴Ra activity. The contribution of ²¹⁹Rn and ²¹¹Bi to this area is low (16.25%) relative to that in the (²¹⁶Po + ²¹⁹Rn + ²¹¹Bi) area; hence this area is particularly useful when the ²²³Ra/²²⁴Ra ratio is high. The ²²⁵Ra daughter ²²¹Fr has a high-yield (84.74%) peak in this area, however; hence its use should be avoided when there is substantial ²²⁵Ra daughter activity present. The lower energy boundary should be chosen to exclude the ²¹²Bi and ²¹⁸Po peaks in the 6.0–6.1 MeV region.

 216 Po + 219 Rn + 211 Bi:

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

- ²¹⁷At: a singlet peak (7.07 MeV, 99.9%).
- ²¹⁵Po: a singlet peak (7.39 MeV, 99.95%).
- ²¹⁴Po: a singlet peak (7.69 MeV, 99.99%).
- ²¹³Po: a singlet peak (8.38 MeV, 100%).

Discussion

RAD224 assumes that the tracer is a ²²⁸Th solution with ²²⁴Ra 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 224 Ra tracer activity remaining at time of counting, integrated over the counting period, is given in the output. Two areas (220 Rn + 211 Bi) and (216 Po + 219 Rn + 211 Bi) may be used as a measure of 220 Rn retention. If either of these areas are not used, input the number of counts as 0. If the 217 At and/or 213 Po peaks are not used, input the number of counts as 0. 213 Po is the daughter of 213 Bi 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 212 Po (daughter of 224 Ra) peak at 8.78 MeV. The decay yield for this peak is therefore measured experimentally using a high-activity source of 229 Th in secular equilibrium with its progeny and input as the ratio of counts observed for 213 Po to counts observed for 217 At.

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

Example output file

```
Using Po-216 peak as a measure of radon retention,
    Ra-224 recovery = 77.7 +/- 1.9 %
    Rn-220 retention = 66.3 +/- 1.7 %
                 Ra-226
                                    Ra-223
           Act conc
                      Error
                              Act conc
                                         Error
                                                 Units
            3377.39
                      90.28
                               151.429 11.444
                                                 mBq/g
         Ra-223/Ra-226
                             Ra-226/Ra-223
Ratio
              0.045
                                 22.304
              0.003
                                  1.615
Error
Note: 1) Disc count started 1.06 days after Th/Ra separation
      2) Ra-223 value adjusted to Th/Ra separation date
      3) Tracer activity at counting = 214.513
      4) Ra-226 activity on disc = 323.120 + - 3.606
      5) Errors are one std deviation due to counting statistics only
```

6) Calculated using program RAD224 v2.01i1

Example input file

05.02.88.133	30 Th/Ra separation date (first)
05.02.88.143	30 Ra/Ac separation date (last)
06.02.88.150	00 Count date start
07.02.88.133	30 Count date finish
80.98	Count time (ks)
20.8629	Tracer mass or volume
13.723	Tracer activity conc
0.12307	Sample mass or 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 d	counts observed in each region. Input = 0. if region not used.
8066.	Ra-226 of Ra-226
4842.	Ra-224 + Rn-222 + Ra-223 + Ac-225measure of Ra-224 + Ra-223
0.	Rn-220 + Bi-211measure of Rn-220
3179.	Po-216 + Rn-219 + Bi-211measure of Rn-220
0.	At-217use if Ac-225 present
230.	Po-215 of Rn-219
355.	Po-214measure of Rn-222
0.	Po-213use 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

RAD225

Determination of 226 Ra by α spectrometry. Tracer isotope: 225 Ra (229 Th/ 225 Ra)

Spectrum

 226 Ra: a doublet (4.78 MeV, 94.45%; 4.60 MeV, 5.55%).

 224 Ra + 223 Ra + 222 Rn + 225 Ac: this region (5.25 - 5.90 MeV) may be measured to apply a tailing correction for the 226 Ra area (see discussion below).

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

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

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

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

Discussion

RAD225 assumes that the tracer is a ²²⁹Th solution with ²²⁵Ra 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.

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

Both 217 At and 213 Po 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 (224 Ra + 223 Ra + 222 Rn + 225 Ac) into the 226 Ra energy region may be applied. If a default value of 0. counts is input, the program calculates the tailing due to 225 Ac, 223 Ra and 222 Rn only via the input 217 At, 215 Po and 214 Po counts.

 213 Po is the daughter of 213 Bi 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 212 Po (daughter of 224 Ra) peak at 8.78 MeV. The decay yield for this peak is therefore measured experimentally using a high-activity source of 229 Th in secular equilibrium with its progeny and input as the ratio of counts observed for 213 Po to counts observed for 217 At.

Example input file

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 (ks)
7.2563	Tracer mass or volume
14.084	Tracer activity conc
0.9904	Sample mass or 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

Example output file

Ra-225 recovery (from At-217 peak) = 80.0 +/- 1.9 %
Ra-226
Act conc Error Units
205.017 5.501 mBq/L
Note: 1) Ra/Ac separation 0.02 days after Ra/Th separation
2) Count start 18.06 days after Ra/Ac separation
3) Ac-225 ingrowth factor = 0.4410
Po-213 ingrowth factor = 0.4411
4) Ra-226 activity on disc = 162.459 +/- 1.855

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

6) Calculated using program RAD225 v2.00i1

RAD226

Determination of $^{223}\mathrm{Ra}$ and $^{224}\mathrm{Ra}$ by α spectrometry.

Used in the following situations:

- ²²⁶Ra is determined separately (e.g. by a later count of the same disc with ²²⁵Ra as a tracer). In this case ²²⁶Ra acts essentially as a tracer for the ²²⁴Ra and ²²³Ra determinations.
- ²²⁶Ra 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 ²²⁵Ra progeny are present.

 226 Ra: a doublet (4.78 MeV, 94.45%; 4.60 MeV, 5.55%).

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

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

 220 Rn + 211 Bi:

this area is used in conjunction with the ²¹⁵Po and the (²²⁴Ra + ²²³Ra) areas to give the ²²⁰Rn retention value and consequently ²²⁴Ra activity. The contribution of ²¹⁹Rn and ²¹¹Bi to this area is low (16.25%) relative to that in the (²¹⁶Po + ²¹⁹Rn + ²¹¹Bi) area; hence this area is particularly useful when the ²²³Ra/²²⁴Ra ratio is high. The ²²⁵Ra daughter ²²¹Fr has a high-yield (84.74%) peak in this area, however; hence its use should be avoided when there is substantial ²²⁵Ra daughter activity present. The lower energy boundary should be chosen to exclude the ²¹²Bi and ²¹⁸Po peaks in the 6.0–6.1 MeV region.

 216 Po + 219 Rn + 211 Bi:

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

- ²¹⁷At: a singlet peak (7.07 MeV, 99.9%).
- ²¹⁵Po: a singlet peak (7.39 MeV, 99.95%).
- ²¹⁴Po: a singlet peak (7.69 MeV, 99.99%).
- ²¹³Po: a singlet peak (8.38 MeV, 100%).

Discussion

Two areas $(^{220}\text{Rn} + ^{211}\text{Bi})$ and $(^{216}\text{Po} + ^{219}\text{Rn} + ^{211}\text{Bi})$ may be used as a measure of ^{220}Rn retention. If either of these areas is not used, input the number of counts as 0. If the ^{217}At and/or ^{213}Po peaks are not used, input the number of counts as 0.

 213 Po is the daughter of 213 Bi 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 212 Po (daughter of 224 Ra) peak at 8.78 MeV. The decay yield for this peak is therefore measured experimentally using a high-activity source of 229 Th in secular equilibrium with its progeny and input as the ratio of counts observed for 213 Po to counts observed for 217 At.

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

There are four tracer options in RAD226:

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

Example output file

Ra-226 recovery = 81.1 +/- 5.5 %

Rn-220	Rn-220	ret	Ra-224		Ra-223		
Peak	%		Act conc	Error	Act conc	Error	Units
Rn-220	69.0	2.4	10.905	0.807	3.604	0.303	mBq/L
Po-216	69.6	2.7	10.941	0.834	3.573	0.307	mBq/L
Both	69.3	2.0	10.898	0.814	3.580	0.318	mBq/L
	Ra-224/Ra	a-226	Ra-223/	'Ra-226	Ra-224/H	Ra-223	Ra-223/Ra-224
Ratio	1.017		0.334		3.044		0.329
Error	0.039		0.020		0.217		0.023

Note: 1) Disc count started 0.25 days after Th/Ra separation 2) Ra-223 & Ra-224 values adjusted to Th/Ra separation date 3) Decay factors: Ra-224 0.8146 Ra-223 0.9356

4) Ra-226 activity on disc = 42.614 +/- 0.975

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

6) Calculated using program RAD226 v2.01i1

Example input file

18.07.89.10	15 Th/Ra separation date (first)
18.07.89.11	25 Ra/Ac separation date (last)
18.07.89.162	20 Count date start
20.07.89.09	15 Count date finish
147.295	Count time (ks)
0.	Mass or volume of added tracer
0.	Tracer Ra-226 activity conc.
10.713	Sample Ra-226 activity conc
0.688	Error in sample Ra-226 conc
4.9077	Sample mass or volume
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 o	counts observed in each region. Input = 0. if region not used.
1950.	Ra-226 Ma-226
2425.	Ra-224 + Rn-222 + Ra-223 + Ac-225measure of Ra-224 + Ra-223
1216.	Rn-220 + Bi-211(16%)measure of Rn-220 retn.
1931.	Po-216 + Rn-219 + Bi-211measure of Rn-220 retn.
42.	At-217use if Ac-225 present
439.	Po-215 measure of Ra-223
110.	Po-214 measure of Rn-222
0.	Po-213use 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	Batio observed Po-213:At-217

RAD346

Determination of 223 Ra, 224 Ra and 226 Ra by α spectrometry. Generally used where radium recovery is determined via a later count for 225 Ra progeny, and 226 Ra activity is low.

Tracer isotope: Radium recovery known.

Spectrum

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

 226 Ra: a doublet (4.78 MeV, 94.45%; 4.60 MeV, 5.55%).

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

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

 220 Rn + 211 Bi:

this area is used in conjunction with the ²¹⁵Po and the (²²⁴Ra + ²²³Ra) areas to give the ²²⁰Rn retention value and consequently ²²⁴Ra activity. The contribution of ²¹⁹Rn and ²¹¹Bi to this area is low (16.25%) relative to that in the (²¹⁶Po + ²¹⁹Rn + ²¹¹Bi) area; hence this area is particularly useful when the ²²³Ra/²²⁴Ra ratio is high. The ²²⁵Ra daughter ²²¹Fr has a high-yield (84.74%) peak in this area, however; hence its use should be avoided when there is substantial ²²⁵Ra daughter activity present. The lower energy boundary should be chosen to exclude the ²¹²Bi and ²¹⁸Po peaks in the 6.0–6.1 MeV region.

 216 Po + 219 Rn + 211 Bi:

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

- ²¹⁷At: a singlet peak (7.07 MeV, 99.9%).
- ²¹⁵Po: a singlet peak (7.39 MeV, 99.95%).
- ²¹⁴Po: a singlet peak (7.69 MeV, 99.99%).
- 213 Po: a singlet peak (8.38 MeV, 100%).

Discussion

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

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

 213 Po is the daughter of 213 Bi 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 212 Po (daughter of 224 Ra) peak at 8.78 MeV. The decay yield for this peak is therefore measured experimentally using a high-activity source of 229 Th in secular equilibrium with its progeny and input as the ratio of counts observed for 213 Po to counts observed for 217 At.

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

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

Example input file

05.08.87.123	30 Th/Ra separation date (first)
05.08.87.135	55 Th/Ra separation date (first)
06.08.87.180	05 Count date start
08.08.87.184	40 Count date finish
171.683	Count time (ks)
84.4	Radium recovery (%)
3.1	Radium recovery error
1.0843	Sample mass or volume
0.3077	Detector efficiency
0.957	Rn-220/Rn-219 retention ratio
0.158	Ra-226 bgd
0.030	Ra-226 bgd error
0.117	Ra-224 bgd
0.033	Ra-224 bgd error
0.029	Rn-220 bgd
0.019	Rn-220 bgd error
0.012	Po-216 bgd
0.008	Po-216 bgd error
0.004	Po-215 bgd
0.002	Po-215 bgd error
Input o	counts observed in each region. Input = 0. if region not used.
68.	Ra-226 measure of Ra-226
109.	Ra-224 + Rn-222 + Ra-223 + Ac-225measure of Ra-224 + Ra-223
58.	Rn-220 + Bi-211(16%)measure of Rn-220 retn.
39.	Po-216 + Rn-219 + Bi-211measure of Rn-220 retn.
25.	At-217use if Ac-225 present
2.	Po-215 measure of Ra-223
11.	Po-214measure of Rn-222
0.	Po-213use 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
0.284	% Tailing (Po-215:Po-214)
0.042	Error
0.9374	Ratio observed Po-213:At-217
Example output file

	Ra-226						
		Act conc	Error	Units			
		0.843	0.204	mBq/L			
Rn-220	Rn-220	ret	Ra-2	24	Ra-2	223	
Peak	%	Act	conc	Error	Act conc	Error	Units
Rn-220	62.2	21.8	1.599	0.972	0.047	0.056	mBq/L
Po-216	67.8	21.7	1.604	0.475	0.043	0.051	mBq/L
Both	65.0	18.5	1.602	0.433	0.045	0.053	mBq/L
	Ra-224/	Ra-226	Ra-22	3/Ra-226	Ra-22	24/Ra-223	3
Ratio	1.	900	(0.053	;	35.811	
Error	0.	681	(0.064	4	43.273	
Note:	1) Disc c 2) Ra-223	ount stari & Ra-224	ted 1.23 values	3 days af adjusted	fter Th/Ra to Th/Ra :	separati separatic	.on on date
	5) Decay	iactors:	Ra-224	0.0577			
			Ra-223 (0.8733	, _		
	4) Ra-226	activity	on disc	= 0.77	(2 + / - 0.1)	184	
	5) Errors	are one s	std devia	ation due	e to count:	ing stati	stics only

6) Calculated using program RAD346 v2.01i2

RAD68

Determination of 228 Ra by α spectrometry.

Tracer isotope: known sample ²²⁶Ra activity concentration

Spectrum

²²⁶Ra: a doublet (4.78 MeV, 94.45%; 4.60 MeV, 5.55%).

- ²²⁴Ra: the upper-energy ²²⁴Ra peak (5.685 MeV, 94.94%) is used as a measure of ²²⁴Ra and consequently its parent ²²⁸Th. The ²²²Rn peak (5.49 MeV, 99.92%) and ²¹⁰Po peak (5.30 MeV, 100%, ingrown on the disc from ²²⁶Ra via ²²²Rn and ²¹⁰Pb) prevent use of the 5.06% ²²⁴Ra peak at 5.44 MeV.
- ²¹⁴Po: a singlet peak (7.69 MeV, 99.99%). This peak is used as a measure of ²²²Rn progeny for calculation of tailing (primarily from the ²¹⁸Po peak) into ²²⁴Ra.

Discussion

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

Due to the proximity of the ²²²Rn peak, only a relatively small energy interval (approximately 0.15-0.17 MeV) can be used for measurement of the ²²⁴Ra peak at 5.685 MeV. Although this peak theoretically represents 94.94% of ²²⁴Ra 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 ²²⁴Ra decays be input. This estimate can be obtained from an analysis of the ²²⁶Ra peaks in the same spectrum. The ²²⁶Ra peak at 4.78 MeV (94.45%) is measured using an energy interval of the same size as that used for the ²²⁴Ra measurement. The required ratio for ²²⁴Ra (measured at 5.685 MeV:total) is then obtained from the ratio for ²²⁶Ra (measured at 4.78 MeV:total) multiplied by (0.9494/0.9445) = 1.005.

Example input file

06.08.87	Th/Ra separation date
29.06.89	Count date
82.438	Count time (ks)
69.14	Sample Ra-226 activity conc
3.76	Error in sample Ra-226 conc
0.9842	Sample mass or 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

```
Ra-226 recovery = 81.4 +/- 5.0 %
                      Ra-228
                           Error
                                   Units
                Act conc
                                   mBq/L
                 112.228
                           7.861
         Ra-228/Ra-226
                             Ra-226/Ra-228
Ratio
              1.623
                                  0.616
              0.072
                                  0.027
Error
Note: 1) Disc counted 693 days after separation
      2) Ra-228 calculated to date of separation
     3) Ra-224 build-up factor = 0.4367
     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 v2.00i1
```

RADPO

Determination of ²²³Ra and ²²⁴Ra by α spectrometry. ²¹²Po used as a measure of ²²⁰Rn. Used in preference to RAD226 when the ²²³Ra/²²⁴Ra ratio is high.

Spectrum

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

 226 Ra: a doublet (4.78 MeV, 94.45%; 4.60 MeV, 5.55%).

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

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

- ²¹⁷At: a singlet peak (7.07 MeV, 99.9%).
- ²¹⁵Po: a singlet peak (7.39 MeV, 99.95%).
- ²¹⁴Po: a singlet peak (7.69 MeV, 99.99%).
- 213 Po: a singlet peak (8.38 MeV, 100%).
- ²¹²Po: a singlet peak (8.78 MeV, 100% of ²¹²Po). This area is used in conjunction with the ²¹⁵Po and the (²²⁴Ra + ²²³Ra) areas to give the ²²⁰Rn retention value and consequently ²²⁴Ra activity.

Discussion

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

- the slow in growth of the parents $^{212}{\rm Pb}$ $(t_{1/2}$ = 10.64 h) and $^{212}{\rm Bi}$ $(t_{1/2}$ = 60.55 m); and
- 212 Po is produced by a 64.06% branch decay of 212 Bi.

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 ²¹²Pb ($t_{1/2} = 10.64$ h) and ²¹²Bi ($t_{1/2} = 60.55$ m) parents of ²¹²Po grow in on the preparation at a constant rate, i.e. that the ²²⁰Rn retention remains constant from the time of Ra/Pb-Bi separation. Although this last condition cannot be achieved in practice using current source preparation steps is kept short (less than 1 hour) and the disc is kept under counting conditions prior to counting, the resultant error should be small.

The ²¹²Po ingrowth factor given is the (time integrated) ratio of the activity of ²¹²Po to that of ²²⁰Rn over the counting period, assuming constant ²²⁰Rn 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 (²¹²Po:²¹³Po) is the ratio of the count rate observed in the ²¹²Po analysis area to that in the ²¹³Po analysis area due to the upper-energy tail of the ²¹³Po peak. This factor varies with detection efficiency. The ²¹³Po:²¹⁷At observed ratio is dependent on a number of factors (analysis area chosen for ²¹³Po; ²¹³Po upper-energy tailing; ²¹³Po is the daughter of ²¹³Bi via a 98% decay branch). Both the % tailing factor (²¹²Po:²¹³Po) and the ²¹³Po:²¹⁷At count rate ratio are measured experimentally using a high-activity source of ²²⁹Th in secular equilibrium with its progeny.

RADPO assumes that the Ra/Pb-Bi separation date is also the last Ra/Ac separation date, and calculates the relative ingrowth of 213 Po and 225 Ac on the source (the half-life of 213 Bi is 45.59 minutes).

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

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

There are four tracer options in RADPO:

No ²²⁶ Ra in sample ²²⁶ Ra tracer added	Input sample 226 Ra concentration as 0.
226 Ra sample conc. known 226 Ra tracer added	RADPO sums $^{226}\mathrm{Ra}$ activity from sample and tracer
226 Ra sample conc. known No 226 Ra tracer added	Input tracer activity concentration as 0.
²²⁶ Ra sample conc. not known No ²²⁶ Ra tracer added	RADPO calculates radium isotope ratios only

Example input file

```
07.08.90.1115 Th/Ra separation date (first)
07.08.90.1310 Ra/Pb-Bi separation date (last)
08.08.90.1515 Count date start
10.08.90.0910 Count date finish
150.948 Count time (ks)
```

0. Mass or volume of added tracer 0. Tracer Ra-226 activity conc 9.188 Sample Ra-226 activity conc 0.435 Error in sample Ra-226 conc 6.6918 Sample mass or volume 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) % Tailing (Ra-226:Ra-224) 0.105 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 Example output file Ra-226 recovery = 81.7 +/- 4.3 % Rn-220 retention = 71.0 +/- 3.0 % Ra-224 Ra-223 Act conc Error Act conc Error Units 4.159 0.317 6.193 0.400 mBq/L Ra-224/Ra-226 Ra-223/Ra-226 Ra-224/Ra-223 Ra-223/Ra-224 0.453 0.674 0.672 1.489 Ratio Error 0.027 0.030 0.048 0.107 Note: 1) Disc count started 1.17 days after Th/Ra separation 2) Disc count started 1.09 days after Ra/Pb-Bi separation 3) Ra-223 & Ra-224 values adjusted to Th/Ra separation date 4) Decay factors: Ra-224: 0.6827 Ra-223: 0.8841 Po-212 ingrowth factor: 1.0375 5) Ra-226 activity on disc = 50.210 +/- 1.195 6) Errors are one std deviation due to counting statistics only 7) Calculated using program RADPO v2.00i1

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RATH228

Determination of 228 Ra by α spectrometry utilising a 228 Th determination on a redissolved radium disc deposit.

Discussion

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

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

 $^{228}\mathrm{Th}$ determination date is the deposition date used in THOR.

Example input file

Details from	n 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
0R066	Disc code
Details from	n 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.
OT154J.01	Disc & count code

Example output file

	Ra-228/Ra-226	Ra-226/Ra-228
Ratio	1.261	0.793
Error	0.083	0.052

Note: 1) Th-228 determined 257 days after separation 2) Ra-228 calculated to date of separation

3) Th-228 build-up factor = 0.2154

4) Calculated using program RATH228 v2.00i1

TAILING

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

Example input file

2	No. of tailing peak areas
148.692	Count time
0.014	Peak #0 bgd
0.007	Peak #0 bgd error
0.004	Peak #1 bgd
0.003	Peak #1 bgd error
0.006	Peak #2 bgd
0.004	Peak #2 bgd error
95328.	Peak #0 counts
223.	Peak #1 counts
248.	Peak #2 counts

Example output file

Peak no.	Tail(%)	error	Count rate	error
0			641.096	2.076
1	0.233	0.016	1.496	0.100
2	0.259	0.017	1.662	0.106

- 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. 0).
 - 2) Errors are one std deviation due to counting statistics only
 - 3) Calculated using program TAILING v2.00i1

THOR

Determination of 232 Th, 230 Th and 228 Th by α spectrometry.

Tracer isotope: ²²⁹Th

Spectrum

 232 Th: essentially a doublet (4.01 MeV, 77.9%; 3.95 MeV, 22.1%; 3.83 MeV, 0.06%).

- ²³⁰Th: essentially a doublet (4.69 MeV, 76.3%; 4.62 MeV, 23.4%; 4.48 MeV, 0.12%; 4.44 MeV, 0.03%) situated just below the broad ²²⁹Th peak band; in addition, some minor (0.25% total) ²²⁹Th peaks lie under the ²³⁰Th upper-energy peak and cannot be separated from it. Hence, the accuracy of the tailing correction is critical for spectra where the ²²⁹Th/²³⁰Th ratio is high.
- $^{229}{\rm Th}:$ this is a complex spectrum. THOR assumes that the 99.75% of counts above the $^{230}{\rm Th}$ peaks are measured.
- ²²⁸Th: essentially a doublet (5.42 MeV, 71.1%; 5.34 MeV, 28.2%; 5.21 MeV, 0.43%; 5.17 MeV, 0.23%; 5.14 MeV, 0.04%). The lower-energy ²²⁴Ra line (5.45 MeV, 5.06%) lies just above the upper-energy ²²⁸Th line (5.42 MeV) and cannot be separated from it. This must be allowed for as ²²⁴Ra is the daughter of ²²⁸Th and will inevitably be present in the spectrum.

 225 Ac can also show significant tailing into 228 Th; it is the grand-daughter of 229 Th and will therefore be present in the spectrum. It may be conveniently measured using one of its progeny, 217 At, 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.

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

 $^{228}{\rm Th}$ activity is corrected to deposition date, allowing for $^{228}{\rm Th}$ decay, and ingrowth from $^{232}{\rm Th}$ via $^{228}{\rm Ra}.$

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

Example input and output files

12.03.94.11	l5 Deposition date
14.03.94.102	20 Count date (start)
15.03.94.100	05 Count date (finish)
82.370	Count time (ks)
5.2687	Tracer mass or volume
15.275	Tracer activity concentration
1.2356	Sample mass or volume
0.2711	Detector efficiency
0.006	Th-232 bgd
0.006	Th-232 bgd error
0.018	Th-230 bgd
0.010	Th-230 bgd error
0.024	Th-229 bgd
0.012	Th-229 bgd error
0.036	Th-228 bgd
0.015	Th-228 bgd error
146.	Th-232 counts
106.	Th-230 counts
1683.	Th-229 counts
428.	Th-228 counts
12.	At-217 counts
4.51	Lower energy boundary for Th-230 area (MeV)
5.23	Lower energy boundary 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

Th-229 recovery = 93.7 +/- 2.3 %

	Th-232		Th-230		Th-228			
	Act conc Error		Error	Act conc	Error	Act conc	Error	Units
	Ę	5.405	0.495	3.555	0.433	16.282	0.889	mBq/L
	•	[h-228/]	Th-232	Th-230/	Th-232	Th-228/	Th-230	
Ratic)	3.0	012	0.	658	4.	581	
Error	-	0.3	304	0.	098	0.	591	
Note:	 2) Th-228 calculate 2) Count midpoint = 3) Theoretical ing: Ra-224 : 0.3711 At-217 : 0.0089 Observed ratio 		ed to date = 2.5 d rowth fact At-217/Th-	of depo ays afte ors: 229: 0.0	sition r depositio 071 +/- 0.0	n 021		

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

5) Calculated using program THOR v2.01i1

THORE

Determination of $^{232}{\rm Th}$ and $^{230}{\rm Th}$ by α spectrometry. $^{228}{\rm Th}$ assumed in secular equilibrium with $^{232}{\rm Th}$ in the sample.

Tracer isotope: ²²⁸Th

Spectrum

 232 Th: essentially a doublet (4.01 MeV, 77.9%; 3.95 MeV, 22.1%; 3.83 MeV, 0.06%).

- ²³⁰Th: essentially a doublet (4.69 MeV, 76.3%; 4.62 MeV, 23.4%; 4.48 MeV, 0.12%; 4.44 MeV, 0.03%).
- ²²⁸Th: essentially a doublet (5.42 MeV, 71.1%; 5.34 MeV, 28.2%; 5.21 MeV, 0.43%; 5.17 MeV, 0.23%; 5.14 MeV, 0.04%). The lower-energy ²²⁴Ra line (5.45 MeV, 5.06%) lies just above the upper-energy ²²⁸Th line (5.42 MeV) and cannot be separated from it. This must be allowed for as ²²⁴Ra is the daughter of ²²⁸Th and will inevitably be present in the spectrum.
- 224 Ra: essentially a doublet (5.685 MeV, 94.94%; 5.45 MeV, 5.06%). Only the upper-energy (5.685 MeV) peak is measured.

Discussion

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

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

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

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

In either case, the 224 Ra contribution to the 228 Th area is calculated using the tailing factor given in the input file (% Tailing 228 Th: 224 Ra). This is the count rate due to 224 Ra observed in the 228 Th area as a percentage of the upper-energy (5.685 MeV) 224 Ra peak only.

Note that use of the 224 Ra 5.685 MeV peak assumes that all of the counts observed in this region are due to 224 Ra. 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 225 Ac, the daughter of 225 Ra which may be present on the detector if sources have previously been counted with 229 Th as tracer. Hence, the presence of 225 Ac *must* be checked for using the 217 At peak at 7.07 MeV before the 5.685 MeV 224 Ra peak can be used.

A second complication in the use of the 224 Ra 5.685 MeV peak appears in the calculation of 228 Th background count rate. Where there is significant 224 Ra present in the background spectrum, its contribution to the 228 Th area must be subtracted from the 228 Th background count rate given to THORN if the 224 Ra 5.685 MeV peak is to be used. This situation is most likely to arise where the counting of a high-activity 228 Th source has resulted in significant 224 Ra on the detector due to recoil.

Example input and output files

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 (ks)
6.9472	Tracer mass or volume
13.585	Tracer activity concentration
1.5217	Sample mass or 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	Lower energy boundary for Th-230 area (MeV)
5.23	Lower energy boundary 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
5.33	% Tailing (Th-228:Ra-224)
0.05	lalling error
Th-:	228 recovery = 87.9 +/- 1.6 %
	Th-232 Th-230
	Act conc Error Act conc Error Units
	3.803 0.270 4.642 0.305 mBq/g
	Th-230/Th-232 Th-232/Th-230
Ratio	1.221 0.819
Error	0.114 0.076
Noto: 1	Deposition 1.1 days after separation
Note: 1) Count midpoint 4.8 days after deposition
2) Ba-224 ingrowth factor
0	Calculated: 0.5953
	Observed: $0.5747 + 7 - 0.0159$
4) Sample Th-228 assumed in equilibrium with Th-232
5) Errors are one std deviation due to counting statistics only
0	, Liters are one but devident due to containing but is bits only

6) Calculated using program THORE v2.00i1

THORN

Determination of $^{232}\mathrm{Th}$ and $^{230}\mathrm{Th}$ by α spectrometry. $^{228}\mathrm{Th}$ concentration in the sample known.

Tracer isotope: ²²⁸Th

Spectrum

 232 Th: essentially a doublet (4.01 MeV, 77.9%; 3.95 MeV, 22.1%; 3.83 MeV, 0.06%).

- $^{230}{\rm Th:}$ essentially a doublet (4.69 MeV, 76.3%; 4.62 MeV, 23.4%; 4.48 MeV, 0.12%; 4.44 MeV, 0.03%).
- ²²⁸Th: essentially a doublet (5.42 MeV, 71.1%; 5.34 MeV, 28.2%; 5.21 MeV, 0.43%; 5.17 MeV, 0.23%; 5.14 MeV, 0.04%). The lower-energy ²²⁴Ra line (5.45 MeV, 5.06%) lies just above the upper-energy ²²⁸Th line (5.42 MeV) and cannot be separated from it. This must be allowed for as ²²⁴Ra is the daughter of ²²⁸Th and will inevitably be present in the spectrum.
- 224 Ra: essentially a doublet (5.685 MeV, 94.94%; 5.45 MeV, 5.06%). Only the upper-energy (5.685 MeV) peak is measured.

Discussion

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

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

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

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

In either case, the 224 Ra contribution to the 228 Th area is calculated using the tailing factor given in the input file (% Tailing 228 Th: 224 Ra). This is the count rate due to 224 Ra observed in the 228 Th area as a percentage of the upper-energy (5.685 MeV) 224 Ra peak only.

Note that use of the 224 Ra 5.685 MeV peak assumes that all of the counts observed in this region are due to 224 Ra. 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 225 Ac, the daughter of 225 Ra which may be present on the detector if sources have previously been counted with 229 Th as tracer. Hence, the presence of 225 Ac MUST be checked for using the 217 At peak at 7.07 MeV before the 5.685 MeV 224 Ra peak can be used.

A second complication in the use of the 224 Ra 5.685 MeV peak appears in the calculation of 228 Th background count rate. Where there is significant 224 Ra present in the background spectrum, its contribution to the 228 Th area must be subtracted from the 228 Th background count rate given to THORN if the 224 Ra 5.685 MeV peak is to be used. This situation is most likely to arise where the counting of a high-activity 228 Th source has resulted in significant 224 Ra on the detector due to recoil.

Example input and output files

03.03.89.1	200 U/Th separation date
04.03.89.1	.430 Deposition date
08.03.89.1	.000 Count date (start)
10.03.89.0	0930 Count date (finish)
171.085	Count time (ks)
9.4286	Tracer mass or 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 or 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	Lower energy boundary for Th-230 area (MeV)
5.23	Lower energy boundary 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
5.33	% Tailing (Th-228:Ra-224)
0.05	Tailing error
Th-22	28 recovery = 92.9 +/- 1.3 %
	Th-232 Th-230
	Act conc Error Act conc Error Units
	0.452 0.038 1.028 0.058 mBg/L
	Th-230/Th-232 Th-232/Th-230
Ratio	2.273 0.440
Error	0.226 0.044
Note: 1)	Deposition 1.1 days after separation
2)	Count midpoint 4.8 days after deposition
3)	Ra-224 ingrowth factor.
	Calculated: 0.5949
	Observed: 0.5993 +/- 0.0132
4)	Sample Th-228 concentration input by user
5)	Errors are one std deviation due to counting statistics only
6)	Calculated using program THORN v2.00i1

URAN

Determination of 238 U, 235 U and 234 U by α spectrometry. 224 Ra used as a measure of 228 Th.

Tracer isotope: ²³²U

Spectrum

- ²³⁸U: essentially a doublet (4.20 MeV, 79%; 4.15 MeV, 20.9%; 4.04 MeV, 0.08%). Two minor ²³⁵U peaks (6.6% total ²³⁵U) overlap this area.
- 235 U: this is a complex spectrum, with inevitable overlap with 238 U and 234 U. URAN assumes that the peaks between 4.25 and 4.45 MeV (total 81.7%) are measured.
- 234 U: essentially a doublet (4.78 MeV, 71.4%; 4.72 MeV, 28.4%; 4.60 MeV, 0.20%). Three minor 235 U peaks (10.8% total 235 U) overlap this area.
- 232 U: essentially a doublet (5.32 MeV, 68.6%; 5.26 MeV, 31.2%; 5.14 MeV, 0.28%). A number of 228 Th peaks (28.9% total 228 Th) overlap this area.
- ²²⁴Ra: the upper-energy ²²⁴Ra peak (5.685 MeV, 94.94%) is used as a measure of ²²⁸Th activity on the disc, and therefore of ²²⁸Th contribution to the ²³²U peak.

Discussion

URAN determines a calculated 235 U figure based upon 0.046 times the observed 238 U activity. This is then used to determine the 235 U contribution to the 238 U and 234 U peaks. This procedure assumes the natural 235 U/ 238 U ratio; the calculation will, therefore, not be correct if applied to a source prepared from 235 U -enriched or -depleted uranium.

The ²²⁸Th activity calculated from the ²²⁴Ra peak is used to give a thorium breakthrough figure. URAN assumes that ²²⁸Th is in secular equilibrium with ²³²U in the tracer solution². The program then calculates Th break-through from the excess of observed thorium activity over the calculated ingrown activity. The ²²⁸Th 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 232 U between calibration date and count date.

In order to allow the program to distinguish the input file from one designed for program URANTH, the first line of the input file must begin with the string "uran".

 $^{^{2}}$ At secular equilibrium, the 228 Th activity is 1.029 times the 232 U activity, due to the relative halflives of the two isotopes

Example input file

uran	Program
15.07.2000	Separation date
17.07.2000	Deposition date
02.08.2000	Count date
279.22	Count time (ks)
7.5418	Tracer mass or volume
6.218	Tracer activity concentration
1.1159	Sample mass or 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
0.122	Ra-224 bgd
0.011	Ra-224 bgd error
1609.	U-238 counts
74.	U-235 counts
3639.	U-234 counts
3403.	U-232 counts
79.	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
15.07.1995	Calibration date (U-232)

Example output file

U-232 recovery = 97.1 +/- 1.7 %

	U-23	38	U-23	4	U-235(m	eas)	U-235(c	alc)	
Act	conc	Error	Act conc	Error	Act conc	Error	Act conc	Error	Units
18	. 752	0.580	42.804	1.037	0.803	0.148	0.863	0.027	mBq/L
		U-234/	ับ-238	U-2:	35/U-238				
Rati	0	2.2	83	(0.043				
Erro	r	0.0	70	(0.008				
Note	: 1)	Disc cou	nted 18	days af	ter separat	ion			
			16	days af [.]	ter deposit	ion			
	2)	Th-228 i	ngrowth fa	ctors: (Calculated: 0.0177				
			(Observed : 0.0148 +/- 0.0031					
	Th-228 breakthrough = -0.3			34 +/- 0.31	% assu	ming no Th-	228 in	sample	
3) Errors are one std deviation du				ion due to	countin	g statistic	s only		
	4)	Calculat	ed using p	rogram U	JRAN v2.01i	1			

URANTH

Determination of 238 U, 235 U and 234 U by α spectrometry. 228 Th measured using upper-energy peak.

Tracer isotope: ²³²U

Spectrum

- ²³⁸U: essentially a doublet (4.20 MeV, 79%; 4.15 MeV, 20.9%; 4.04 MeV, 0.08%). Two minor ²³⁵U peaks (6.6% total ²³⁵U) overlap this area.
- 235 U: this is a complex spectrum, with inevitable overlap with 238 U and 234 U. URAN assumes that the peaks between 4.25 and 4.45 MeV (total 81.7%) are measured.
- 234 U: essentially a doublet (4.78 MeV, 71.4%; 4.72 MeV, 28.4%; 4.60 MeV, 0.20%). Three minor 235 U peaks (10.8% total 235 U) overlap this area.
- 232 U: essentially a doublet (5.32 MeV, 68.6%; 5.26 MeV, 31.2%; 5.14 MeV, 0.28%). A number of 228 Th peaks (28.9% total 228 Th) overlap this area.
- ²²⁸Th: the upper-energy ²²⁸Th peak (5.423 MeV, 71.1%) is used as a measure of ²²⁸Th activity on the disc, and therefore of ²²⁸Th contribution to the ²³²U peak.

Discussion

URANTH determines a calculated 235 U figure based upon 0.046 times the observed 238 U activity. This is then used to determine the 235 U contribution to the 238 U and 234 U peaks. This procedure assumes the natural 235 U/ 238 U ratio; the calculation will, therefore, not be correct if applied to a source prepared from 235 U -enriched or -depleted uranium.

The ²²⁸Th activity calculated from the ²²⁴Ra peak is used to give a thorium breakthrough figure. URANTH assumes that ²²⁸Th is in secular equilibrium with ²³²U in the tracer solution³. The program then calculates Th break-through from the excess of observed thorium activity over the calculated ingrown activity. The ²²⁸Th 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 232 U between calibration date and count date.

In order to allow the program to distinguish the input file from one designed for program URAN, the first line of the input file must begin with the string "uranth".

 $^{^{3}}$ At secular equilibrium, the 228 Th activity is 1.029 times the 232 U activity, due to the relative halflives of the two isotopes

Example input file

uranth	Program
15.07.2000	Separation date
17.07.2000	Deposition date
02.08.2000	Count date
279.22	Count time (ks)
7.5418	Tracer mass or volume
6.218	Tracer activity concentration
1.1159	Sample mass or 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
3639.	U-234 counts
3403.	U-232 counts
82.	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
15.07.1995	Calibration date (U-232)

Example output file

U-232 recovery = 97.0 +/- 1.7 %

U-238 U-234 U-235(meas) U-235(calc) Act conc Error Act conc Error Act conc Error Act conc Error Units mBq/L 18.771 0.581 42.847 1.038 0.803 0.148 0.863 0.027 U-235/U-238 U-234/U-238 Ratio 2.283 0.043 0.070 0.008 Error Note: 1) Disc counted 18 days after separation 16 days after deposition 2) Th-228 ingrowth factors: Calculated: 0.0177 Observed : 0.0183 +/- 0.0032 Th-228 breakthrough = 0.01 + - 0.32 % assuming no Th-228 in sample 3) Errors are one std deviation due to counting statistics only 4) Calculated using program URANTH v2.01i1

B Radionuclide decay data

The following tables give the radionuclide decay data which have been assumed in the programs discussed in Appendix A. As such, they are not intended to be definitive and researchers requiring accurate data are advised to consult primary sources. The data given here have been derived from Firestone (1996). Intensities are given as % of all decays of the isotope. Transformations with intensities of less than 0.01% have not been included in these tables, nor are they accounted for in the programs.

Polonium tracer isotopes								
Isotope	Half-life	Decay Mode	${ m Energies} \ ({ m MeV})$	$\frac{Intensities}{\%}$	Daughter			
Po-208	2.898 y	alpha	5.115	100	Pb-204			
Po-209	102 y	alpha99.52 $%$	$\begin{array}{c} 4.883\\ 4.622\end{array}$	$\begin{array}{c} 98.60 \\ 0.92 \end{array}$	Pb-205			
		$\begin{array}{c} \mathrm{EC} \\ 0.48 \ \% \end{array}$			Bi-209			

Thorium s	eries (4n series)				
Isotope	Half-life	Decay Mode	${ m Energies}\ { m (MeV)}$	$\begin{array}{c} \text{Intensities} \\ \% \end{array}$	Daughter
U-236	$2.342\times10^7~\mathrm{y}$	alpha	$\begin{array}{c} 4.494 \\ 4.445 \\ 4.332 \end{array}$	$73.8 \\ 25.9 \\ 0.26$	Th-232
U-232	68.9 y	alpha	$5.321 \\ 5.264 \\ 5.137$	$68.6 \\ 31.2 \\ 0.28$	Th-228
Th-232	$1.405 \times 10^{10} \text{ y}$	alpha	4.013 3.954 3.830	$77.9 \\ 22.1 \\ 0.06$	Ra-228
Ra-228	5.75 y	beta		100	Ac-228
Ac-228	$6.15~\mathrm{h}$	beta		100	Th-228
Th-228	1.9131 y	alpha	5.423 5.340 5.211 5.173 5.138	$71.1 \\ 28.2 \\ 0.43 \\ 0.23 \\ 0.04$	Ra-224
Ra-224	3.66 d	alpha	$5.685\\5.449$	$\begin{array}{c} 94.94\\ 5.06\end{array}$	Rn-220
Rn-220	$55.6 \ \mathrm{s}$	alpha	$6.288 \\ 5.747$	$\begin{array}{c} 99.89\\ 0.11\end{array}$	Po-216
Po-216	$0.145 \ \mathrm{s}$	alpha	6.778	100	Pb-212
Pb-212	10.64 h	beta			Bi-212
Bi-212	$60.55 \mathrm{~m}$	beta		64.06	Po-212
		alpha 35.94 %	$\begin{array}{c} 6.090 \\ 6.051 \\ 5.768 \\ 5.626 \\ 5.607 \end{array}$	$9.75 \\ 25.13 \\ 0.64 \\ 0.06 \\ 0.43$	Tl-208
Po-212	$0.299~\mu{ m s}$	alpha	8.784	100	Pb-208
Tl-208	$3.053 \mathrm{\ m}$	beta		100	Pb-208

Uranium series (4n + 2 series)

Isotope	Half-life	Decay Mode	$rac{\mathrm{Energies}}{\mathrm{(MeV)}}$	$\frac{Intensities}{\%}$	Daughter
U-238	$4.468 \times 10^9 { m y}$	alpha	$\begin{array}{c} 4.198 \\ 4.151 \\ 4.038 \end{array}$	$79.0 \\ 20.9 \\ 0.08$	Th-234
Th-234	24.10 days	beta		100	Pa-234m
Pa-234m	1.17 m	beta IT		$\begin{array}{c} 99.84\\ 0.16\end{array}$	U-234 Pa-234
Pa-234	$6.70~\mathrm{h}$	beta		100	U-234
U-234	$2.455 \times 10^5 { m y}$	alpha	$\begin{array}{c} 4.775 \\ 4.722 \\ 4.604 \end{array}$	$71.38 \\ 28.42 \\ 0.20$	Th-230
Th-230	$7.538\times10^4\mathrm{y}$	alpha	$\begin{array}{c} 4.688 \\ 4.621 \\ 4.480 \\ 4.438 \end{array}$	$76.3 \\ 23.4 \\ 0.12 \\ 0.03$	Ra-226
Ra-226	1600 y	alpha	$\begin{array}{c} 4.784\\ 4.602 \end{array}$	$94.45 \\ 5.55$	Rn-222
Rn-222	3.8235 d	alpha	$5.490\\4.987$	$\begin{array}{c} 99.92 \\ 0.08 \end{array}$	Po-218
Po-218	$3.10 \mathrm{~m}$	alpha	6.002	100	Pb-214
Pb-214	26.8 m	beta		100	Bi-214
Bi-214	19.9 m	beta		99.98	Po-214
		$\substack{\text{alpha}\\0.021~\%}$	$5.516 \\ 5.452 \\ 5.273$	$0.0082 \\ 0.0113 \\ 0.0012$	Tl-210
Po-214	$164.3~\mu{\rm s}$	alpha	$7.687 \\ 6.902$	$\begin{array}{c} 99.99\\ 0.01 \end{array}$	Pb-210
Tl-210	$1.30 \mathrm{\ m}$	beta		100	Pb-210
Pb-210	22.3 у	beta		100	Bi-210
Bi-210	$5.013 \mathrm{d}$	beta		100	Po-210
Po-210	138.376 d	alpha	5.304	100	Pb-206

Isotope	Half-life	Decay Mode	$rac{\mathrm{Energies}}{\mathrm{(MeV)}}$	$\frac{Intensities}{\%}$	Daughter
U-233	1.592×10^5 y	alpha	$\begin{array}{c} 4.824\\ 4.804\\ 4.796\\ 4.783\\ 4.758\\ 4.758\\ 4.751\\ 4.751\\ 4.729\\ 4.701\\ 4.681\\ 4.664\\ 4.634\\ 4.600\\ 4.513\\ 4.507\end{array}$	84.4 0.05 0.28 13.2 0.02 0.16 0.01 1.61 0.06 0.01 0.04 0.01 0.04 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.02 0.01 0.01 0.01 0.01 0.01 0.01 0.02 0.01 0.01 0.01 0.01 0.01 0.02 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.02 0.01 0.02 0.01 0.02 0.01	Th-229
Th-229	7340 y	alpha	5.078 5.053 5.036 5.009 4.978 4.968 4.930 4.901 4.878 4.865 4.861 4.852 4.845 4.845 4.833 4.815 4.809 4.798 4.754 4.754 4.754 4.694 4.690 4.690 4.484	0.05 6.6 0.24 0.09 3.17 5.97 0.16 10.2 0.03 0.28 0.03 56.2 5.0 0.29 9.30 0.22 1.5 1.0 0.05 0.01 0.12 0.23 0.05 0.02 0.03	Ra-225
Ra-225	14.9 d	beta		100	Ac-225

Neptunium series (4n + 1 series)

Isotope	Half-life	Decay	Energies	Intensities	Daughter
		Mode	$({ m MeV})$	%	
Ac-225	10 0 d	alpha	5830	50.7	Fr-221
110 220	10.0 4	aipiia	5.805	0.3	11 221
			5.000 5.793	18 1	
			5.791	8.6	
			5.732	9.32	
			5 731	0.82	
			5.701 5.724	3.1	
			5.682	13	
			5.637	4 4	
			5.609	1 1	
			5.598	0.04	
			5.580	1.2	
			5.563	0.03	
			5.554	0.1	
			5.545	0.03	
			5.540	0.02	
			5.443	0.14	
			5.436	0.07	
			5.321	0.07	
			5.286	0.23	
			5.270	0.01	
			5.211	0.03	
Fr-221	4.9 m	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	$32.3 \mathrm{\ ms}$	alpha	7.067	99.9	Bi-213
			6.812	0.06	
			6.609	0.01	
			6.483	0.02	
Bi-213	$45.59~\mathrm{m}$	beta		97.91	Po-213
		alpha	5.869	1.94	Tl-209
		2.09%	5.549	0.15	11 200
		,	0.010	0.10	
Po-213	$4.2 \ \mu s$	alpha	8.376	100	Pb-209
Tl-209	2.20 m	beta		100	Pb-209
Pb-209	3.253 h	beta		100	Bi-209

Isotope	Half-life	Decay Mode	${ m Energies}\ { m (MeV)}$	$\frac{\rm Intensities}{\%}$	Daughter
U-235	$7.038 \times 10^8 \text{ y}$	alpha	$\begin{array}{c} 4.596\\ 4.556\\ 4.502\\ 4.435\\ 4.414\\ 4.398\\ 4.366\\ 4.345\\ 4.324\\ 4.271\\ 4.219\\ 4.215\\ 4.150\end{array}$	$\begin{array}{c} 4.9\\ 4.2\\ 1.7\\ 0.7\\ 2.1\\ 56\\ 18\\ 1.5\\ 3\\ 0.4\\ 0.9\\ 5.7\\ 0.9\end{array}$	Th-231
Th-231	25.52 h	beta		100	Pa-231
Pa-231	$3.276 \times 10^4 \text{ y}$	alpha	5.059 5.032 5.028 5.014 4.986 4.975 4.975 4.951 4.934 4.853 4.795 4.736 4.713 4.681 4.643 4.632 4.599 4.566	$11.0 \\ 2.5 \\ 20.0 \\ 25.4 \\ 1.4 \\ 0.4 \\ 22.8 \\ 3.0 \\ 1.4 \\ 0.04 \\ 8.4 \\ 1 \\ 1.5 \\ 0.1 \\ 0.1 \\ 0.02 \\ 0.01 $	Ac-227
Ac-227	21.773 у	beta alpha 1.38 %	$\begin{array}{r} 4.953 \\ 4.941 \\ 4.873 \\ 4.855 \\ 4.796 \\ 4.768 \\ 4.36 - 4.74 \end{array}$	$98.62 \\ 0.66 \\ 0.55 \\ 0.09 \\ 0.08 \\ 0.01 \\ 0.02 \\ 0.01$	Th-227 Fr-223

Actinium series (4n + 3 series)

Isotone	Half-life	Decay	Energies	Intensities	Daughter
Isotope	man-me	Mode	(MeV)	%	Daughter
		1120 40	(11201)	,,,	
Th-227	18.72 d	alpha	6.038	24.2	Ra-223
			6.009	2.90	
			5.978	23.5	
			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	
Fr-223	21.8 m	beta			Ra-223
Ra-223	$11.435 \ d$	alpha	5.871	0.87	Rn-219
			5.858	0.32	
			5.747	9.1	
			5.716	52.6	
			5.607	25.7	
			5.540	9.1	
			5.502	0.80	
			5.481	0.01	
			5.434	2.27	
			5.366	0.11	
			5.339	0.10	
			5.287	0.13	
			5.283	0.10	
			5.259	0.04	
			$5.259 \\ 5.236$	$\begin{array}{c} 0.04 \\ 0.04 \end{array}$	
			$5.259 \\ 5.236 \\ 5.173$	$0.04 \\ 0.04 \\ 0.03$	

Isotope	Half-life	Decay Mode	Energies (MeV)	$\frac{Intensities}{\%}$	Daughter
Rn-219	3.96 s	alpha	$\begin{array}{c} 6.819 \\ 6.553 \\ 6.529 \\ 6.425 \\ 6.312 \\ 6.159 \end{array}$	$79.4 \\12.9 \\0.12 \\7.5 \\0.05 \\0.02$	Po-215
Po-215	1.781 ms	alpha	$7.386 \\ 6.957 \\ 6.950$	$99.95 \\ 0.03 \\ 0.02$	Pb-211
Pb-211	$36.1 \mathrm{~m}$	beta		100	Bi-211
Bi-211	2.14 m	beta		0.276	Po-211
		alpha $99.724~\%$	$\begin{array}{c} 6.623 \\ 6.278 \end{array}$	$\begin{array}{c} 83.54\\ 16.18\end{array}$	Tl-207
Tl-207	4.77 m	beta		100	Pb-207
Po-211	0.516 s	alpha	8.883 8.305 7.995 7.275	$7.04 \\ 0.25 \\ 1.66 \\ 91.05$	Pb-207