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Barium sulphate method for consecutive determination of radium-226 and radium-228 on the same source

P Medley

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Determination of two isotopes of radium – ^{226}Ra and ^{228}Ra – has been an important part of the monitoring and research program of the Environmental Radioactivity group of ***eriss***. Difficulties were encountered with a routine electrodeposition method for the determination of both isotopes in 2001, at which point a faster and more reliable method for the determination of ^{226}Ra by co-precipitation with barium was developed (the barium sulphate method). This new method was not suitable for the determination of ^{228}Ra and a reliable method for assessing this isotope was needed. The barium sulphate method for ^{226}Ra determination was thus expanded to allow for determination of the ^{228}Ra isotope via measurement of the ingrown daughters, either ^{228}Ac via gamma spectrometry or ^{228}Th via alpha spectrometry.

This report provides a detailed description of the radiochemical separation and radiation measurement techniques for the determination of ^{228}Ra via the barium sulphate method. Detection limits, uncertainty estimation and the applicability of the method to various sample matrices are presented and discussed.

Barium sulphate method for consecutive determination of radium-226 and radium-228 on the same source

P Medley

1 Introduction

Radium was identified as a significant environmental pollutant in the 1950s and since then has been primarily studied due to its hazard to human health. Radium pollution has come mainly from uranium, phosphate and gold production and radium is also an important pollutant in fly ash (Williams & Kirchmann 1990).

There are four naturally occurring radium isotopes (Table 1), of these radium-226 (^{226}Ra) and radium-228 (^{228}Ra) have been the most widely studied as they are the most radiotoxic. This is for several reasons, for ^{226}Ra they have been described in detail in IR501 (Medley 2005), for ^{228}Ra they are:

- its relatively short half-life,
- emitted beta particles have a high potential for causing biological damage,
- short lived alpha-emitting daughters will build up over approximately 10 years if ^{228}Ra is trapped in the body.

Table 1 Details and dose conversion factors [Sv/Bq] of the four naturally occurring isotopes of radium

	^{228}Ra	^{226}Ra	^{224}Ra	^{223}Ra
Half life ($t_{1/2}$)	5.75 years	1600 years	3.66 days	11.44 days
Primary Alpha particle decay energies and probabilities	None*	4.784 (94.4%) 4.602 (5.6%)	5.685 (94.9%) 5.449 (5.1%)	5.747 (9.1%) 5.716 (52.6%) 5.607 (25.7%) 5.540 (9.1%)
Parent of decay chain	232Th	238U	232Th	235U
ICRP dose conversion factor (Adult)*	6.9×10^{-7}	2.8×10^{-7}	6.5×10^{-8}	1.0×10^{-7}

* Dose conversion factors (DCF) convert actual activity of a radionuclide someone has ingested into an effective committed radiation dose (in Sv) that will be received from the given exposure over their lifetime. The DCFs given are for adults, taken from ICRP Publication 72. All half-lives and alpha decay energies are taken from Martin & Hancock (2004b).

The much lower importance given to the other two naturally occurring isotopes of radium (^{223}Ra and ^{224}Ra) is partly due to their very short half lives (approximately 3 and 11 days respectively). ^{223}Ra, as the progeny of Uranium-235 (^{235}U – 0.7% of natural uranium), has a comparatively low abundance compared with the other naturally occurring radium isotopes. ^{224}Ra is also usually of less importance due to the lower mobility of its parent ^{228}Th (and ultimately Thorium-232) in the environment. Consequently these two isotopes do not pose a significant threat to human health.

In biological systems radium tends to follow the biochemical pathway of analogue elements barium, strontium and particularly calcium (Iyengar 1990, Jeffree 1990). This has been demonstrated in several animal species, including humans (Jeffree 1990). It is for the above reasons that ^{226}Ra and ^{228}Ra both have high dose conversion factors (Table 1) and a combined proscribed limit in drinking water quality guidelines in many parts of the world, including Australia (NHMRC & NRMMC 2004).

^{226}Ra being in the uranium series decay chain makes it exceptionally important for any monitoring regime looking at impacts of uranium mining, milling and associated activities (Sauerland et al 2005) and thus is more intensively studied than ^{228}Ra. ^{228}Ra is the more radiotoxic but the lesser studied of the 2 isotopes, due to the lower mobility of the parent isotope thorium-232 (^{232}Th). Thorium principally occurs in refractory heavy minerals and is not easily leached (Jaworowski 1990), and the short half life of ^{228}Ra will not allow this isotope to be readily removed from these minerals.

1.1 Radium in the environment

Radium isotopes occur in ultra trace levels in the natural environment due to their short half lives, and the relatively long half lives of parent nuclides. As a result of this, radium tends to follow the behaviour of chemically similar elements, and also tends to adsorb easily to particulate matter (Molinari & Snodgrass 1990, Frissel & Koster 1990, Dickson 1990).

^{226}Ra is most notably associated with U mining & milling activities, but is also of environmental concern in many other activities including gold mining, coal production and phosphate fertiliser production (eg Leopold et al 2007, Othman & Al-Masri 2007, Williams & Kirchmann 1990). ^{228}Ra is associated in industry with thorium mining (Campos et al 1986), oil production (Vegueria et al 2002) and can be much more significant to radiological dose than ^{226}Ra in natural environments (Malanca et al 1995, Iyengar 1990).

Table 2 A range of reported concentrations of ^{226}Ra and ^{228}Ra in different environmental sample types, highlighting the considerable range of activities found in the natural environment. Data are summarised from Iyengar (1990).

Matrix	Activity concentration of ^{226}Ra	Activity concentration of ^{228}Ra
Rocks	0.037–2220 Bq/kg	
Soil	3.7–126 Bq/kg	
Continental waters:		
Rivers	0.074–314 mBq/L	0.53–133.2 mBq/L
Lakes	0.37–145 mBq/L	
Groundwater	0.74–55500 mBq/L	14.8–5610 mBq/L
Deep oceans	2.22–54.4 mBq/L	
Land crops	0.01–21.5 Bq/kg (wet weight)	0.074–34.4 Bq/kg (wet weight)
Freshwater biota	0.05–8930 Bq/kg (wet weight)	
Marine biota	0.015–66.6 Bq/kg (wet weight)	0.12–33.3 Bq/kg (wet weight)
Terrestrial animals	0.0004–64.2 Bq/kg (wet weight)	

The study of radium activity ratios has a wide variety of potential applications. It has been used to trace movement and behaviour of the uranium and thorium parent ions for assessing their movement and sources in groundwater (eg Martin & Akber 1999) or to assess movement of oceanic waters (Jaworowski 1990). Activity ratios have also been used as seepage indicators of tailings water from uranium mining (Martin & Akber 1994) and to gauge erosion and sedimentation rates (Joshi et al 1983). Finally, of importance for the development of the method described in this report, it has been applied to characterising the uptake pathway of radium isotopes in water lilies, a native bush food (Johnston et al 1985).

Radium is known to follow the chemistry of calcium in biological systems, and will accumulate in bones and through the food chain (Iyengar 1990, Vandecasteele 2004). It is for this reason that radium has been studied (primarily ^{226}Ra) in many different natural systems (Maul & O'Hara 1989, IAEA 1994). These studies have often been used for building radiological dose models to estimate contribution of radium to radiological dose in humans (IAEA 1994, Sam & Eriksson 1995, Lasheen et al 2007, Martin et al 1998).

A range of reported values for ^{226}Ra and ^{228}Ra are shown in Table 2.

1.1.1 Radium in drinking water

Radium is a relatively mobile ion, being readily soluble in water and is found in a wide range of environments (Kirby 1964, Iyengar 1990, Maul & O'Hara 1989).

Radium is routinely analysed in drinking water. ^{226}Ra and ^{228}Ra are the most likely isotopes to be found in drinking water and they are more commonly found in drinking water supplies derived from groundwater where chloride, carbonate and sulphate anions (among others) tend to increase the mobility of radium (NHMRC & NRMMC 2004, Dickson 1990).

The Australian drinking water quality guidelines (NHMRC & NRMMC 2004) state that analysis for ^{226}Ra and ^{228}Ra isotopes is required if gross alpha/beta activity exceeds 0.5 Bq/L. Radium concentrations in Australian drinking water are generally below 0.02 Bq/L, though it is not uncommon for small groundwater sources to exceed these limits (NHMRC & NRMMC 2004, Qureshi & Martin 1996).

1.2 Analysis of radium

High resolution gamma spectrometry, alpha spectrometry techniques, Liquid Scintillation counting and Emanometry are the most common techniques used for radium activity concentration measurements. ^{226}Ra is usually measured via its direct alpha decay, though it is not uncommon for ^{222}Rn and daughters to be used to indirectly measure ^{226}Ra (Marten 1992). ^{228}Ra, a beta emitter, is often measured via the alpha decay of its daughter ^{228}Th (Martin & Hancock 2004a), though ^{228}Ra determinations can also be performed via gamma spectrometry, using the decay lines of the immediate daughter ^{228}Ac, or by measuring the beta radiation directly (eg Santos et al 2002).

At the Environmental Research Institute of the Supervising Scientist (***eriss***) both high resolution gamma spectrometry and alpha spectrometry techniques are used for radium activity concentration measurements. Two separate methods of radium determination via alpha-spectrometry have been used at ***eriss***, the first of these methods (Martin & Hancock 2004b) could be used for determination of all 4 naturally occurring radium isotopes (Table 1), though was a long and costly method. A new method for alpha spectrometric analysis of the isotope ^{226}Ra only – the $BaSO_4$ method (Medley et al 2005), based on a method by Sill (1987) – has been used since implementation in 2001, when difficulties with the previous method emerged.

At ***eriss*** gamma spectrometry is also routinely used for radium determination, however, with the lower detection limit and the high voltage applied to the high purity germanium (HPGe) gamma detectors (and thus the potential for serious damage if water samples were to leak), this method of analysis is not used for water samples. Thus, ^{228}Ra determinations on water samples via alpha or gamma spectrometry have not been performed at ***eriss*** since early 2001, when difficulties with the ion exchange method were first experienced. With the much higher limits of detection compared with alpha spectrometry, gamma spectrometry is still not suitable for many types of environmental samples other than soil, sediments and water.

This project has extended the Sill (1987) method for evaluation of ^{226}Ra, to enable analysis on the same sample for ^{228}Ra. This method for ^{228}Ra determination is particularly suited for projects requiring very low detection limits, or where significant differences in ^{226}Ra and ^{228}Ra activities may be expected, such as bioaccumulation studies on both aquatic and terrestrial biota, ground and surface water monitoring and research, and on sites impacted by uranium mining and milling activities.

2 Methodology

The $BaSO_4$ precipitation method utilises micro-filtration, rather than electro-deposition to deposit radium as a thin source for alpha counting. Poorer resolution as compared to electro-deposition techniques, and unquantifiable radon retention means that only ^{226}Ra can be effectively resolved from the spectrum on these sources (Sill 1987, Medley et al 2005).

A method has been developed for counting the sources prepared for ^{226}Ra determination by the $BaSO_4$ precipitation method, with a High Purity Germanium (HPGe) detector for ^{228}Ra determination. The gamma decay lines of the fast ingrowing ^{228}Ac daughter of ^{228}Ra are utilised for this. The low efficiency, high background counts and low peak decay probabilities of the high energy lines of ^{228}Ac, gives relatively high detection limits for this method. However, the detection limits are lower than the standard gamma method using a pressed geometry due to the thin, flat geometry of the source which improves the efficiency for counting.

To achieve very low-level detection limits for ^{228}Ra determination a complementary method for digestion of the filter paper after a sufficient time for ingrowth of the ^{228}Th daughter and measurement of ^{228}Th via alpha spectrometry has also been developed.

2.1 Gamma spectrometry method development

This section describes the preparation of samples and calibration of the spectrometry systems for determination of ^{228}Ra by the $BaSO_4$ method, utilising high resolution gamma spectrometry. Instrument Detection Limits (IDLs), Method Detection Limits (MDLs), Efficiency, Energy, Recovery and Region of Interest (ROI) calibrations are included.

2.1.1 Source preparation

Source discs for alpha and gamma spectrometry are prepared by methods described in Medley et al (2005). The system set-up and configuration for the alpha and gamma spectrometry systems are described in Martin & Hancock (2004b) and Marten (1992) respectively. Prepared sources are initially counted via alpha spectrometry for ^{226}Ra determination, then for ^{228}Ra via gamma spectrometry.

To accurately analyse prepared sources from the $BaSO_4$ method via gamma spectrometry, the sources must be mounted in a standard geometry. To enable this, sample holders were custom made from PVDF. This material was deemed the most suitable material for the following reasons:

- Easy to work to necessary dimensions with a high degree of accuracy
- High chemical resistance, including to H_2SO_4 and caustic agents – this helped in preparation of standard sources (see method for sealed standards)

- Resistance to temperatures up to at least 80°C
  - Necessary for preparation of sealed standards
  - Essential for cleaning of holders which uses an alkaline (pH 10.6) 0.2 M DTPA wash at 80°C for removing Ba/$RaSO_4$
- Relatively low cost; PTFE has a higher chemical resistance and melting point than PVDF but was ruled out due to significantly higher cost

The inner diameter of the PVDF holders is 24 mm to ensure the source discs are not bent while in the holder. The outer diameter is not a factor that will influence the gamma counting efficiency. The thickness of the PVDF holder must be consistent for standards and source discs. Source discs are placed in the base of the holder then the top is placed on to hold the disc centrally and pressed flat to maintain the same geometry.

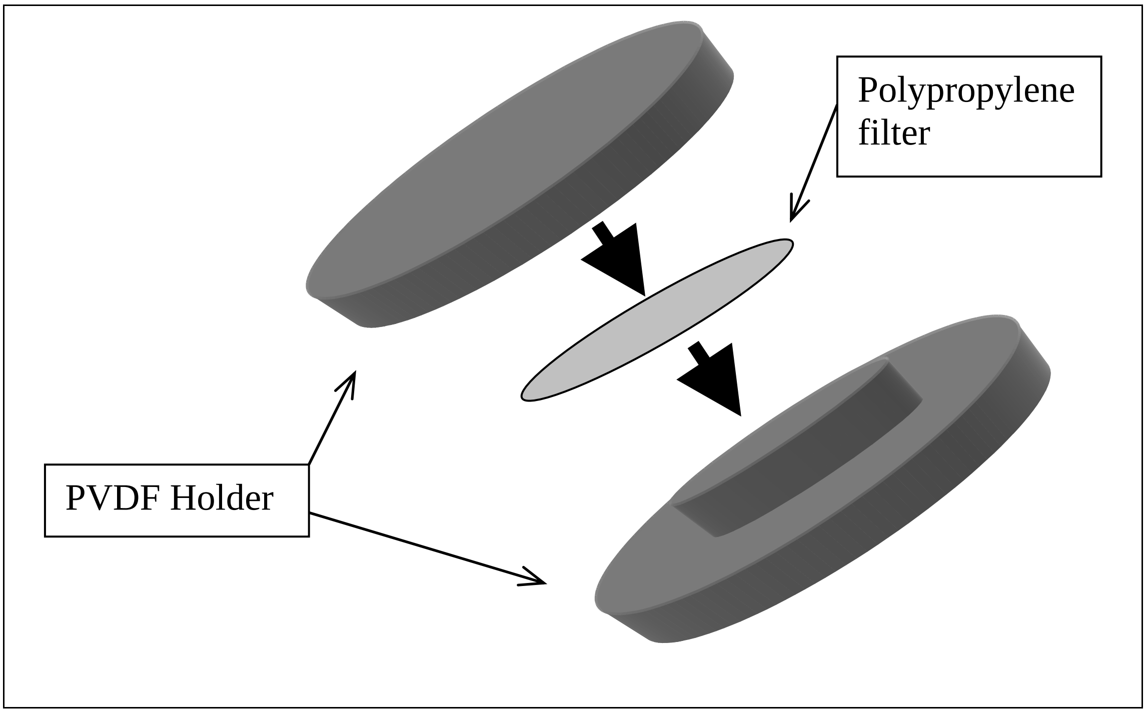

Figure 1 Illustration of mounting radium source discs in PVDF holders for gamma spectrometry. Polypropylene filters have a 17.5 mm active diameter, and a total diameter of 22 mm.

^{228}Ra is a beta emitter, and cannot be directly measured via alpha or gamma spectrometry. ^{228}Ac, the direct daughter of ^{228}Ra, is very short lived with a half-life of only 6.15 hours (Martin & Hancock 2004b). After a short ingrowth period ^{228}Ac will have sufficiently ingrown to have reached secular equilibrium with ^{228}Ra (Figure 2).

This is calculated using the radioactive decay and ingrowth equation (Equation 1) adapted from Friedlander (1981).

$$A_{Ac} = \frac{\lambda_{Ra} \times \lambda_{Ac}}{\lambda_{Ac} - \lambda_{Ra}} \times \frac{A_{Ra}}{\lambda_{Ra}} \times \left(e^{-\lambda_{Ra} \times t} - e^{-\lambda_{Ac} \times t}\right)$$

Ingrowth of ^{228}Ac from the parent isotope ^{228}Ra. Equation 1

Where –

A_{Ac} – Activity of ^{228}Ac

A_{Ra} – Activity of ^{228}Ra

λ_{Ra} – Decay constant of ^{228}Ra

λ_{Ac} – Decay constant of ^{228}Ac

As $\lambda_{Ra} << \lambda_{Ac}$ equation 1 can be written as:

$$A_{Ac} = A_{Ra} \times \left(1 - e^{-\lambda_{Ac} \times t}\right)$$

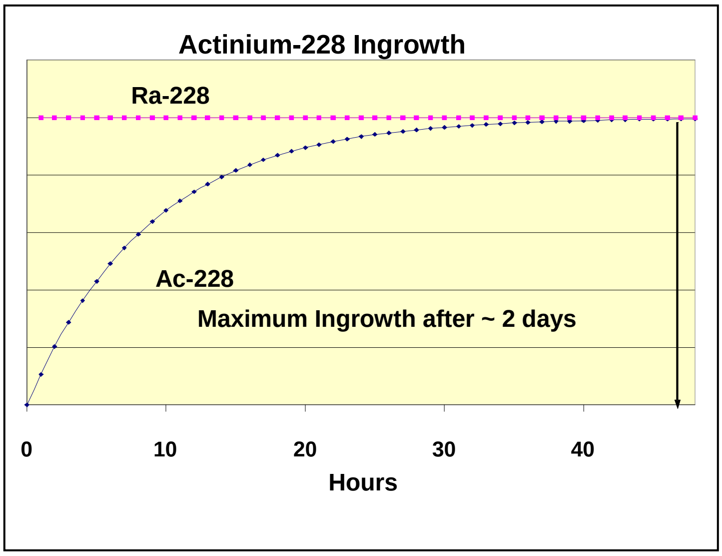

Figure 2 Time taken for ^{228}Ac to reach equilibrium with ^{226}Ra parent after radium separation. Calculated using Equation 2

2.1.2 Gamma counting

The 911 keV and 969 keV gamma lines of ^{228}Ac are used as they are sufficiently separated from interfering lines from the ^{133}Ba tracer, ^{226}Ra and daughters, and have a high decay probability (Table 3). Figure 3 shows a typical spectrum with major lines of ^{133}Ba, ^{226}Ra and daughters and shows that there are no lines interfering in the region of interest of the 911 keV and 969 keV peaks.

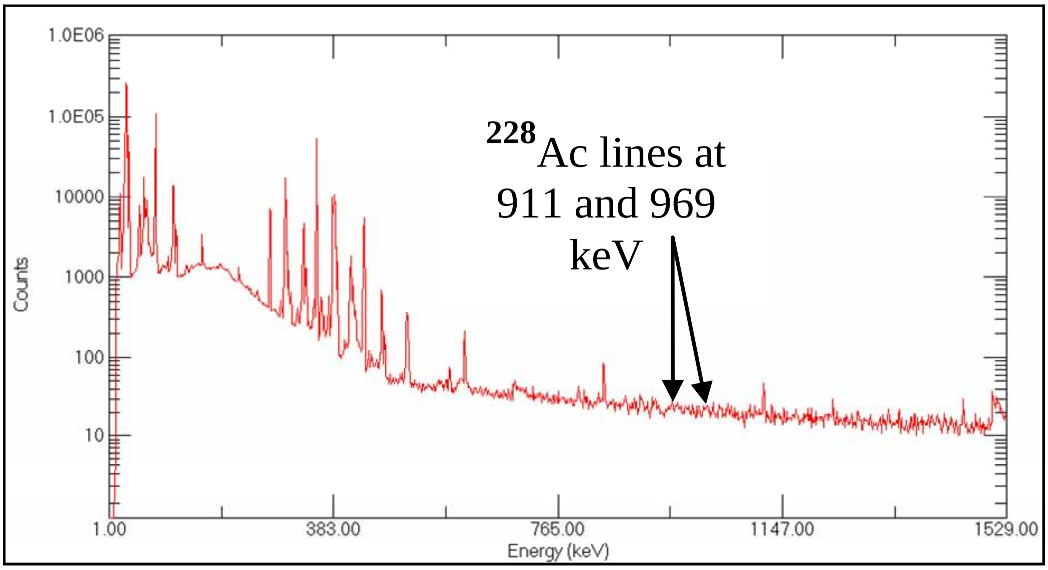

Figure 3 Spectrum of sample with ^{133}Ba and ^{226}Ra, counted on an HPGe spectrometer. Major peaks of these 2 isotopes can be seen to be distinctly separate from ^{228}Ac decay lines at 911 and 969 keV. Spectrum produced at ***eriss***.

Table 3 Gamma decay energies and emission probabilities for relevant nuclides and decay lines in samples and standards prepared for ^{226}Ra and ^{228}Ra analysis via the $BaSO_4$ method. All gamma energies are taken from Canet & Jacquemin (1990), except for ^{228}Ac which are taken from Marten (1992).

Isotope	Main gamma emissions (keV)	Probability (%)	Isotope	Main gamma emissions (keV)	Probability (%)
^{232}Th	59	1.9	^{226}Ra	186	3.28
^{228}Ac	338	12.3	^{214}Pb	295	18.7
	911	26.6		352	35.8
	969 & 964 (doublet peak)	20.4	^{228}Th	84	1.2
			^{224}Ra	241	3.9
^{214}Bi*	609	46.1	^{133}Ba**	53	2.2
	934	3.16		81	33.8
	964	0.38		223	0.5
	1120	15.0		303	18.4
	1238	5.9		356	62.1

2.1.3 Detection system calibration

Calibration of the gamma spectroscopy system is necessary before any results can be calculated. The parameters that need to be determined are:

- Channel/energy calibration
- Detector efficiency
- Background
- Detection limits.

2.1.3.1 Energy calibration

Energy calibrations are performed with the sealed standards used for efficiency determination and the ^{133}Ba standard discs. Quality control checks with a standard of known activity, with a broad energy range of gamma emitting nuclides, are counted after each sample to ensure energy calibration is maintained.

2.1.3.2 Efficiency

The efficiency of an HPGe gamma spectrometer varies with source geometry, sample matrix and the energy of the gamma decay line, thus a gamma spectrometry system requires accurate efficiency determination for the geometries used and for each peak of interest to be calculated. To do so a source of known activity with the same geometry and sample matrix (as close as possible) is used. Typical efficiency curves for a series of spectrometers calibrated with a source containing isotopes with a range of gamma photon energies are shown in Figure 4.

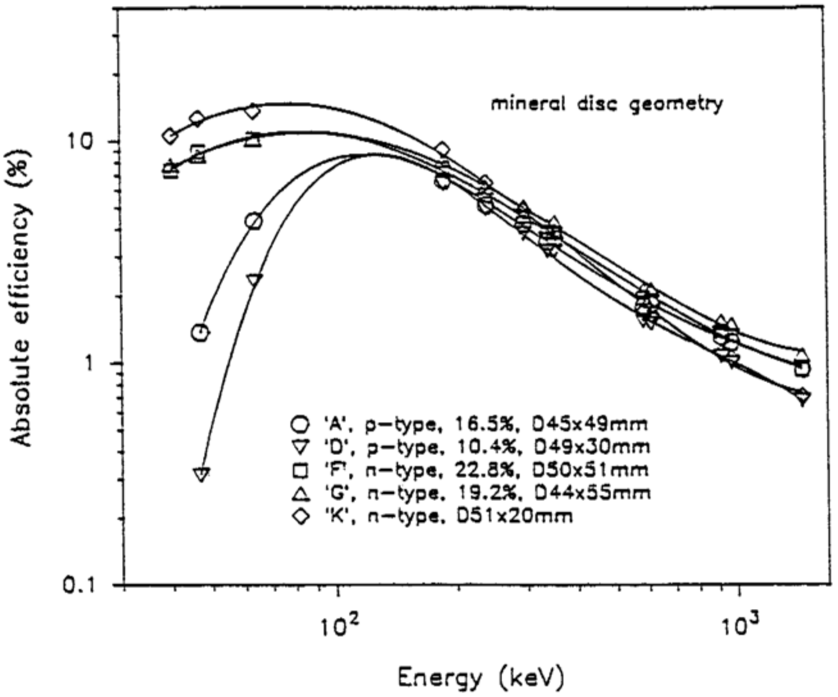

Figure 4 Typical efficiency curves for a series (A, D, F, G & K) of gamma spectrometer configurations. Reproduced from Marten (1992).

For this method the chemical recoveries of the sources are determined by comparison with a standard of known activity so determination of the efficiencies of the decay lines for the ^{133}Ba peaks is not necessary. However, the system needs calibration for the ^{228}Ac.

The preparation of standards is often the most critical step in the use of radiation detection systems. For gamma spectrometric measurement of ^{228}Ra via the gamma decay of ^{228}Ac, a pure source of ^{228}Ra is ideally used to calibrate the system. Due to the short half of ^{228}Ra, it is not easily available and quite expensive to obtain as a pure source. Pure thorium salts however are easy to obtain and relatively inexpensive. An isotopically pure ^{232}Th (t½ = 1.41 x 10^{10} years, Joshi et al 1983) salt will reach secular equilibrium with the daughter ^{228}Ra (t½ = 6.7 years, Joshi et al 1983) after approximately 5 half lives, and thus can be used as an essentially pure ^{228}Ra standard. It is important that ^{230}Th contamination of the thorium salt is negligible, as the daughter ^{226}Ra is unwanted in calibration standards. A review of the main gamma emissions from ^{232}Th and daughters other than ^{228}Ra showed no significant interferences with the high energy ^{228}Ac gamma emissions, though the lower energy emissions could not be used (338 keV, Table 3).

2.1.3.3 Background

There are essentially 2 types of background that need to be considered in gamma spectrometry systems. The background introduced by the source falls in two main categories, either Compton scattering or Bremsstrahlung. Compton scattering is caused by gamma photons imparting energy to weakly bound electrons which in turn release photons. Bremsstrahlung creates a broad spectrum and is caused by beta particles (electrons) interacting with the semiconductor detector and the absorbing material of the sample and holder (Canet & Jacquemin 1990). The type and magnitude of background interference will vary with each source (Marten 1992).

There may also be systematic background as a result of contamination of the counter or counting well and natural system (ie – electronic interference in old counting systems, cosmic and other natural radiation). Lead and other types of shielding are routinely used to minimise natural background. Interferences in the production of a final spectrum will vary with each detector system (Marten 1992).

2.1.3.4 Detection limits

Detection limits represent the point at which a detection system can no longer be considered to have detected a peak.

There are several types of detection limits described for radiation detection systems – instrument detection limits, IDLs, method detection limits, MDLs, and overall detection limits, DDLs. There are also a number of ways to determine the detection limits.

Detection limits are essentially the measure of the relative effectiveness of:

- IDL – the detector system configuration only
- MDL – IDL and the method components – any processing that affects each sample
- DDL – MDL and the preparation and counting conditions that are unique for each prepared source.

Instrument detection limit

The IDL for ^{228}Ra for this method can be determined by measuring:

- the efficiency of the detector for the ^{228}Ac peaks to be used
- the background spectrum as a result of the detector and sample holder configuration only.

Detector efficiencies for the method were determined from a series of sealed standards prepared at varying activities from an isotopically pure, calibrated thorium nitrate ($Th(NO_3)_2$) solution in secular equilibrium with ^{228}Ra. The solution was pipetted onto a small disc of absorbent paper (17.5 mm diameter – the same size as polypropylene filter papers) in the PVDF sample holders for gamma measurement. A small volume of 60% ethanol was added. $Th(NO_3)_2$ is highly hygroscopic so it is essential the standards are dried when weighed to ensure accurate calibration (this was performed on a hotplate at 70°C), once dried, it is also essential that the standards are sealed. The sealed standards were counted under identical conditions to those as for samples, and the efficiency of each ^{228}Ac line was determined (assuming 100% recovery). The IDL can be calculated after measuring a number of instrument background spectra, using methods derived by Currie (1968).

Method detection limit

The method detection limit, uses the same factors as for the IDL, but also takes into account the processes samples undergo for sample preparation. For this method these are:

- chemical separation and associated typical recovery of the analyte of interest
- additional background counts resulting from trace contaminants in chemical solutions and laboratory equipment
- the accuracy of other preparation steps – eg weighing of the sample (only has a small influence on uncertainty in radiation measurement techniques, De Regge & Fajgelj 1999)
- Appropriate sample size and type may also be influencing factors – for example there are limits on the amount of organic material that can be tested before the chemical separation and deposition of the analyte is adversely affected.

Unsealed standards were prepared to determine the method detection limit and to assess whether it is significantly affected by the ^{133}Ba activity which is used as a tracer to determine the chemical recovery of radium from the procedure. These standards were made from the prepared and calibrated $Th(NO_3)_2$ tracer solutions in secular equilibrium, and an isotopically pure ^{133}Ba tracer solution.

Unsealed standards were also prepared with varying amounts of the ^{133}Ba tracer solution only in order to assess the correlation of ^{133}Ba activity to background counts in the ^{228}Ac peaks.

After counting, these standards were given a period of time (approximately 6 ½ months) to allow ingrowth of the ^{228}Th daughter from ^{228}Ra, so they could be used for calibration of the ingrowth part of this method.

Overall detection limit

Overall detection limits, are affected by all of the above considerations, but vary with each sample, this is due to several factors:

- Counting time – the most significant source of uncertainty in radiological measurements are counting statistics (De Regge & Fajgelj 1999), with longer count times uncertainty is reduced, and therefore the detection limits are reduced
- Individual sample composition
  - Some samples contain much higher levels of trace contaminants which may affect the chemistry (such as barium) than others
  - Samples with higher levels of ^{226}Ra can affect the overall Compton background due to the 934 keV gamma line of ^{214}Bi (Table 3), and in extreme cases (very high ^{226}Ra: ^{228}Ra activity ratios, eg >1000) another very low probability gamma emission of ^{214}Bi at 964 keV can also affect the spectrum due to its proximity to the ^{228}Ac peak at 969 keV
- Chemical recovery of the sample.

2.1.4 Chemical recovery determination

A barium standard disc is prepared, and the chemical recovery of the disc determined using a NaI detector according to methods described by Medley et al (2005).

This disc is then counted in an HPGe detector and the count rate compared with that of the sample is used for chemical recovery determination. Actual tracer activities are not needed as the relative recovery of each sample is determined by comparison with the count rates obtained for the standard disc, using the same amount of tracer.

Thus the chemical recovery is determined according to the following basic principle:

$$R_{Sample} = \frac{N_{Sample}}{N_{Standard}}$$

Principle of chemical recovery determination. Equation 2

Where –

R_{sample} – Sample recovery

N_{sample} – Net count rate for the sample

$N_{standard}$ – Net count rate for the standard disc

The 302 keV and 356 keV gamma decay lines of ^{133}Ba are used, other lines with a high decay probability are interfered with by lines from daughters of ^{226}Ra, and so cannot be used for accurate recovery determination. To account for the varying peak decay probabilities of the two gamma decay lines, and the varying count times and tracer masses of the sample and standard, the following set of Equations 3–5 are used for chemical recovery determination:

$$R_{Sample} = \frac{R_{302} + R_{356}}{2}$$

Chemical recovery determination. Equation 3

Where –

R_{302} – Sample Recovery calculated using the 302 keV gamma line

R_{356} – Recovery calculated using the 356 keV gamma line

Recovery at each ^{133}Ba decay line is calculated using Equation 4.

$$R_{Peak} = \frac{C_{Peak} - (B_L + B_R)}{t \times PDP \times M_{Sample} \times CF_{STD}}$$

Chemical recovery determination for each peak. Equation 4

Where –

R_{Peak} – The sample recovery at a given peak

C_{Peak} – The gross counts in the peak

B_L – The background counts in a region to the left of the gamma line spanning half the width of the main region of interest

B_R – The background counts in a region to the right of the gamma line spanning half the width of the main region of interest

t – The count time in kiloseconds (ks)

PDP – The Peak Decay Probability of the peak. For the 302 keV peak this is 0.1833, and the 356 keV peak is 0.6205

M_{sample} – The mass of the tracer used in the sample

CF_{Std} – The ^{133}Ba standard correction factor

Equation 5 is used to calculate the ^{133}Ba standard correction factor.

$$CF_{STD} = \frac{\left(C_{STD} - \left(B_L + B_R\right)\right) \times R_{STD}}{t \times PDP \times M_{STD}}$$

^{133}Ba standard correction factor determination. Equation 5

Where –

CF_{Std} – Gross counts of a given peak of the standard disc

R_{Std} – The recovery of the standard disc, this is calculated from methods described in Medley et al (2005)

M_{Std} – The mass of the tracer used in the sample.

All other parameters are the same as described above, though for the standard disc.

2.1.5 ^{228}Ra activity determination

Based on the above calibrations of the spectroscopy system ^{228}Ra activity is determined using Equation 6.

$$A_{Sample} = \frac{N_C \times R_{STD}}{t \times PDP_C \times \varepsilon}$$

Back calculation of ^{228}Ra activity from ^{228}Ac activity measured. Equation 6

Where –

$$N_C = C_{911} + C_{969} - \left(B_{L911} + B_{L969} + B_{R911} + B_{R969}\right)$$

Net count rate determination. Equation 7

and –

N_c – Combined net counts of the 911 and 969 keV regions of interest

C_{911} – Counts in the 911 keV region of interest

C_{969} – Counts in the 969 keV region of interest

BL_{911}, BL_{969}, BR_{911}, BR_{969} – The background counts in a region to the left and right of the 911 keV and 969 keV gamma lines spanning half the width of the main region of interest

PDP_c – The Combined Peak Decay Probability of the 911 and 969 keV which is 0.4705

ε – The calculated combined efficiency of the 911 and 969 keV peaks which is 2.70%.

2.1.6 Quality control and quality assurance

Quality assurance and quality control (QA/QC) is an important part of implementing a developed method to ensure calibrated parameters remain within acceptable limits.

Counting of a high activity energy calibration source for 10 minutes after each sample count provides a means of ensuring energy calibration of each spectrum can be adjusted for minor variations after counting.

Regular background checks are conducted for a standard pressed geometry, though this does provide relevant information regarding the background spectrum of the detector system, these shall be implemented for unused and chemical blank polypropylene discs at bi-monthly intervals. It will take some time to fill control charts with sufficient data points to provide meaningful QC data (>20 data points, Currie 1968).

Due to the discs being used for determination of ^{226}Ra by alpha spectrometry as well as ^{228}Ra by gamma spectrometry, all samples are counted with a NaI detector for chemical recovery determination prior to alpha counting. Alpha counting should always precede gamma counting to prevent losses on the PVDF containers used for gamma counting from affecting final results.

Comparison of the chemical recovery obtained through NaI and HPGe spectrometers provides an additional QA process. The calibration of high resolution gamma spectrometers allows for accurate determination of chemical recovery in samples for ^{226}Ra analysis where ^{226}Ra activity levels are very high. The gamma emissions of radon daughter ^{214}Pb, and increased Compton background from higher energy gamma emissions of ^{210}Bi and others (Table 3) can increase the number of counts in the broad region of interest used for chemical recovery determination through the NaI spectrometer, increasing the measured recovery.

2.2 Alpha spectrometry method development

This section describes the preparation of samples and calibration of the spectrometry systems for determination of ^{228}Ra by the $BaSO_4$ method and subsequent separation and measurement of the ^{228}Th daughter utilising high resolution alpha spectrometry. Instrument Detection Limits (IDLs), Method Detection Limits (MDLs) and Recovery calibrations are included. Efficiency, Energy and Region of Interest (ROI) calibrations are detailed in (Martin & Hancock 2004b).

2.2.1 Methodology

Prepared sources are screened for ^{228}Ra activity via HPGe gamma spectrometry using the ^{228}Ac daughter. If the activity is below the detection limit for this method, the samples are stored until the ^{228}Th daughter has ingrown sufficiently to be measured via alpha spectrometry (Figure 5). The maximum activity of ^{228}Th is reached after approximately 1650 days, or just over 4 years. Suitable activities for analysis of many environmental can be reached after 12 months ingrowth.

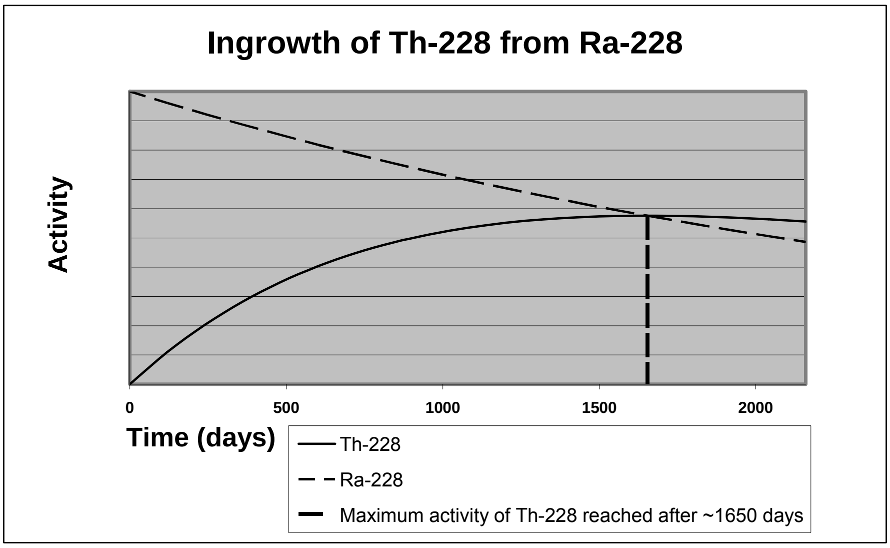

Figure 5 Ingrowth of ^{228}Th from the parent isotope ^{228}Ra, based on Equation 1. Note that this ingrowth curve is valid regardless of the initial activity of ^{228}Ra.

^{228}Th activity was determined by methods described in Martin & Hancock (2004b), and ^{228}Ra activity was back calculated using Equation 8 given below.

$$A_{Ra} = A_{Th} \times \frac{1}{\left(\frac{\lambda_{Th}}{\lambda_{Th} - \lambda_{Ra}}\right) \times \left(e^{-\lambda_{Ra} t} - e^{-\lambda_{Th} t}\right)}$$

Back calculation of ^{228}Ra activity from measured ^{228}Th activity. Equation 8

Where –

A_{Ra} - The activity of a ^{228}Ra at time t

A_{Th} - The initial activity of ^{228}Th

λ_{Ra} – The decay constant of ^{228}Ra

λ_{Ra} – The decay constant of ^{228}Th

t - Time since separation of ^{228}Ra from the sample

2.2.2 Source preparation for ^{228}Th measurement

A standard method for separation of thorium isotopes and analysis via alpha spectrometry used is described in Martin & Hancock (2004b), a flow diagram summary is given in Figure 6. Based on a number of assumptions, this method has been modified for the current application.

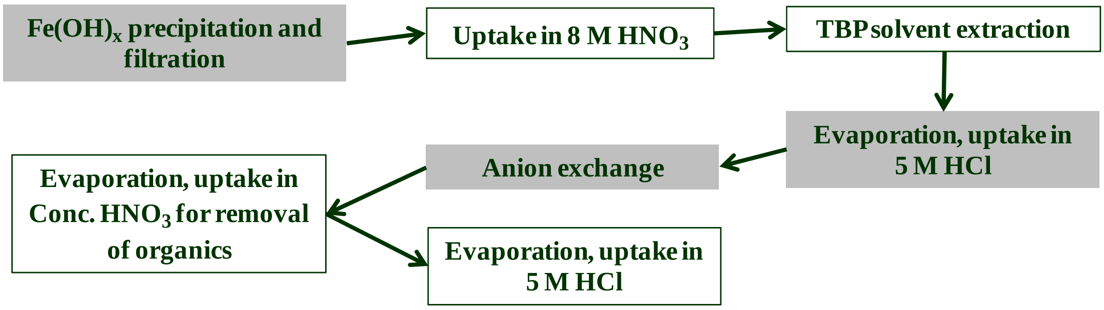

Figure 6 Flow diagram of standard method for thorium isotope analysis (Martin & Hancock 2004b). Steps highlighted have been omitted for this project.

The source disc filter paper used in radium determination is 100% polypropylene. To break this down into a suitable chemical form and release for thorium analysis, a digestion process is required (Figure 7). Concentrated sulphuric acid (98% H_2SO_4), is used first to char the filter, and then concentrated nitric acid/hydrogen peroxide (69% HNO_3/35% H_2O_2) treatment is used to remove excess carbon from the sample matrix. Once the digestion is complete, the sample can be taken up in appropriate acid medium, and undergo tributyl phosphate (TBP) extraction for thorium, eliminating the iron hydroxide precipitation step.

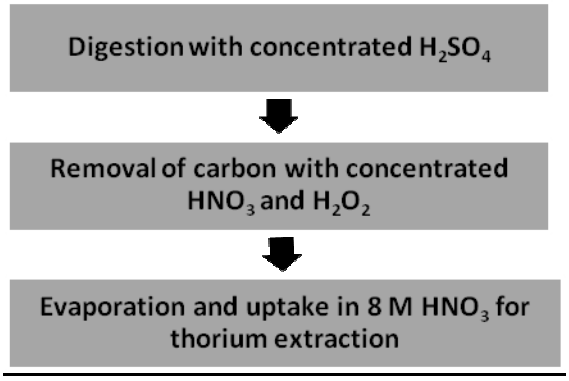

Figure 7 Flow diagram of digestion procedure for ^{228}Th ingrowth method

Due to the very similar chemical properties of thorium and uranium, an anion exchange step is usually employed to ensure complete separation of these two elements (Martin & Hancock 2004b). For the current application it can be assumed that uranium has already been effectively removed from the sample in the initial radium separation, and thus the anion exchange step can be eliminated. To prevent from allowing organic residue to carry through from the TBP extraction step (usually removed in the anion exchange step), after evaporation of the extract, concentrated HNO_3 is added, and evaporated at moderate heat (approximately 80°C).

The solution is then passed through the electrodeposition process, whereby thorium is electroplated onto a stainless steel planchet, and counted via alpha spectrometry according to methods described Martin & Hancock (2004b).There are several assumptions to this approach for ^{228}Ra determination, and a number of calibration and performance assessment procedures were undertaken to ensure the validity of this method.

$Th(SO_4)_2$ is very soluble in water and acid media (Hyde 1960), and there is an assumption that there is a 100% recovery of ^{228}Th from the digestion procedure. This was confirmed by the analysis of unsealed standards prepared initially for calibration of both the gamma and alpha spectrometric techniques.

2.2.3 Alpha counting

Alpha counting for ^{228}Th calibration of the detection system, and QA/QC for the alpha spectrometry determinations is performed according to procedures detailed in Martin & Hancock (2004b) and others detailed below:

- Bi-monthly blanks are counted to monitor background levels
- Efficiency calibration of the spectrometry system is performed by calibration with a known activity alpha-emitting standard
- Peak tailing calibrations are performed with prepared standards of isotopically pure ^{228}Th, ^{229}Th and ^{230}Th
- Energy calibrations are performed with a prepared standard of ^{232}Th in secular equilibrium with its decay series
- Chemical blanks are run with each batch of samples to monitor procedural contamination
- All equipment used for chemical separation and handling is washed according to procedures described in Appendix 1, section A1.4.1 of IR501 (Medley et al 2005).

2.2.4 ^{228}Ra activity determination

Back calculation of ^{228}Ra activity from ^{228}Th determination is performed using Equation 8.

3 Method calibration and results

3.1 Gamma spectrometry method calibration

3.1.1 Efficiency determination

5 sealed standards were prepared and counted to determine the efficiency of the detection system at the 911 and 969 keV peaks of ^{228}Ac. ^{228}Ac was allowed sufficient time to equilibrate with ^{228}Ra. Table 4 shows the activity of the standards, net count rates and the calculated efficiency for each standard disc at each peak. The peak decay probability (PDP) for the 911 keV peak is 26.6%, and combined PDP for the doublet peak at 969 keV is 20.45% (Martin & Hancock 2004b).

Table 4 Efficiency calibration data

Standard disc activity (Bq)	911 keV (net counts per kilosecond)	969 keV (net counts per kilosecond)	Efficiency at 911 keV (%)	Efficiency at 969 keV (%)
55.7	401	310	2.71	2.72
40.6	295	233	2.73	2.81
21.3	153	120	2.70	2.75
11.4	81.1	64.0	2.67	2.74
8.42	56.8	44.9	2.54	2.60

Efficiency was determined using Equation 9.

$$\varepsilon_{Peak} = \frac{C_{Peak} - (B_L - B_R)}{t \times PDP_C \times A_{STD}}$$

Gamma decay line efficiency determination. Equation 9

Where –

ε_{Peak} – The efficiency in the peak of interest

C_{Peak} – The gross counts in the peak

B_L– The background counts in a region to the left of the gamma line spanning half the width of the main region of interest

B_R – The background counts in a region to the right of the gamma line spanning half the width of the main region of interest

PDP_c – The Combined Peak Decay Probability of the 911 and 969 keV which is 0.4705

A_{Std} – The ^{228}Ra activity of the standard disc

t – Count time (kiloseconds)

Average efficiency and standard deviation for each peak was 2.67±0.08 and 2.72±0.07 for the 911 and 969 keV peaks respectively. Due to the negligible difference between the efficiency calculated for the 2 peaks, a combined efficiency for both peaks was determined, using a combined average of all efficiencies calculated for each peak for each standard, to be **2.70%**, with a standard deviation of **0.08%**. Figure 8 shows net count rates of all sealed standards versus activity of those standards.

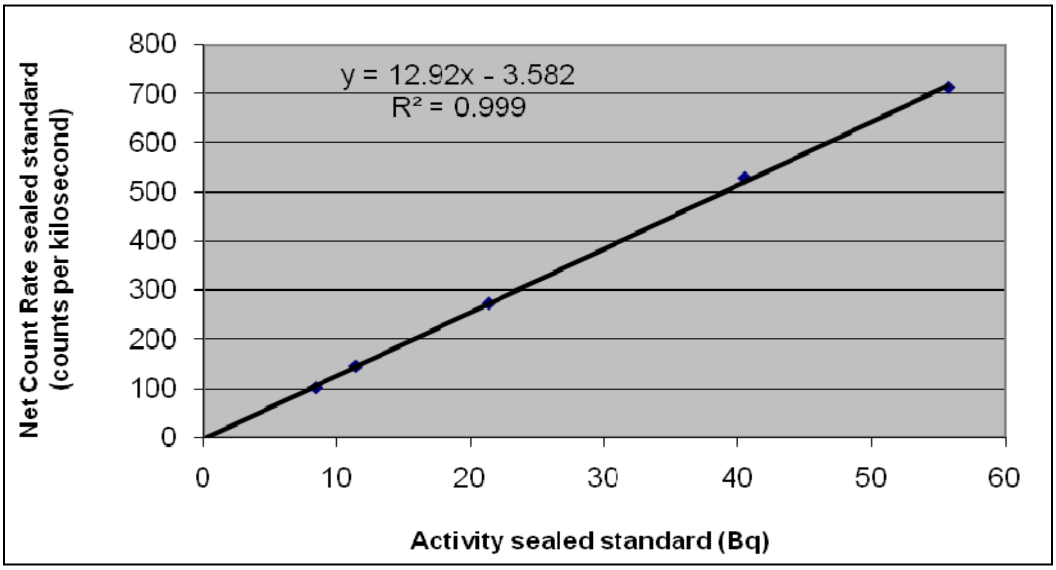

Figure 8 Combined net count rates of ^{228}Ac decay lines at 911 and 969 keV of sealed standards vs. activity of sealed standards

The R^2 value of 0.999 indicates clear correlation between activity of the standards and the net count rates across a wide range of activities. The apparently negative intercept signified in the equation from Figure 8 is not statistically significantly different from zero ($p=0.54$).

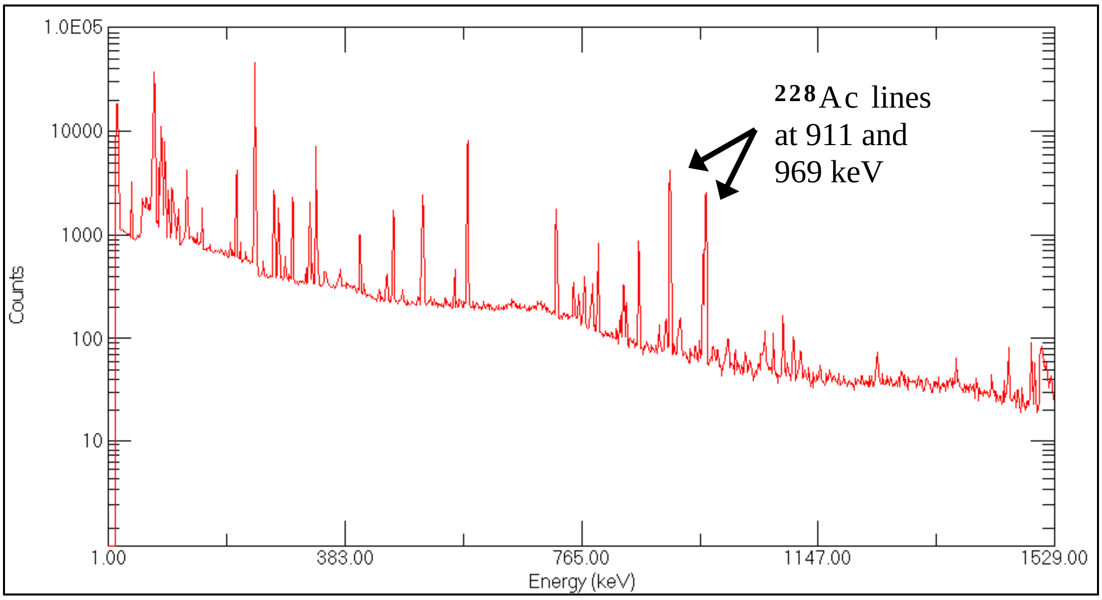

Figure 9 HPGe gamma spectrum of the most active of the sealed standards. No additional lines close to the 911 and 969 keV lines of ^{228}Ac can be seen, even in the logarithmic scale.

Comparison of the separated ^{228}Ra spectra (see Figure 9) with those of the sealed standards also showed that the assumptions of no interference in the ^{228}Ac lines from ^{232}Th or daughters in secular equilibrium were correct.

In addition a clean PVDF sample holder and chemical blanks prepared with the sealed and unsealed standards, and ^{133}Ba blanks with increasing volumes of ^{133}Ba tracer ranging from 1/20 of that used in normal samples (Ba-133 Blank #1) to an equal volume as that used in normal samples (Ba-133 Blank #5). No upward trend in count rates in the combined 911 and 969 peaks was observed, and no significant variations, within uncertainty, in the count rates of the blanks can be observed when compared with that of the blank PVDF sample holder (Table 5).

Table 5 Blank count rates after Compton and natural background subtraction of various blanks

Blank type	**Count rate (counts per kilosecond) in 911 and 969 keV peaks**	**Uncertainty (counts per kilosecond)**
Blank PVDF sample holder	0.524	0.141
Sealed standard Chemical Blank, average of 2 counts	0.309	0.135
Unsealed standard Chemical Blank, average of 2 counts	0.707	0.155
^{133}Ba Blank #1	0.316	0.094
^{133}Ba Blank #2	0.305	0.089
^{133}Ba Blank #3	0.576	0.089
^{133}Ba Blank #4	0.419	0.132
^{133}Ba Blank #5	0.122	0.131
Average of ^{133}Ba Blanks	0.348	0.167[1]

[1] This is the standard deviation of the count rate of the ^{133}Ba blanks.

A similar analysis of net count rates of the unsealed standards, after net count rates were corrected for chemical recovery of radium, was performed. The results of this are shown in Figure 10.

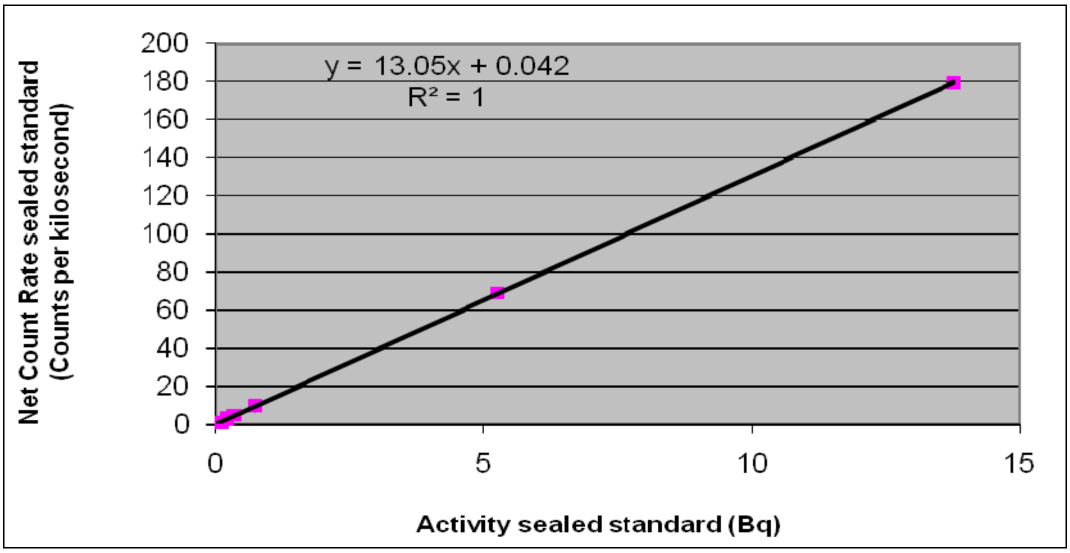

Figure 10 Recovery corrected combined net count rates of ^{228}Ac decay lines at 911 and 969 keV of unsealed standards vs. activity of unsealed standards

The R^2 value of 1, and the low background count rate for these standards which were significantly lower in activity than the unsealed standards, shows the method is suitable for ^{228}Ra determination for a variety of samples, and can achieve relatively low detection limits. The data also indicates the assumptions of equal chemical recovery of radium and barium, enabling chemical recovery determination with ^{133}Ba are accurate.

3.1.2 Chemical recovery comparison HPGe vs NaI

As a quality control check on chemical recovery determinations, a set of freshwater mussels (Ryan et al 2005) prepared by the $BaSO_4$ method (Medley et al 2005) was counted in both the NaI and HPGe gamma spectrometers calibrated for these geometries. Table 6 shows a comparison of chemical recovery determined via both of these systems.

Table 6 Chemical recovery data for a set of freshwater mussels using ^{133}Ba as a tracer and counted on HPGe and NaI gamma spectrometers.

Sample ID	Gamma spectrometry (HPGe)		For alpha spectrometry (using NaI)	
	Recovery (%)	%RSD	Recovery (%)	%RSD
MI02025	68.5	0.3	68.0	1.0
MI02026	35.1	0.3	36.4	1.5
MI02027	38.8	0.2	40.3	1.4
MI03135	67.2	0.4	68.5	1.1
MI03137	102.4	0.6	104.0	1.0
MI03138	93.3	0.5	93.3	1.0
MI03139	65.9	0.4	68.4	1.1

These results show very good agreement between the results obtained for both methods. This indicates that in ^{226}Ra activity determinations for very active samples, the HPGe spectrometer can be used after alpha counting to accurately determine chemical recovery without the interference of radon daughters encountered on the lower resolution NaI spectrometer.

3.1.3 Detection limits

Six unsealed standards were prepared for determining the MDL. Table 7 details net counts (which are normalised to a 1 day count so as to accurately reflect standard deviation for this counting period), chemical recovery and percent relative standard deviation (%RSD). Variations in chemical recovery and count time inversely affect the MDL.

Table 7 Detection limit determination data

Sample activity (Bq)	Normalised net counts	%RSD	Chemical recovery (%)
0.137	110	24.0	83
0.253	238	12.1	83
0.461	434	7.77	80
0.946	820	5.38	78
6.43	5999	1.39	82
18.3	15551	0.88	76

In this report, the MDL is assumed to be the point at which % relative standard deviation (RSD) is 30%. It must be noted %RSD takes into account uncertainty associated with counting statistics only. Counting statistics in this technique can reliably be assumed to account for over 90% of total uncertainty (except for samples very close to detection limits, De Regge & Fajgelj 1999, Currie 1998).

The net count rate of the standards in both peaks combined versus %RSD was charted to determine the normalised net counts at 30% RSD in order to back calculate the MDL, this is shown in Figure 11.

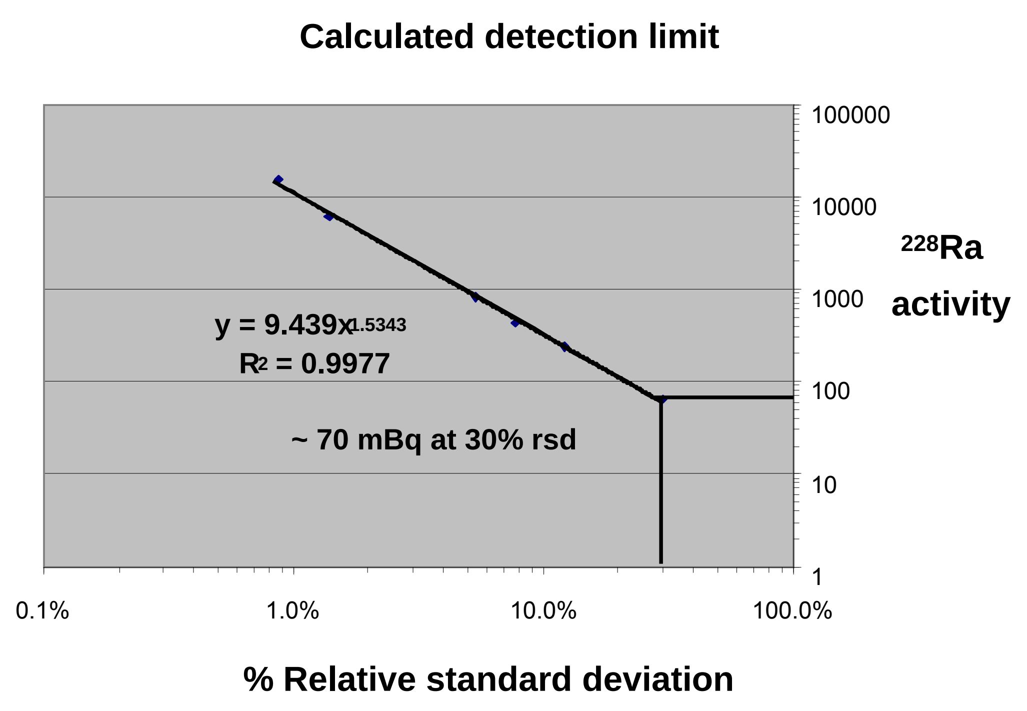

Figure 11 Combined normalised net counts of ^{228}Ac 911 and 969 keV peaks vs. %RSD for 6 unsealed standards

A MDL was determined to be **70 mBq** by:

- back calculating net count rates using the equation determined in Figure 11 assuming %RSD is 30%
- back calculating ^{228}Ra activity using Equation 7.
- making the following assumptions:
  - 85% chemical recovery of analyte
  - 1 day (86.4 ks) count time
  - 2.70% combined efficiency for 911 and 969 keV peaks
  - Stable, repeatable geometry of samples

The standard adopted for calculating detection limits by IUPAC and other organizations (ISO 1993) is based on Currie (1968), and gives the general equations detailed below (Table 8) for calculating the critical value (IDL), the Minimum Detectable Value (MDL) and the limit of quantification, or overall detection limit.

Using the standard deviation of the ^{133}Ba blanks shown in Table 5 and the formula in Table 8 and assuming we have a well-known blank to calculate the net count rate in the combined 911 and 969 keV peaks and dividing by the calculated efficiency of 2.70% for these peaks, we can calculate an IDL of 10 mBq, a MDL of 20 mBq and an overall detection limit of 62 mBq.

This is quite similar to the detection limit of 70 mBq calculated using 30% RSD as the cut-off point.

Table 8 General formulae for calculating various detection limits, taken from Currie (1968). $б_B$ is the standard deviation of the net count rate of the blank.

Limit type/type of measurement	Critical Value (IDL)	Limit of Detection (MDL)	Limit of quantification
Paired observations	2.33 x $б_B$	4.65 x $б_B$	14.1 x $б_B$
'Well-known' blank	1.64 x $б_B$	3.29 x $б_B$	10.0 x $б_B$

The flat nature of the sources prepared for radium determination gave a higher counting efficiency at the high energy gamma lines of ^{228}Ac than expected. 2.70% efficiency for this technique compares with efficiencies of 1.03% for the large geometry and 1.59% for the small geometry for a standard pressed geometry method (pers. comm. Andreas Bollhoefer). This high efficiency is primarily responsible for the relatively low MDL of 70 mBq.

As counting statistics follow a normal distribution, uncertainty will decrease proportionally to the inverse square of the count time, so a fourfold increase in count time will half the uncertainty and approximately halve the MDL.

3.2 Alpha spectrometry method calibration

3.2.1 ^{228}Ra determination with alpha spectrometry

The unsealed standards prepared were allowed an ingrowth period until ^{228}Th activities were high enough for alpha spectrometric determination. Separation of thorium was performed using the methods developed in this project, and counted via alpha spectrometry.

Figure 12 shows the results obtained for ^{228}Ra activity of the unsealed standards after back calculation from the determined ^{228}Th activity at the time of thorium separation.

The measured versus expected activity shows an R^2 of 1 and a slope of nearly 1, indicating 100% recovery and good accuracy over a wide range of standard activities. Additional quality control for assessing recovery of the digestion process was performed indirectly through measurement of the ^{133}Ba recovery in the digest solution.

$BaSO_4$ is less soluble than $ThSO_4$ and therefore 100% recovery for ^{133}Ba is considered indicative of 100% recovery for thorium (Chaudhary et al 2006, Kirby 1964, Hyde 1960). Three polypropylene ^{133}Ba blank discs were digested by the method developed for this project, filtered through 0.45 µm into a plastic bottle and count rates from a NaI spectrometer in a selected region of interest were compared. Overall recovery was determined by methods described in Medley et al (2005) and is shown in Table 9. Recovery was essentially shown to be 100%, within uncertainty.

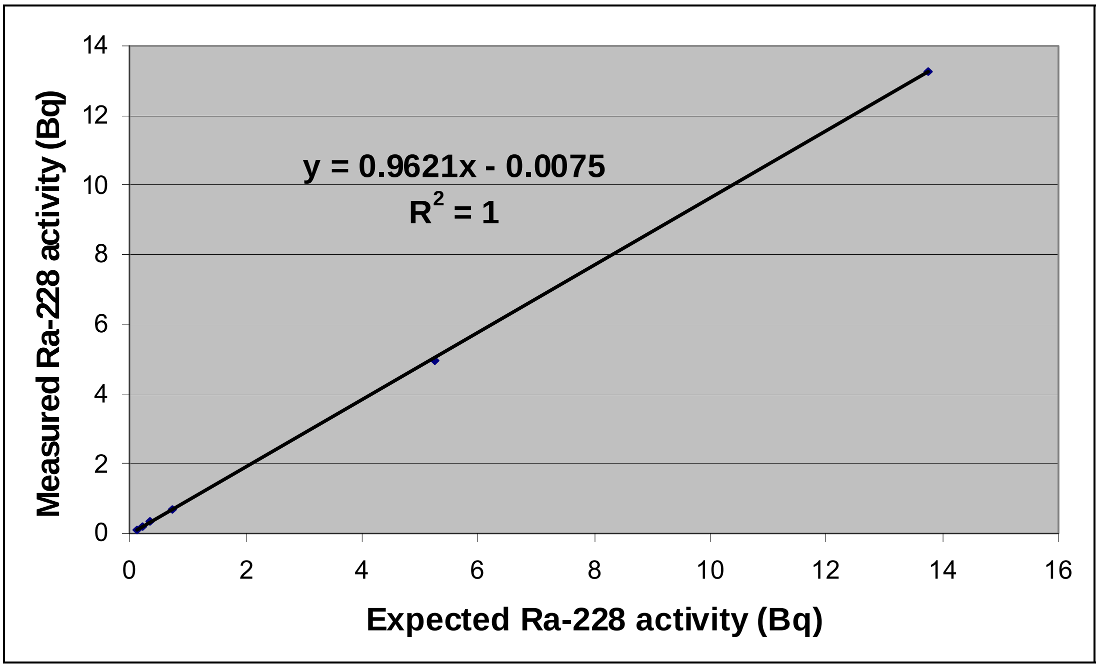

Figure 12 Measured vs actual ^{228}Ra activity in unsealed standards as determined by ingrowth of ^{228}Ra and measurement via alpha spectrometry

Table 9 ^{133}Ba chemical recovery for 3 standards after charring with concentrated sulphuric acid, digestion with concentrated hot nitric acid and hydrogen peroxide, then filtered through 0.45 μm. Methods used for gamma spectrometric (NaI) analysis are described in Medley et al (2005).

Standard identification number	^{133}Ba Standard 1	^{133}Ba Standard 2	^{133}Ba Standard 3
Chemical recovery and uncertainty in % (based on counting statistics only)	99±4.7	101±5.2	102±5.8

3.2.2 Detection limits

A detection limit of **5 mBq** for the ingrowth method was calculated using Equation 11, and based on the following assumptions:

- 85% recovery for both the ^{228}Ra and ^{228}Th separation steps
- A 12 month ingrowth period
- A detection limit of 1 mBq for the alpha spectrometric determination of ^{228}Th (Martin & Hancock 2004b, this is based on Currie 1968).

$$A_{Ra} = \frac{A_{Th}\left(\lambda_{Th} - \lambda_{Ra}\right)}{\lambda_{Th} \times R_{Ra} \times R_{Th}\left(e^{-\lambda_{Ra}\times t} - e^{-\lambda_{Th}\times t}\right)}$$

Detection limit determination for ^{228}Ra via ingrowth of ^{228}Th. Equation 10

Where –

A_{Ra} – Initial activity of ^{228}Ra

R_{Ra}– Sample Recovery from radium separation

R_{Th} – Recovery calculated from thorium separation

t – The count time in kiloseconds (ks)

A_{Th} – The ^{228}Th activity concentration at the date of initial thorium separation.

λ_{Th} – The decay constant of ^{228}Th

λ_{Ra} – The decay constant of ^{228}Ra

Very low backgrounds in alpha detector systems and from laboratory equipment, as well as the 100% efficiency demonstrated for the chemical recovery of the polypropylene source filter digestion, help to give the low detection limits of 5 mBq after 12 months ingrowth for this technique. The wide range of activities used for the unsealed standards also demonstrates that this method is suitable across a broad range of potential activities found in samples.

4 Conclusions

Calibration of the gamma spectrometric method for ^{228}Ra measurement via the ^{228}Ac daughter, and development of a digestion procedure for radium sources prepared by $BaSO_4$ co-precipitation to enable alpha spectrometric measurement of the ^{228}Ra daughter, ^{228}Th, was undertaken. A detection limit of 70 mBq was determined for the indirect measurement of ^{228}Ra via gamma spectrometry. A detection limit of 5 mBq, after a 12 month waiting period, was determined for indirect measurement of ^{228}Ra through ingrowth of ^{228}Th.

The developed technique showed suitability for relatively fast, cheap and accurate analysis of drinking water for assessment of compliance with the Australian Drinking Water Quality Guidelines which sets a guideline limit of 0.5 Bq/L for combined ^{226}Ra and ^{228}Ra if gross alpha/beta activity exceeds 0.5 Bq/L (excluding radon and ^{40}K; NHMRC & NRMMC 2004). Analysis of ^{226}Ra and ^{228}Ra activity to ADWG guidelines via this method is more rapid and has lower detection limits than common methods currently employed (Medley 2007, Table 8, p 39).

The developed technique showed suitability for analysis of potentially contaminated water form uranium mining and milling activities and the low detection limits provided with the ^{228}Th ingrowth method for ^{228}Ra measurement also provides an excellent tool for analysis of low-level environmental samples and ^{226}Ra/^{228}Ra activity ratios for a wide range of applications.

The high backgrounds associated with the gamma spectrometry techniques and peak tailing interferences from higher energy alpha particles with the alpha spectrometry techniques limit the range of ^{226}Ra /^{228}Ra activities that can be measured on the same prepared source. With the gamma spectrometry method for ^{228}Ra determination developed in this project it is estimated that ^{226}Ra can be at least 4 orders of magnitude higher that ^{228}Ra activity before the interference from the 964 keV ^{214}Bi in the 969 keV ^{228}Ac peak becomes significant (Table 3). Even so, the 911 keV peak could still be used alone (with reduced MDL due to lower overall counts) for ^{228}Ra determination. With the complementary ^{228}Th ingrowth method for ^{228}Ra determination there is no realistic difference in activity of ^{226}Ra and ^{228}Ra isotopes that could not be measured.

With ^{226}Ra and ^{228}Ra concentrations spanning ranges shown in Table 2 in natural environments, these techniques are useful for low-level studies of radium transport in the environment, especially if time to allow for ingrowth of ^{228}Th is possible. Examples of this include movement of radium from past and present coal, uranium and radium mining activities (Fernandes et al 2006, Carvalho et al 2007, Leopold et al 2007) and assessment of radium uptake in natural bush foods (Martin & Ryan 2004). If combined with additional pre-concentration steps such as manganese dioxide precipitation this method could prove useful for studies in environmental transport of radium in saline coastal, estuarine and ocean waters (Okubo 1990).

Combined with pre-concentration techniques such as dry-ashing to remove excess organics for large volumes, this technique may be applied to more in-depth studies of radium migration within terrestrial and marine biota (Justyn & Havlik 1990, Simon & Ibrahim 1990, Ryan et al 2005). Difficulties of such techniques with radium due to plating of radium on walls of nickel containers or fusion with ceramics can make expensive platinum crucible or microwave digestions (pers comm Elizabeth Manickam) the only alternative.

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Appendix 1 Apparatus & method description for ^{228}Ra determination

Samples are prepared for ^{228}Ra determination using the same methods for source preparation for ^{226}Ra determination as described in IR501 (Medley 2005). The system set-up and configuration for the alpha and gamma spectrometry systems are described in SSR180 (Martin & Hancock 2004) and IR76 (Marten 1992) respectively.

Additional apparatus required to the above referenced publications include only a calibrated ^{232}Th tracer solution, and the PVDF holders described in the main text (Figure 1).

Appendix 2 Calibration of gamma and alpha spectrometers

Calibration of the spectroscopy system is necessary before any results can be calculated. The gamma spectrometry system requires accurate efficiency determination for each peak of interest to be calculated. Counting of a high activity energy calibration source for 10 minutes after each sample count provides a means of ensuring energy calibration of each spectrum can be adjusted for minor variations after counting. Although there are several types of detection limits described for these systems – IDLs, MDLs, overall DDLs, the detection limits used in this report are based on a 30% relative standard deviation cut-off limit.

A2.1 Preparation of sealed standards

Sealed standards prepared to determine the Instrument detection limits for the method. These standards were prepared from a relatively isotopically pure, calibrated thorium nitrate ($Th(NO_3)_2$) solution in secular equilibrium with ^{228}Ra, a beta emitter, and its direct daughter ^{228}Ac, a gamma emitter.[1]

A2.2 Preparation of unsealed standards

Unsealed standards were prepared to determine the method detection limit and if it is significantly affected by the ^{133}Ba activity which is used as a tracer to determine the chemical recovery of radium from the procedure. These standards were prepared from a calibrated $Th(NO_3)_2$ tracer solution in secular equilibrium, and an isotopically pure ^{133}Ba tracer solution (reference to standard material details here).

Unsealed standards were also prepared from varying amounts of the ^{133}Ba tracer solution only in order to assess the correlation of ^{133}Ba activity to background counts in the ^{228}Ac peaks.

After counting, these standards were held for approximately 8 months to allow ingrowth of the ^{228}Th daughter from ^{228}Ra, then digested according to the procedure given in Appendix 3, section A3.3.

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[1] It is essential the standards were sealed due to the hygroscopic nature of $Th(NO_3)_2$.

Appendix 3 Methods

A3.1 Preparation of sealed standards

1. Cut a 25 mm disc from thin absorbent paper and place in the base of a sample holder, use the top of the holder to press it flat (remove the top of the holder after pressing) – provide a photograph here.
2. Weigh, then add a known volume of calibrated $Th(NO_3)_2$ tracer solution in secular equilibrium
3. Add a small volume of 60% EtOH to prevent the acid in the tracer solution from reacting with the absorbent paper
4. Heat the sample holder at 60°C on a hotplate until completely dry
5. Once dry, leave the sample holder on the hotplate to avoid the $Th(NO_3)_2$ adsorbing moisture from the air (see footnote)). Place the top of the sample holder on firmly, then seal the holder with a high strength plastic glue (brand name given here)
6. Count in an HPGe gamma spectrometer (for how long? How many counts?)

A3.2 Preparation of unsealed standards

1. Measure into a 50 mL centrifuge tube approximately the same amount (weighed to 4 decimal places) of ^{133}Ba standard as used per sample
2. Evaporate the samples in a water batch to near dryness (low recovery was noted for original standards prepared, and this step is a modification of procedures followed for initial calibration of the method).
3. Add desired volume of $Th(NO_3)_2$ tracer solution (see footnote or something)
4. Add 0.5 mL of Ba carrier solution
5. Add 10 mL 0.2 M DTPA, 1 drop of thymol blue and 2 drops of methyl red
6. Simultaneously add 6 mL of 5:1, 20% Na_2SO_4:Acetic acid mix, and 0.5 mL Ba seeding solution, then leave to stand for at least 30 minutes before proceeding to the next step
7. Filter as per samples (steps 18–23 from A1.4 of IR501), then remove filter and allow to air dry
8. After drying place in the base of a PVDF gamma sample holder, use the top of the holder to press it flat, then count using an HPGe gamma spectrometer.

A3.3 Digestion of polypropylene filter, thorium extraction and deposition

1. Place the filter to be digested in a tall form 50 mL beaker, and heat to ~80°C. The filter paper should go semi-transparent after 5–10 minutes.
2. Add 5–10 drops of concentrated (98%) H_2SO_4, to char the remaining filter paper and continue heating (ensure all of the filter paper is charred before proceeding to the following steps) until most of the H_2SO_4has evaporated
3. Add 10 mL concentrated (69%) HNO_3 and heat the solution to 140°C

4 Add 2 mL of 30% H_2O_2 in 0.2 mL aliquots, waiting for the foaming to subside between addition of each aliquot

5 Repeat step 3 every 30 minutes for ~1–2 hours or until the black colour has been completely removed from the sample. Add extra concentrated HNO_3 when necessary to prevent the solution from drying out

6 Evaporate the sample to dryness.

7 Uptake in 20 mL 8 M HNO_3, and separate and deposit ^{228}Th using method ‘8.3 Separation and deposition procedure’ from SSR180 with the following exceptions:

   a. The Anion Exchange step is eliminated.

   b. TBP extraction is followed by gently heating the solution with concentrated HNO_3 to remove excess organic material from the extraction step – add 10 mL conc. HNO_3 and evaporate to dryness at 60°C

8 Continue with the electrodeposition step as for a normal sample

9 Count the sample in an alpha spectrometer (see SSR180 for system set-up) for ^{228}Th determination.