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Introduction

Radium-226 (^{226}Ra) is an alpha-emitting radionuclide. It is part of the naturally occurring uranium-238 (^{238}U) decay series, and the direct progeny of thorium-230 (^{230}Th) (figure 1). 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***.

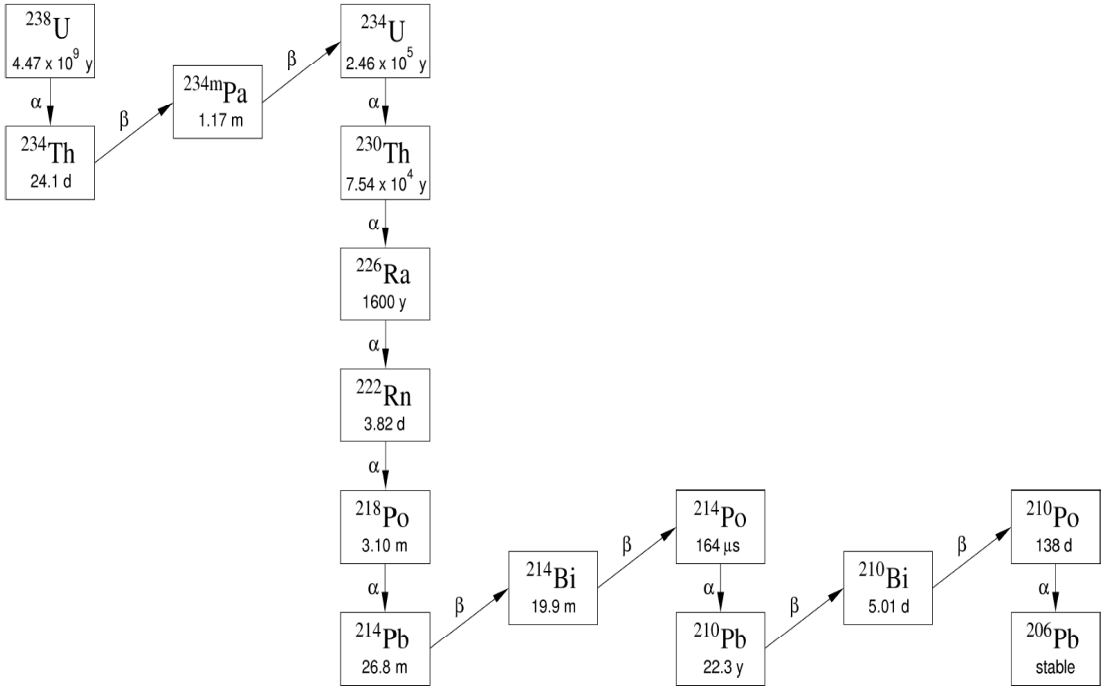

Figure 1 The Uranium decay series (4n + 2 series)

The barium sulphate ($BaSO_4$) precipitation method, based on Sill (1987), is used when only the isotope ^{226}Ra is determined. If ^{223}Ra, ^{224}Ra and/or ^{228}Ra isotope determinations are required a number of sequential separations are required – refer to methods described in chapter 9 of SSR180 (Martin & Hancock 2004).

The aim of this report is to provide a description of radiochemical techniques and administrative procedures for radium-226 (^{226}Ra) determination of internal research and monitoring, and external commercial samples at the Environmental Radioactivity laboratory of ***eriss***; and to present standard operating procedures for the $BaSO_4$ precipitation method – commonly referred to in-house as the 'Sills' method.

The main body of this report contains discussions of radium chemistry, analytical methods and applications of radium analyses used at ***eriss***. The appendices contain the standard operating procedures for all components of the $BaSO_4$ precipitation method of analyses, including instructions on:

- preparation of samples and standards,
- counting of sources,
- calculation of results, and
- calibration/quality control of all components.

The $BaSO_4$ precipitation method described here is suitable for ^{226}Ra activity measurements of water samples (dissolved and particulate), sediments, and biota.

Radium

Radium was first discovered by Marie Curie in 1898 and was soon hailed as a wonder drug for its shown ability to destroy cancers. The activity equivalent from 1g of pure radium was used to define the first standard unit of radioactivity (1 Curie(Ci) = 3.70×10^{10} decays per second). Later, when the health hazards of radiation were discovered, radium became the basis for the first standard of radiotoxicity (The MPBB, Maximum permissible body burden, for occupational exposure was set at 0.1Ci).

Radium has over 20 known isotopes, with mass numbers ranging from 206-234. All radium isotopes are unstable and only four are found naturally. Table 1 shows the four naturally occurring radium isotopes.

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 ($t_{1/2}$)(ICRP, 1983)	5.75 years	1620 years	3.66 days	11.44 days
ICRP dose conversion factor (Adult)*	6.9×10^{-7}	2.8×10^{-7}	6.5×10^{-8}	1.0×10^{-7}
Parent of decay chain	^{232}Th	^{238}U	^{232}Th	^{235}U
ICRP Dose conversion factor* for parent of decay chain	2.3×10^{-7}	4.5×10^{-8}	2.3×10^{-7}	4.7×10^{-8}

* 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 DCF's given are for adults, taken from ICRP Publication 72.

Radium has been primarily studied due to its hazard to human health. Of the naturally occurring isotopes ^{226}Ra has been the most widely studied as it is the most radiotoxic of the radium isotopes, for several reasons:

- due to its long half-life,
- the high relative abundance of its parent ^{238}U in the earths crust and the fact that most radium bearing wastes are produced from the milling of uranium ores,
- emitted alpha particles have a high potential for causing biological damage,
- radium's very similar chemical properties to calcium means exposure may lead to build-up of radium in bones and teeth and it has been shown to cause bone sarcomas,
- the very short half-lives of daughter nuclei (figure 1), will result in a rapid build-up of ^{222}Rn (Iyengar 1990) and daughters (most of which are alpha-emitters), until equilibrium with the parent is reached, if radium is trapped in the body.

Radium has a relatively mobile ion, being readily soluble in water; analysis for radium is routine in drinking water. ^{226}Ra and ^{228}Ra are the most likely isotopes to be found in drinking water. ^{224}Ra has a very short half-life, and due to the lower mobility of its parent ^{232}Th, is usually of less importance. As the progeny of ^{235}U, and due to its short half-life, ^{223}Ra has a comparatively low abundance compared to the other naturally occurring radium isotopes.

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

Radium activity ratios can be used to trace movement and behaviour of the U and Th parent ions, eg for assessing movement of uranium mining ore waste in groundwater (Martin 1998). ^{226}Ra in addition has broader applications in radioactive dating techniques (see Ivanovich & Harmon 1982).

At ***eriss*** ^{226}Ra determinations are performed routinely for bio-accumulation studies, ground-water studies, and surface water monitoring for the protection of people and the environment from the impacts of uranium mining.

The method described here is only used for ^{226}Ra analysis. However, after allowing for in-growth of ^{228}Th after radium separation, and subsequently performing a ^{228}Th determination, this process could be adapted to determine ^{228}Ra on the same sample (detection limits for ^{226}Ra ~1mBq; for ^{228}Ra ~40mBq after 18 months in-growth).

Chemical behaviour of radium

This section discusses the relevant behaviour of radium in relation to the $BaSO_4$ method, more detail can be found in Appendix 1.

Radium is an alkaline earth metal (a Group II metal), and has chemical properties very similar to that of barium and other members of the Group II metals (Be, Mg, Ca & Sr). Radium exhibits only one oxidation state in solution (+2). Because of its highly basic nature the divalent ion is not easily complexed, hence most radium compounds are simply ionic salts.

Radium reacts readily with water forming a soluble hydroxide. The chloride, bromide and nitrate complexes are all soluble in water (with this solubility decreasing as the concentration of the respective mineral acid increases), explaining the high mobility of the ion, particularly in groundwater, where these anions are generally in elevated concentrations.

Due to its relatively short half-life as compared to parent isotopes, trace levels of ^{226}Ra can have significant activity (for example a ^{226}Ra alpha activity of 0.5Bq/L, which exceeds drinking water guidelines represents only 0.6×10^{-13} M Ra). Radium tends to follow the behaviour of chemically similar elements, particularly to Ba>Sr>Ca (in that order). As a result of very low radium concentrations in the environment, radium tends to be associated with minerals of these elements. This similar chemistry is the basis for the chemical separation of radium in most analytical techniques, though many previously used methods for radium determination have also been inhibited by this similarity in chemistry and required lengthy chemical separations to remove other Group II elements, especially barium.

Precipitation of an element occurs when the solubility product of the element is exceeded. Co-precipitation is a phenomenon where similar chemical behaviour is used to precipitate more than one element, even though the solubility product of only one element may have been exceeded. In this way, through the addition of a carrier solution, radium co-precipitates with all barium compounds, and to a lesser extent with strontium, lead, and calcium compounds.

Radium salts are generally less soluble than barium salts, with the exception of $Ra(NO_3)_2$, which is more soluble; fractional crystallisation techniques have exploited these differences and have been used extensively in the past for separation of barium and radium. $Ra(NO_3)_2$ is also insoluble in >80% HNO_3, and this has often been used for the separation of radium from other elements.

It must be noted that incomplete precipitation of barium, may still be accompanied by almost 100% precipitation of radium during co-precipitation, this has important implications for recovery determinations where barium is used as a tracer (eg ^{133}Ba), for a more detailed discussion on co-precipitation of radium with barium see Kirby (1964).

The very low solubility of radium compounds in organic substances has often been used in separating radium from other nuclides. Currently at ***eriss*** multiple nuclides can be analysed on the same sample concurrently, firstly Po and Pb are extracted with diethyldithiocarbamic acid (DDTC) into chloroform ($CHCl_3$), then uranium and thorium are extracted into tri-butyl-phosphate (TBP), (Martin & Hancock 2004) finally radium (which remains in the aqueous phase) is precipitated with $PbSO_4$ using a barium carrier.

Radium does form a limited number of 1:1 stable complexes, most notably with diethylenetriaminepentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA). Barium also forms stable and slightly stronger complexes than radium, and this has been used widely in separating barium and radium via anion exchange.

Radium sulphate is the most insoluble of the alkaline earth sulphates, and probably the most insoluble compound of radium known. Barium sulphate is such an excellent carrier for radium that radium is quickly adsorbed even when preformed crystals of barium sulphate are added to a radiferous solution. Initially the adsorbed radium, can be removed by washing, but after a short time the radium becomes incorporated in to the crystal lattice and can no longer be removed by washing. The migration of the radium into the barium sulphate lattice continues slowly until isomorphous mixed crystals are formed.

Strontium sulphate co-precipitates radium in a similar way to barium sulphate but less completely and co-precipitation of radium on calcium sulphate is quite poor, but if either of these elements is in significantly high concentration, they may cause interference (refer to the Method discussion on page 11 for how to overcome this).

Selection of analytical technique

Due to the short half lives of radium isotopes, ICPMS (Inductively Coupled Plasma Mass Spectrometry) cannot be used for their determination, with typical concentrations well below detection limits. Thus radium concentrations are usually determined through their decays using alpha or gamma spectrometry. However, some studies have measured radium using TIMS (Thermal Ionisation Mass Spectrometry), (eg Staubwasser et al 2004).

The most widely used methods for the determination of ^{226}Ra involve either alpha particle or gamma-ray spectrometry, or emanation methods.

Emanation methods

Emanation methods involve collection of the ^{222}Rn daughter and measuring its activity through the alpha decay. The precision of these techniques is very good (Lucas et al 1990), though time is needed for ^{222}Rn to reach equilibrium with ^{226}Ra after preparation of the sample. Emanometry can only be performed accurately on a liquid sample, instrument processing times can be long (requiring heavy investment in equipment for high turnover), and detection limits are higher than those with alpha spectrometry. If very large water samples need to be analysed, however, the emanation method may be the cheapest and most suitable due to its ability to handle very large volume samples (up to 20 L for some types, Bland 1990).

High resolution gamma spectrometry

Gamma ray spectrometry directly measures gamma rays emitted from the analyte. As gamma rays have a much greater ability to penetrate materials than alpha particles, no chemical separation of the radionuclide of interest from the sample matrix is required. Lead shielding is required to minimise background radiation interfering with the spectrum. The main advantage of gamma spectrometry lies in this fact, allowing minimal sample processing to prepare a source for gamma counting. At ***eriss*** solid samples for gamma analysis are crushed to a desired consistency, then pressed, and sealed prior to counting.

At ***eriss*** the HPGe gamma spectrometers used for ^{226}Ra determinations are not set-up for analysing large volumes of water. With the high voltage applied to these instruments (and very low operating temperatures), and the potential for serious damage if water samples were to leak, it is not a desirable analytical technique for large volumes of water.

Gamma spectrometry also requires equilibration between radon progeny, ^{222}Rn and ^{226}Ra, which is not always successful, due to potential radon loss from the sample. It is also quite time-consuming (>3 weeks is required for equilibration after preparation for analysis at ***eriss***). The gamma method also requires homogeneous distribution of the radon progeny throughout the sample and a standard having the same configuration, similar mineral composition and density as the samples, neither of which is necessarily easy to achieve. The minimum mass required for gamma analysis is 15 g and detection limits are typically ~2–3 Bq/kg. Where these criteria are met for a given sample, gamma spectrometry is by far the easiest and cheapest method of analysis.

High resolution alpha spectrometry

Alpha spectrometry for radium utilises direct measurement of the alpha radiation from radium isotopes. In general, alpha particles have much higher energies than beta or gamma rays (table 2) – energies are given in electron Volts (eV), but due to the very large mass and higher charge of alpha particles compared with beta particles or gamma rays, alpha particles are easily stopped by a few microns of air. Therefore very thin sources need to be prepared to allow adequate transmission of the alpha particles to the detector surface without significant interference from within the source itself. There are two main techniques for preparing sources for alpha spectrometry:

- Sequential extraction followed by electrodeposition
- microfiltration.

Table 2 Table of Radioactive Isotopes of the ^{238}U decay series (taken from Tinker 1995)

Nuclide	Half-life (t ½)	Alpha Decay		Beta Decay		Gamma Decay	
		Energy (MeV)	Abundance (%)	Energy (keV)	Abundance (%)	Energy (keV)	Abundance (%)
^{228}Ra	5.75 days			9.865	100%		
^{226}Ra	1620 y	4.784	94.45	-	-	186.1	3.28
		4.801	5.55			262.4	0.01
^{222}Rn	3.823 d	5.490	99.92	-	-	510	0.07
		4.987	0.08				
^{218}Po	3.10 m	6.003	100	-	-	510	<0.01
^{214}Pb	27 m	-	-	220 (average)	100	351.9	37.1
						295.1	19.2
						241.9	7.46
^{214}Bi	19.9 m	5.513	0.01	-	-	609.3	46.1
						1764.5	15.9
						1120.3	15.0
^{214}Po	164 μs	7.687	99.99	-	-	797.9	0.01
		6.904	0.01				
^{210}Pb	22.3 y	-	-	6.5	100	13.07	10.4
						10.82	9.2
						46.5	4.1
^{210}Bi	5.01 d	4.648	<0.001	389	100	305.2	<0.01
^{210}Po	138.4 d	5.304	100	-	-	803.1	<0.01
^{206}Pb	STABLE LEAD						

Alpha spectrometry requires the use of tracers to determine the recovery from the radiochemical procedures used to separate the element of interest. Preparation of thin sources for alpha spectrometry often requires lengthy and complex chemical separations, which may reduce recovery of radium isotopes in sample matrices which are difficult to separate, especially silicates and insoluble phosphates (Sill 1987).

Alpha spectrometry has many distinct advantages however:

- as, in most cases, a radioisotope of the same element is added before element separation from the sample matrix, detailed knowledge and calibration of detector efficiencies is not required and uncertainties only arise from uncertainties in tracer calibration and mass, and counting statisitics.
- it does not require any considerations of radon equilibria, or loss, in the sample (except for possible contamination of the detector).
- modern silicon surface barrier detectors have very few spectral interferences, very low backgrounds and they are relatively easy to set-up and operate (not requiring high voltages or extreme cooling like gamma spectrometers), achieving high resolution and high precision (Bland 1990).

Electrodeposition

Sensitive electrodeposition techniques had been the most common method of preparing sources suitable for alpha spectrometry. The very nature of electrodeposition can be part of the problem with these techniques however. Electrolysis of a solution causes bubbling and therefore uneven plating, any metals present in the final solution will interfere with plating efficiency and residual metals may electroplate on the source and decrease resolution.

These procedures (eg Decaillon 2004), have only been marginally successful for radium deposition because addition of too much barium carrier (used to prevent low recoveries) which co-precipitates the radium, leaves a much thicker than desirable deposit for counting, and seriously degrades resolution of the spectra (figure 2).

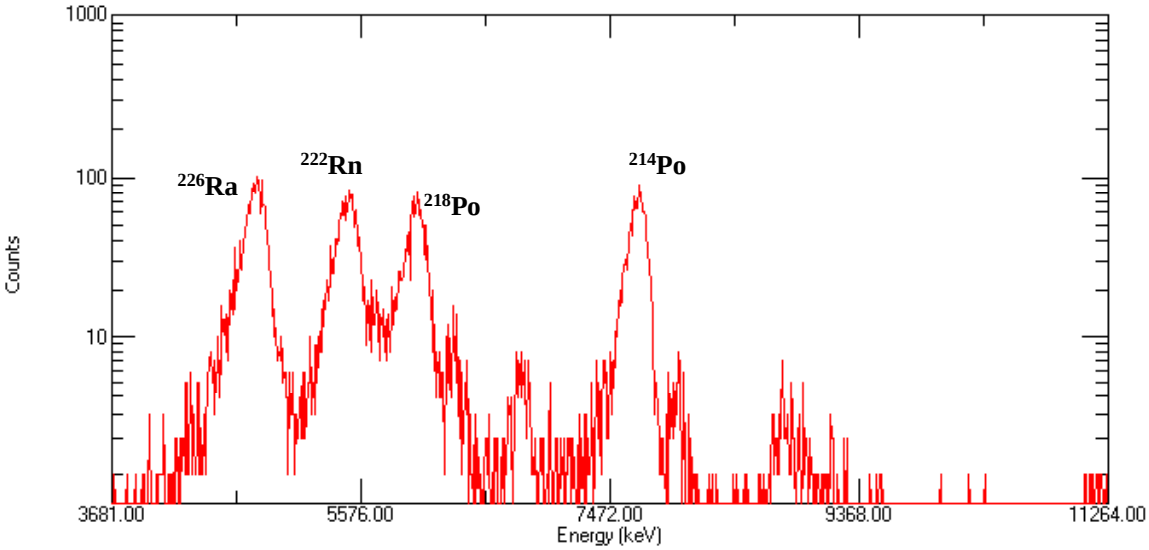

Figure 2 Very poorly resolved spectrum from Ba interference on disc

An electrodeposition technique refined at ***eriss*** (SSR180 Chapter 9) has the advantage of allowing determination of all four naturally occurring radium isotopes. However, significant problems with the ion exchange step have been encountered following changes to the properties of the recommended cation exchange resin, such that this method no longer separated barium from radium adequately. It is not used at ***eriss*** at the moment, and further reviewing of the method is required before employing it again.

Alpha-counting of ^{226}Ra must take into account the rapid in-growth of its radioactive progeny (figure 1). This presents a special problem for many methods determining ^{226}Ra, particularly interference between ^{226}Ra daughters and tracer peaks.

With electrodeposition techniques, ^{133}Ba cannot be used as a tracer as it retards deposition. As there are no alpha-emitting radium isotopes with suitable half-lives (^{225}Ra is a beta emitter), using an isotopic tracer for radium determination requires time for ingrowth of alpha-emitting daughters which are consequently measured (figure 3).

^{225}Ra is the most common isotopic tracer for radium determination, though not an alpha-emitter, ^{225}Ra is measured through the peak of its decay product ^{217}At. The direct daughter of ^{225}Ra, (^{225}Ac) is also an alpha emitter, though this cannot be used due to spectral interference with a ^{226}Ra daughter (^{222}Rn). Due to the short half-life of ^{225}Ra (14.9 days) there is also only a short window for optimal counting of the ^{217}At peak (figures 4–5).

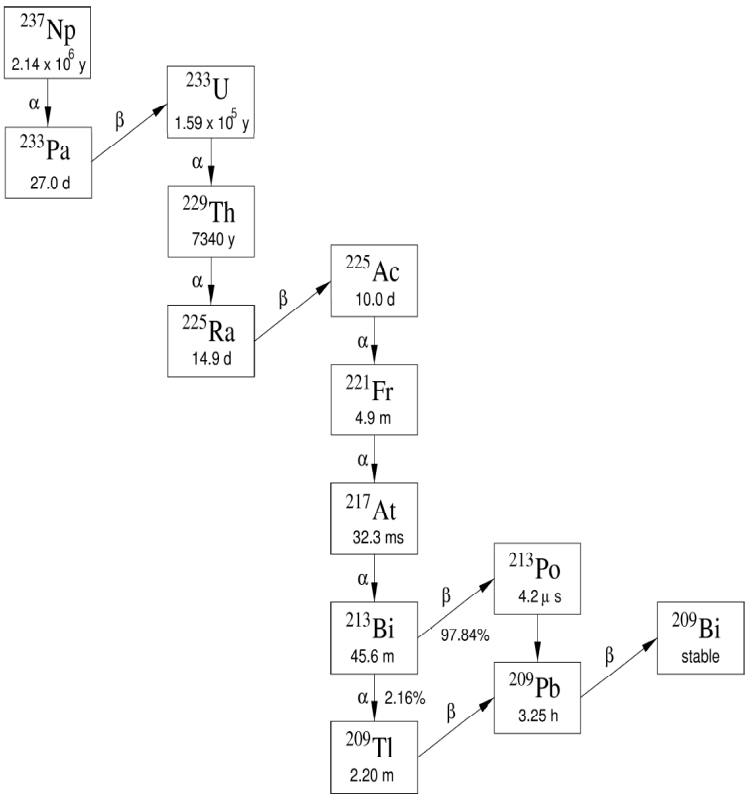

Figure 3 The Neptunium decay series (4n + 1 series)

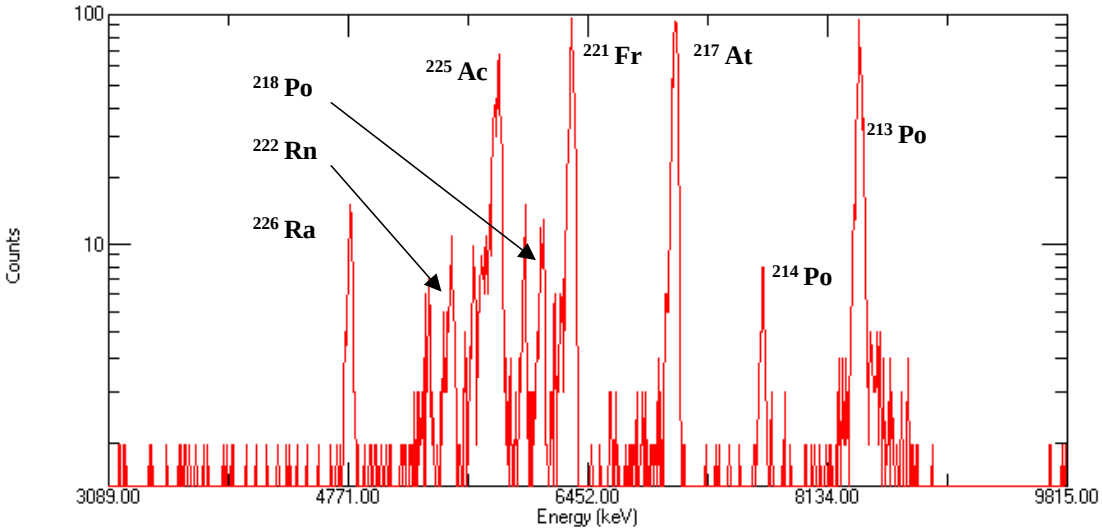

Figure 4 Ingrowth of ^{225}Ra daughters

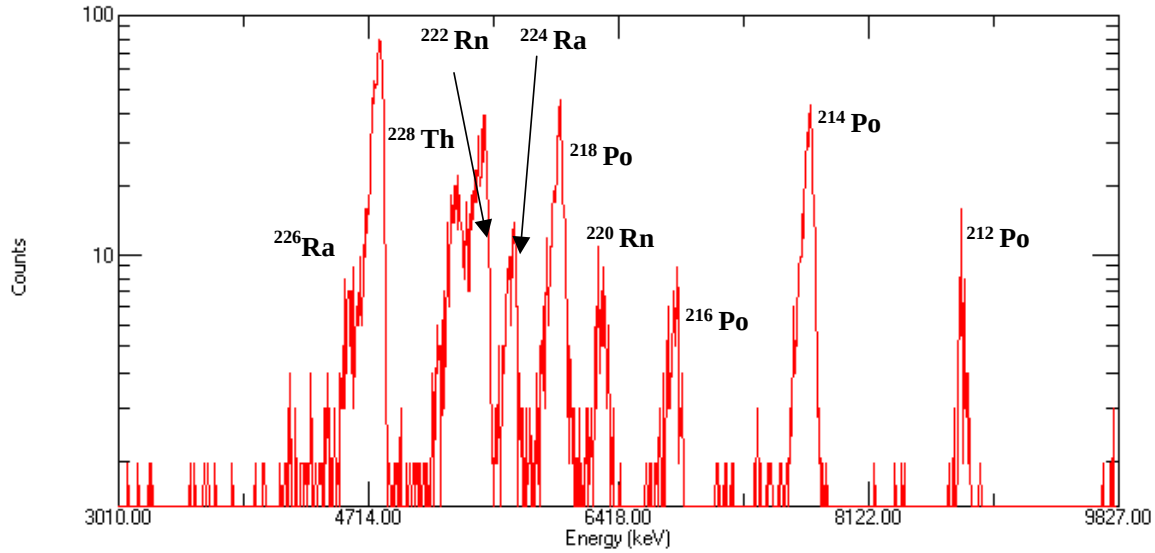

Figure 5 Well resolved spectra, after ^{228}Th ingrowth

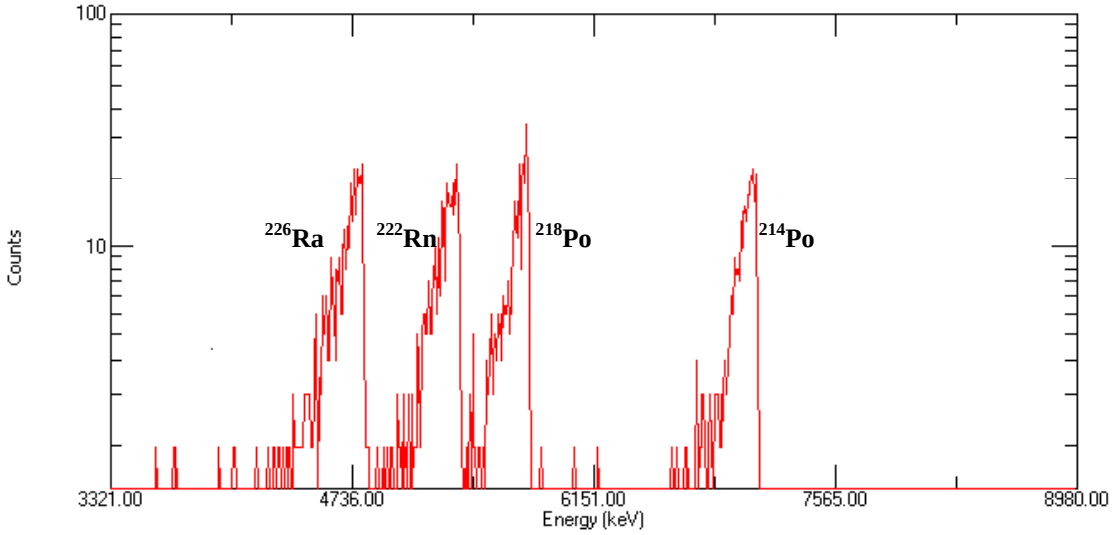

Figure 6 Normal spectrum showing ^{226}Ra and daughters

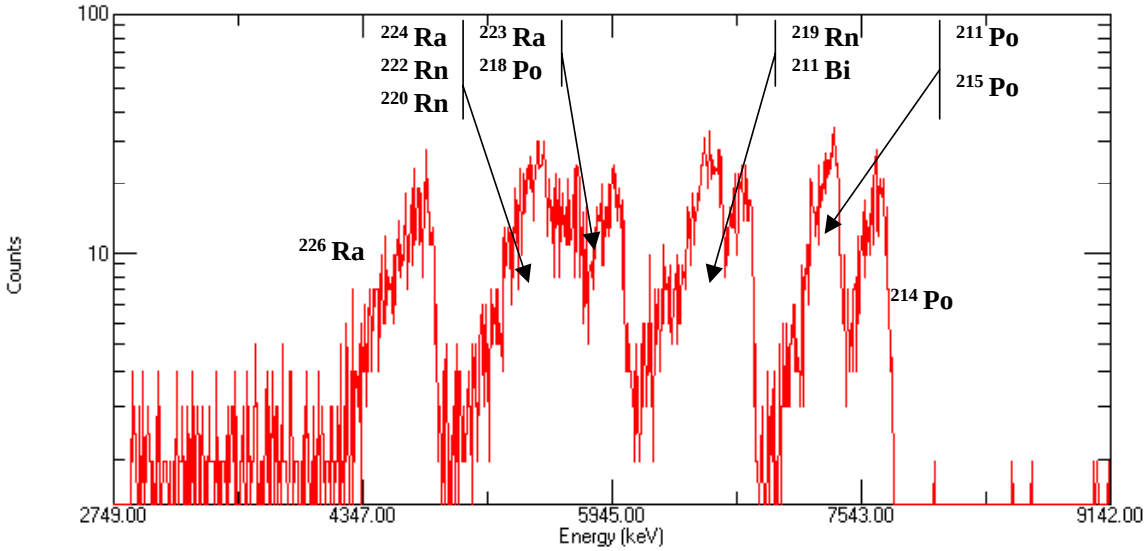

Figure 7 Spectrum including ^{223}Ra, ^{224}Ra, ^{226}Ra and daughters of all 3 isotopes

In 1987 Sill proposed a method for ^{226}Ra determination that differed from many previous techniques. This technique utilised micro-filtration of co-precipitated colloidal $Ba/RaSO_4$, with a non-radium tracer being used – ^{133}Ba.

Many other radionuclides (such as thorium and uranium) are being determined through micro-filtration today, (in the USA it is the industry standard), and in general these methods are quicker, produce very even deposition of the analyte, and are much more tolerable to the presence of other metals. However, reduced resolution of the alpha peaks due to a thicker source for alpha counting prevents determinations of radium isotopes other than ^{226}Ra with the method proposed by Sill (1987).

With the use of ^{226}Ra and ^{133}Ba standards Sill (1987) investigated the differences between yield (also known as recovery) of radium and barium for various steps throughout the method. Sill (1987) did not find any significant difference between radium and barium recoveries in the sources prepared after completion of all steps, though there were minor variations in recovery for different steps throughout the method. Sill (1987) suggests that these variations relate to slight differences in the size of the Ba^{2+} and Ra^{2+} ions.[1]

The $BaSO_4$ method has been suitable for a wide range of sample types, though it is sensitive to large amounts of very fine particulate matter (especially particles between 0.1 µm and 0.45 µm), which tend to clog the filter membrane, and can provide loose material that may easily dislodge and contaminate alpha detectors.

The most significant potential contaminant in this technique is Ba, which, in excess of ~500µg, begins to severely retard the resolution of Alpha peaks (figure 8).

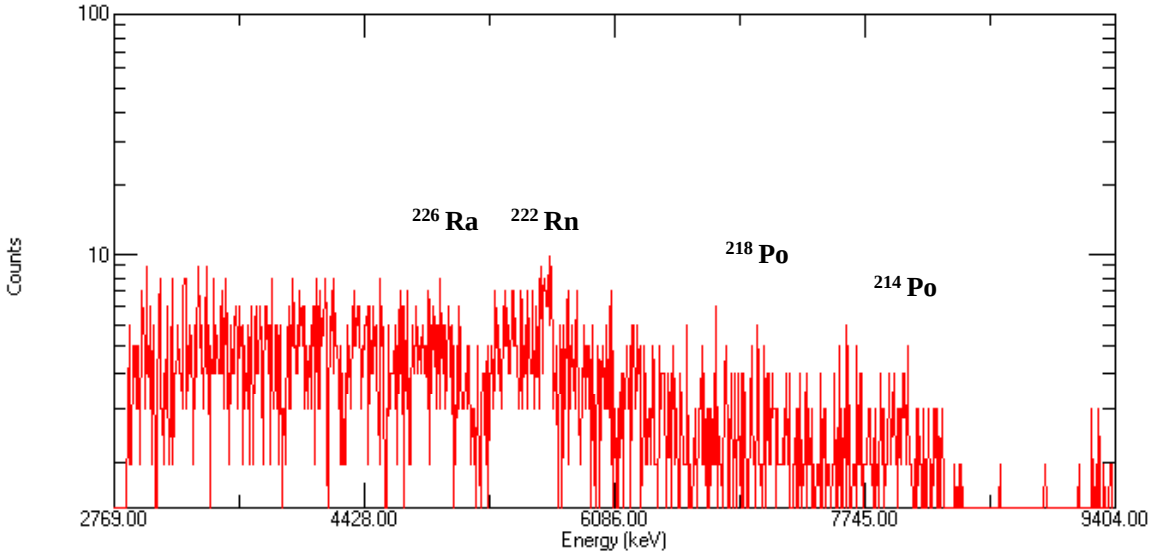

Figure 8 Very poorly resolved spectrum. Likely Ba contamination.

The only solution to this problem so far has been to reduce sample sizes, which is not suitable for all samples high in Ba.

Overall, with suitable digestion procedures, the $BaSO_4$ method is a very fast, and cost effective way of achieving excellent Ra separation for Alpha spectrometric analysis.

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[1] Lozano (1997) indicated a small systematic difference in radium and barium recoveries due to modifications of the original method by Sill (1987); these modifications were made to handle purer solutions than those handled by Sill (1987), and are similar (higher volume of Na_2SO_4 in initial precipitation step) to those employed at ***eriss***, and though the variations in chemical recovery were very small, it may be worth further investigation.

Method

Wet chemistry

Radium is isolated from the gross sample by wet chemistry techniques. Radium is co-precipitated with lead sulphate, using $BaCl_2$ as a carrier, to separate it from the gross sample constituents. Thorium, uranium and other radionuclides (Zikovsky 2001) are also precipitated in this step, with varying recoveries, so further decontamination of the sample is needed. An 80% ethanol wash is used to dry the precipitate after decanting. This helps to remove organic soluble salts, and to remove any supernate that has carried through. This is followed by a mildly acidic (~0.5% H_2SO_4) solution of 20% Na_2SO_4 which is used to further remove traces of remaining acid-soluble substances and to remove excess EtOH. If excess Calcium is present, Kirby (1964) suggests washing the precipitate in a saturated NaOH solution to remove this (this step will also remove some silicates, alumina and lead sulphate).

The washed precipitate is taken up in alkaline diethylenetriaminepentaacetic acid (DTPA), and re-precipitated upon the addition of acetic acid simultaneously with a Barium seeding solution. The seeding solution acts as a carrier; through sonication prior to addition, this seeding solution provides very fine preformed crystals for the Ra to adsorb to, and allows the formation of a very fine crystal lattice, within which the Ra becomes isomorphously distributed (at least 30 minutes is allowed for this isomorphous distribution to take place, and to allow the Ra to be fully absorbed into the Ba crystal lattice). This is a very important step, as demonstrated by Sill (1987) by viewing particle sizes and their effect on resolution through varied steps of this procedure.

All other naturally occurring alpha emitting nuclides that may have carried through to this stage, remain as stable DTPA complexes in the aqueous phase (Sill 1987) with the exception of protactinium isotopes, the half-lives of which preclude them from reaching significant levels after the complete chemistry has been performed.[2]

The colloidal $Ba/RaSO_4$ is mounted on a 0.1 μm polypropylene filter, and again washed with 80% Ethanol and a mildly acidic (~0.5% H_2SO_4) solution of 20% Na_2SO_4 to remove any traces of other radionuclides, in particular ^{230}Th which as the parent of ^{226}Ra may contribute to overall ^{226}Ra and because it has an alpha energy directly beneath the ^{226}Ra peak, which cannot be resolved due to poor resolution of the final source. Sill (1987) suggests ^{230}Th may contribute up to 30% of counts in the ^{226}Ra peak before it can be distinguished.

Due to the adsorptive properties of $RaSO_4$ and its relative insolubility, a heated alkaline solution of DTPA is used to clean any equipment in significant contact with the $Ba/RaSO_4$ to prevent any build up of contamination of the equipment.

[2] ^{231}Pa, which as the daughter of ^{235}U occurs at low activities, is an exception, in theory if 100% of the initial Pa was carried through it would be at 0.046 times ^{226}Ra activity at equilibrium, this is low but still a significant contaminant. Sill (1987) observed a small peak of ^{231}Pa (4.934–5.059 MeV) just to the right of the ^{226}Ra peak on some spectra. Though most of the ^{231}Pa alpha particle energies do fall to the right of the of the ^{226}Ra, some ~11% of alpha energies occur underneath the ^{226}Ra peak. Sill (1987) suggests subracting this amount (11% relative to the ^{231}Pa peak) from the ^{226}Ra peak to accurately reflect measurement of alpha particles from ^{226}Ra only.

Determination of the chemical recovery

To determine the chemical recovery of the procedure a ^{133}Ba tracer is added to each sample. Chemical recovery is quantitatively determined by comparing a ^{133}Ba standard disc with each source. The ^{133}Ba standard disc has an equivalent amount of tracer as per samples, and comparison is made by counting both standard and sample in a thallium dotted sodium iodide, NaI(Tl), detector (figure 9).

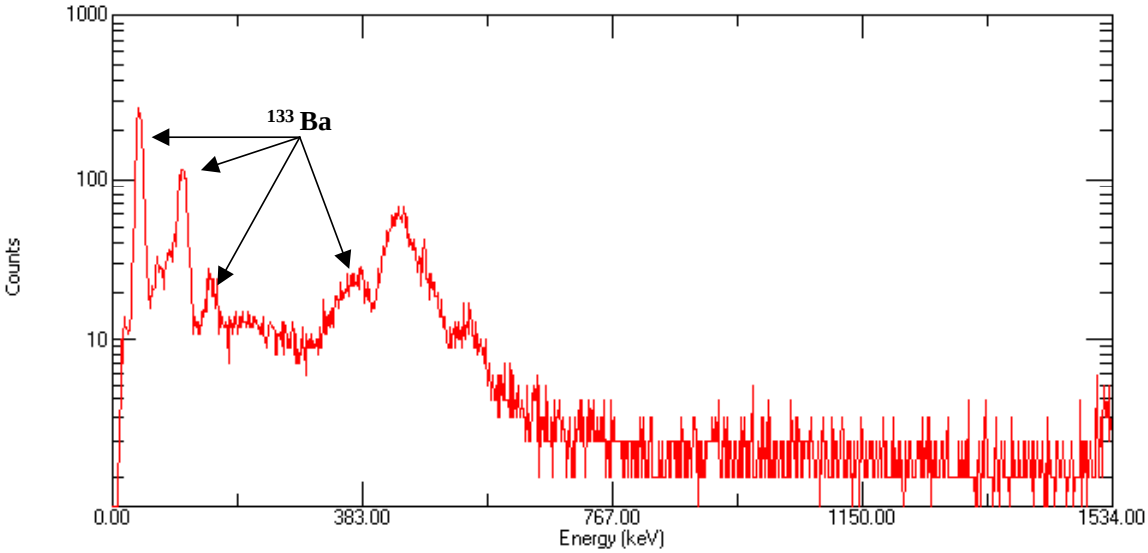

Figure 9 Typical NaI(Tl) spectrum of ^{133}Ba tracer peaks

Each time a new tracer solution is prepared a new Ba standard disc is made for chemical recovery determination. The ^{133}Ba standard disk is made by mounting a known amount of ^{133}Ba as a sulphate in the same manner as samples, excepting that the filtrate and washings from the filtration process are collected in a bottle, counted on a NaI(Tl) gamma spectrometer and compared to an equivalent, known activity of ^{133}Ba in the same geometry. The losses incurred in mounting the standard are calculated from these measurements, allowing the efficiency of mounting, and therefore the fractional recovery of the ^{133}Ba standard disk, to be calculated. Barium standard discs should have a minimum recovery of 95%,[3] and are prepared according to A1.5 ‘Making a Ba-133 standard disc’.

The chemical recovery is required to determine the efficiency of the chemical separation of radium from the sample matrix.

Very active sources of ^{226}Ra can produce enough activity in daughters (namely ^{214}Bi and ^{214}Pb, see figure 1) with spectral lines that will interfere with the ^{133}Ba energy regions. If this is suspected, then NaI(Tl) counting of the source immediately after the final deposition step is required to accurately assess the ^{133}Ba activity before ingrowth of ^{226}Ra daughters reaches significant levels.

Alpha spectrometry

The ^{226}Ra is measured using an high resolution alpha spectrometer fitted with a low background silicon surface barrier detector. Preparation of a radium standard is performed to determine the efficiency of the alpha counting system, to set the regions of interest for peak

[3] see Sill (1987) for discussion of co-precipitation of Ra with Ba for a discussion on the yields of each element during co-precipitation

count determination, and to perform energy calibration of the alpha spectrometer (Appendix 4). This is done in the same manner as a Barium standard, with the addition of ^{226}Ra tracer (A1.6 'Making a ^{226}Ra Standard disc').

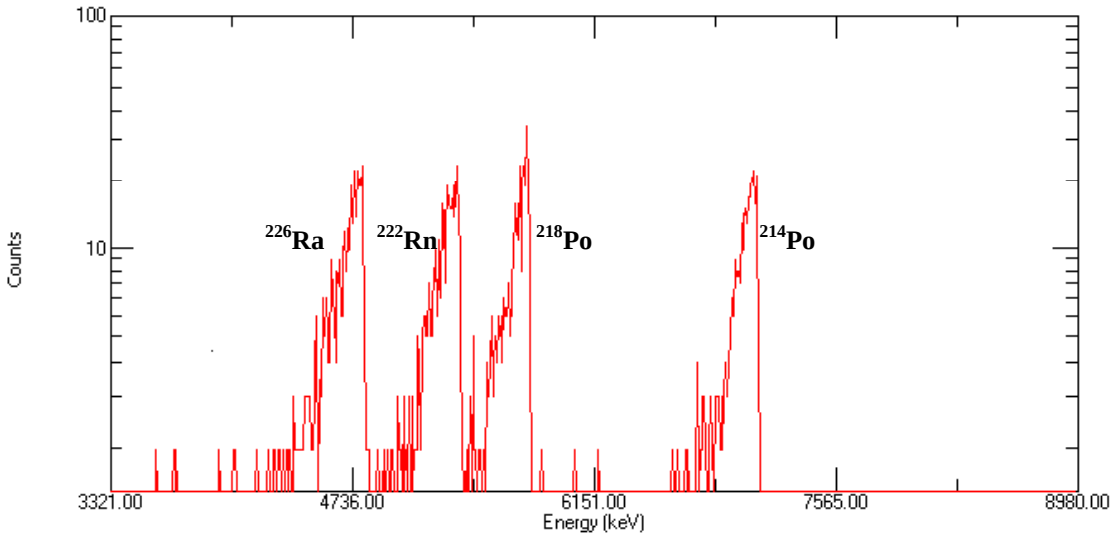

Figure 10 Typical standard disc spectrum

Determination of alpha activity is based on the counts in the ^{226}Ra peak (left-most peak), after accounting for tailing from the ^{222}Rn peak directly to the right. The tailing is calculated as such:

- by assuming equal peak properties for ^{226}Ra and ^{222}Rn
- using a region of interest to the left of the ^{226}Ra peak to measure ^{226}Ra tailing
- Assuming this tailing to peak ratio is equal to that for the ^{222}Rn peak the spectral interference can be accounted for.

For complete information on alpha detector set up and system configuration see SSR180 (Hancock & Martin 2004).

QA/QC

Routine QA/QC checks are performed on the alpha spectrometric system.

The main QA procedures specific to this method are as follows:

- Backgrounds
- Chemical Blanks
- Efficiencies
- Energy calibrations.

Detector backgrounds

The background contamination level of all detectors is monitored with a bi-monthly background count. This involves counting of a blank filter in the same manner as a source for 604.8 ks (exactly 1 week). Control charts monitor variations in count rate in the main peak area of ^{226}Ra.

Chemical blanks

Chemical blanks (or reagent blanks) are volumes of ultra pure water equivalent in size to the samples to allow for determination of contaminants that may arise from reagents and apparatus used in the method. A chemical blank is put through with each batch of samples and counted in each detector in which samples from that batch are counted. Net counts are calculated from subtracting chemical blank counts from source counts.

Detector efficiencies

Calculation of the efficiency of the alpha detection system is required to perform accurate determinations with this method. This is done by counting a ^{226}Ra standard disc (as mentioned previously) of known activity in each alpha spectrometer and comparing the counts per second in the ^{226}Ra peak with the activity of ^{226}Ra (Becquerel = decays per second) on the standard disc.

Detector energy calibrations

After counting of the ^{226}Ra standard disc, the energy of each alpha spectrometer is calibrated to the peaks on the standard disc. This is not essential in ^{226}Ra determinations, but does allow much simpler and more accurate evaluation of potential alpha emitting contaminants where this has occurred by allowing energy evaluation of extra peaks or counts that are obtained in spectra.

Again, for complete information on Alpha detector set up and system configuration see SSR180 (Hancock & Martin 2004).

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Appendices

Appendix 1 Sample and standard preparation

A1.1 Apparatus

Note: All equipment that comes into direct contact with samples, and is to be reused must be separated into Low/Medium and High activity equipment. High activity equipment is kept in the Source laboratory, and should **not** be **removed** from this room.

- Alpha Spectrometers with low background silicon surface barrier detector
- Source holders with a -6 V bias
- NaI gamma detector
- Glass beakers and pipettes; assorted sizes
- Disposable 25 mL, and 50 mL syringes
- Centrifuge and 50 mL centrifuge tubes, Nalgene PC, 50 mL. (Order #3118-0050)
- Hot plate
- Magnetic stirrer plate, bars and retriever
- Vortex stirrer
- Sonic bath
- Vacuum apparatus
- PALL PES (PES – Polyethersulphone) filtration units with stainless steel support screens
- 0.1 μm, 25 mm diameter polypropylene, PALL, Metricel filters (Order #M5PU025)
- 0.45 μm, 47 mm diameter Cellulosic, MicronSep filters (Order #1215281)
- 0.45 μm 25 mm syringe filters – CAMEO 25SS, PES (Order #DDS04025S0); Millipore, MILLEX HV, PVDF (Order #SLHV 025 NB).
- 250 mL side arm flasks.
- Millipore 47 mm petrislides (Order #PD1504700)

A1.2 Reagents

All reagents are to be Analytical Grade or better unless otherwise stated.

Barium carrier solution: $BaCl.2H_2O$ solution: Dissolve 0.92 g $BaCl.2H_2O$ in 1 L Milli-Q, then filter through 0.45 μm. Note, if a filamentous growth forms, make up a fresh solution.

Na_2SO_4 solution (20%): Dissolve 400 g of anhydrous Na_2SO_4 in Milli-Q and make up to 2 L.

Lead nitrate solution (3.2%): Dissolve 32 g of $Pb(NO_3)_2$ in Milli-Q and dilute to 1 L. Filter through a 0.45 μm MicronSep filter.

Sodium sulfate wash solution: Dissolve 100 g of anhydrous Na_2SO_4 in 2 L of 0.5% H_2SO_4. Filter through a a 0.45 μm MicronSep filter

Alkaline DTPA (0.2 M): Dissolve 72 g of NaOH in 1.6 L of Milli-Q and add 160 g of DTPA while stirring. Cool, adjust pH to 10.6 with 10 M NaOH and dilute to 2 L with Milli-Q. Filter through a 0.45 μm MicronSep filter.

Alkaline DTPA (0.5 M): Prepare 100 mL, using 9.5 g of NaOH and 20 g of DTPA, diluting with Milli-Q.

NaOH (10 M): Dissolve 410 g of NaOH in Milli-Q and make up to 1 L. Note that this is a highly exothermic reaction, take care when mixing reagents, and perform in a fume hood.

Conc. H_2SO_4: (98%) AR Grade.

70% Sodium hydrogen sulphate ($NaHSO_4$) solution: Dissolve 70 g of $NaHSO_4$ in Milli-Q in a 100 mL volumetric flask. Filter through a 0.45 μm disposable syringe (Millipore, PVDF). Note, this is highly endothermic and should be placed in a lightly heated (<60°C) water bath for 10-20 minutes to ensure complete dissolution.

$BaSO_4$ seeding suspension: Weigh between 0.012-0.016 g of $BaCl_2$ $2H_20$ into a tall 150 mL beaker. Add approximately 0.4 mL of Milli-Q water to completely dissolve the $BaCl_2.2H_20$. In a fume hood designated for perchloric acid use, add 10 mL of the 70% sodium hydrogen sulphate solution, and 2 drops of 72% $HCLO_4$. Evaporate the solution on a hot plate at high heat with continuous swirling until most of the excess sulphuric acid has been expelled and a pyrosulphate fusion is obtained. Cool the beaker while rolling the melt around the sides so that the cake is deposited on the sides as uniformly as possible to facilitate rapid dissolution. Cool the beaker and contents to room temperature in a dessicating chamber. Using a 0.45 μm disposable syringe filter (Millipore, PVDF), add a solution of 50 mL 20% Na_2SO_4 to the beaker. Swirl continuously until the cake is completely dissolved. (Place in an ultrasonic bath for 10 minutes before each use).

Note: If a build up of particulate matter occurs then make a fresh solution.

Sodium sulphate/acetic acid: Mix 5 parts 20% Na_2SO_4 with 1 part glacial acetic acid. Always make this fresh and ensure the solution is adequately mixed prior to use.

80% EtOH dewetting agent: Add 400 mL of AR grade Ethanol (EtOH) to 100 mL Milli-Q.

Methyl Red indicator

Bromothymol Blue indicator

Thymol Blue

DTPA Cleaning Solution: Place 50 g of DTPA in 2.5 L of Milli-Q, add 0.125 mL of 0.25% bromothymol blue indicator into a graduated 3 L beaker and heat to approx. 80°C in a fume hood. Add 10 M sodium hydroxide until the DTPA has dissolved and the darkest permanent blue colour of the alkaline form of the indicator is produced (about 15 mL per litre of cleaning solution). Cover with a watch glass and leave in the beaker for storage (the beaker should be kept in a fume hood for use). Replace evaporation losses with Milli-Q to keep the volume at about 2.5 L.

HCl 32%: AR Grade.

0.5% H_2SO_4: Mix 10 mL of concentrated H_2SO_4 in 2 L of Milli-Q

0.1 M HCl: Mix 8.3 mL of HCL 32% in 1 L of Milli-Q.

A1.3 Sample pre-treatment and preparation

Samples will be prepared differently according to the needs of the project or client concerned.

The following pre-treatment methods are routine for all samples unless otherwise specified by a client.

Note: Tracer is added prior to commencement of the digestion procedure unless otherwise specified, and the digest is filtered through 0.45 μm, prior to initial precipitation.

A1.3.1 Water samples:

All samples are filtered through 0.45 μm

- then acidified with 5 mL concentrated HCl per litre for surface-water chemistry monitoring samples
- or acidified with 1% HNO_3 for other samples.

If residual or total analysis is required the residue is digested according to the Filtration Residue Digestion Method, DFR001 (described below), unless otherwise specified.

A1.3.2 Soil/sediment/biota samples: EnRad Method DSB-002

1. Weigh the digest mass in an appropriate size beaker. Remember, many biota samples may spit and react strongly upon addition of concentrated acids, so selection of a larger beaker than usual may be required
2. Add an appropriate mass of tracer, weighed to an accuracy of 0.0005 g (refer to A1.4, step 2 for ^{133}Ba tracer volume in ^{226}Ra determination)
3. Add enough conc. HNO_3 to cover the digest mass, transfer the beaker to a hotplate set at 60°C and cover with a watchglass for approx. 24 hours (overnight is sufficient) and allow to reflux. Remove the cover and allow to evaporate to near dryness
4. Repeat step 3 once
5. After evaporating to near dryness add enough Aqua Regia (3-4 parts conc. HCl to 1 part conc. HNO_3) to cover the digest mass, transfer the beaker back to the hotplate and cover with a watchglass cover for approx. 24 hours (overnight is sufficient) and allow to reflux. Evaporate the solution to dryness
6. Repeat step 5 as many times as necessary to break down all organic matter present
7. Take up near dry digest solution in appropriate solution for analysis.

A1.3.3 High volume air samples

Digestion is carried out according to EPA method EPA/625/R-96/010a “Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air”, Compendium Mehtod IO-3.1 “Selection, Preparation and Extraction of filter Material”.

A1.3.4 Filtration Residues: EnRad Method DFR-001 (Digest, Filtration Residue. Method 001)

Glassware is cleaned according to set procedures (refer to A1.4.1) for the alpha spectrometry laboratory. Glassware is also separated into high/medium/and low activity.

Always include a filter paper blank in each batch of digests.

1. Add an appropriate mass of tracer, weighed to an accuracy of 0.0005 g (refer to A1.4, step 2 for ^{133}Ba tracer volume in ^{226}Ra determination) to a 100 mL beaker

2. Transfer the dried filter paper(s) to the beaker. Add enough conc. HNO_3 to cover the filter paper(s), transfer the beaker to a hotplate set at 60°C and cover with a watchglass for approx. 24 hours (overnight is sufficient), allow to reflux
3. Remove the cover and allow to evaporate to near dryness, repeat step 2
4. Take up the near dry residue in 20 mL of a mix of 40:1, HCl:H_20, heat for 30 minutes at 60°C, or until residue is dissolved, then filter through 0.45 μm.

A1.4 Radiochemical procedure for sample preparation

A chemical blank must be prepared with each batch of samples, using an approximately equal volume of Milli-Q water to the sample volume.

1. Weigh approximately the following volumes of the sample into a beaker (assuming a specific gravity of 1:

- Filtrates
  - Approrimately 800 mL for low level filtrate samples (<10 mBq/L)
  - For higher activity samples the volume should be adjusted to give between 20-50 mBq of activity for analysis. This will reduce chances of equipment and detector contamination. Samples with activity concentrations >5 Bq/L should be stored and handled solely in the Source Lab
- Residue, soil and sediment digests are prepared according to Appendix 3; refer to step 4 for suggested minimum volumes of digest solutions.

Acid concentrations in the sample should be reduced below 0.15 M to ensure efficient removal of barium & radium during the $Pb(NO_3)_2$ precipitation step.

Record weight of sample on the $BaSO_4$ worksheet (form L4, see Appendix 5).

2. Using a disposable pipette add approx. 2 mL of ^{133}Ba tracer. Weigh tracer volume to an accuracy of 4 decimal places and record on the $BaSO_4$ worksheet (form L4)
3. Add 0.4 mL of barium carrier solution (~365 μg of barium)
4. For 800 mL filtrate samples, add 10mL of conc. (98%) H_2SO_4 and 50 mL of 20% Na_2SO_4 to the beaker and mix with magnetic stirrers. This ratio can be adjusted according to the volume being precipitated. Generally a minimum of 2 mL of conc. H_2SO_4 and 10 mL of 20% Na_2SO_4 is required). For residue sediment and biota digests this is suggested to be a minimum volume of 4 mL of conc. H_2SO_4 and 20 mL of 20% Na_2SO_4, with a minimum 100 mL sample volume to reduce matrix interference
5. Precipitate Pb/Ba/Ra/SO_4 by adding five 1 mL aliquots of 3.2% $Pb(NO_3)_2$ solution through a dripper while stirring. Keep stirring for 1-2 minutes. Remove stirrer bars, washing with a small amount of 0.1 M HCl and Milli-Q (allow washings to drip into the beaker) to reduce loss of precipitate and prevent cross contamination between samples
6. Cover with watch glass and allow to settle overnight for large samples, >100 mL, smaller volume samples, <100 mL, will settle adequately in 3–4 hours. For samples <40 mL, settling and decanting is not necessary, and you may proceed directly to step 8, washing the entire solution into the centrifuge tube
7. Decant supernatant liquor to as low a volume as possible. Discard decanted supernatant

8. Wash precipitate into a 50 mL centrifuge tube using 80% $^{v}/_{v}$ EtOH (this acts as a de-wetting agent) and centrifuge at 3500 rpm for five minutes
9. Pour out supernatant
10. Repeat steps 7 and 8 once
11. Wash sides of the centrifuge tube with 5–10 mL of the sulphate wash solution. Vortex to mix thoroughly, then add a further 5–10 mL to wash down the walls. Re-centrifuge at 3500 rpm for five minutes
12. Pour out supernatant. Invert the tube and wash the walls with Milli-Q to remove excess acid and SO_4 (take care not to disturb the precipitate)
13. Add 10 mL of 0.2 M DTPA solution, and 1 drop of <0.25% thymol blue. The solution should turn deep blue, if not add 10 M NaOH drop wise until a deep blue colour is reached (pH>9)
14. Vortex to dissolve the precipitate
15. If a whitish turbidity is present and the pH is above 9, add 50 µL aliquots of 0.5 M alkaline DTPA until the solution clears upon standing in a hot water bath for 1 minute *(refer to Sill 1987, p242);* or, if the turbidity is of a darker colour, the solution can be filtered through a CAMEO 25SS PES 0.45 µm disposable syringe filter; the syringe filter should be pre-washed with 10 mL 0.2 M DTPA, and an extra 1–2 mL of 0.2 M DTPA should be added after filtering to wash through the solution and to make the solution up to 10 mL
16. Begin sonicating the Ba seeding solution to be used in step 18. Sonicate for 10 minutes
17. Add two drops of <0.25% methyl red solution, the solution should turn a deep green, and remain pink (pH 4–5) following stage 18.

Mounting the Sample

18. Before beginning this step, note that once this stage has been performed, the procedure **must** be completed that day. Using a syringe with a Millipore MILLEX HV, PVDF 0.45 µm disposable syringe filter, rapidly inject 4 mL of the mixed NA_2SO_4/Acetic acid solution. Add 0.4 mL of the Ba seeding solution as soon as possible (2–3 s). pH is reduced to 4.8 as indicated by the colour change to a bright red. Allow to sit for at least 30 minutes
19. Filter the colloidal suspension of Ba/Ra/SO_4 through a pre-wetted (60% $^{v}/_{v}$ EtOH) PALL, Metricel 0.1 µm pore size, 25 mm diameter polypropylene filter mounted in a PALL PES filter unit
20. After the sample has filtered rinse the centrifuge tube walls with 4–5 mL of sodium sulphate wash solution and filter
21. Rinse the sides of the centrifuge tube walls with 4–5 mL of 60% $^{v}/_{v}$ EtOH and filter
22. Rinse the sides of the filter holder with 15–20 drops of 60% $^{v}/_{v}$ EtOH in a circular motion just above the previous aqueous level to wash down any Ba\Ra\SO_4 on the funnel sides
23. Allow the filter to dry and place in a Millipore 47 mm petrislide before transferring to the counting room. **Note:** Count the ^{133}Ba on the same day, or as soon as practicable
24. Discs (mounted filters) are labelled according to a set standard for alpha counting. This is detailed in Appendix 2.2.

A1.4.1 Cleaning of equipment

25. In between uses, the PALL filter units are heated to near boiling in a DTPA wash solution to remove residual Ba/Ra/SO_4 precipitate. Air dry. DO NOT wipe dry. This may cause a static electricity build up which will attract dust and Ba/Ra/SO_4 precipitate. Do not heat above 120°C as this may damage the PES surfaces

26. All glassware, plastic, Teflon and stainless steel is washed in 3% DECON 90 for several hours, rinsed and left to soak in 2% HNO_3 for several hours. Items are then rinsed in deionised water and air dried.

Teflon circlips, stainless steel, and plastic support screens are cleaned using both of the above procedures, starting with step 1, followed by step 2.

A1.5 Making a ^{133}Ba standard disk.

A ^{133}Ba standard disc is prepared to determine the chemical recovery of prepared sources.

A new standard disk should be made and calibrated each time a new batch of ^{133}Ba tracer is used.

The ^{133}Ba standard disk is made by mounting a known amount of ^{133}Ba as a sulphate in the same manner as samples are mounted (steps 18–23).

The filtrate and washings from the mounting process are collected in a bottle, counted on a NaI(Tl) gamma spectrometer and compared to an equivalent, known activity of ^{133}Ba in the same geometry (ie – in the same type of bottle filled to the same height). The losses incurred in mounting the source are calculated from these measurements, allowing the efficiency of mounting, and therefore the fractional recovery of the ^{133}Ba standard disk, to be calculated.

Additional Apparatus

- 60 ml plastic bottles (x3).

A1.5.1 Mounting the ^{133}Ba standard disc

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. Add 0.5 mL of Ba carrier solution

3. Add 10 mL 0.2 M DTPA, 1 drop of thymol blue and 2 drops of methyl red

4. Simultaneously add 6 mL of 5:1, 20% Na_2SO_4:Acetic acid mix, and 0.5 mL Ba seeding solution

5. Leave to stand for at least 30 minutes

6. Filter as per samples (steps 18–23 from A1.4), collecting all of the filtrate (including washings) into a side arm flask

7. Remove filter and allow to air dry.

A1.5.2 Collecting the filtrate & washings

1. Heat 10 mL of 0.2 M DTPA in the centrifuge tube to dissolve any remaining particles, use this to wash the funnel and collect the washings

2. Add these washings to the filtrate in a counting bottle and make up to a known height with Milli-Q

3. To make a ^{133}Ba standard bottle, measure into an identical counting bottle approximately the same amount (weighed to 4 decimal places) of ^{133}Ba standard as used in the first step. Dilute this to the same height as the combined washings and filtrate
4. Make a Blank bottle by filling a third counting bottle to the same height with Milli-Q.

Discs and bottles are labelled according to procedures desribed in Appendix 2.

A1.5.3 Determining fractional recovery of the Ba133 standard disc

Refer to Appendix 3.3.

A1.6 Making a ^{226}Ra standard disk.

A ^{226}Ra standard disk is used to determine the efficiency and perform an energy calibration of each alpha spectrometer. The disk is made by mounting a known amount of calibrated ^{226}Ra solution, and ^{133}Ba solution, as a sulphate in the same manner[1] as samples are mounted (steps 18–23 from A1.4).[4]

Additional Apparatus

- 60 ml plastic bottles (x3).

Additional Reagents

- ^{226}Ra standard solution.

A1.6.1 Mounting the ^{226}Ra standard disc

1. Measure into a 50 mL centrifuge tube approximately 1.3 mL (weighed to 4 decimal places) of ^{226}Ra standard solution (Ra–226 #7)
2. Measure into a 50 mL centrifuge tube approximately the same amount (weighed to 4 decimal places) of ^{133}Ba standard as used per sample
3. Mount the ^{226}Ra standard disc as per the ^{133}Ba standard disc (steps 18–23 from A1.4).

A1.6.2 Collecting the filtrate and washings

1. Collect the filtrate and washings as per the Ba standard disc (steps 8–11 from A1.5.2)

Refer to Appendix 2.2 for labelling discs and bottles.

A1.6.3 Determining fractional recovery of the ^{226}Ra standard disc

Refer to Appendix 3.3.

A1.7 Gamma and alpha counting

A1.7.1 Alpha counting procedure

Details of the system setup and maintenance can be found in SSR180. Alpha detectors must be properly calibrated before mounting samples for counting. For recoil protection calibration see SSD Explorer at:

\\Equipment and Techniques\Alpha Spec\Procedures\Recoil_prot_pressure2.doc

All other calibration procedures for ^{226}Ra alpha counting (including efficiency, energy, ROIs and detector backgrounds) can be found in Appendix 4.

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[4] See footnote on p10.

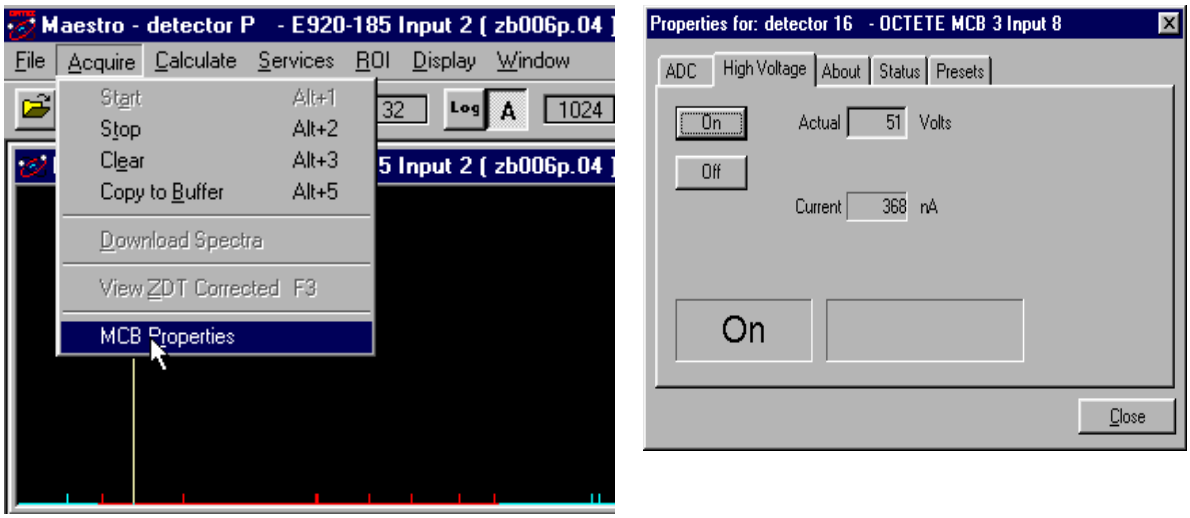
To handle samples, tweezers are designated for specific purposes:

- For handling ^{226}Ra samples only, further designated for high, medium and low activity samples
- For handling ^{226}Ra standards only
- For handling very high activity samples only, all isotopes (of Ra, U, Th & Po)
- For handling Blank discs only
- Tweezers should be wiped with a dry tissue after handling each sample.

Alpha detectors for counting ^{226}Ra samples are designated for High, Medium and Low level samples due to differences in detection limits (related to background contamination of detectors).

Turn off the bias to the detector in which a sample is to be counted, either manually, or using Maestro V6 for the Octete™ (figure A1.1).

1. While in the active detector window, select Acquire\MCB Properties to open the properties dialog box. Select the High Voltage tab, then click the Off button, (follow this procedure , clicking the On button to turn the bias back on)



A1.1 Turning bias ON/OFF for OCTETE™ detectors

2. After ensuring the bias is turned off, set the vacuum knob to 'Vent', then open the chamber door and remove the sample holder
3. Place the sample centrally in a custom built sample holder with the sample facing upwards, then fix into place using a clean Teflon circlip
4. Place the sample holder back into the counting chamber. Check that the gasket seal is in place and free of dust; ensure enough vacuum grease is on the gasket seal to seal the door before closing
5. Set the chamber to pump and bring the chamber pressure down to as low a pressure as possible. This is done by switching the pump on, then turning on the solenoid switch located above the OCTETE™
6. Using the pressure adjustment knob attached to the pressure gauge, bring the chamber back up to the pressure labeled on the door (this is calculated from recoil protection calibration procedures detailed on the previous page), give the preamplifier about 30

seconds to reach the desired voltage and leakage current across the detector; turn on the bias, either manually or using Maestro V6 for the Octete™ (figure A1.1)

7. Samples are counted for a minimum of 400 ks, or until 500 counts are recorded in ROI B, the central ^{226}Ra peak
8. To remove samples, first turn off the bias; then set the vacuum switch to vent. Remove the sample holder, then the circlip, placing it into the used circlip container, place the sample back in the Millipore petrislide
9. Even if the detector is not going to be used, the pressure and bias must be set as normal.

A1.7.2 Saving spectra and recording data

To save spectra from Maestro V6, select the 'File' drop down menu, then 'Save as'. Refer to Appendix 2.2 for protocols on saving spectra.

Count details are recorded on the $BaSO_4$ worksheet (form L4), and then entered into the Sills Calculations worksheet. Refer to Appendix 3 for details of setting up Sills Calculations worksheets and the calculations involved here.

A1.7.3 Gamma counting procedure

1. Open the chamber, place the plastic Petri dish containing the source centrally on the NaI detector then close the chamber
2. Set the counting 'Live time' for 3.6 ks to obtain 25–30,000 counts in the standard Region of Interest under the ^{133}Ba peak at 356 keV. The Ba133.roi is set from 323 to 646 keV to cover the major gamma emissions of ^{133}Ba. The NaI detector is calibrated according to IR 76 (Marten R 1992)
3. Acquire the spectrum using Maestro V6 on the Gamma computer.
4. Clear the previous spectrum, then press GO to start counting.

A1.7.3 Saving spectra

Refer to Appendix 2.2.

A1.8 Source storage procedure

For storage of sources refer to the Source Control Plan on SSD Explorer at:

\\OH & S\Safety Manuals\Radiation_Safety\Radiation_Source_Control_Plan\Versions\ RadSourceControlPlan_v6.doc

In general sources are stored in the original boxes (located in the shelving in the filtration laboratory) in which the plastic petri-slides are purchased, and when these are full, they are kept in the Source Store. Most sources at eriss are below exemption limits for classification as a radioactive source, however for good safety practice, and to avoid contamination of the laboratory areas from radon and daughters, sources are removed to the source store as soon as practicable.

Standard discs are stored in the top drawer of the wooden filing cabinet in the counting room.

Appendix 2 Labelling and saving sources and spectra

A2.1 Labelling of discs and bottles for the $BaSO_4$ method

A2.1.2 Discs

All discs (except ^{133}Ba standard discs) are given a 5 or 6 digit code to identify them. This begins with a 2 letter prefix, followed by a 3 or 4 digit number:

- The 2 letter prefixes used are SR, SZ, YS and ZB.
- SR : Sills Radium. This is for sources prepared from a sample, (the $BaSO_4$ method is based on a method by C.Sills).
- YS : Background Sills. This is for chemical and procedural blanks.
- SZ : Sills Standard. This is for all standard sources prepared for the calibration of detectors and instrumentation used in the $BaSO_4$ method.
- ZB : Standard Blank. This is for all blank discs (filters) used for counting instrument blanks in the $BaSO_4$ method.

ZB discs have a card prepared detailing the batch from which they were taken, and recording the count times and detectors for each count. The details recorded on the card are given below, followed by an example card.

ZB (blank disc) card for ^{226}Ra blank discs

'Disc ID'			Ra226	
- 0.1 μm filter paper from 'Batch #'				
- For use in chamber backgrounds for Ra226 detectors only				
'Specify for L/M/H detectors'		'Date created, initialled'		
'Count Code' 'Count date start'–'Count date finish' 'File archive (eg Alpha-21)'				

Example ZB (blank disc) card for ^{226}Ra blank discs

ZB007			Ra226	
- 0.1 μm filter paper from Lot. #93322				
- For use in chamber backgrounds for Ra226 detectors only				
MED/HIGH detectors			06.07.04 PSM	
ZB007(10).01	06.07.04	-	13.07.04	α-21
ZB007(12).01	17.08.04	-	24.08.04	α-21

- ZB spectra are saved in:
    - Alpha-21\Alphadata\Spectrum\Z\ZB sub-folder
- Data for discs with prefix ‘ZB’ counting is recorded in:
    - Alpha-21\Alphadata\BgdCrates\Ra226BlankFilterCounts.xls.
- A new worksheet for each detector is used in this workbook and a template of this worksheet can be found in ‘spreadsheet solutions’ on the alphaone computer.

- The digits following the prefix represent the number of that type of sample, 4 digits for SR samples, 3 digits for all others. For example, a batch of 5 radium samples is prepared. The previous batch had a chemical blank labelled ys035, with the last source in the batch labelled sr1075. The new batch being prepared will be labelled sr1076–sr1080, with the chemical blank being labelled ys036. With this batch, a Ra standard, sz025 is used to calibrate the detector, this is the 25th Ra standard disc made for the $BaSO_4$ method in the laboratory.
- ^{133}Ba standard discs are labelled ‘BaStd##.#’, followed by 3 digits. The first 2 digits represent the Ba Tracer Solution being used, the next digit represents the number of ^{133}Ba standards made from that solution. For example, if 3 Ba standards were prepared from Ba Tracer solution #12, the first would be labelled BaStd12.1, the second BaStd12.2 and the third BaStd12.3.
- There is a worksheet titled ‘Standard List’. This worksheet has a current list of all standard and blank discs/bottles, and is to be used when assigning codes for newly prepared discs/bottles. This list **must** be updated as new ones are prepared. The Standard List worksheet can be found in the Ba-133.xls workbook on the Alphaone computer at:
    - D:\Alpha21\Results\Sillscalculations\Ba133\Ba-133.xls

A2.1.3 Bottles

Bottles are only used for preparing a ^{133}Ba standard, and are labelled according to their purpose. There are 3 types of bottle used:

- A blank bottle: filled with Milli-Q
- A standard bottle: filled with Milli-Q and a known volume of ^{133}Ba tracer
- A bottle with the filtrate and washings from the preparation of the ^{133}Ba standard disc.

These bottles are labelled accordingly:

- Blank bottles: ‘BLB###’, where the numbers represent the number of the blank bottle prepared. For example, the 10th blank bottle prepared will be labelled BLB010.
- Standard bottles: ‘STB##.#’, where the first 2 numbers represent the tracer solution being used, and the last digit is the number of the standard bottle prepared. Eg – The third standard bottle prepared from ^{133}Ba Tracer solution 12 will be labelled STB12.3.
- Filtrate and washings bottles for Barium Standards: ‘F&W##.#’, where the last 3 numbers represent the number of the ^{133}Ba standard disc these were collected from. For example, the filtrate and washings from ^{133}Ba standard disc BaStd12.2 will be labelled F&W12.2.
- Filtrate and washings bottles for Radium standards: F&WSZ##, where the 3 numbers represent the number of the Ra standard disc. For example, the filtrate and washings from Ra standard disc SZ026 will be labelled F&WSZ026

A2.2 Saving spectra for the $BaSO_4$ method

^{133}Ba counts of these bottles are saved in:

- Alphaone\D:\Alpha-21\Spectrum\GammaBa133, as .chn files.

Spectra are saved beginning with the bottle code, then the count number, eg the 1st count for the filtrate and washings from Barium Standard 12.2 will be saved as F&W12.2.01.chn.

NaI Spectra are saved on the Alphaone computer as .chn files in the following sub- folders of the GammaBa133 folder:

- Bgd for backgrounds,
  - This is further split into sub-folders for every 100 discs, eg
    - ys001-ys099
    - ys100-ys199 etc.
- Samples for samples,
  - This is further split into sub-folders for every 500 discs, eg
    - sr001-sr499
    - sr500-sr999 etc.
- Std for standards, this is further split into sub-folders:
  - StandardBottle for standard bottles,
  - BlankBottle for blank bottles,
  - Filtrate&Washings for the filtrate and washings,
  - and BaStd for Barium standard disc counts.
- Region of Interest files for NaI spectra are saved in:
  - D:\User\ROI\New ROI\Ba133.

All NaI spectra for discs are saved beginning with the disc code, followed by the count number, eg sr2001.01.chn for the first count, sr2001.02.chn for the second.

Write the gross counts in the Ba133 counts column in form L4. Required details of the Ba133 standard used are listed below, these are to be recorded in the appropriate row in the laboratory worksheet L4:

- Ba133 standard disc ID,
- Ba133 standard disc count date,
- Ba133 standard disc counts,
- Ba133 standard disc count time.

Count the Ba standard disc for the specific barium standard solution being used each time a new batch of samples is counted.

All alpha spectra are saved beginning with the disc code, followed by the detector code then the count number, eg sr2001q.01.chn for the first count, sr2001q.02.chn for the second in that detector. Brackets are used if the detector code is a number, eg sr2001(13).01.chn.

All files are saved in:

- Alphaone\D:\Alpha-21\Spectrum\Sills.

The Sills folder is further split into sub-folders:

- S for samples and standard discs, which is then split into 2 further sub-folders:
    - S for samples:
        - This is further split into sub-folders for every 100 discs, eg–
            - sr2201-sr2300
            - sr2301-sr2400 etc.
    - SZ for standard discs:
        - This is further split into sub-folders for every disc, eg–
            - sz026
            - sz027 etc.
- Y for chemical Backgrounds:
        - This is further split into sub-folders every for every 100 discs, eg–
            - ys001-ys099
            - ys100-ys199 etc.

Appendix 3 Data storage and calculations

A3.1 Blank filters

Recording and calculation of the blank filter count rates is performed in the spreadsheet Ra226BlankFilterCounts.xls, on the Alphaone computer at:

- D:\Alpha21\Alphadata\BgdCrates

This workbook contains a spreadsheet for each alpha detector, new worksheets are opened from the template Ra226BlankFilter.xlt in Spreadsheet solutions, these worksheets are named after the detector they relate to.

The Ra226BlankFilterCounts.xls worksheet calculates the gross count rate in each region of interest (ROI) and the mean count rate for successive blank filter counts. The worksheet also plots the gross counts from ROI B (the ^{226}Ra peak) over time. Calculations from this worksheet are detailed below.

The gross count rate in region of interest A, G_A, and its uncertainty, ΔG_A are calculated using:

$$G_A = \frac{b_{cA}}{t_b}$$

$$\Delta G_A = \frac{\sqrt{b_{cA}}}{t_b}$$

with:

b_{cA}: Blank filter counts in ROI A (Ra-226 peak tailing region).

t_b: Blank filter count time.

Similarly, the gross count rates in ROI B and C are calculated:

$$G_B = \frac{b_{cB}}{t_b}$$

$$\Delta G_B = \frac{\sqrt{b_{cB}}}{t_b}$$

$$G_C = \frac{b_{cC}}{t_b}$$

$$\Delta G_C = \frac{\sqrt{b_{cC}}}{t_b}$$

with:

$b_{cB:}$ Blank filter counts in ROI B (Ra-226 peak).

$b_{cC:}$ Blank filter counts in ROI C (Rn-222 peak).

A3.2 Samples

Sills calculations worksheets are used to calculate the ^{226}Ra activity concentrations for all samples. Sills calculations worksheets can be found on the Alphaone computer, and are divided into folders according to the year in which the work order was begun. A separate worksheet is created in each workbook for the data set of each report sent. – Check in the Report table of the Universal2000a database for the latest report number to be used, as reports may be issued against a work order for non-Ra226 analyses.

- For example, the first data set for work order 200325, will be placed in a worksheet called 200325.01, and found in workbook Sillscalculations2003.xls. Subsequent worksheets (and their associated reports) from that work order will be called 200325.02, 200325.03 etc.
- Blank worksheets are created from the template Ra226_Calculations.xlt (found in the Spreadsheet solutions tab on the Alphaone computer), and then moved into the appropriate workbook in the InProgress sub-folder, which is located at:
    - Alphaone\D:\Alpha21\Results\Sillscalculations\InProgress

^{226}Ra activity concentrations, A_{226}, and associated uncertainty, ΔA_{226} are calculated in the Sills calculations template using:

$$A_{226} = \frac{N_{226}}{m_S \cdot \varepsilon_{corr} \cdot R_S}$$

$$\Delta A_{226} = \frac{\Delta N_{226}}{m_S \cdot \varepsilon_{corr} \cdot R_S}$$

with:

A_{226}: ^{226}Ra activity concentration in [Bq/kg].

N_{226}: Net count rate of ^{226}Ra, in counts per kiloseconds [cpks].

m_S: Mass of sample in [g].

R_S: relative ^{133}Ba recovery of sample (refer to A3.3.2 for details).

ε: corrected efficiency of alpha spectrometer (refer to A3.4 for details).

The net count rate of ^{226}Ra, N_{226},is given by:

$$N_{226} = N_A + N_B - (\frac{N_A}{N_B} \cdot N_C)$$

if $N_{CB} > N_{CA}$, or:

$$N_{226} = N_A + N_B - (\frac{N_A}{N_C} \cdot N_C)$$

if $N_{CB} < N_A$

with:

N_A: net count Rate of ROI A in [cpks].

N_B: net count Rate of ROI B in [cpks].

N_C: net count Rate of ROI C in [cpks].

N_A and associated uncertainty, ΔN_A are given by:

$$N_A = \frac{S_{CA}}{t_S} - \frac{b_{CA}}{t_B}$$

$$\Delta N_A = \sqrt{\frac{S_{CA}}{t_S}^2 + \frac{b_{CA}}{t_B}^2}$$

with:

S_{CA}: Sample counts ROI A (Ra-226 peak tailing region).

b_{CA} : Background counts ROI A.

t_b: Background count time in [ks].

Similarly, the net counts in ROI B and ROI C are calculated:

$$N_B = \frac{S_{CB}}{t_S} - \frac{b_{CB}}{t_B}$$

$$\Delta N_B = \sqrt{\frac{S_{CB}}{t_S}^2 + \frac{b_{CB}}{t_B}^2}$$

and

$$N_C = \frac{S_{CC}}{t_S} - \frac{b_{CC}}{t_B}$$

$$\Delta N_C = \sqrt{\frac{S_{CC}}{t_S}^2 + \frac{b_{CC}}{t_B}^2}$$

with:

S_{CB} : Sample counts ROI B (Ra-226 peak).

S_{CC}: Sample counts ROI C (Rn-222 peak).

B_{CB}: Background counts ROI B.

B_{CC}: Background counts ROI C.

The error in the net count rate of Ra-226, ΔN_{226}, is calculated using:

$$\Delta N_{226} = \sqrt{\left(\frac{dN_{226}}{dN_A}\cdot\Delta N_A\right)^2 + \left(\frac{dN_{226}}{dN_B}\cdot\Delta N_B\right)^2 + \left(\frac{dN_{226}}{dN_B}\cdot\Delta N_B\right)^2}$$

with:

$$\frac{dN_{226}}{dN_A} = 1 - \frac{N_C}{N_B}$$

$$\frac{dN_{226}}{dN_B} = 1 + \frac{N_A \cdot N_C}{N_B^2}$$

$$\frac{dN_{226}}{dN_C} = -\frac{N_A}{N_B}$$

For blank count rates that can be neglected compared to the count rates in the sample, ΔN_{226} can be written as:

$$\Delta N_{226} = \sqrt{\left(1 - \frac{S_{CC}}{S_{CB}}\right)^2 \cdot S_{CA} + \left(1 + \frac{S_{CA}\cdot S_{CC}}{S_{CB}^{\ 2}}\right)^2 \cdot S_{CB} + \left(\frac{S_{CA}}{S_{CB}}\right)^2 \cdot S_{CC}} \cdot \frac{1}{t_s}$$

A3.3 Barium standard recovery calculations

Data from the bottle counts are recorded in the Ba-133.xls workbook.

A new worksheet is set up for each standard disc from the template Ra226_StdDisc.xlt found in Spreadsheet Solutions on the Alphaone computer. New standard disc worksheets are placed in the Ba-133.xls workbook, which is located at:

- Alphaone\D:\Alpha21\Results\SillsCalculations\Ba133

Relative barium standard recoveries in percent are determined by:

$$R_{BStd} = 100 \cdot \left(1 - \frac{N_{F\&W} / N_{STB}}{m_{STB} / m_{BStd}}\right)$$

And associated uncertainy:

$$\Delta R_{BStd} = 100 \cdot \frac{m_{BStd}}{m_{STB}} \cdot \sqrt{\frac{\Delta N_{F\&W}^{\ 2}}{N_{STB}^{\ 2}} + (\frac{N_{F\&W}}{N_{STB}^{\ 2}})^2 \cdot \Delta N_{STB}^{\ 2}}$$

With:

R_{BStd}: Barium Standard Disc Recovery.

$N_{F\&W}$: Net Counts of Filtrate and Washings.

m_{BStd}: Tracer Mass added to Barium Standard Disc.

N_{STB}: Net counts in barium standard bottle.

m_{STB}: Tracer mass in barium Standard bottle.

and

$$N_{F\&W} = S_{F\&W} - S_{BLB}$$

and

$$\Delta N_{F\&W} = \sqrt{S_{F\&W} + S_{BLB}}$$

With:

$S_{F\&W}$: ^{133}Ba Filtrate and washings counts.

S_{BLB} : ^{133}Ba Blank Bottle counts.

Similarly:

$$N_{STB} = S_{STB} - S_{BLB}$$

$$\Delta N_{STB} = \sqrt{S_{STB} + S_{BLB}}$$

With:

S_{STB}: ^{133}Ba Standard bottle counts.

A3.3.1 Sample recovery calculations

Sample recovery is calculated using:

$$R_S = \frac{(S_C - b_C)/m_S}{(Std_C - b_C)/m_{BStd}} \cdot R_{BStd}$$

$$\Delta R_S = m_{BStd}/m_S \cdot \sqrt{\frac{(S_C - b_C)^2}{(Std_C - b_C)^2} \cdot \Delta R_{Std}{}^2 + R_{Std}{}^2 \cdot \frac{S_C + b_C}{(Std_C - b_C)^2} + R_{Std}{}^2 \cdot \frac{(S_C - b_C)^2}{(Std_C - b_C)^4} \cdot (Std_C + b_C)}$$

with:

S_C: ^{133}Ba sample Counts.

b_C : ^{133}Ba Background counts.

m_S: Tracer mass in sample.

Std_C: ^{133}Ba Barium standard disc counts.

R_S: Sample ^{133}Ba recovery.

m_{BStd}: Tracer Mass in Barium Standard Disc.

R_{BStd}: Barium Standard Disc Recovery.

A3.3.2 Radium standard recovery calculations

Ra standard recovery calculations are determined through the ^{133}Ba recovery on the disc, and this is calculated in the same manner as for a ^{133}Ba standard disc, with:

R_{RStd}: Radium Standard Disc Recovery

A3.4 Alpha spectrometer efficiencies

Efficiency spreadsheets are found at:

Alphaone\D:\Alphadata\Efficiencies\Efficiencies.xls.

Efficiencies and associated errors are calculated using:

$$\varepsilon_{corr} = \varepsilon / R_{RStd} \cdot 100$$

$$\Delta\varepsilon_{corr} = 100 \cdot \sqrt{(\frac{\Delta\varepsilon}{R_{RStd}})^2 + \varepsilon / R_{RStd}^{\ 2} \cdot \Delta R_{RStd}}$$

with:

ε_{corr}: Efficiency corrected for standard disc recovery

R_{RStd}: Radium Standard Disc Recovery.

Uncorrected efficiencies and associated uncertainty are calculated using:

$\varepsilon = N_{226}/A_{RStd}$

$\Delta\varepsilon = \Delta N_{226}/A_{RStd}$

with:

ε: Efficiency.

N_{226}: ^{226}Ra standard Net Count Rate [cps].

A_{RStd}: Expected activity on disc in [Bq].

The ^{226}Ra Net Count Rate (N_{226}) is calculated using calculations identical to those in Sills calculations worksheets for $N_{CB} > N_{CA}$, using the most recent blank filter count. The blank filter count can usually be neglected as it reflects less than 0.01 per cent of the total count rate, therefore in the standard operating procedure at ***eriss*** a blank count with 1 count in ROI A and C, 0 counts in ROI B, and a count time of 2ks is assumed; for detectors with high background contamination a blank filter should be counted with each count of the standard disc.

Appendix 4 ^{226}Ra detector calibrations

A4.1 Efficiency calibration

Efficiency calibrations are done by counting a Ra standard disc of known activity (Note: A fresh disc should be made with each new batch of ^{133}Ba tracer solution prepared, see A1.5 'Making a ^{226}Ra standard disc', for details of Ra standard disc preparation).

Discs should be prepared with an activity of 20–25Bq to give ~10000 counts in the ^{226}Ra region of interest over a 3ks count.

$BaSO_4$ method Radium and Barium standards are found in the top drawer of the wooden filing cabinet in the count room eg ^{226}Ra – SZ025.

Standards cards are in the QC section of the card box in the counting office.

After counting the standard disc for 3 ks, the sprectrum is saved (refer to Appendix 2.2), and a Region Of Interest (ROI) file needs to be set.

In the spectrum 4 peaks can be seen from left to right, in order: ^{226}Ra, ^{222}Rn ^{218}Po and ^{14}Po (figure A4.1).

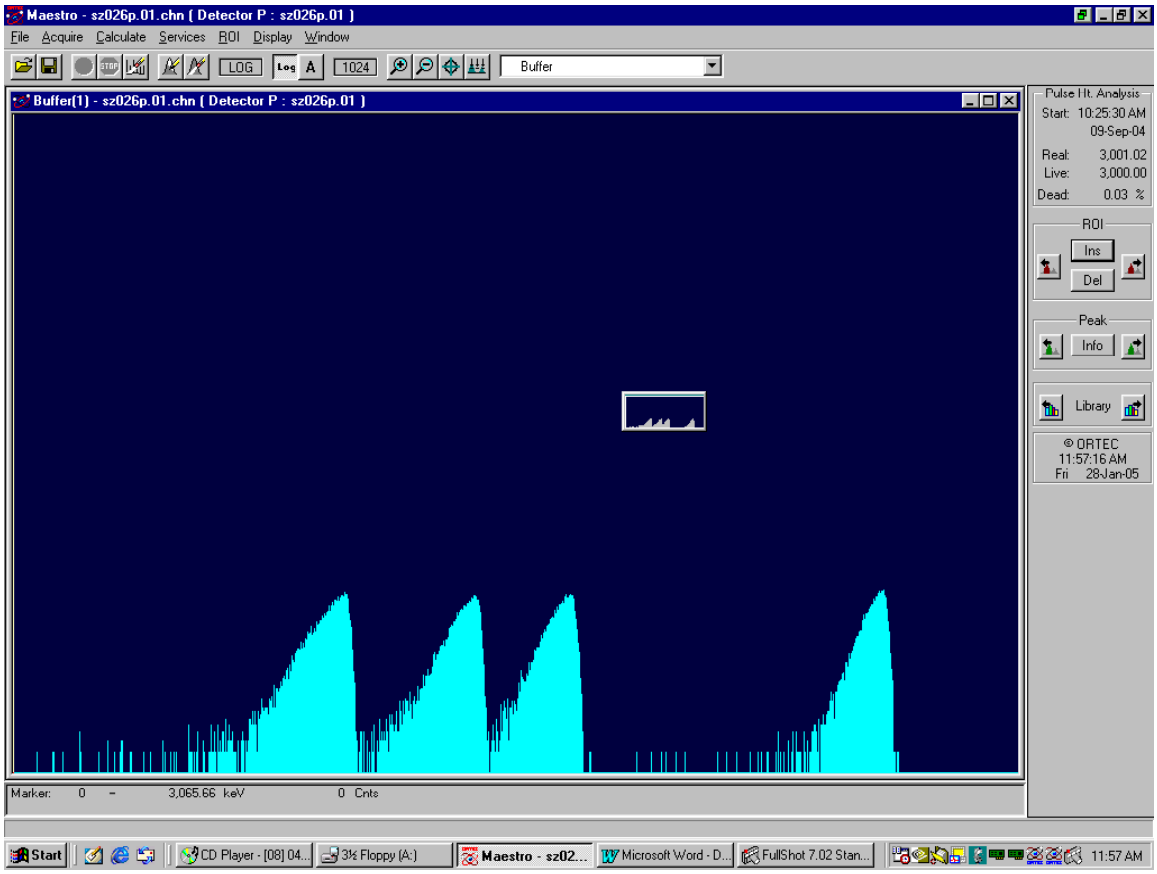


Figure A4.1 Standard disc spectrum view in MAESTRO V6

Expand and adjust view (in Log scale), to highlight the second peak from the left. Place the marker where the peak begins on the right side (SZ026p.01 starts at channel 481). Select ROI then Mark ROI from the drop down list. Using the left arrow, key highlight the peak beginning from the marker position to a point 2 channels from where the next peak begins (figure A4.2).

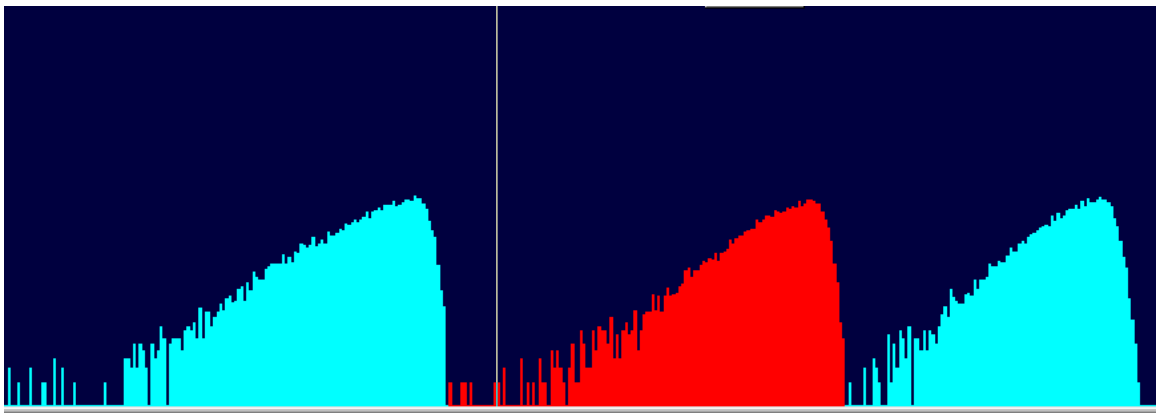


Figure A4.2 Marking ROI C

Note the number of channels in this 'region of interest' (ROI C). The next 2 ROIs for this detector will be set at exactly the same length as ROI C.

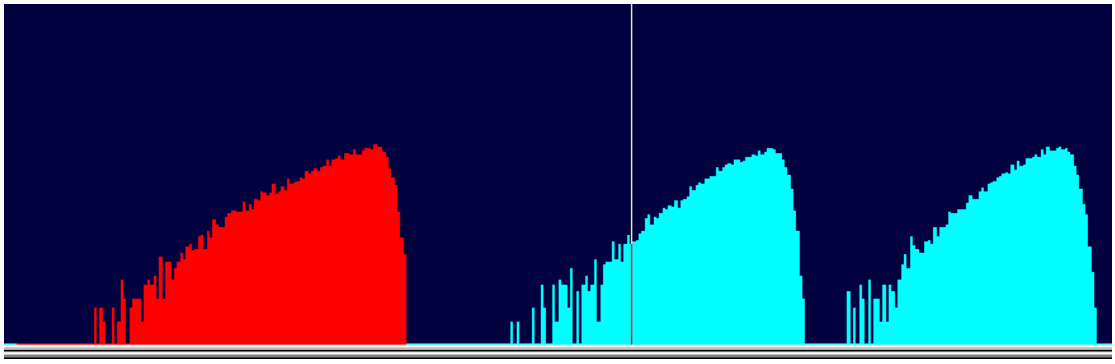


Figure A4.3 Marking ROI B

Select ROI, then Off from the dropdown list, move the marker one channel to the left, then select ROI, Mark ROI. Again, using the left arrow key, highlight the next peak (^{226}Ra), ensuring this ROI (ROI B) occupies the same number of channels as ROI C.

Repeat the above process to highlight a 3rd ROI (ROI A) of the same size to the left of ROI B, This 3rd peak does not correspond to any specific radionuclide, but is used as a means of calculating peak tailing from ^{226}Ra (in the final calculations this is extrapolated to remove the effect of peak tailing from the ^{222}Rn peak into the ^{226}Ra peak).

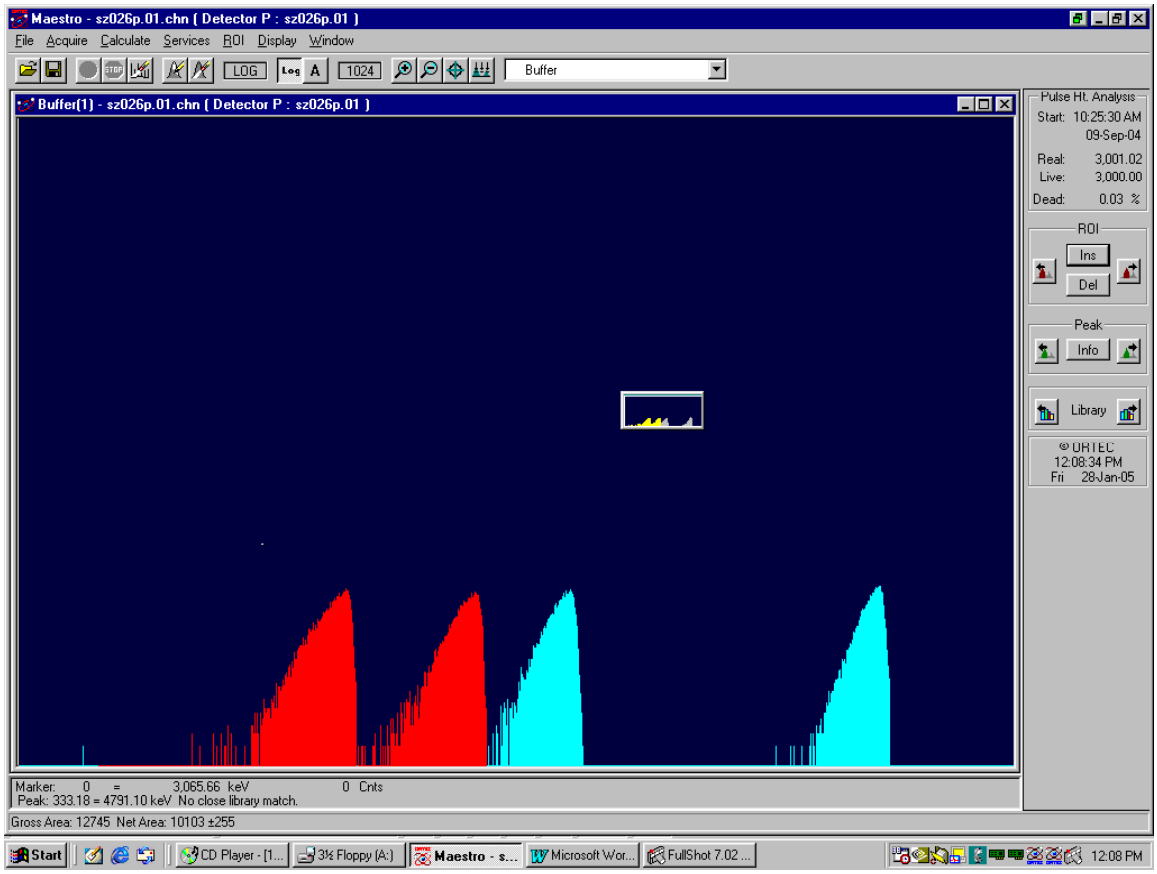


Figure A4.4 A complete set of ROIs for ^{226}Ra analysis

Go to:

D:\Alphadata\Detectors\Efficiencies.xls\Ra Detector Effy Jan2005-ongoing.

Cut the old efficiency calculation and paste in:

D:\Alphadata\Detectors\Efficiencies.xls\Old Ra Detector Effy Jan2005-ongoing.

Fill in the details of the tracers, count time etc, and calculate the new efficiency. To check the chemical efficiency for the Ra standard see Ba-133.xls spreadsheet:

- D:\Alpha21\Results\SillsCalculations\Ba133\Ba-133.xls

Note that the sample spectrum given here has quite good resolution, not all detectors will have as clear cut peaks as the above spectrum (see figure A4.5). In these cases it may be easier to view the sprectrum in normal scale, then to zoom in around the area where the ^{222}Rn peak begins to rise. There will be a point at which the counts per channel increases sharply in the peak, 2–3 channels to the right of this point is usually the most ideal point at which to start setting ROIs for detectors with poor resolution.

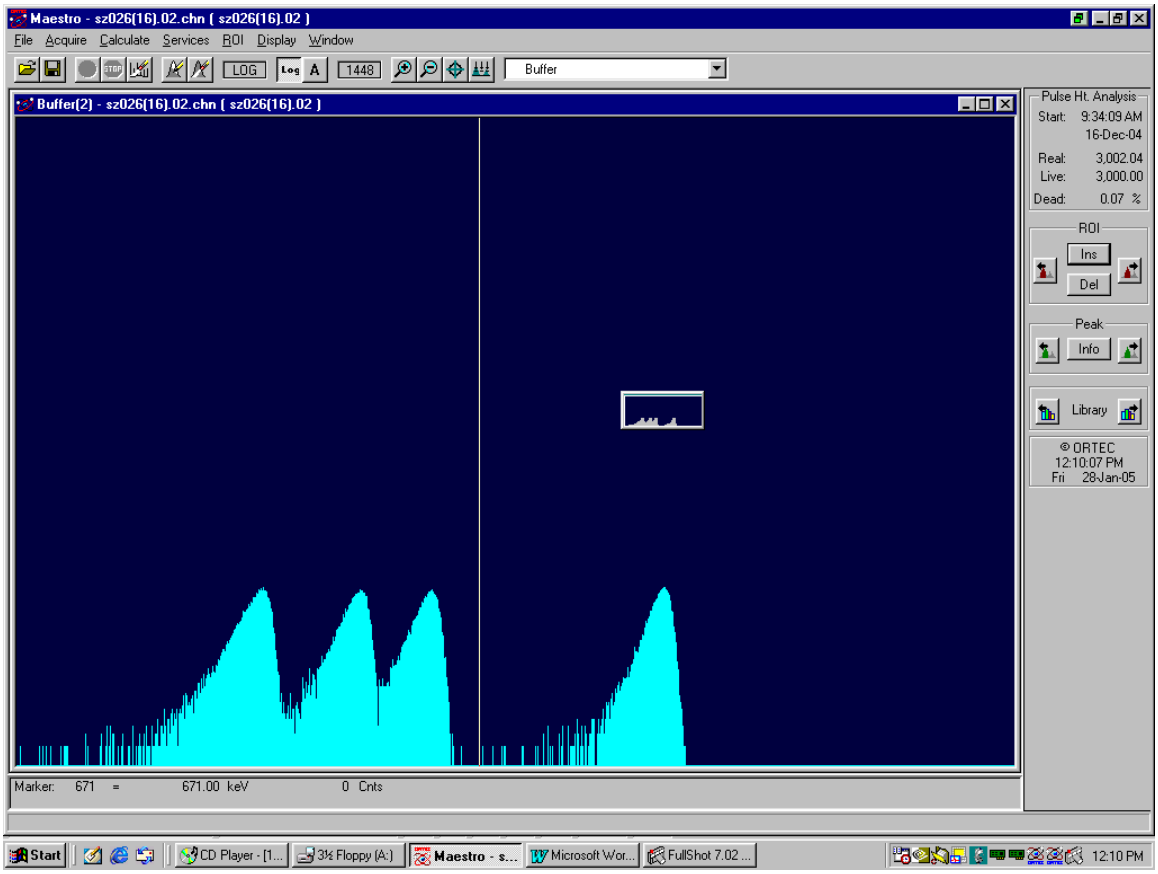


Figure A4.5 Spectrum with poor resolution of peaks

A4.2 Energy calibration

After setting the new ROI, clear the ROI from the detector/buffer window to proceed with energy calibration (energy cannot be calibrated with active ROIs).

Select Calculate then Calibration to bring up the calibration dialog box. Select destroy calibration to prevent old calibrations from interfering with the new energy calibration.

Place the marker in the channel with the highest counts (this should be 5-6 channels to the left of the rightmost channel of the ROI) in ROI B. Select Calculate, then Calibration again, type 4784 for this channel then press enter. Place the marker in the channel with the highest counts in the ^{214}Po peak (the peak furthest to the right of the screen). Select ‘Calculate’ then

Calibration again, type 7687 for this channel then press enter, a dialog box will appear asking for the units, type keV then press enter.

The energy calibration is now complete. To check that the calibration is accurate, the highest counts in the ^{222}Rn (ROI C) and ^{218}Po (1st peak to the right of ROI C) channel should be roughly equal to 5490 keV and 6002 keV respectively.

A4.3 ^{226}Ra chamber backgrounds

Chamber backgrounds are counted in each detector once in every 2 month period, starting with Jan–Feb. Chamber backgrounds are counted using a blank filter paper in the source holder to replicate conditions under which sources are being counted. Chamber backgrounds are counted for 604.8 ks (exactly one week).

Details of preparing the source card and labelling of the filters is detailed in Appendix 2.1; Appendices 2.2 and 3.1 detail protocols for saving and recording chamber background data.

A4.4 Reporting of ^{226}Ra results

When a batch of samples has completed counting and is ready for reporting:

Transfer the worksheet (see Appendix 3.2 for details on naming of Sillscalculations worksheets) from the Alphaone computer:

D:\Alpha21\Alphadata\Sillscalculations\InProgress\Sillscalculations<year>.xls

to:

D:\Alpha21\Alphadata\Sillscalculations\Reported\<year>.xls

Adjust the data to 3 significant figures, then protect the datasheet using Tools\Protect Sheet. The password used is the name of the worksheet.

Copy the worksheet to a floppy disc to transfer onto the network.

Check out the files:

ENRADAdministration\Analysis_and_Sample_register\Database_results\Universal_2000 a.mdb

and :

ENRAD Administration\Analysis_and_Sample_register\Database_results\importSills.xls

from SSD explorer.

Open a new worksheet in importSills.xls, name this worksheet the same as the worksheet being transferred. Cut and paste the appropriate columns from a previous worksheet in importSills.xls to the worksheet being transferred, the columns to use and the order in which they must be in importsills.xls to be transferred to the appropriate columns in the Universal200a.mdb database are listed below.

For water samples:

		error (filtrate)	Ra226 (mBq/l) residue	error (residue)	Ra226 (mBq/L) Total		Ra226 (mBq/L) Unfiltered	error (Unfiltered)

For soil/sediment/biota samples:

Eriss ID	Ra226 (Bq/kg)	error

For High Volume Air (HVAS) Samples :

	Ra226 Digest mBq/L	err

Cut and paste the column Eriss ID, and those columns containing the Ra226 results/error required into the new worksheet created in importSills.xls, from the SillsCalculations worksheet on the floppy disk.

Cut and and paste the column Eriss ID, and those columns containing the Ra226 results/error required from the new worksheet created in importSills.xls, to the Universal_2000a.mdb database using the 'Paste Append' command from the Edit drop down menu.

Using Tools\Protect Sheet, protect the worksheet in importSills, again using the name of the worksheet as the password. Check importSills.xls back in to SSD Explorer.

Update the Report table in the Universal2000a.mdb database, by entering the report number, location in SSD Explorer and work order ID. The Report date is the date the report is sent, this must be updated upon sending of reports. When all work for a work order is complete, update the Finish date column for that work order in the Order table to reflect the date the last report was sent.

Use the [Sills result_xxx] queries to retrieve the data from the database (for example, Sills result_H2O, or Sills result_HVAS). Copy those records to be reported (take care not to report previously reported results from the same work order) then paste into the report (see below for creating a report). Adjust the data to reflect the 1 mBq/L reporting limit for ^{226}Ra by the $BaSO_4$ method for commercial reports.

To create a report from Microsoft Word, select the File drop down menu, then New. In the 'General' document list choose ERA_Report1, then enter details as prompted. If the report is for a different client, be sure to change the Address, File Ref. and the details of the receiving officer(s). Ensure all information given regarding methodology and validation. is correct for the sample analyses being reported.

Reports are saved in SSD Explorer in

'ENRAD Administration\Commercial\Clients', there are sub-folders for different clients, and further sub-folders for reports (grouped by year).

Save internal reports in

'ENRADAdministration\Radioanalytical analysis for eriss projects' (there are sub-folders for various projects).

Appendix 5 Laboratory and Count room Form

Ra-226 ($BaSO_4$ method) worksheet

$BaSO_4$ ppt date: **Ba-133 standard disk ID:** **Ba-133 standard disk count date:**

Project details: **Ba-133 standard tracer mass:** **Ba-133 standard disk counts**

Analyst(s): **Ba-133 count time:**

WorkOrder	SampleID	Volume (ml)	Ba-133 (ml)	Countsource code	Detector	Ba-133 counts	Ra-226 count time (ks)	ROI A counts	ROI B counts	ROI C counts	ROI File used	Comments

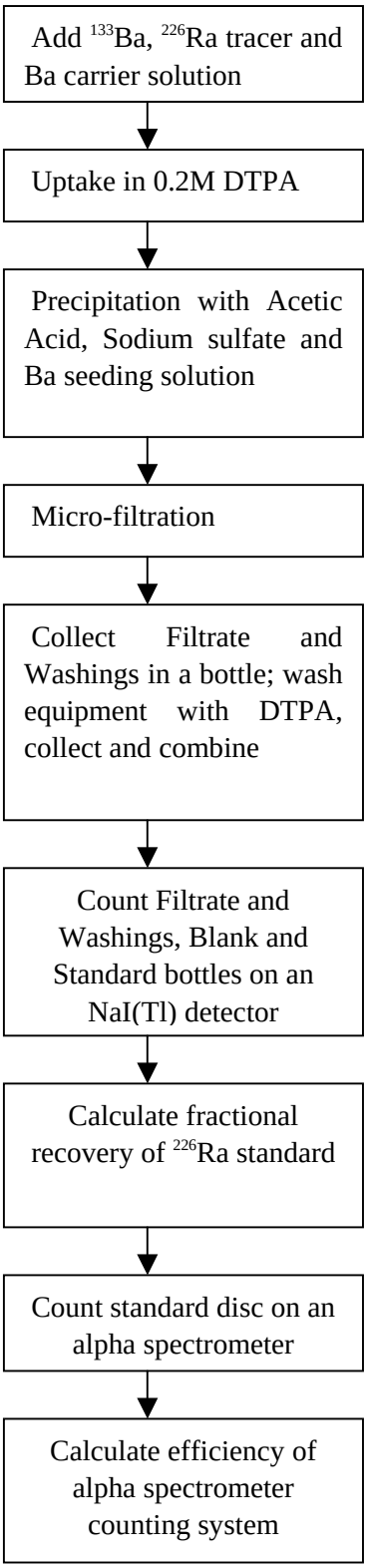
Comments:

WorkOrder	SampleID	Volume (ml)	Ba-133 (ml)	Countsource code	Detector	Ba-133 counts	Ra-226 count time (ks)	ROI A counts	ROI B counts	ROI C counts	ROI File used	Comments

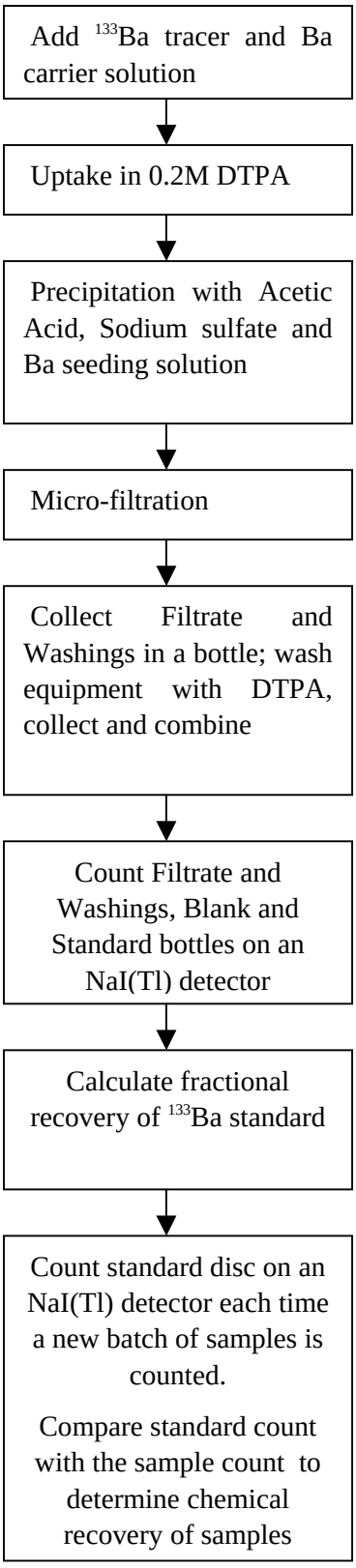
Comments:

Appendix 6 Method Flowcharts

Alpha Efficiency calculation



Chemical recovery calculation



Sample treatment