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Pb-210 determination
using liquid scintillation
counting (LSC)

Peter Medley

November 2016

Release status – unrestricted

The Department acknowledges the traditional owners of country throughout Australia and their continuing connection to land, sea and community. We pay our respects to them and their cultures and to their elders both past and present.

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Executive summary

Lead-210 (^{210}Pb) is a beta particle emitting radionuclide in the uranium decay series and has therefore been an important part of the monitoring and research program of the environmental radioactivity group of *eriss*. The *eriss* radioanalytical laboratories have routinely used gamma and alpha spectrometric methods for ^{210}Pb determination, though current techniques have some limitations. For gamma spectrometry, analysis can be performed immediately after sample preparation, but, the detection limits are quite high, thus this technique cannot be used for determination of radionuclide activity in environmental samples with low activity concentrations. In contrast, detection limits are very low for alpha spectrometric measurement but ^{210}Pb must be determined via its direct daughter polonium-210, requiring complex separation chemistry and long ingrowth periods in order to achieve the low detection limits.

Liquid scintillation counting (LSC) provides an alternative technique for ^{210}Pb determination that allows measurement via the beta decay. Although LSC methods have some limitations, the detection limits approach those of alpha spectrometry and are approximately two orders of magnitude lower than gamma spectrometry. When compared to the alpha spectrometric method for ^{210}Pb determination, LSC can significantly reduce the time taken for separation chemistry and therefore lead to faster analysis.

This report provides a detailed description of a radiochemical separation and radiation measurement technique developed in the *eriss* radioanalytical laboratories for the determination of ^{210}Pb via LSC. Detection limits, uncertainty estimation and the applicability of the method to various sample matrices are presented and discussed.

1. Introduction

Lead-210 (^{210}Pb) is part of the uranium decay series. With a relatively short half-life of 22.2 years (LNHB, 2013), sources of ^{210}Pb in the environment are essentially the radioactive decay of Radon-222 (^{222}Rn) and Radium-226 (^{226}Ra) in various environmental media. Lead-210 is a beta-emitting radionuclide, with beta emission energies of 17.0 and 63.5 keV, and a low energy gamma emission at 46.5 keV (LNHB, 2013). The direct daughter, bismuth-210 (^{210}Bi) is also a beta emitter (maximum beta energy of 1162 keV), and grows in quickly after separation of ^{210}Pb due to its short half-life of only 5 days (LNHB, 2013). For details of ^{210}Pb and significant decay products of ^{210}Pb and their properties see table 1.

Table 1 Nuclear properties of ^{210}Pb and significant decay products

Isotope	Daughter isotope	Half-life	Decay type	Emission probability	Decay energy
^{210}Pb	^{210}Bi	22.23 years	Beta	80.2% 19.8%	17.0 keV 63.5 keV)
^{210}Bi	^{210}Po	5.012 days	Beta	100%	1162.1 keV
^{210}Po	^{206}Pb (Stable)	138.4 days	Alpha	99.99% 0.001%	5.304 MeV 4.517 MeV

There are numerous measurement techniques for ^{210}Pb . The most commonly used methods include Gas Flow Proportional (GFP) counting (eg – Benedik & Vrecek, 2001), gamma spectrometry (eg – Marten, 1992), alpha spectrometry (eg – Martin and Hancock, 2004; García-Orellana and García-León, 2002), and liquid scintillation counting (LSC), (eg – Biggin et al., 2002; Kim et al., 2001). Gamma and alpha spectrometric methods for ^{210}Pb determination are routinely used in the radioanalytical laboratory of *eriss* in Darwin. Recent advances in inductively coupled plasma mass spectrometric (ICP-MS) techniques are allowing non-radiometric techniques to be used for ^{210}Pb analysis despite its relatively short half-life (eg – Amr et al 2010, Lariviere et al 2006).

There are limitations to many of the current methods used for analysis of ^{210}Pb . For gamma spectrometry, analysis can be performed immediately after sample preparation, but, due to the low energy gamma emission and low number of gamma emissions per nuclear transformation (0.0405), the detection limits are quite high at around 4 Bq kg⁻¹ or higher (Marten, 1992), preventing the use of this technique for many low level environmental samples. In contrast, detection limits are very low for alpha spectrometric measurement (2 mBq L⁻¹), but ^{210}Pb must be determined via its direct daughter polonium-210 (^{210}Po). This requires complex separation chemistry and long ingrowth periods in order to achieve the low detection limits (eg – Martin and Hancock, 2004; García-Orellana and García-León, 2002). Complex separation chemistry is also required for GFP analysis, but detection limits are comparatively higher (eg – Benedik & Vrecek, 2001) and attenuation from the source can also be a problem (Packard Instrument Company, 1992). Figure 1 shows the relative degree of ingrowth of ^{210}Pb daughters, highlighting the necessary delays in measurement using the daughter products.

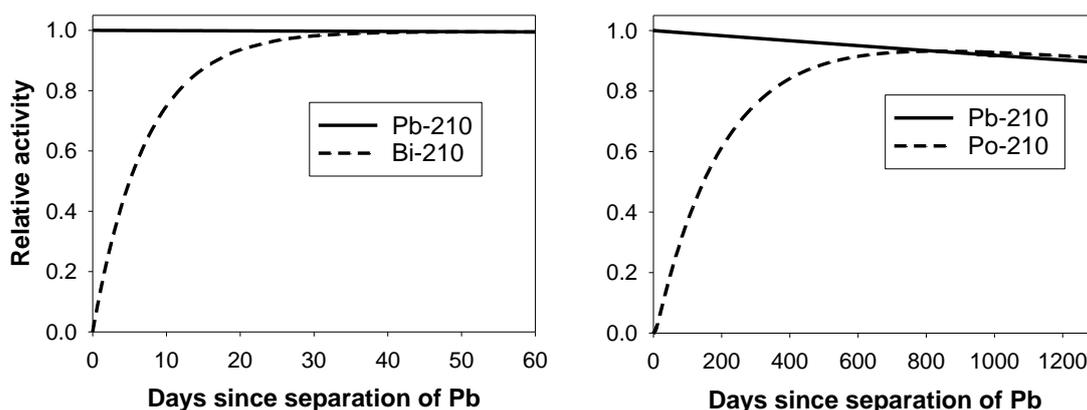


Figure 1 Ingrowth curves for ^{210}Bi and ^{210}Po after initial separation from ^{210}Pb

LSC for ^{210}Pb has some limitations, as it also requires complex separation chemistry (particularly for biota samples due to the effects of chemical and colour quenching, discussed below). The detection limits however, are approaching those of alpha spectrometry partly due to the ability to effectively double the counting efficiency by including the beta decay of ^{210}Bi in the measurement. Although detection limits using LSC are usually several times higher than alpha spectrometry (eg – Blanco et al, 2004, Jia et al, 2000, Kim et al, 2001 and Garcia-Orellana and Garcia-Leon, 2002), LSC overcomes several of the disadvantages of other techniques, allowing relatively rapid measurement with detection limits two orders of magnitude lower than gamma spectrometry (active shielding, such as a bismuth germanate (BGO) guard can improve detection limits in LSC even further (L'Annunziata, 2012)).

Determination of the chemical recovery from ^{210}Pb separation is necessary and a stable Pb tracer is most commonly used for this, though some techniques use a radioisotope tracer such as lead-212 (^{212}Pb ; eg Biggin et al., 2002).

In the environmental radioactivity laboratory the use of LSC is attractive, primarily because, when compared to the current methods using either alpha spectrometry (Martin and Hancock, 2004) or gamma spectrometry (Marten, 1992) it has the ability to dramatically reduce separation chemistry and turnaround times as well as improve detection limits.

When conceptualising the development of a method for the analysis of ^{210}Pb in the *eriss* radioanalytical laboratory it was considered whether to use an established method published elsewhere, or to develop a method in-house. The use of an 'off-the-shelf' published method has distinct advantages:

- there is a peer-reviewed process supporting the methodology
- often multiple users have employed the method and many issues that may arise with new methods have been resolved
- calibrations and calculations (should) have been thoroughly checked before publication.

These factors contribute to a significant potential to save time in implementation of a new method in the laboratory. However, there are also distinct disadvantages in using a published method:

- the method may not be capable of attaining appropriate performance characteristics using the LSC model that we have available for use;

- often, all of the calibration parameters, performance characteristics and some measurement parameters required to implement the method are not reported (which makes an assessment of suitability very difficult).

In contrast, methods developed in-house can be tailored to specific needs, which can be advantageous in situations with unusual or unique analytical requirements, and you can optimise it for best performance to suit your needs. Nonetheless, the preparation for development and implementation of a new method should include an evaluation of the suitability of already published methods due to the considerable potential to save time.

The performance characteristics of a new method introduced to the laboratory is the most important consideration in choosing the method to use – if performance measures such as precision, accuracy or achievable detection limits of a method are not suitable then there is no use implementing it. The types of samples that need to be analysed are also an important consideration as sample characteristics can have a major impact on the effectiveness of a method.

It is also of major benefit to evaluate potential methods for compatibility with methods already used in the laboratory – this can lead to significant savings, eg in the management of chemical inventories.

The performance characteristics we needed were:

- a minimum detection limit of 4 mBq
- reduced turnaround times (compared to alpha spectrometry) – although 3–4 months is still acceptable
- stable performance for different samples (and ‘difficult’ sample matrices)
- the ability to store samples for longer periods after collection prior to analysis (2–3 months).

It was also desirable to achieve a high level of compatibility (ie – with equipment, chemicals and separation techniques) with current methods used in the environmental radioactivity laboratories.

There are many published methods for the analysis of ^{210}Pb . In these methods there are 2 main ways for the determination of chemical recovery – using stable Pb, or milking ^{212}Pb from a solution of the parent isotope (or isotopes – thorium-228, radium-228 or thorium-232). Lead-212 has a half-life of 10.6 h, and we measure all parent isotopes at low levels in the environmental radioactivity laboratory. Thus, the high activity of the ^{212}Pb parent solution required makes this a very undesirable option for a low-level laboratory.

There are many methods for chemical separation of Pb, however, our current separation technique is very effective and meets our required performance characteristics. This method could be adapted for ^{210}Pb measurement with LSC.

LSC involves mixing a sample with a scintillation cocktail. The cocktail consists of organic solvents and fluors. When a radioactive particle strikes the fluor a burst of light is emitted and this is measured via a photo-multiplier tube. There are several major publications that provide an in-depth discussion of the principles and practice of LSC (eg L’Annunziata, 2012)

To optimise a LSC technique for best performance a number of parameters can be adjusted. The primary parameters are:

- the volume of sample and cocktail (that is the sample cocktail ratio)

- the selection of cocktail for the isotope to be measured, desired chemical stability and possible detection limits
- The count conditions – eg count time.

It is this optimisation where the difficulties in adopting published methods begin. Whereas chemical separation methods are usually quite detailed and reproducible, many of the count conditions on the LSC are omitted in publications. Only specific details each author believes are the most important are published. Parameters that are not often reported include:

- chemical stability of cocktails with sample solutions
- variability of quench in samples
- optimisation of counting windows.

Two more parameters that can be varied on some instruments are not often reported, these are:

- delay before burst timing
- anti-coincidence timing.

Although these final 2 settings can't be adjusted on many instruments, the default settings are unknown to those not using those instruments. These settings will be discussed in more depth later.

Given the suitability of our current Pb separation technique and the lack of published methods suitable for low-level counting that are compatible with our liquid scintillation counter, the development of a new method was considered the most effective option for achieving the performance characteristics required in the EnRad radioanalytical laboratory.

2. Liquid scintillation counting (LSC)

2.1 General

LSC is based on properties of some organic compounds enabling them to convert energy absorbed from nuclear radiation into photons of light. These photons, in turn, are then converted to a burst of electrons using a photomultiplier tube (PMT) which can be measured as an electric pulse (L'Annunziata, 2012). Organic compounds that emit photons, or 'fluoresce', when bombarded by nuclear radiation are called 'fluors'. The basic practice of LSC involves mixing a sample with a scintillation cocktail (comprising one or more fluors dissolved in a suitable solvent) and measuring the fluorescent light emissions. Although early LSC instruments were not suitable for low-level radioanalysis, due to excessively high backgrounds, advances in organic scintillants, low-background vials and microcomputing have allowed LSC to progress into low-level analysis (L'Annunziata, 2012).

2.2 The TriCarb 3100TR

The TriCarb 3100TR is a modern LSC instrument from PerkinElmer, with several components and functions designed to enable low-level analysis of radioactivity. The most important of these are:

- the use of two PMTs, enabling coincidence counting to reduce background events
- a minimum thickness of 2 inches of lead as passive shielding surrounding the sample counting chamber

- time-resolved liquid scintillation counting using advanced pulse shape analysis to discriminate between true radioactive decay events and background pulses.

These properties make this instrument suitable, therefore, for low-level analysis of environmental radioactivity.

2.3 Selection of scintillation cocktail, vials and count conditions,

Pre-selection of some conditions prior to experimentation was undertaken based on our knowledge of the radiochemical procedure and the properties of reagents and equipment such as the scintillation cocktail and counting vials.

The starting point for our method was directly after separation of Pb via anion exchange with a final solution of 25 mL of 9 M HCl. The difference in blank count rates between glass and plastic vials has been widely reported and shows that plastic vials generally have a lower blank count rate than glass (L'Annunziata, 2012). Routinely used 20 mL plastic (HDPE) LSC vials are suitably compatible with 9 M HCl to enable evaporation of the final solution in them, so these vials were selected for this method.

As the scintillation cocktail Ultima Gold AB (UGAB) is already used in the environmental radioactivity laboratory for gross α/β analysis, this was the preferred cocktail for this method to reduce administration of chemicals and limit the generation of different types of organic waste. The environmental radioactivity laboratory typically only runs a low number of samples per year and the long-term stability of UGAB demonstrated by Feng et al (2012) was a factor in deciding to use this cocktail (although at present the throughput of samples for gross α/β counting is not high enough to use a full bottle before reaching the expiry date). Based on data available for the UGAB cocktail it should be able to reach the required detection limits.

The PbCl_2 remaining after evaporation of the 25 mL 9 M HCl has low solubility in water (4.5 g L^{-1} at 20°C) so a dilute acid or base solution is required to ensure complete dissolution prior to mixing with a scintillation cocktail. Ultima Gold cocktails have low phase stability in alkali (ie NaOH), but are generally phase stable in acid solutions (PerkinElmer, 2002). HCl has a lower blank count rate than HNO_3 due to sample quenching effects and is less reactive than H_2SO_4 (L'Annunziata, 2012), therefore HCl was selected as the aqueous component of the scintillation cocktail.

2.4 CPM counting vs Alpha/beta discrimination

Many methods for ^{210}Pb analysis via LSC rely on the discrimination of alpha and beta pulses to separate beta counts from ^{210}Pb and ^{210}Bi from alpha counts from ^{210}Po (see L'Annunziata (2012) for a complete description of how α/β discrimination functions operate). In some cases this is to allow analysis of multiple isotopes (eg simultaneous determination of ^{226}Ra and ^{210}Pb by Kim et al (2001)), in others simply to remove interference from ^{210}Po ingrowth in the sample (eg Blanco et al (2004)). In the method developed here, however, to maximise the number of counts registered for each sample and therefore achieve lower detection limits, the direct CPM (counts per minute) mode was used with no α/β discrimination. This also has the advantage that the uncertainty associated with spill-over events is eliminated, reducing the overall uncertainty in the sample and blank signals and therefore reducing the limits of detection and quantification as defined by Currie (1968).

2.5 Time-resolved LSC: delay before burst (DBB) and coincidence time

A typical beta scintillation event is composed of at least two components as a function of time – a fast and slow component.. The length and duration of afterpulse(s) following the fast component can differentiate true beta scintillation events from non-quenchable blank

pulses – which tend to have a longer slow component. The TriCarb 3100TR has time-resolved pulse shape analysis software that provides the ability to analyse these pulses and adjust the timing for accepting and rejecting them (Figure 2).

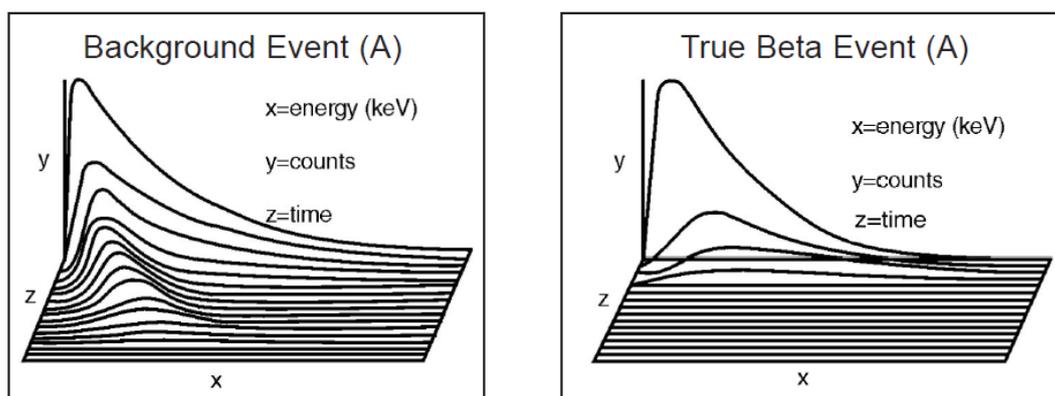


Figure 2 Three Dimensional plots of pulse height spectra for a background and true beta event, respectively (from Passo J R 2015).

Adjusting the delay before burst (DBB) setting changes the time delay before afterpulses are counted, this allows discrimination of true beta events from blank pulses. Afterpulses, which occur after the fast pulse and the specified delay time interval, indicate that a scintillation event is due to background. The actual length of the afterpulses from true beta events will vary depending on the cocktail used and the energy of the beta emissions. Some scintillants, such as the Packard Ultima Gold produce afterpulses that make a beta event appear similar to a typical background event (Passo and Cook, 1996).

The use of two PMTs in the TriCarb 3100TR allows coincidence counting to take place which reduces the background from radiation external to the source. The coincidence timing on the TriCarb 3100TR can be adjusted from 10–100 ns. The Coincidence timing function rejects pulses that are received from the scintillation counter's two photomultiplier tubes outside a specified timeframe – decreasing this time will increase the number of events rejected, reducing both the efficiency and the blank count rate. Sensitivity of a measurement technique can be measured using the figure of merit (L'Annunziata, 2012) which is the square of the efficiency divided by the blank counts (E^2/B), as such parameters that influence the background and/or efficiency can influence the optimised count conditions.

2.6 Counting windows

Selecting an optimum counting window is a challenge due to the ingrowth of ^{210}Bi and ^{210}Po into the sample after initial Pb separation. If only using a ^{210}Pb window, measurements can be taken directly after separation of lead, though after time some counts from ^{210}Bi will contribute to the ^{210}Pb counting window. If including ^{210}Bi then either time must be taken to allow for ingrowth of ^{210}Bi , or calibration must be performed to calculate the relative contribution from ^{210}Bi in the ^{210}Pb window over time. ^{210}Bi reaches equilibrium within 53 days, which is suitable for our purposes and provides significantly increased sensitivity. Use of a window including ^{210}Po can further be used in CPM count mode as there is no discrimination between alpha and beta particles, though long ingrowth times are required due to the longer half-life of ^{210}Po .

The figure of merit was used to select appropriate windows based on the relative stage of ingrowth for ^{210}Bi and ^{210}Po .

2.7 Quench and tSIE

Quench correction can often be a critically important factor in accurate LSC measurements. However, with the preparation of a highly consistent matrix for all samples, this is not always necessary. To measure quench in the samples and standards we use the quench indicating parameter tSIE – the transformed spectral index of the internal standard. This is measured by the instrument through the use of a high activity internal ^{133}Ba standard. In our samples, there is very low variability in tSIE and insignificant variation in the efficiency for potential values of tSIE over an extended range of possible values. Thus, quench correction was not an important consideration for this method.

3. Methods

3.1 Cocktail optimisation

Solutions of 1 mL and 2 mL of HCl at concentrations of 1 M and 2 M HCl with levels ranging from 2–20 mL of Ultima Gold AB (UGAB) were tested to check for completeness of dissolution and to optimise the solution to scintillant ratio in the cocktail. The activity added to each standard was 16.3 Bq of a ^{210}Pb solution in equilibrium with the ^{210}Bi and ^{210}Po decay products.

3.2 Optimisation of count parameters

3.2.1 Delay before burst and anti-coincidence timing

A series of 6 standards were prepared from a ^{210}Pb standard solution in equilibrium with daughter isotopes ^{210}Bi and ^{210}Po . The standards were prepared with an analytical blank using an optimised scintillation cocktail mix of 2 mL 1 M HCl with 10 mL UGAB. The total activity of ^{210}Pb added to each standard ranged from 292–294 Bq. All standards were counted for 1 min and the analytical blanks were counted for 100 min across a range of anti-coincidence timing settings from 10–100 ns while also varying the DBB timing from 75–800 ns. Counting of these standards and the analytical blank took place over a period of 51 days after initial preparation.

3.2.2 Efficiency calibration and cocktail stability

A series of standards were counted in CPM mode over a period of >300 days to give a relative efficiency calibration that takes into account the amount of both ^{210}Bi and ^{210}Po that have ingrown in the sample to allow both rapid measurement directly after separation of ^{210}Pb and later measurement for maximum ingrowth of ^{210}Bi and ^{210}Po leading to lower detection limits. The relative efficiency was calculated as a function of the activity of ^{210}Pb in the sample (equations 1 and 2). Relative efficiencies of greater than 100% were achieved as all counts from the isotopes ^{210}Bi and ^{210}Po were summed with the counts from ^{210}Pb for a given count window.

Equation 1

$$\epsilon_{Relative} = \frac{N_{CR}}{A_{Pb-210}}$$

Where:

$\epsilon_{Relative}$ = The relative efficiency in a given count window

N_{CR} = The net count rate in a given count window (counts s⁻¹)

A_{Pb-210} = The activity of ^{210}Pb in the sample or standard

$$N_{CR} = \frac{G_C - B_C}{t}$$

Where:

N_{CR} = The net count rate in a given count window (counts s⁻¹)

G_C = The gross counts in a given count window

B_C = The background counts in a given count window

t = The count time (s)

These standards were prepared from a stock solution of ²¹⁰Pb that had been chemically purified so that ²¹⁰Bi and ²¹⁰Po had been removed. Standards were prepared fresh at suitable intervals to give a representative estimation of the relative efficiency of counting with ingrowth of ²¹⁰Bi and ²¹⁰Po. A number of these prepared standards were re-counted over a period of >300 days to assess the stability of the cocktail mixture. Efficiency calibrations were calculated for freshly prepared and aged cocktail solutions.

3.2.3 Selection of counting windows

Data from the standards used for relative efficiency calibration was used to calculate optimum count windows for 3 selected counting phases. These phases related to the relative stage of ingrowth of daughters ²¹⁰Bi and ²¹⁰Po. Optimisation using the figure of merit was performed by an iterative process on a selected number of channel ranges corresponding to windows for ²¹⁰Pb only, ²¹⁰Bi and ²¹⁰Pb and a final window count primarily for ²¹⁰Po (with some counts from ²¹⁰Bi).

3.2.4 Method comparison

As a quality control check on the accuracy of the method a comparison of results with a gamma spectrometric method using a set of freshwater mussels samples was done. The freshwater mussels were collected from Mudginberri and Sandy Billabongs in the Northern Territory, Australia. The sample preparation technique used an epoxy resin to cast 2–5 g of dried mussel tissue into 42 mm diameter discs (Marten, 1992). Activity concentrations of ²¹⁰Pb were determined using a HPGe gamma spectrometer and an in-house analysis program, VisualGamma (methods are described in Esparon and Pfitzner, 2010). Approximately 0.2–1 g of dried mussel tissue was used for the ²¹⁰Pb analysis via LSC using the method described in this study.

4. Results

4.1 Transformed spectral index of the internal standard (tSIE)

Solutions of 1 mL and 2 mL of HCL at concentrations of 1 M and 2 M HCl were tested and the tSIE determined (using the internal ¹³³Ba source) with levels of UGAB ranging from 2–20 mL. There were no differences in blank levels and relative efficiency between the 1 M and 2 M HCl solutions. However, 1 mL of 1 M HCl was insufficient to ensure complete dissolution of the sample..

Figure 3 shows the results from variations of UGAB volume with 2 mL of 1 M HCl. The quench parameter (tSIE) sharply falls at UGAB volumes below 10 mL.

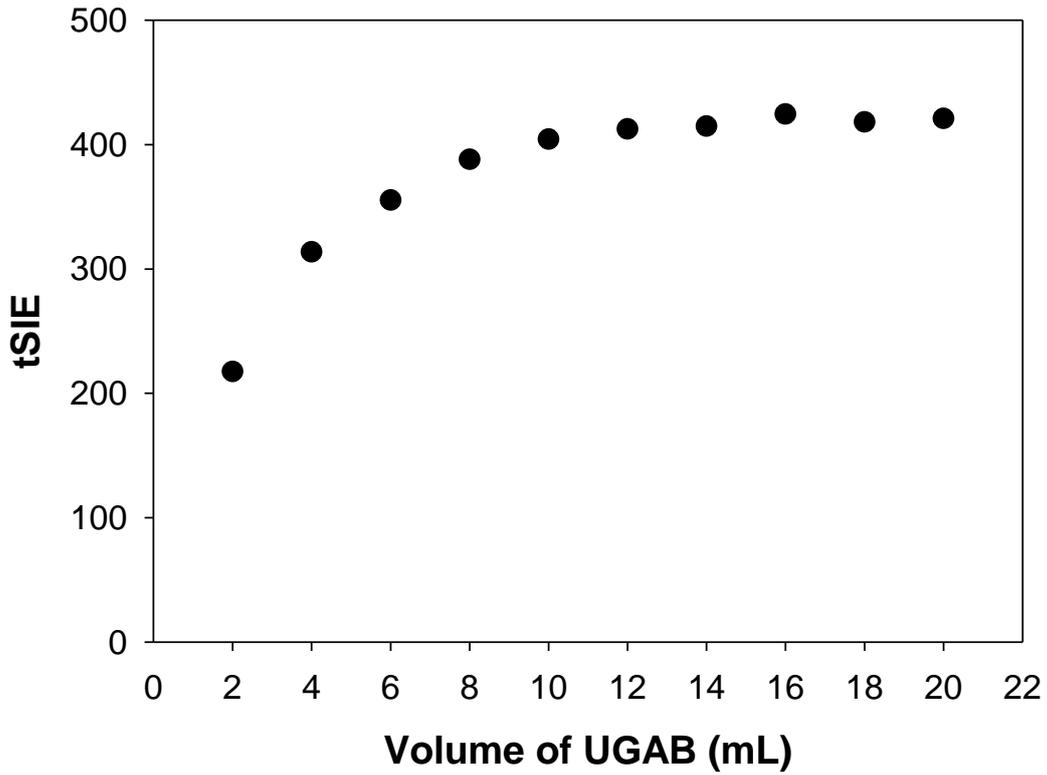


Figure 3 Quench indicating parameter tSIE variation relative to the volume of UGAB scintillant mixed with 2 mL of 1 M HCl

4.2 Optimising E²/B for varying volumes of UGAB

Figures 4 and 5 (next page) show the relationships between relative efficiency and the blank count rate, and the volume of UGAB in the scintillation cocktail. Both the relative efficiency and blank count rate increase with increasing volume of UGAB.

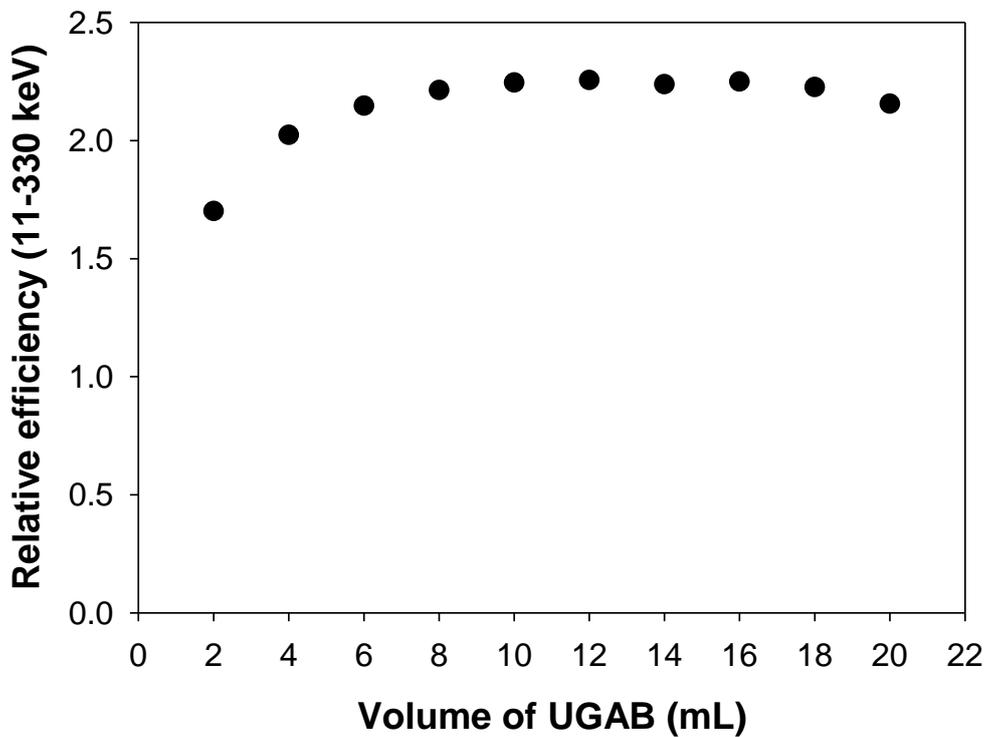


Figure 4 Relative efficiency plotted against the volume of UGAB scintillant in 2 mL of 1 M HCl. The relative efficiency was determined using equation 1.

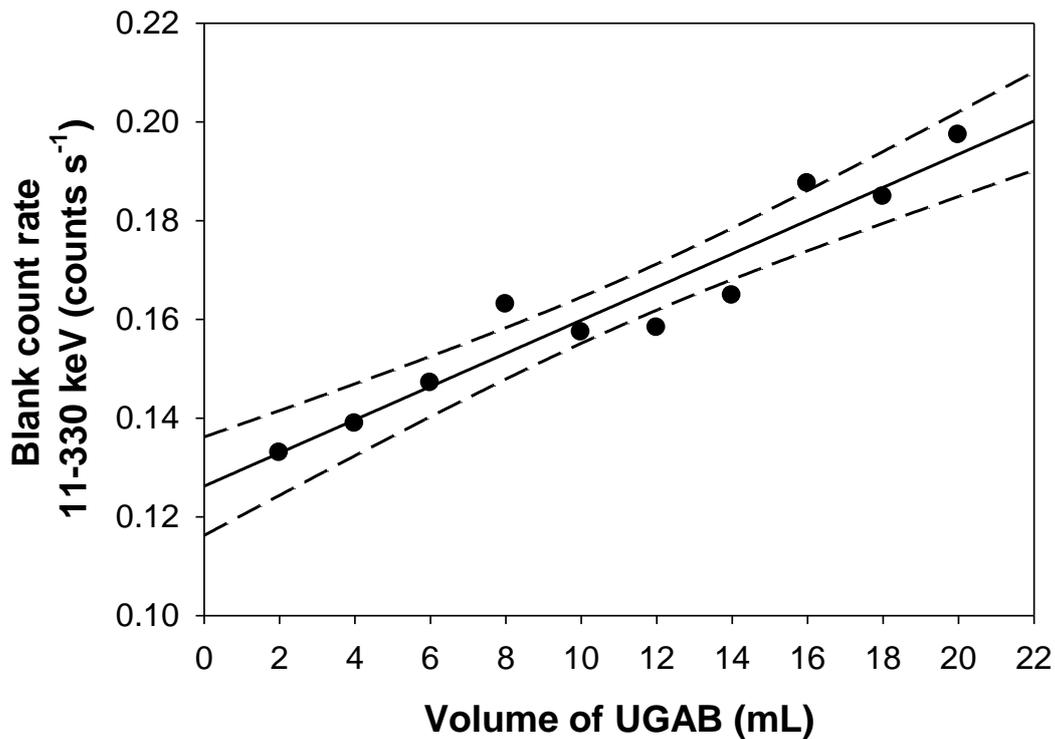


Figure 5 Background plotted against the volume of UGAB scintillant in 2 mL of 1 M HCl. Linear regression fitted with 95% confidence intervals shown.

The efficiency reached an effective maximum at between 10–18 mL of UGAB, whereas a linear increase in the background was correlated to an increase in the volume of UGAB ($R^2=0.92$, $p<0.0001$). Using the figure of merit parameter ($E2/B$) it was determined that a 10–12 mL volume of UGAB gave the optimum result sample to scintillant ratio (Figure 6). Consequently, the lower value of 10 mL of UGAB with 2 mL of 1 M HCl was chosen for this method to minimise the generation of organic waste.

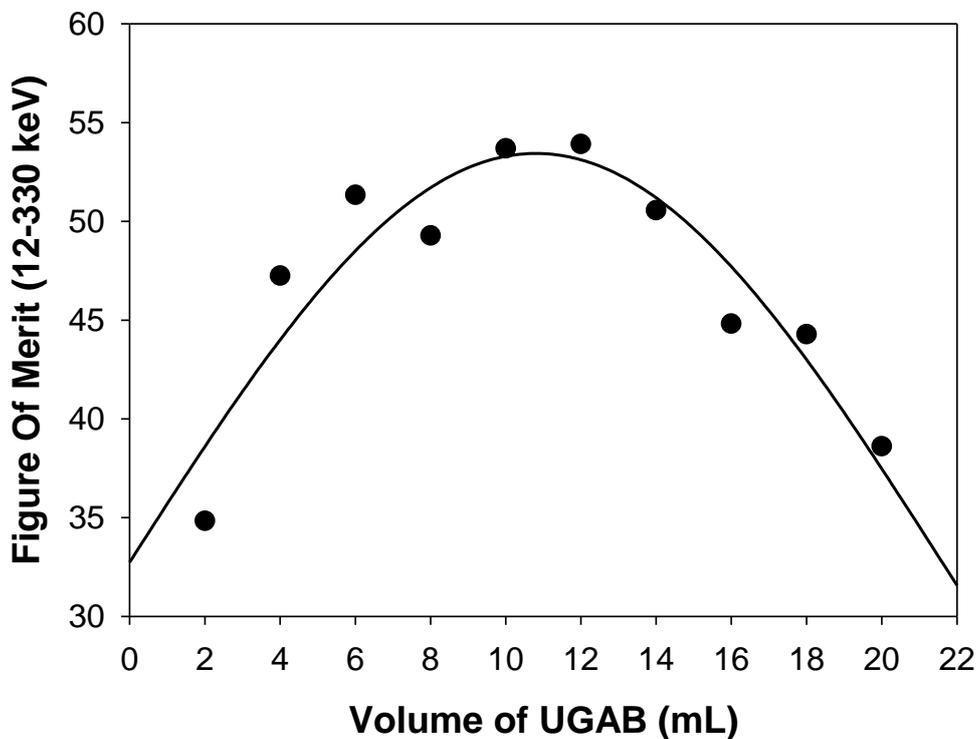


Figure 6 Figure of merit parameter ($E2/B$) plotted against the volume of UGAB scintillant in 2 mL of 1 M HCl. DBB 400 ns, anti-coincidence 30 ns. A peak fit has been applied for visual purposes only.

4.3 Optimising E²/B for varying anti-coincidence (AC) timing

Measurement of a series 6 standards, prepared from a ²¹⁰Pb standard solution in equilibrium with daughter isotopes ²¹⁰Bi and ²¹⁰Po, was undertaken. These measurements were conducted over a range of coincidence timings from 10–100 ns while also varying the DBB timing from 75–800 ns was performed. Increments of 25 ns for DBB timing with an increment of 20 ns for coincidence timing were tested, in addition at every 100 ns interval for the DBB timing, 5 ns increments were tested for with the coincidence timing.

Due to the large number of coincidence timing and DBB timing settings that were tested, there was a delay of 51 days between the first count and the final count of the standards prepared for this calibration step. A decrease in the blank count rate over the time taken to obtain data for all settings tested was observed (Figure 7).

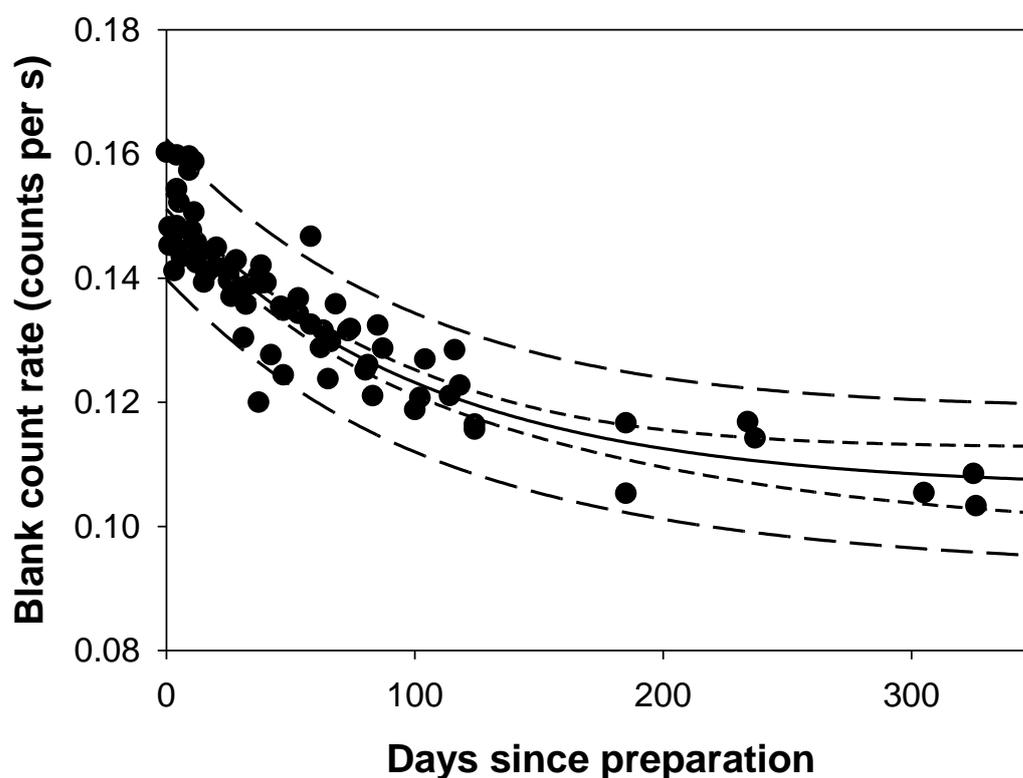


Figure 7 Blank count rate in aged blanks relative to the number of days since preparation of the blank, with 95% confidence (short dash) and prediction (long dash) bands.

The relative change (%) in the blank count rate was determined as a function of the days since preparation. The fitted function was a single 3-parameter exponential decay function ($R^2=0.83$, $p<0.0001$) and from this a correction factor was determined (equation 3, plotted in figure 8). This was then used to correct the count rates in the standards used for DBB and coincidence timing optimisation. Although the cause of the decreasing background is not known, it is likely to be related to a chemical reaction and/or the presence of low levels of environmental radioactivity introduced to the sample during separation and preparation for counting. Both of these potential explanations lead to the choice of the exponential decay function as the best fit to the data.

$$E_{CR} = \frac{CR_B}{0.7054 + 0.2977 \times e^{-0.0103 \times t}}$$

Where:

E_{CR} = The expected count rate of the blank (counts per ks) at $t = 0$

CR_B = The measured count rate of the blank at time t

t = The number of days since preparation of the sample in a scintillation cocktail

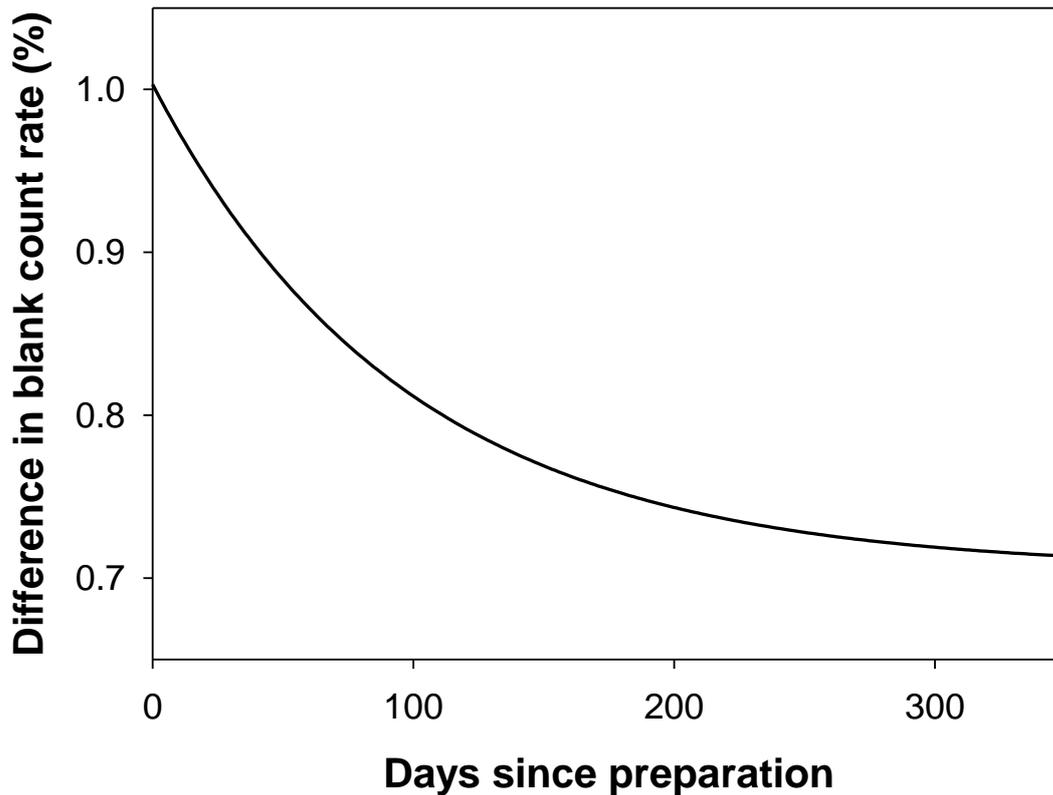


Figure 8 Difference (%) in the blank count rate in aged blanks relative to the number of days since preparation of the blanks

A significant decrease in the relative efficiency across this time period was not found for these standards, although in later measurements of other standards a decrease in the relative efficiency over time was observed (see section 4.5).

The efficiency and blank count rate (and thus figure of merit) did not vary significantly when the coincidence timing was varied (figure 9). Figure of merit values measured across the different coincidence timing settings were normalised and tested for normality and variance. All normalised distributions passed the Shapiro-Wilk normality test ($P=0.139$) and a one-way ANOVA comparing normalised distributions showed no significant difference across all groups tested ($P=0.998$).

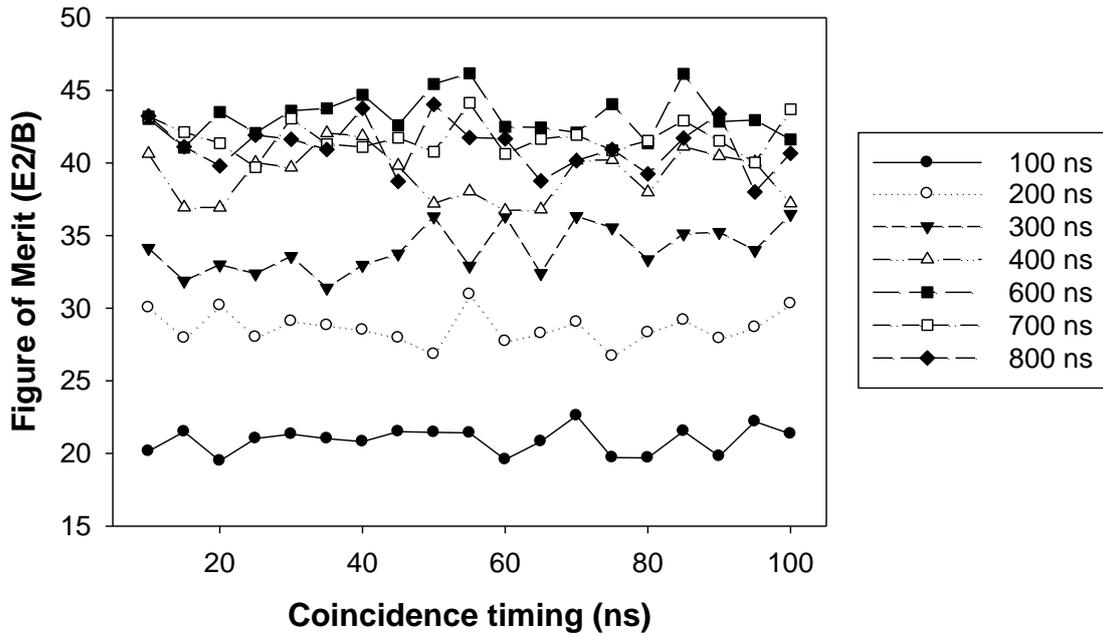


Figure 9 Average figure of merit for varied coincidence timing (10–100 ns)

The blank count rate, efficiency and figure of merit varied with varying DBB timing, with both the blank count rate and efficiency increasing as the DBB timing increased (figures 10 and 11).

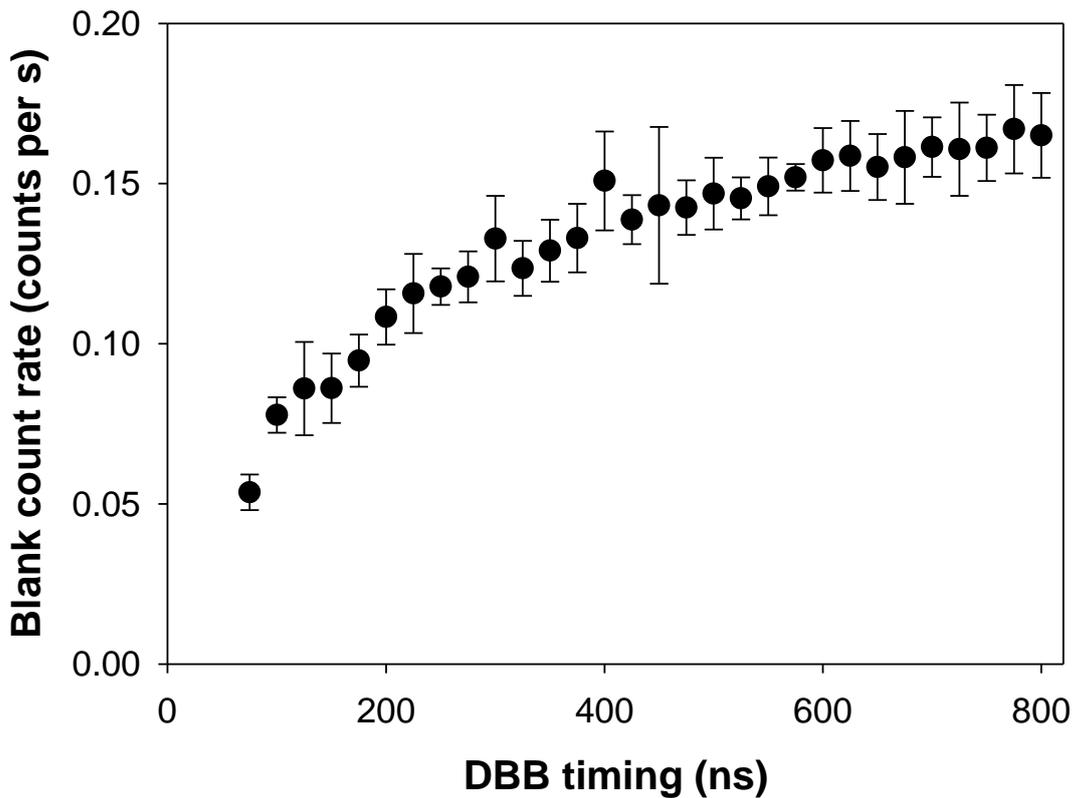


Figure 10 Average blank count rate (counts per second; time delay corrected) for DBB timing (ns; values averaged for all AC timing values tested) showing a general increase in the blank count rate with increasing DBB timing. Error shown is 2 standard deviations.

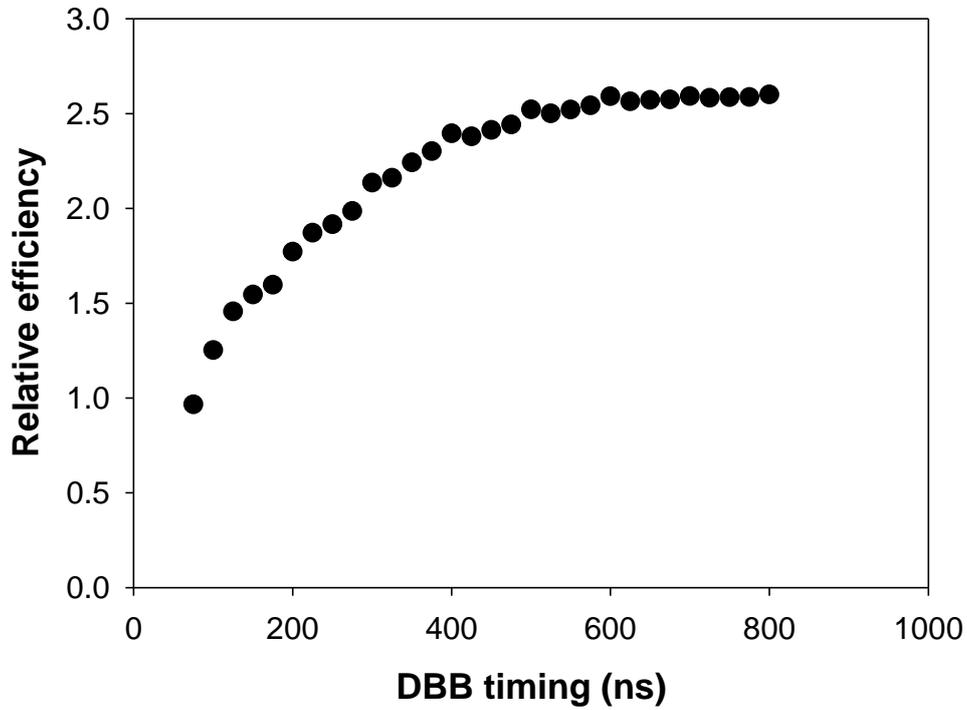


Figure 11 Average efficiency (11–330 keV) for AC timing values of 10–100 for a range of DBB timing (ns) showing a general increase in the efficiency with increasing DBB timing. Error is not shown as it is too small to display.

As there was no significant difference in the figure of merit for different coincidence timing settings an average of measured values across the range of DBB timing tested was used to assess the optimum DBB timing (figure 12). The figure of merit increased initially with increasing DBB timing, however, as the blank count rate increased proportionately more relative to the efficiency, a maximum was reached at a DBB timing of approximately 600 ns (figure 12).

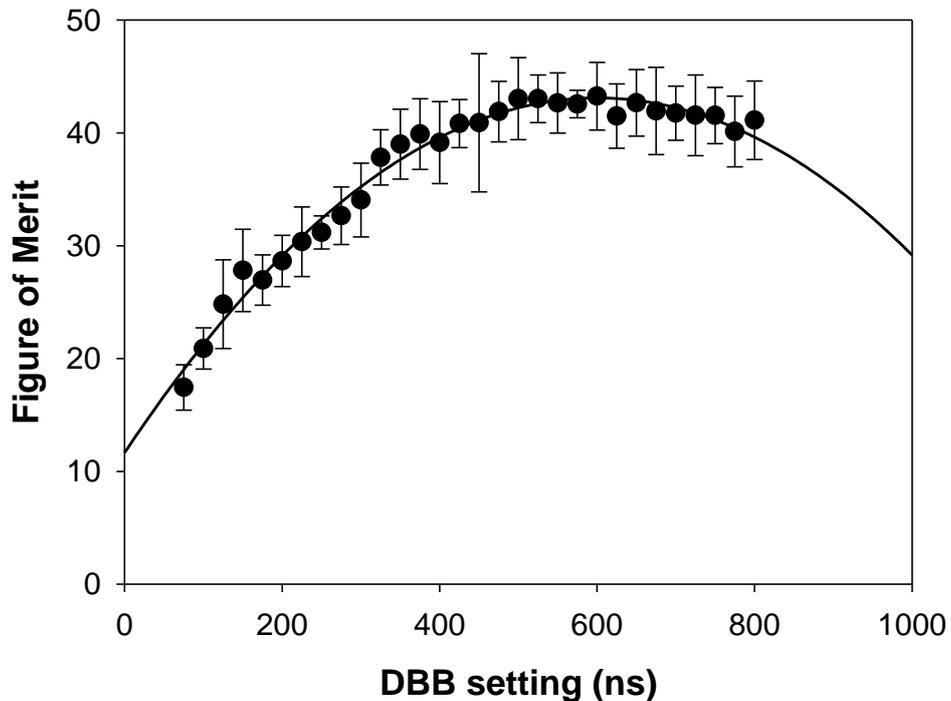


Figure 12 Average FoM (averaged for all AC timing values tested) vs DBB timing (ns) showing a general increase in FoM with increasing DBB timing, with a peak around a DBB setting of 600 ns. Error is one standard deviation from the mean of values from all AC timing settings tested. A fitted curve has been added to aid with visualisation only.

Based on the measured values an coincidence timing of 50 ns and DBB timing of 600 ns were chosen as the optimum settings for this method.

A range of different counting windows were assessed for their FoM to determine if there was any effect on the optimum count window with varying DBB timing. No differences in the general trends (ie – the increase in the blank count rate and the efficiency with increasing DBB timing) were found with variations in the counting window. Thus optimisation of the counting window was undertaken only with the optimised settings selected for coincidence timing and DBB.

4.4 Optimisation of the counting windows

The signal measured in the LSC is a function of the energy of the beta or alpha particles measured. Although the maximum energies of ^{210}Pb and ^{210}Bi beta emissions are 63.5 and 1162 keV, the best window to select for best performance will not necessarily cover these entire energy ranges. The alpha particle energy emitted from ^{210}Po is 5.41 MeV, however, as the entire energy is not transferred at once, the maximum peak height for ^{210}Po in our spectra is at approximately 200 keV. The optimum count window(s) will be where the efficiency relative to the blank count rate is at an optimum, this is measured by the FoM.

Three count windows were selected and investigated in this study using an iterative process, to determine the best window to use, accounting for various relative ingrowth of ^{210}Bi and ^{210}Po after initial separation from Pb.

Figure 13 shows several spectra from the LSC measurement of ^{210}Pb standard solutions under the optimised conditions determined from this study, ie – 2 mL of 1 M HCl mixed with 10 mL UGAB in 20 mL scintillation vials with a DBB setting of 600 ns and a coincidence timing setting of 50 ns. The spectra were selected to highlight the various stages of ingrowth of ^{210}Bi and ^{210}Po . The large peak to the left is from the beta emission of ^{210}Pb and has a peak centred at ~ 16 keV, the central peak is from the alpha emission of ^{210}Po , with a peak centred at ~ 200 keV at equilibrium with the ^{210}Pb parent. The ^{210}Bi beta emissions span a large range up to 1162 keV and no clear peak is discernible. Counts from the ^{210}Bi in the standards are seen as a relative increase in the counts measured in channels across the whole spectrum up to the 2000 keV it is most visible in the range between the ^{210}Pb and ^{210}Po peaks and there is relatively no difference between the background spectrum above ~ 400 keV (not shown in the figure).

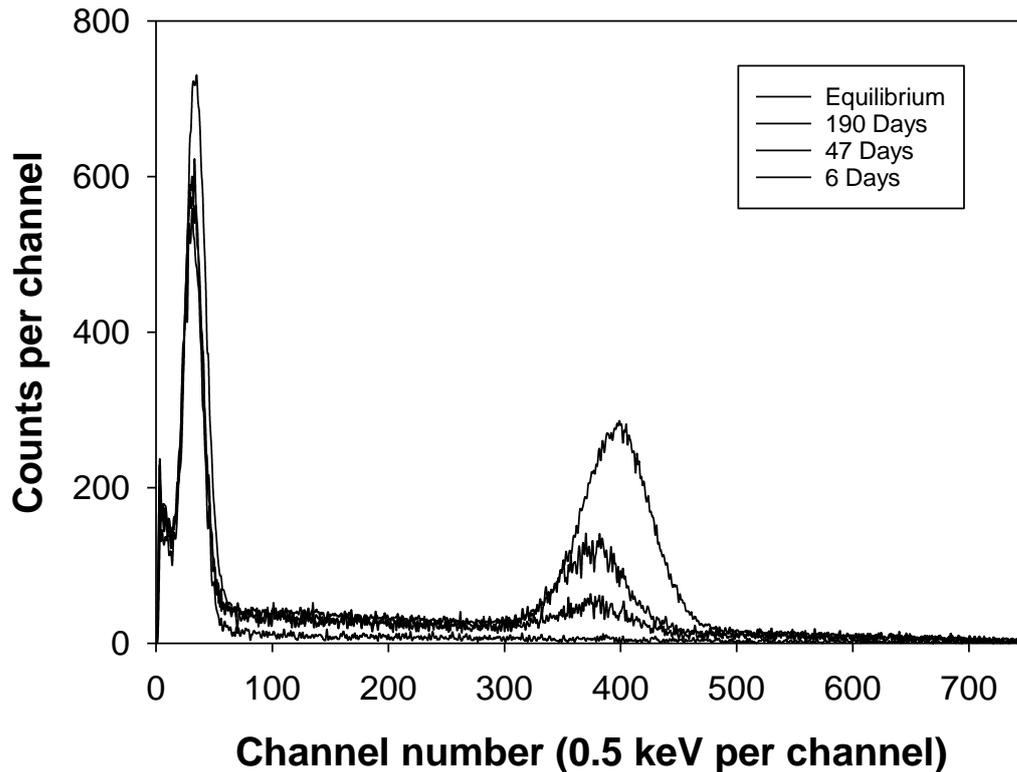


Figure 13 LSC spectra from ^{210}Pb standard solutions

Standards prepared both 5 days after chemical separation of Pb (i.e. with some ^{210}Bi grown in) and at secular equilibrium with the daughters (^{210}Bi and ^{210}Po), were used to select windows for counting of ^{210}Pb only, ^{210}Bi , ^{210}Po and ^{210}Pb combined or ^{210}Po only. The average counts per channel from 3 standards used for efficiency calibration (taken 5 days after separation of Pb) were used for determining the window for measuring ^{210}Pb only. The average counts per channel from 6 standards used for DBB and coincidence timing optimisation (ie – with ^{210}Bi , ^{210}Pb and ^{210}Po in equilibrium) were used to select the other two optimum windows after sufficient ingrowth of ^{210}Bi and ^{210}Po .

Calculation of the optimum windows was done by calculating the FoM for the entire spectrum (Channels 1–4000), then reducing the window by 1 channel at a time from the highest channel down to channel 1. This determined the upper bounds of the optimum count windows. With this upper boundary set, the width of the counting windows was then reduced by 1 channel at a time starting from the lowest channel (ie – channel 1) up to the upper boundary. From these FoM calculations, the 3 optimum windows were determined to be 11–22 keV (Channels 23–44), 11–330 keV (Channels 23–660) and 173–330 keV (Channels 345–660). These windows are optimum at different stages of ingrowth after separation of Pb (Figure 14). The 11–22 keV count window is optimal up to ~16 days after separation, the 11–330 keV is optimal up to ~246 days. These windows reflect the initial counting of ^{210}Pb only, then counting of ^{210}Pb , ^{210}Bi and ^{210}Po together and finally counting of primarily ^{210}Po (with some counts from ^{210}Bi). This final window has the lower boundary at a much higher energy (173 keV) than the other 2 windows. This is because this window is across a region where the blank count rate is significantly lower than across the optimum window for counting emissions from ^{210}Pb and ^{210}Bi . The fitted curves in Figure 14 are a visualisation aid only and are there to assist the reader in identifying the approximate crossover times where the FOM for one window is superior to another.

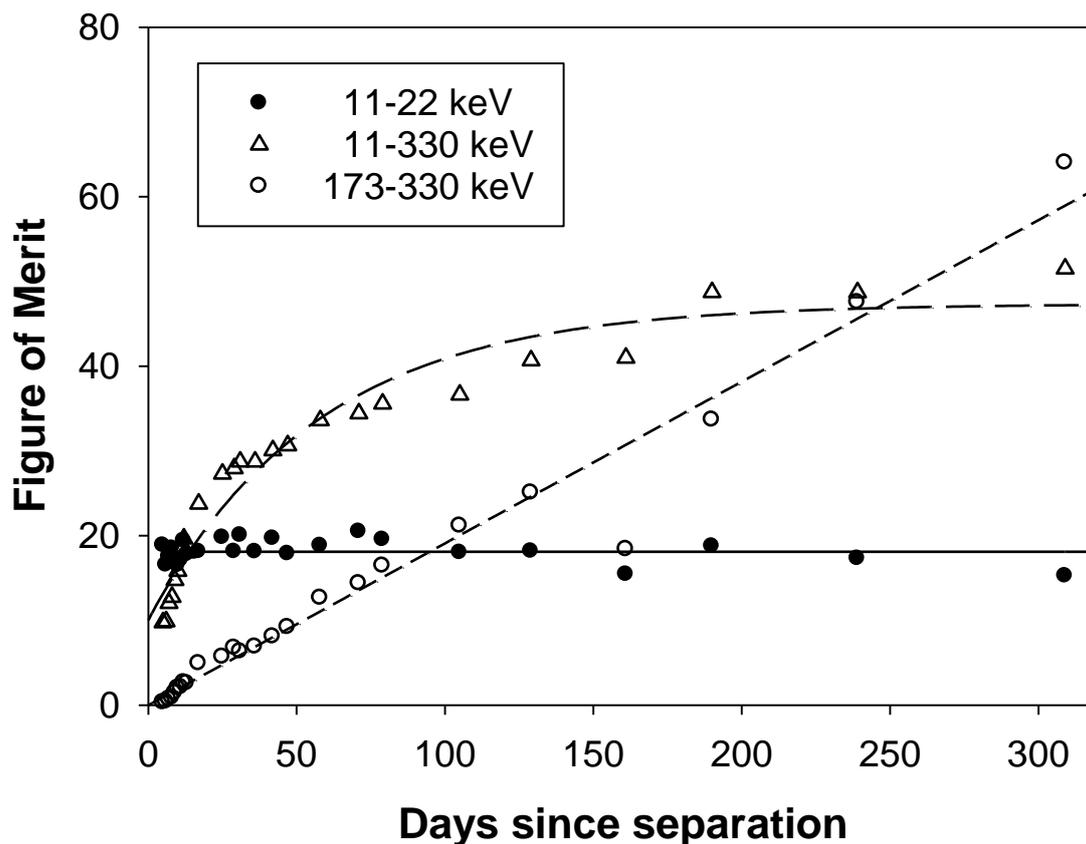


Figure 14 FoM for optimised count windows relative to the stage of ingrowth of ^{210}Pb daughters ^{210}Bi and ^{210}Po

4.5 Efficiency determinations

The relative counting efficiency of all 3 isotopes was determined under the optimised count conditions with the optimised count windows, 11–22 keV and 11–330 keV window, for different stages of ingrowth. This was done by measuring sub-samples taken from a calibrated ^{210}Pb solution at regular intervals (after initial chemical separation of ^{210}Pb). Sub-samples were taken from 5 days to 309 days after separation and were prepared fresh prior to counting, allowing at least 3 hour's time to settle after mixing with the scintillant, 3 standards and a single blank were prepared for each measurement and individual values given are an average of these 3 standards.

In addition to the freshly prepared standards above, 2 sets of 3 standards (including a blank) were prepared (i.e. mixed with the cocktail) soon after preparation of the purified ^{210}Pb solution and re-counted at regular intervals to assess the stability of the scintillation cocktail. The relative efficiency was measured as a function of the activity of ^{210}Pb in the sample (see equation 1). Relative efficiencies of greater than 100% were achieved by summing counts from the isotopes ^{210}Bi and ^{210}Po with the counts from ^{210}Pb .

The combined efficiency measured for both the fresh and the aged standards for the 11–330 keV count window is shown in figure 15. In this figure the data for the aged samples is a combination of data from both sets of aged standards, where they were counted on the same day an average value is used, in other cases values from a single set are used.

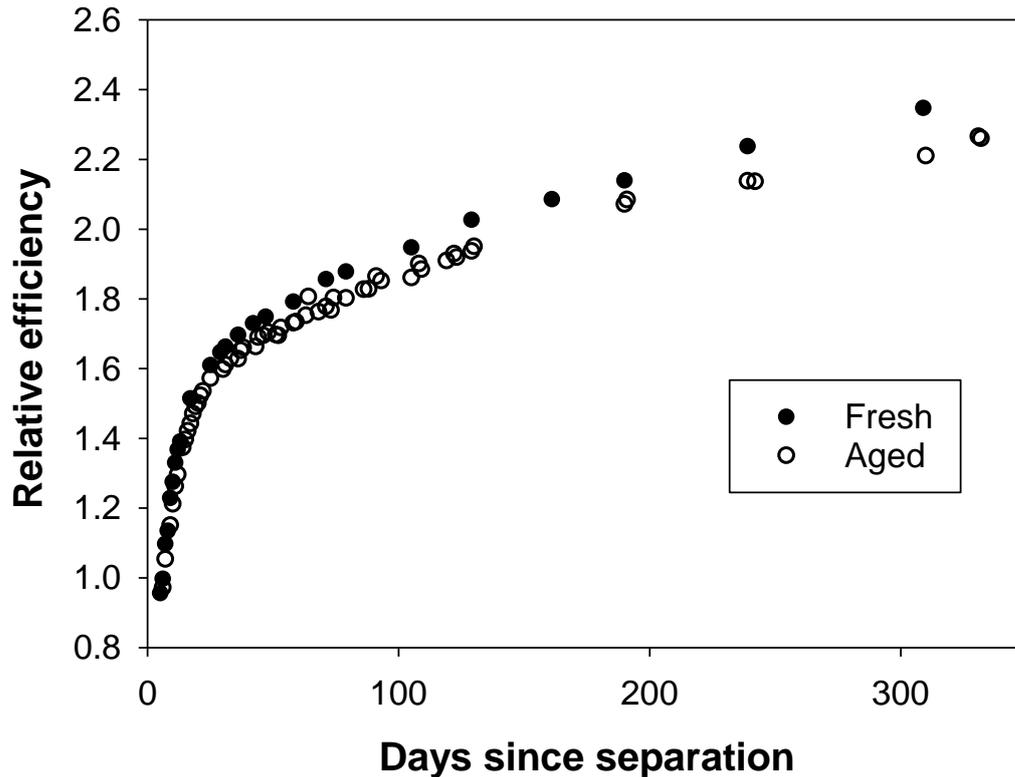


Figure 15 Measured efficiencies in fresh and aged standards

For the fresh standards a relative efficiency of 2.35 is reached after 309 days, corresponding to a ^{210}Po activity of 77% of the initial ^{210}Pb activity (which has decayed to 97.4% of the initial activity at this stage). Assuming a 100% counting efficiency for ^{210}Po , this corresponds to a peak relative efficiency of 2.60 at equilibrium. This compares to the relative efficiency determined in the DBB/AC timing optimisation of 2.59 under the same counting conditions.

The overlapping energies of the three radionuclides, ^{210}Pb , ^{210}Bi and ^{210}Po could be effectively resolved due to initial separation of ^{210}Pb from the daughter isotopes and because a counting efficiency of 100% can be assumed for the alpha emissions of ^{210}Po (Packard Instrument Company, 2015).

The efficiency determined for ^{210}Pb for freshly prepared standards in the 11–22 keV (Channels 23–44) counting window was $70\pm 1\%$, based on 6 measurements between 5 and 10 days after initial Pb separation. A maximum determined efficiency of $73\pm 1\%$ was reached between 17 and 25 days after preparation (the midpoint is 21 days); the difference is only 3% and the increase in efficiency for this window is likely to be due to increasing counts from the overlapping ^{210}Bi region, with a maximum reached nearing secular equilibrium.

The efficiency determined for ^{210}Bi was $85\pm 1\%$ in the 23–330 keV window (Channels 45–660) and was based on 7 measurements taken between 36 and 105 days after initial separation of Pb where ^{210}Bi is at maximum ingrowth, with the total activity equivalent to 99% of the initial ^{210}Pb activity. This efficiency for ^{210}Bi was determined by subtracting both the efficiency determined for the 11–22 keV window and the efficiency of ^{210}Po (based on the relative amount of ingrown ^{210}Po) from the efficiency determined for the 11–330 keV window.

Figure 16 shows the measured efficiency for the count window 11–330 keV as a function of time since separation of ^{210}Pb plotted with the predicted efficiency based on the

maximum achieved efficiency for ^{210}Bi (85%) and ^{210}Pb (70% to day 21 and 73% thereafter) and assuming 100% efficiency for ^{210}Po . Equation 4 is used to calculate the predicted (combined) efficiency, taking into account the ingrowth of ^{210}Bi and ^{210}Po after initial separation of ^{210}Pb (equation amended from Johansson, 2008).

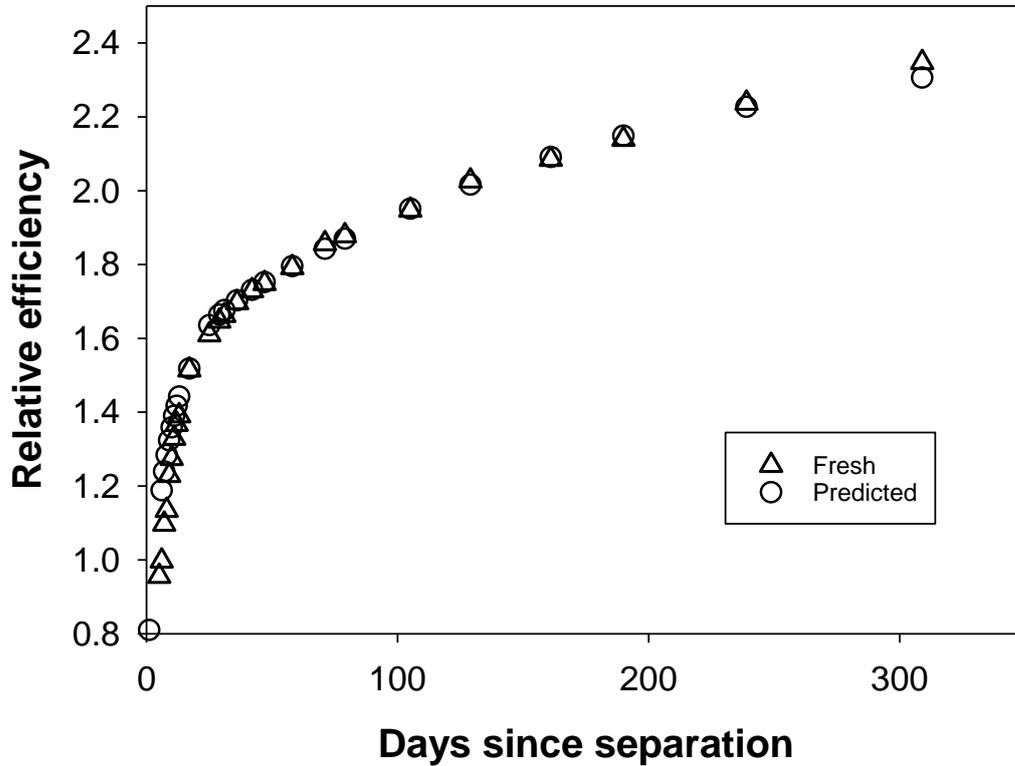


Figure 16 Measured and predicted combined efficiencies in fresh standards

Equation 4

$$\begin{aligned} \varepsilon_{Combined} = & (e^{-\lambda_{Pb}t}) \times \varepsilon_{Pb} + (1 - e^{-\lambda_{Bi}t}) \times (e^{-\lambda_{Pb}t}) \times \varepsilon_{Bi} + \lambda_{Bi} \times \lambda_{Po} \\ & \times \left[\left(\frac{e^{-\lambda_{Pb}t}}{(\lambda_{Bi} - \lambda_{Pb}) \times (\lambda_{Po} - \lambda_{Pb})} \right) + \left(\frac{e^{-\lambda_{Bi}t}}{(\lambda_{Pb} - \lambda_{Bi}) \times (\lambda_{Po} - \lambda_{Bi})} \right) \right. \\ & \left. + \left(\frac{e^{-\lambda_{Po}t}}{(\lambda_{Bi} - \lambda_{Po}) \times (\lambda_{Pb} - \lambda_{Po})} \right) \right] \end{aligned}$$

Where:

$\varepsilon_{Combined}$ = The summed relative efficiencies of ^{210}Bi , ^{210}Pb and ^{210}Po at time t

t = The time since ^{210}Pb separation (days)

ε_{Pb} = The relative efficiency of ^{210}Pb . This is set at 0.70 for days 0–21 and 0.73 thereafter

ε_{Bi} = The relative efficiency of ^{210}Bi . This is set at 0.85 (0.8 for samples aged over 25 days, see below for details)

ε_{Po} = The relative efficiency of ^{210}Po . This is set at 1

λ_{Bi} = The decay constant of ^{210}Bi

λ_{Pb} = The decay constant of ^{210}Pb

λ_{Po} = The decay constant of ^{210}Po

The aged standards showed a deterioration of relative efficiency over time, though measurements up to 250 days after cocktail preparation display repeatable and stable measurements if a correction is applied to the relative efficiency for ^{210}Bi .

The deterioration in efficiency between fresh and aged standards does not appear to be related to the 11–22 keV ^{210}Pb window as there is no discernible difference in efficiency in this peak between fresh and aged standards. Consequently, the decrease can be attributed to a combination of ^{210}Bi and ^{210}Po but, due to overlapping peak areas, it is not possible to accurately determine the relative decrease in efficiency for the individual isotopes. As the ^{210}Pb count window is not affected it is unlikely to be due to quenching. A possible explanation for the deterioration in efficiency in the aged standards may be due to a delay in diffusion of the daughter nuclides (^{210}Bi and ^{210}Po) into the scintillant cocktail after initial preparation, rather than a change in the properties of the scintillation cocktail.

Data for ^{210}Bi efficiency in the aged standards for the same date range (36–105 days) as used for the fresh standards shows a 5% reduction in counting efficiency to $80 \pm 1\%$. Assuming 80% as the efficiency for ^{210}Bi , with all other parameters the same as for the fresh standards, combined efficiencies for aged standards at different stages of ingrowth were calculated using equation 4 and results are shown in Figure 17.

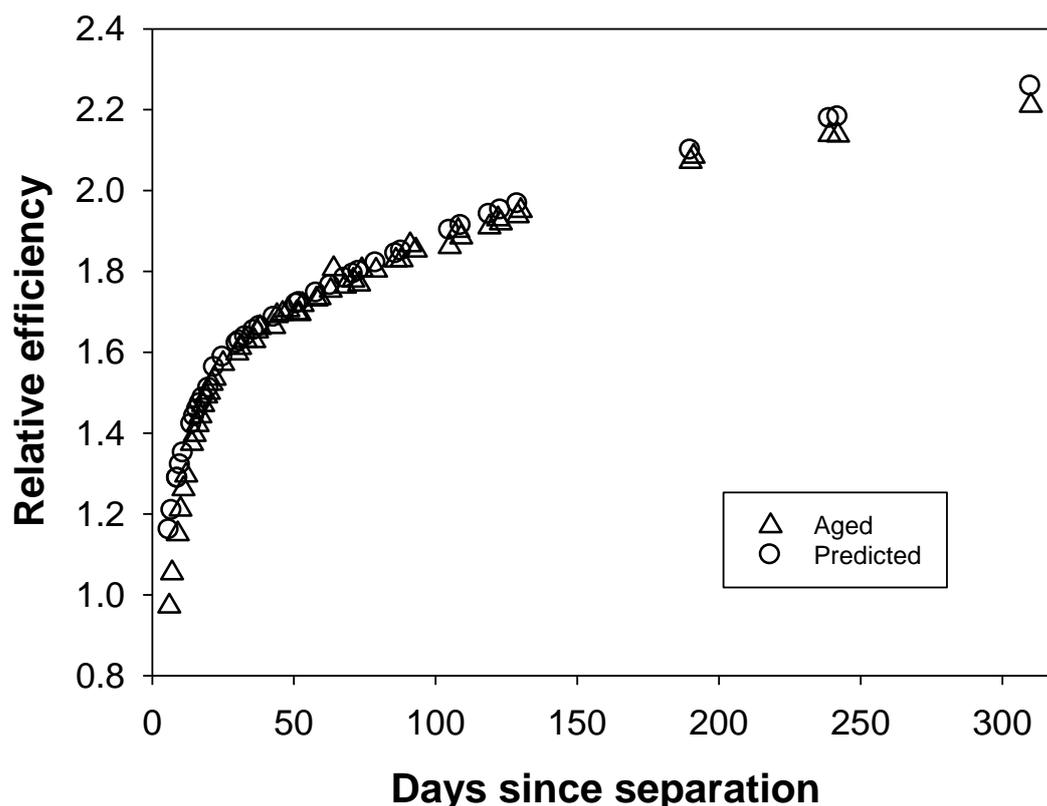


Figure 17 Measured and predicted combined efficiencies in aged standards

The relative efficiencies for the fresh and aged standards with the corrected ^{210}Bi efficiency show good agreement and therefore an efficiency for ^{210}Bi of 0.8 is used for samples aged greater than 25 days. The limitation of 25 days is recommended as the counting efficiency of ^{210}Bi in fresh standards was also lower than the 85% predicted, taking ~25 days to reach the maximum determined efficiency (figure 18). The relative efficiency of ^{210}Bi in the aged

standards does not reach the full predicted efficiency due to the steady decrease in efficiency noted previously for the aged standards (see figure 15), though the marked reduction in measured efficiency (greater than 50%) in the early count period is not understood, though it was also noted in the aged standards (figure 19).

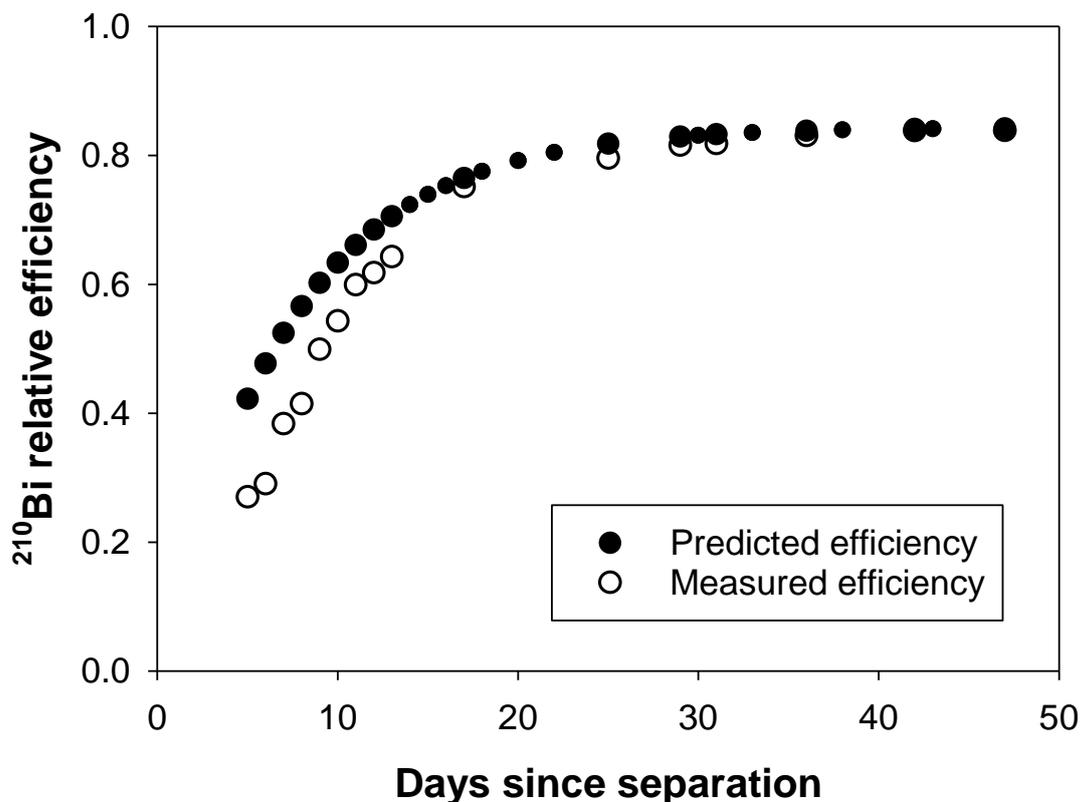


Figure 18 Measured and predicted ^{210}Bi relative efficiencies in freshly prepared standards

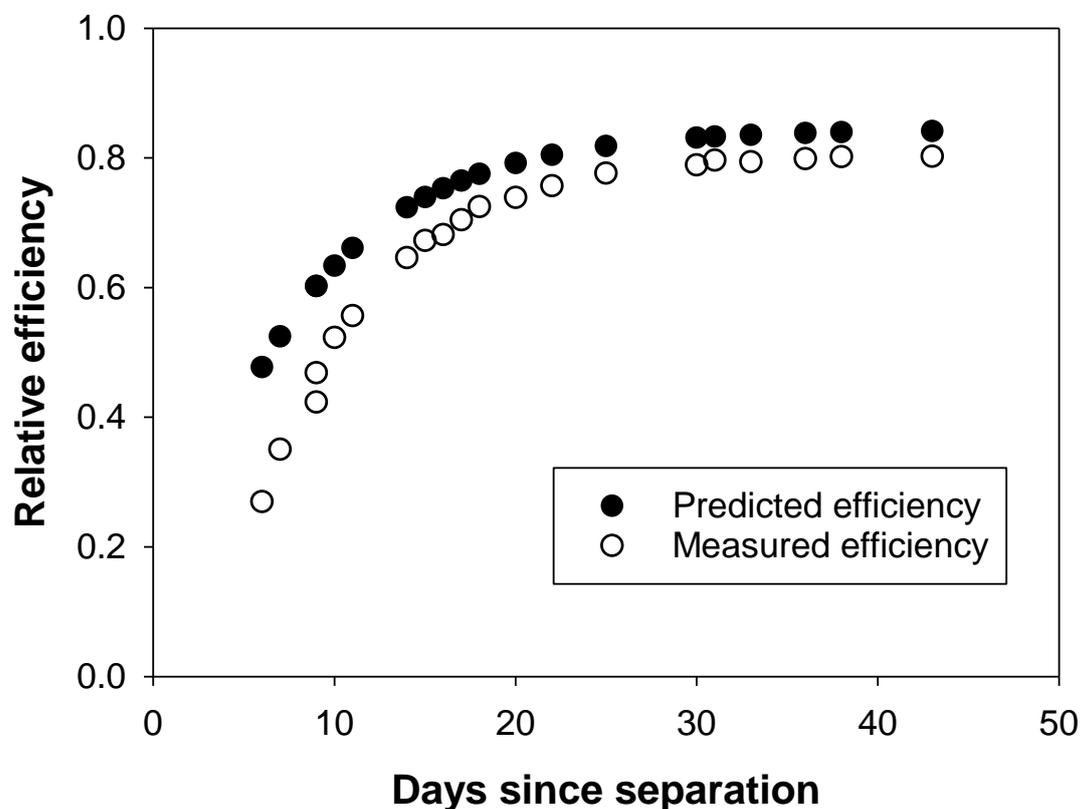


Figure 19 Measured and predicted ^{210}Bi relative efficiencies in aged standards

It is important to note that the reduced counting efficiencies in the ^{210}Bi counting window was very similar for each standard in both sets of aged standards. In addition to this, the standards used for optimising DBB and coincidence timing did not show a lower efficiency in the initial stages of counting. This indicates a probable systematic effect and may be due to losses of ^{210}Bi to the walls of the stock solution container that was used for preparing the standards, thereby increasing the time taken for full ingrowth of ^{210}Bi . Either waiting for at least 25 days after sample preparation, or only using the ^{210}Pb window (11–22 keV) in the first 25 days, would limit the potential for this effect to have any impact on results for actual samples.

4.6 Calculation of ^{210}Pb activity concentrations from LSC

To calculate results from samples there are several steps that need to be taken to ensure that results are corrected appropriately to the sample collection date. This includes accounting for any ingrowth of ^{210}Pb in the sample after collection and prior to separation of Pb from ^{226}Ra .

The following set of equations are used to calculate the activity concentration in samples at the date of sample collection and assumes no radon loss.

Equation 5

$$A_{\text{Sample}} = \frac{A_{\text{Measurement}}}{e^{-\lambda_{\text{Pb}}t_{\text{C}}}} - A_{\text{Ra}} \times (e^{\lambda_{\text{Pb}}t_{\text{C}}} - 1)$$

Where:

A_{Sample} = The activity concentration of ^{210}Pb in the sample at the date of collection (Bq kg^{-1})

$A_{\text{Measurement}}$ = The activity concentration of ^{210}Pb in the sample on the date it was counted on the LSC (Bq kg^{-1})

λ_{Pb} = The decay constant of ^{210}Pb

A_{Ra} = The activity concentration of ^{226}Ra in the sample at the date of collection (Bq kg^{-1})

t_{C} = The time between separation and collection (days)

Equation 6

$$A_{\text{Measurement}} = \left(\frac{A_{\text{Total}}}{m_{\text{S}} \times R_{\text{Pb}} \times F_{\text{Measured}}} \times 1000 \right) - A_{\text{Tracer}} \times m_{\text{Tracer}}$$

Where:

m_{S} = The sample mass used for analysis (g)

R_{Pb} = The chemical recovery of stable Pb in the sample solution (1 equals 100% recovery)

A_{Tracer} = The activity concentration of ^{210}Pb in the stable Pb tracer at the measurement date (Bq g^{-1})

m_{Tracer} = The mass of stable Pb tracer added for analysis (g)

F_{Measured} = The fraction of sample extract measured after removal of a sub-sample for stable Pb recovery via ICPMS

Equation 7

$$A_{Total} = \frac{N_C}{\varepsilon_{Combined}}$$

Where:

A_{Total} = The total activity of ^{210}Pb in the scintillation cocktail source prepared for counting (Bq)

N_C = The net count rate in the sample

$\varepsilon_{Combined}$ = The combined efficiency (from equation 4)

Equation 8

$$N_C = \frac{S_C}{t_S} - \frac{B_C}{t_B}$$

Where:

N_C = The net count rate in the sample

S_C = The gross counts in the sample

B_C = The gross counts in the analyte blank

t_S = The count time of the sample (s)

t_B = The count time of the analyte blank (s)

4.7 Calculation of the uncertainty associated with calculated ^{210}Pb activity concentrations

The measurement uncertainty is calculated according to the spreadsheet method described by Kragten (1994). This is a relatively quick and easy method where the standard deviation is calculated numerically without violating the condition of mutual independence. Another advantage of this technique is that the relative contribution to the total uncertainty from each parameter can be easily determined (Kragten (1994)). The formula for calculating the relative uncertainty is shown in equation 9.

Equation 9

$$U_{Sample} = \sqrt{\sum_{i=1}^n (A_{Sample}(X_i + U_i) - A_{Sample})^2}$$

Where:

U_{Sample} = The total absolute uncertainty for the activity concentration of ^{210}Pb in the sample at the date of collection (Bq kg⁻¹)

$A_{Sample}(X_i + U_i)$ = The activity concentration of ^{210}Pb in the sample at the date of collection (Bq kg⁻¹), calculated with the value of the parameter X being substituted for the value 'X plus the absolute uncertainty of X'

A_{Sample} = The activity concentration of ^{210}Pb in the sample at the date of collection (Bq kg⁻¹)

When calculating the total absolute uncertainty all sources of uncertainty should be included, where this is not achievable the major sources of error should be included at a minimum. For this method, the gross count rate of the sample and analyte blank and the stable Pb chemical recovery will usually be the most significant parameters contributing to the total uncertainty.

It must be noted, that this technique is only valid when the relative uncertainty of each parameter is small and the function $y(X_1, X_2, \dots, X_n)$ is linear with respect to all parameters (Holmes, 2004). Holmes (2004) notes that although this isn't always the case, the method still gives a good estimate of the overall uncertainty.

4.8 Linearity test

An additional series of standards were prepared with ^{210}Pb activities varying from 18–220 mBq to test the linearity of the calibration. Results from these standards are shown in Figure 20. The test shows a very strong linear response ($R^2 = 0.99$, $p < 0.0001$) across a range of activities typically measured in our research projects, though there appears to be a systematically lower than expected response of 6% (slope = 0.94). Certified reference materials, therefore, should be run with samples to ensure corrections can be made to results from actual samples if necessary.

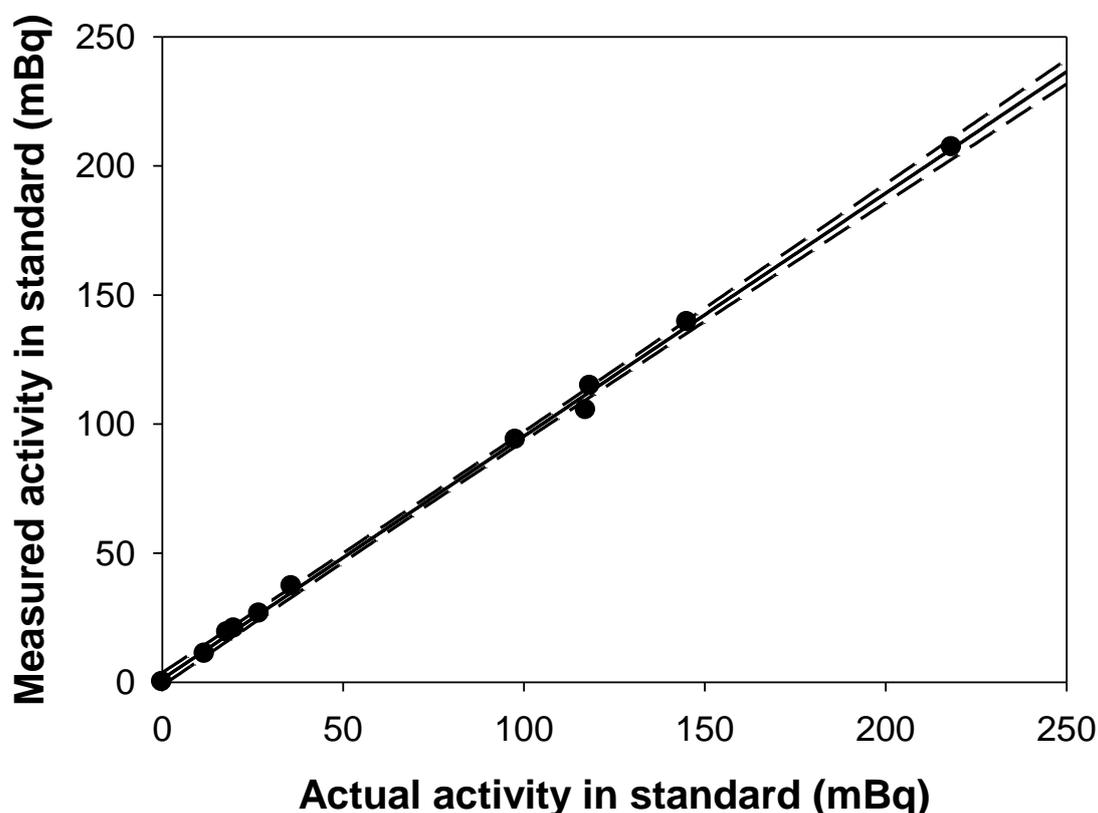


Figure 20 Measured vs actual activities in 10 standard solutions of varying activity (18–220 mBq) in the 11–330 keV counting window (solid line, 95% confidence intervals are shown as dashed lines).

4.9 Performance with actual samples

Comparison of results with a set of freshwater mussel samples from gamma analysis (Marten, 1992).

Using a set of age-classes composite mussel samples that have previously been measured by gamma spectrometry (Supervising Scientist, 2013 & 2014) a comparison of the gamma and LSC techniques was done. Results from this comparison are shown in Figure 21, activity concentrations as measured by gamma spectrometry and LSC are plotted against

the age class of the composite mussel samples (the age plotted for the LSC measurements has 0.2 y added to the age to prevent overlapping data points on the figure). The results from both techniques are in good agreement and this indicates that this technique is suitable for analysis of samples from *eriss* research projects and validates the method.

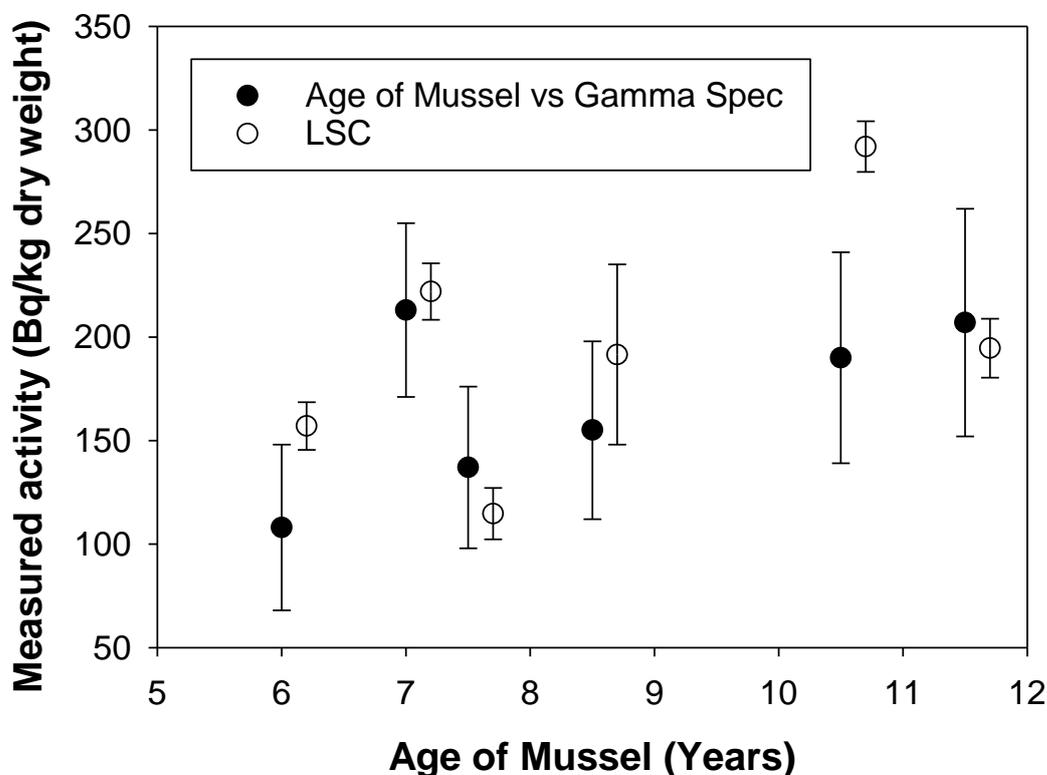


Figure 21 A comparison of the developed LSC method with an *eriss* gamma spectrometry method using a set of freshwater mussels

From this set of mussel samples, 4 were re-counted in the LSC several times over a period of several months to check the stability of the scintillation cocktail with actual samples. Although the variability in measured values was relatively high for one of the samples (23% RSD for the 8½ y old sample), overall the stability of the scintillation cocktail was good and low variability was observed in repeat measurements. It is important to note that the activity of ²¹⁰Bi as measured by the efficiency of the ²¹⁰Bi window, was as expected in those samples counted within days after preparation, and that the reduced counting efficiencies previously seen in the fresh and aged standards (figures 18 and 19) was not observed.

4.10 Analytical blank and limits of detection

The limits of detection were determined using formulae from Currie (1968), where the limit of detection (L_D) and limit of quantification (L_Q) are defined as functions of the standard deviation of the blank count rate (table 1).

Table 1: Currie's (1968) formulae for calculating L_D and L_Q (σ_B is the standard deviation of the blank)

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

The blank count rate used here for calculating detection limits is based on a single 1500 minute (90 ks) count of the blank from analysis of the set of mussels. This was chosen as the count time was 1500 minutes (which is the minimum count time for samples and much higher than the 6 ks maximum count time for the calibration standards) and it was believed to be more representative of the blank count rate that can be expected in actual samples.

The count rate in the blank was 155.56 ± 1.31 counts per ks (uncertainty is based on counting statistics only). Estimated detection limits for the 11–330 keV and 173–330 keV count windows, based on the predicted combined efficiency for freshly prepared samples, assuming a chemical recovery of 80% and relative to the number of days since separation of Pb, are shown in figure 22.

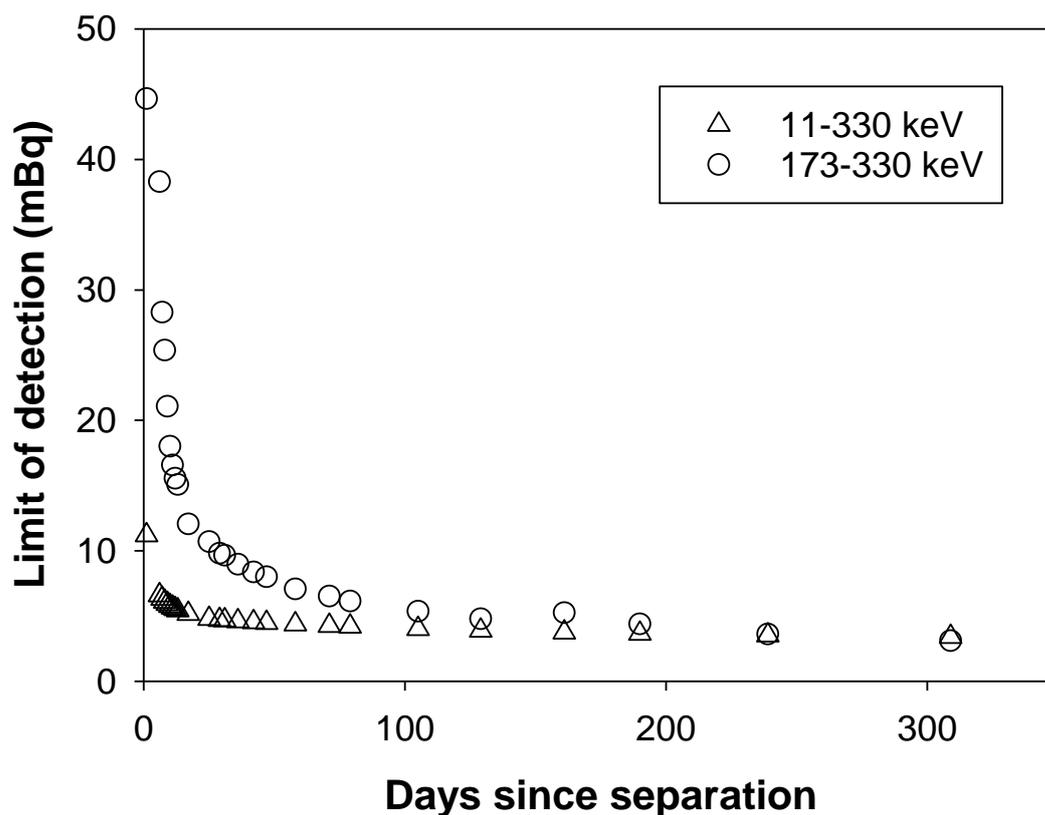


Figure 22 Detection limits (L_D) in mBq for the 11–330 keV and 173–330 keV count windows relative to the time since initial separation of Pb

Our desired L_D of 4 mBq can be reached ~ 80 days after separation of Pb. The same L_D can be achieved 3 days after separation of Pb if a 4 day count time is used. The lowest detection limits are achieved using the 173–330 keV count window at ~ 250 days after initial separation of Pb, with detection limits of ~ 3 mBq achievable after 300 days.

If we consider the 11–22 keV window only, a L_D of 11 mBq can be achieved directly after separation of Pb (given the same parameters). For rapid analysis, using just the 11–22 keV window, an L_D of 54 mBq can be achieved with a 100 minute count time (assuming 80% chemical recovery). This will allow rapid screening and analysis for ^{210}Pb , at relatively low levels, in the event of a radiological emergency.

Although it is not used in the calculations for L_D shown in figure 23, the decrease in the blank count rate in aged samples (figures 7 and 8) is greater than the deterioration in the combined efficiency. As such, re-counting samples after allowing them to age for a period of time may lead to a lower L_D for aged samples than that estimated above.

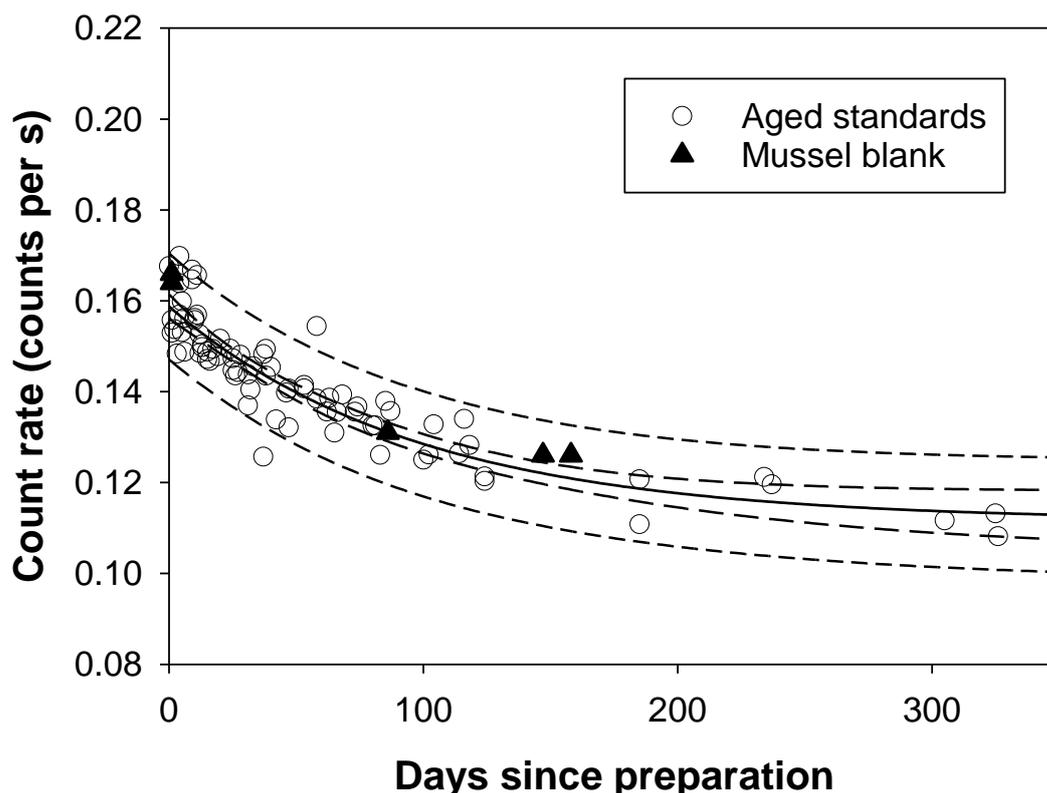


Figure 23 Relative decrease in the blank count rate relative to the time since cocktail preparation. Data from aged standards is reproduced from Figure 7 and presented with 4 repeated counts of the analytical blank for the mussels used for the method comparison shown in section 4.9. 95% confidence (inner dashed line) and prediction bands (outer dashed line) are shown.

In practice, a paired-blank should be counted within 5 days of aged samples, however, if this is not possible, the expected blank count rate from the measurement process can be calculated using an exponential decay function that has been fitted to Figure 23 above (equation 10).

Equation 10

$$E_{CR} = 0.1116 + 0.0471 \times e^{-0.0103 \times t}$$

Where:

E_{CR} = The expected count rate of the blank (in counts per ks) at time t

t = The number of days since preparation of the sample in a scintillation cocktail

4.11 Quench effects

The level of quenching in the samples (as measured by tSIE) prepared for counting will have an effect on the combined counting efficiency. Therefore, maintaining a stable range of tSIE values for sample counting is important.

The radiochemical separation and purification of lead required before analysis will limit the potential for various quenching agents to be introduced to samples and will therefore limit the potential for variability of quenching. When evaporating the 9 M HCl solution from the sample vials in preparation for counting, care should be taken to ensure complete evaporation as any residual acid will increase quench. Samples should be also be free of colour, if colour is noticed the samples may be treated with concentrated HCl and HNO₃

with addition of 35% H₂O₂ until the sample is completely colourless (see Appendix 1 for a standard operating procedure for the method which is to be incorporated into the EnRad procedures manual (Medley & Evans 2015).

The tSIE values in the freshly prepared standards used for optimisation of this method ranged from 365–450, with values in this range having no discernible difference on the combined counting efficiency.

For the aged standards a decrease in tSIE over time was observed (see figure 24).

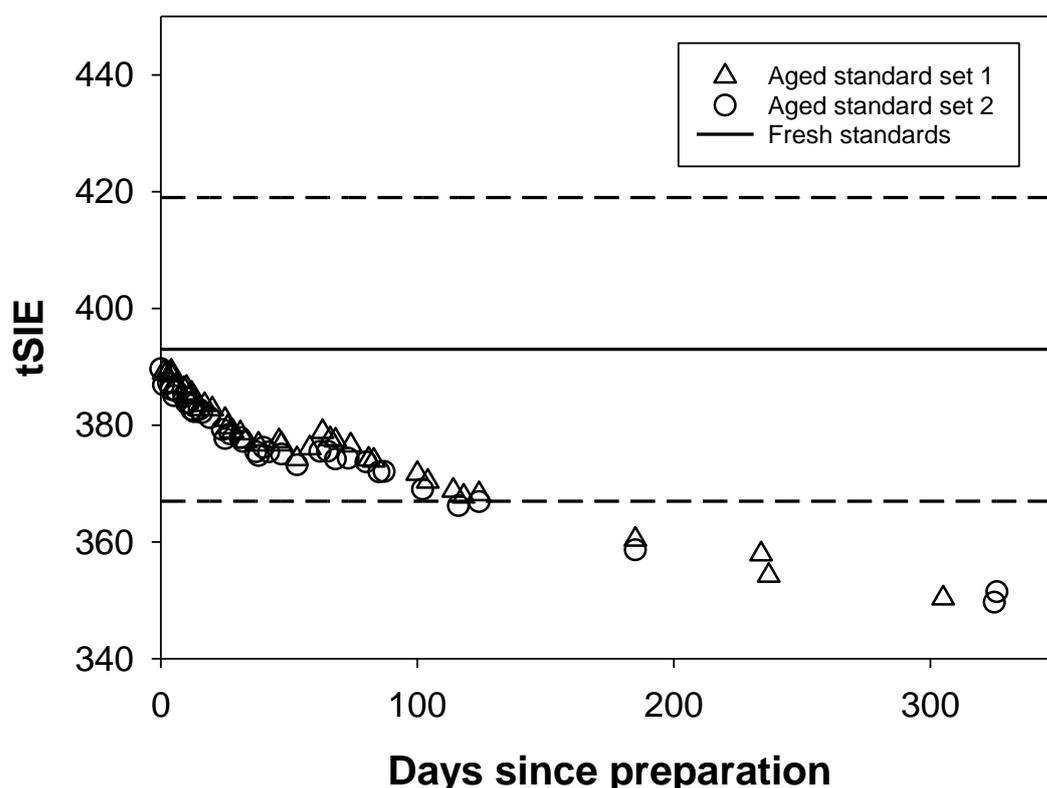


Figure 24 Average decrease in tSIE (increase in quench) relative to the number of days since cocktail preparation for 2 sets of 3 aged standards. Exponential decay functions have been fitted to data from each set of standards. The mean tSIE (solid line) and two times the standard deviation (dashed lines) for all freshly prepared standards is included to highlight the relative decrease in the aged standards.

The decrease in efficiency measured across the optimised count window (11–330 keV) for the aged standards may be a result of the increase in quench (ie – decrease in the tSIE value), though, as previously mentioned, the data showing that the efficiency in the ²¹⁰Pb count window is unaffected suggests an alternative explanation as increased quench would likely result in a reduced spectral endpoint for the ²¹⁰Pb peak (Passo and Cook, 1996).

The complexity of the optimisation techniques for this method limited the possibility of assessing the effect of quench in relation to DBB timing, AC timing, count window selection and the relative stage of ingrowth of ²¹⁰Bi and ²¹⁰Po. All but one of the freshwater mussel samples showed initial tSIE values within the same range as for the standards (one value of 283 was observed). These values decreased over time, with no apparent effect on the counting efficiency other than that observed previously for the aged standards (figure 25).

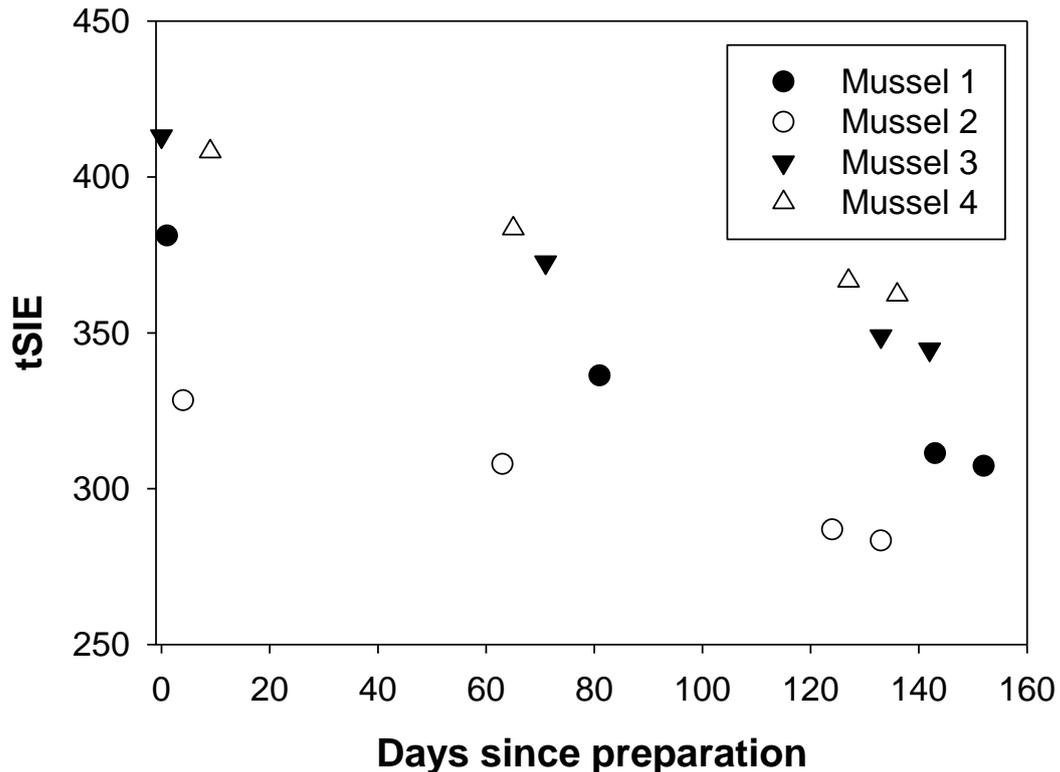


Figure 25 tSIE relative to the number of days since cocktail preparation for 4 mussels each counted 4 times up to 157 days after initial sample preparation.

The lowest tSIE value recorded for the freshwater mussel samples was 283, counted 133 days after initial preparation. As such, for samples with tSIE values of 283 or higher, quenching effects are not expected to have a noticeable effect on the relative efficiency. For samples with tSIE values below 283 caution should be exercised as the relative efficiency predicted may be higher than the actual efficiency for the measurement. Several steps can be taken to aid in the assessment of the potential effects of stronger quench, reflected by lower tSIE values, and these should be included as part of the ongoing quality control system when this method is introduced to the radiochemistry laboratory for routine analysis. These steps are:

- the use of certified reference materials (for example NIST seaweed SRM 4359)
- after initial counting, samples with high quench can be spiked with a calibrated ^{210}Pb solution and any difference in expected activity measured can be checked
- re-counting highly quenched samples using the Automatic Efficiency Compensation (AEC) function of the TriCarb 3100TR which can adjust the observed spectral endpoint of the quenched samples
- recording the peak shifts in quenched samples to improve count window optimisation for highly quenched samples.

5. Summary and Discussion

Development of a new technique for the measurement of ^{210}Pb in environmental samples in the *eriss* radiochemistry laboratory via LSC was undertaken for 2 main reasons:

- (1) To reduce separation chemistry and turnaround times for analysis as compared to the previous technique developed by Martin & Hancock (2004) and
- (2) because there were no suitable published methods that met the requirements of the environmental radioactivity research programs.

The requirements were a minimum detection limit of 4 mBq, reduced turnaround times, stable performance for different samples and the ability to store samples for longer periods after collection prior to analysis¹ (2–3 months). Desirable outcomes were also compatibility, with the current chemical separation technique used for ^{210}Pb (Martin & Hancock 2004), and with the scintillation cocktail UGAB which is currently used in the environmental radioactivity laboratory for another technique. All of these requirements/outcomes have been achieved with the method presented in this study.

Achieving the low limit of detection for the method was a particular focus as the instrument available for method development (a Tri-Carb 3100 TR) is not set up for very low-level counting. Optimisation of the time resolved settings, delay before burst (DBB) and anti-coincidence timing (AC), of the instrument were undertaken with an optimum DBB setting of 600 ns found. There was no significant difference found from varying the AC timing, and a setting of 50 ns was selected as a suitable setting for routine analysis. Count windows were optimised using the figure of merit parameter and 3 optimum windows suitable for different times after separation were found. A window at 11–22 keV is optimum up to 10 days after scintillation cocktail preparation, with a detection limit of 11 mBq per sample. A window at 11–330 keV was found to be optimum from 11 days to ~250 days, with detection limits decreasing over time but below 4 mBq from 11 days for a 2 day count time, slightly lower detection limits of ~3 mBq can be achieved with the 173–330 keV window after 300 days. Efficiencies of 73% for ^{210}Pb and 85% for ^{210}Bi were achieved. This compares to 65.7% for ^{210}Pb and 14.7% for ^{210}Bi from Blanco et al (2004). Kim et al (2001) achieved 73% for ^{210}Pb in the beta window using gross α/β discrimination to also measure ^{226}Ra . Biggin et al (2002) achieved efficiencies of 92% for ^{210}Pb and 89% for ^{210}Bi using a more recent model of the Tri-Carb series (a 3170 TR/SL) with a BGO guard. Biggin et al (2002) optimised the DBB timing setting and, as in this study, found the optimum value to be 600 ns, though the count windows were not optimised and the higher efficiencies can be explained in part by the use of a 0–40 keV window for ^{210}Pb and the full 0–2000 keV window for ^{210}Bi . As the instrument used in this study does not have a BGO guard to reduce the background, optimisation of the count windows was critical to ensuring the lowest possible limits of detection.

This report presents a suitable method for low-level analysis of ^{210}Pb , with reduced handling times and radiochemical separation techniques required compared to the previous method (Martin & Hancock 2004). With an L_D of 54 mBq for a 100 minute count time the method is also suitable for rapid analysis of ^{210}Pb in radiological emergency situations.

New laboratory methods detailing ^{210}Pb measurement techniques that have been introduced in this report are included in Appendix 1 and are also included in the radiochemistry laboratory procedures manual.

¹ Without this time delay as an option the dual ^{210}Po measurement technique for ^{210}Pb requires separation of initial ^{210}Po soon after collection and therefore all ^{210}Pb samples take priority over all others.

6. References

- Amr MA, Al-Saad KA & Helal AI 2010. Ultra-trace measurements of ^{210}Pb in natural occurring radioactive materials by ICP-MS. *Nuclear Instruments and Methods in Physics Research A*. 615, 237–241.
- Benedik L & Vrecek P 2001. Determination of ^{210}Pb and ^{210}Po in environmental samples. *Acta Chimica Slovenica*. 48, 199–213.
- Biggin CD, Cook GT, MacKenzie AB & Pates JM 2002. Time-Efficient Method for the Determination of ^{210}Pb , ^{210}Bi , and ^{210}Po Activities in Seawater Using Liquid Scintillation Spectrometry. *Analytical Chemistry*. 74, 671–677.
- Blanco P, Lozano JC, Gómez Escobar V & Vera Tomé F 2004. A simple method for ^{210}Pb determination in geological samples by liquid scintillation counting. *Applied Radiation and Isotopes*. 60, 83–88.
- Currie LA 1968. Limits for Qualitative Detection and Quantitative Determination: Application to Radiochemistry. *Analytical Chemistry*. 40, 586–593.
- Esparon A & Pfitzner J 2010. Visual gamma: *eriss* gamma analysis technical manual. Internal Report 539, December, Supervising Scientist, Darwin.
- Feng X-g, He Q-g, Wang J-c & Chen J 2012. The long-term stability on basic performances of a diisopropylnaphthalene-based liquid scintillation cocktail. *Applied Radiation and Isotopes*. 70, 1536–1540.
- García-Orellana I & García-León M 2002. An easy method to determine ^{210}Po and ^{210}Pb by alpha spectrometry in marine environmental samples. *Applied Radiation and Isotopes*. 56, 633–636.
- Holmes, I., 2004. Alpha-spectrometric analysis of environmental samples – spreadsheet approach. IAEA TECDOC-1401, IAEA, Vienna, 141–148.
- Jia, G., Belli, M., Blasi, M., Marchetti, A., Rosamilia, S., Sansone, U., 2000. ^{210}Pb and ^{210}Po determination in environmental samples. *Applied Radiation and Isotopes* 53, 115–120.
- Johannsen LY, 2008. Determination of Pb-210 and Po-210 in aqueous environmental samples. PhD thesis, Gottfried Wilhelm Leibniz Universität Hannover.
- Kim Y-J, Kim C-K & Lee J-I 2001. Simultaneous determination of ^{226}Ra and ^{210}Pb in groundwater and soil samples by using the liquid scintillation counter – suspension gel method. *Applied Radiation and Isotopes*. 54, 275–281.
- Kragten, J., 1994. Tutorial review. Calculating standard deviations and confidence intervals with a universally applicable spreadsheet technique. *Analyst* 119, 2161–2165.
- L'Annunziata M 2012. Handbook of Radioactivity Analysis, third ed. Elsevier, New York
- Lariviere D, Taylor VF, Evans RD & Cornett RJ 2006. Radionuclide determination in environmental samples by inductively coupled plasma mass spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy*. 61(8), 877–904.
- LNHB, 2013 Laboratoire National Henri Becquerel. Decay Data Evaluation Project. http://www.nucleide.org/DDEP_WG/Nuclides. Accessed 04 Sep 2013.
- Marten R 1992. Procedures for routine analysis of naturally occurring radionuclides in environmental samples by gamma-ray spectrometry with HPGe detectors. Internal report 76, Supervising Scientist for the Alligator Rivers Region, Canberra. Unpublished paper.

- Martin P & Hancock GJ 2004. Routine analysis of naturally occurring radionuclides in environmental samples by alpha-particle spectrometry. Supervising Scientist Report 180, Supervising Scientist, Darwin NT.
- Packard Instrument Company 1992. High throughput screening of samples containing alpha and beta radionuclides: An overview of methods. Alpha Beta Application Note ABA-005. Packard Instrument Company Meriden, CT.
- Packard Instrument Company 2015. The effect of quench on quantitating alpha radionuclides by liquid scintillation counting, alpha/beta, ABA-003. PerkinElmer TR-LSC™ Application Note
http://www.perkinelmer.com/pdfs/downloads/app_quenchquantalpharadionucl.pdf
accessed 12/11/2015. accessed: 12/11/2015.
- Passo JR, 2015. Time Resolved Liquid Scintillation Counting: (TR-LSC™) for Environmental 3H Analysis. PerkinElmer TR-LSC™ Application Note
http://www.perkinelmer.com/pdfs/downloads/app_trlsctimeresolvedliquidscintcounting.pdf
accessed: 21/10/2015.
- Passo Jr., C.J., Cook, G.T., 1996. Handbook of Environmental Liquid Scintillation Spectrometry. A Compilation of Theory and Methods. Packard Instrument Company, Meriden, USA.
- PerkinElmer 2001. Counting Solutions LSC Technical Tips (2002) Counting Aqueous Samples by LSC. PerkinElmer. CS-005.
- Supervising Scientist 2013. Annual Report 2012–13. Supervising Scientist, Darwin.
- Supervising Scientist 2014. Annual Report 2013–14. Supervising Scientist, Darwin.

Appendix 1 Laboratory Methods

 Australian Government Department of the Environment and Energy Supervising Scientist		SOP #	LSC01
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LSC01 – Liquid Scintillation Counting for ^{210}Pb

1. Purpose/ Scope

This procedure is used for the counting of sources for prepared for LSC determination of ^{210}Pb . This procedure follows from procedure [RLR12](#), starting after the completion of step 11 in section 3.2 Analytical Procedure.

1.2 Considerations prior to starting

The detection limits for ^{210}Pb determination via LSC are dependent on the relative stage of ingrowth of the daughter products ^{210}Bi and ^{210}Po . Where rapid determination of ^{210}Pb is required this method can be utilised immediately after chemical separation of Pb, with an adjusted count time. For samples where a lower detection limit is required a longer count time can be used (6 ks) and a minimum of 25 days should be allowed after separation before preparation of sources for LSC; the lowest detection limits can be achieved 33 days or more after separation of Pb.

2. Risks/Responsibilities

Strong acids are used in the preparation of sources for ^{210}Pb analysis via LSC, though these are thoroughly mixed with a scintillation cocktail when prepared for counting. The emulsion formed is very stable and poses a low risk to staff.

2.1 PPE

Minimum PPE is required in all laboratories. No specific PPE is required when handling sources prepared for LSC once they are ready for counting – care should be taken and gloves used if necessary due to leakage or spillage of the scintillant cocktail.

2.2 Other considerations

Any waste organic chemicals (ie – UGAB) generated must be stored in a designated container for the storage of this waste. The designated container must be registered in the most recent ‘Time sensitive chemical and organic waste register’, and a required disposal date recorded (by default this is 12 months unless otherwise specified) in this logbook.

Disposal dates (again the default is 12 months) must also be recorded for samples prepared with UGAB, this is recorded in the ‘LSC ^{210}Pb – Method batch log’ logbook (form S6).

3. Procedure

3.1 Equipment/Apparatus preparation

TriCarb 3100TR liquid scintillation counter (TriCarb)

Racks for use in the TriCarb

3.2 Counting Procedure

- 1) Select a rack and a protocol flag to use for counting, attach the protocol flag to the rack (see the reference manual – PerkinElmer, 2004 – for details)
- 2) Place all samples in the rack and note the position of each sample on the rack, the counting order is from left to right

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- 3) Push the protocol flag to the left as far as it will go to ensure the rack is recognised as requiring counting then close the lid on the TriCarb
- 4) Open the QuantaSmart program on the computer attached to the LSC (the LSC computer), the homescreen will look similar to the display shown in Figure 1, depending on the source being counted at the time

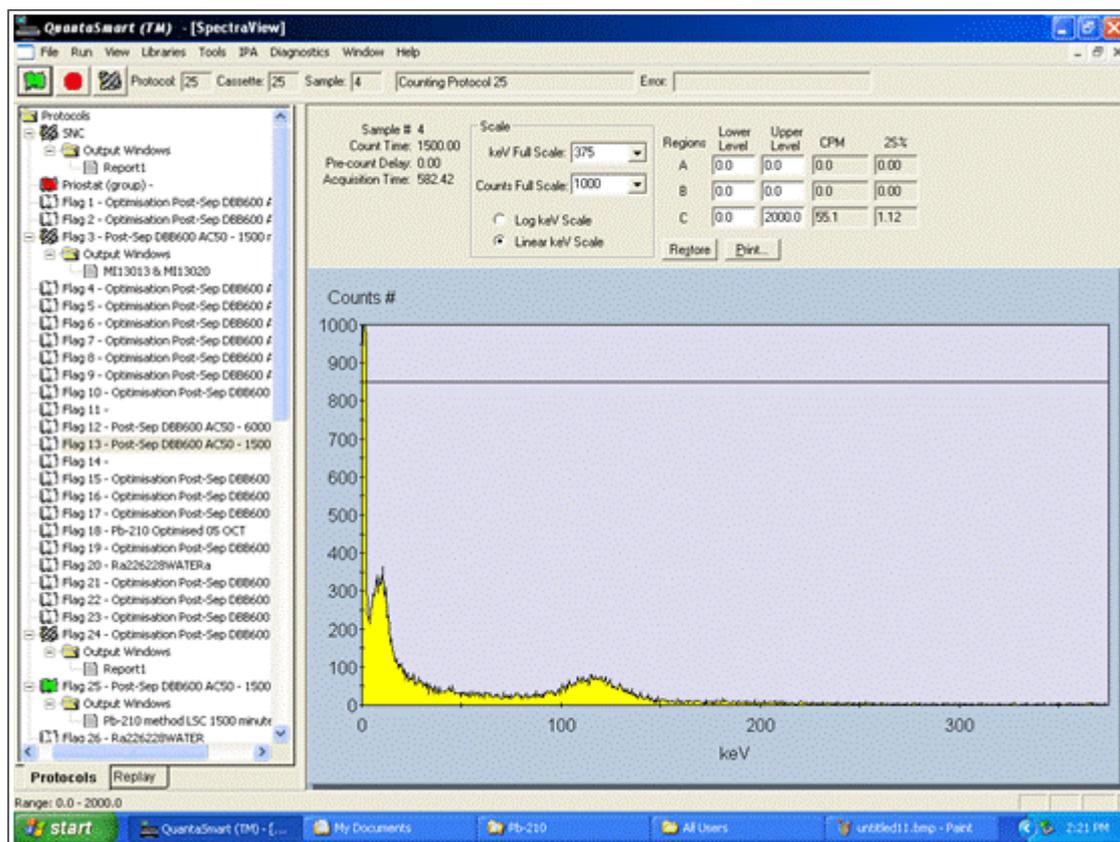


Figure 1 Home page screen for the QuantaSmart program on the TriCarb

- 5) Select the flag number for the rack that is being used, in this example flag 13 is used (figure 2a), then right click to bring up a dialog box and select 'Associate Assay' (figure 2b). A new dialog box will appear, scroll through to select the assay to be used then click on 'Open'. For this method there are 2 assays set up for routine analysis, these are 'Post-Sep DBB600 AC50 – 1500 minute count.lsa' and 'Post-Sep DBB600 AC50 – 6000 minute count.lsa'. These 2 assays use the same count conditions but different count times – counting for approximately 1 day or 4 days. In this example the assay with a 1500 minute count time is selected (figure 2c).
- 6) Once the assay is associated with the selected flag the program will open a 'Data Paths' dialog box on the home screen (figure 3). From this screen select your User ID from the dropdown list and enter an additional header for the assay if desired (for routine analysis the 'Additional header field is left blank), then click 'OK'.



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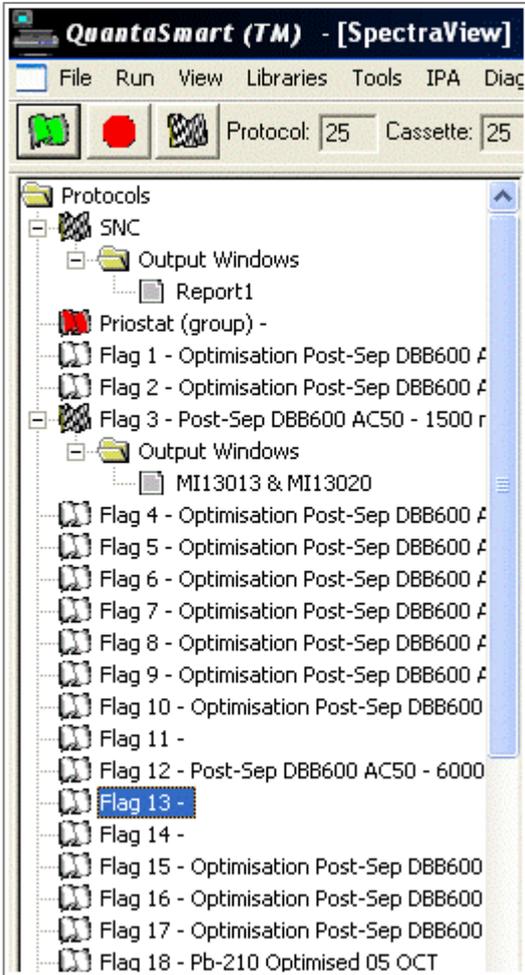


Figure 2a

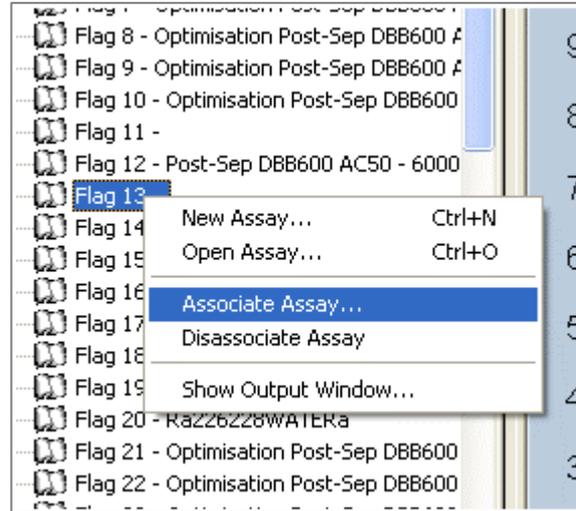


Figure 2b

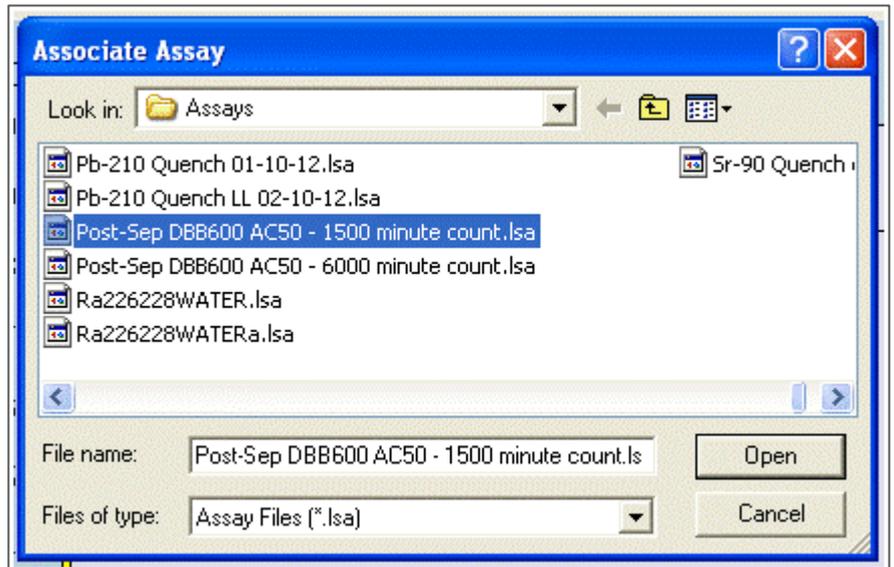


Figure 2c

Figures 2a to 2c Selecting the flag for counting and associating an assay

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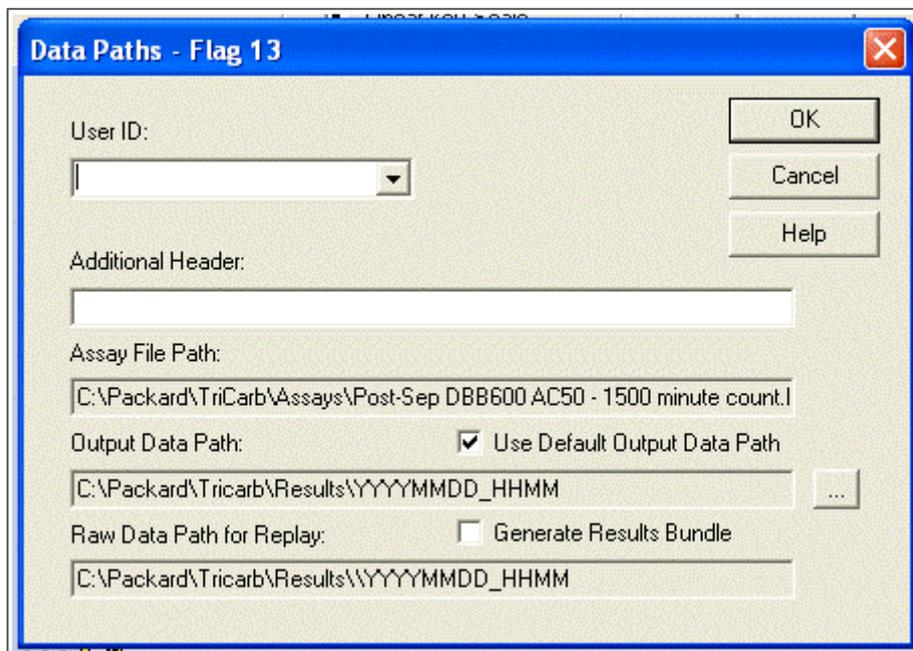


Figure 3 Enter User ID details and additional information about the assay

- 7) Once the assay is associated with the selected flag and the User ID is entered the program will return to the home screen (figure 1). Double click on the selected flag (eg – flag 13), to open the Assay Definition tab (figure 5). Note that if the assay is currently in use (ie – there are samples being counted using that protocol) a dialog box will appear stating that only changes to ‘Count Time a 2 Sigma%’ (figure 4) – select OK if this is acceptable, if not, a new assay will need to be created.

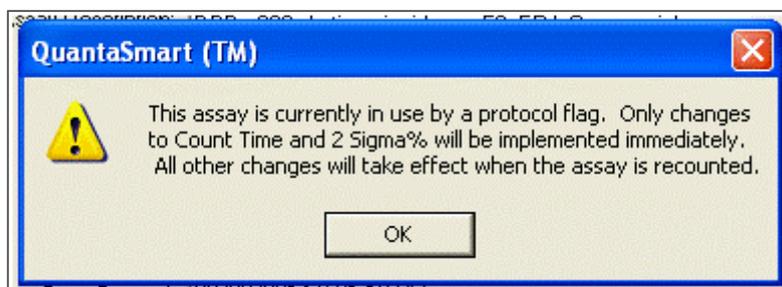


Figure 4 Dialog box information when an assay currently in use is opened

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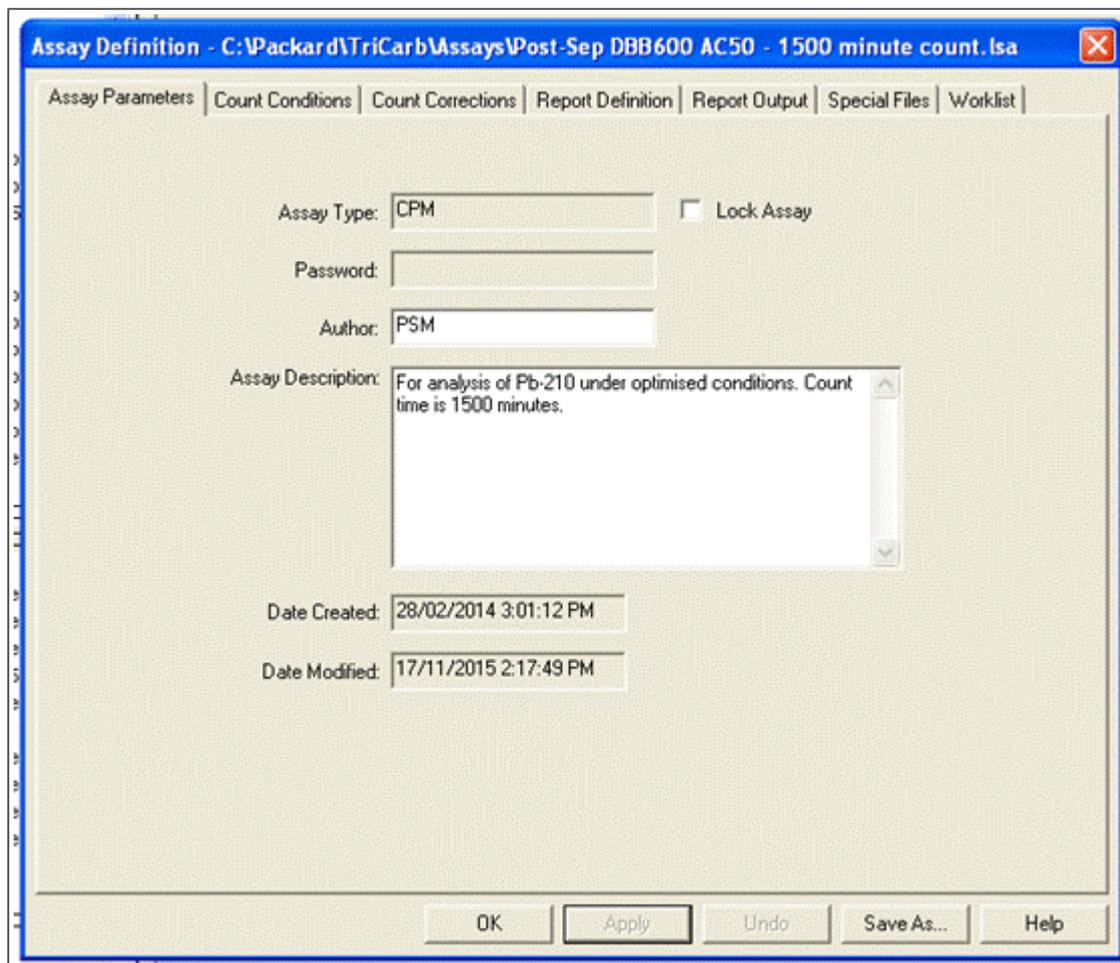


Figure 5 Dialog box information when an assay currently in use is opened

- 8) Enter in further details in the Assay description text box in the Assay Parameters tab if required
- 9) Open the Worklist tab (figure 6) and enter in details of the samples to be counted
 - a. The PID is the flag number (eg – 13 or 25)
 - b. The sample number is the position in the rack – number 1 is the sample position on the far left of the rack
 - c. Sample Name is the unique 7 digit code assigned to the count source by method ASA07 plus the count number, eg – LSC0024.02 is the second count for a source with count source ID LSC0024.

NOTE: For routine analysis changes should only be made to the Assay description text box in the Assay Parameters tab and the sample details in Worklist tab.

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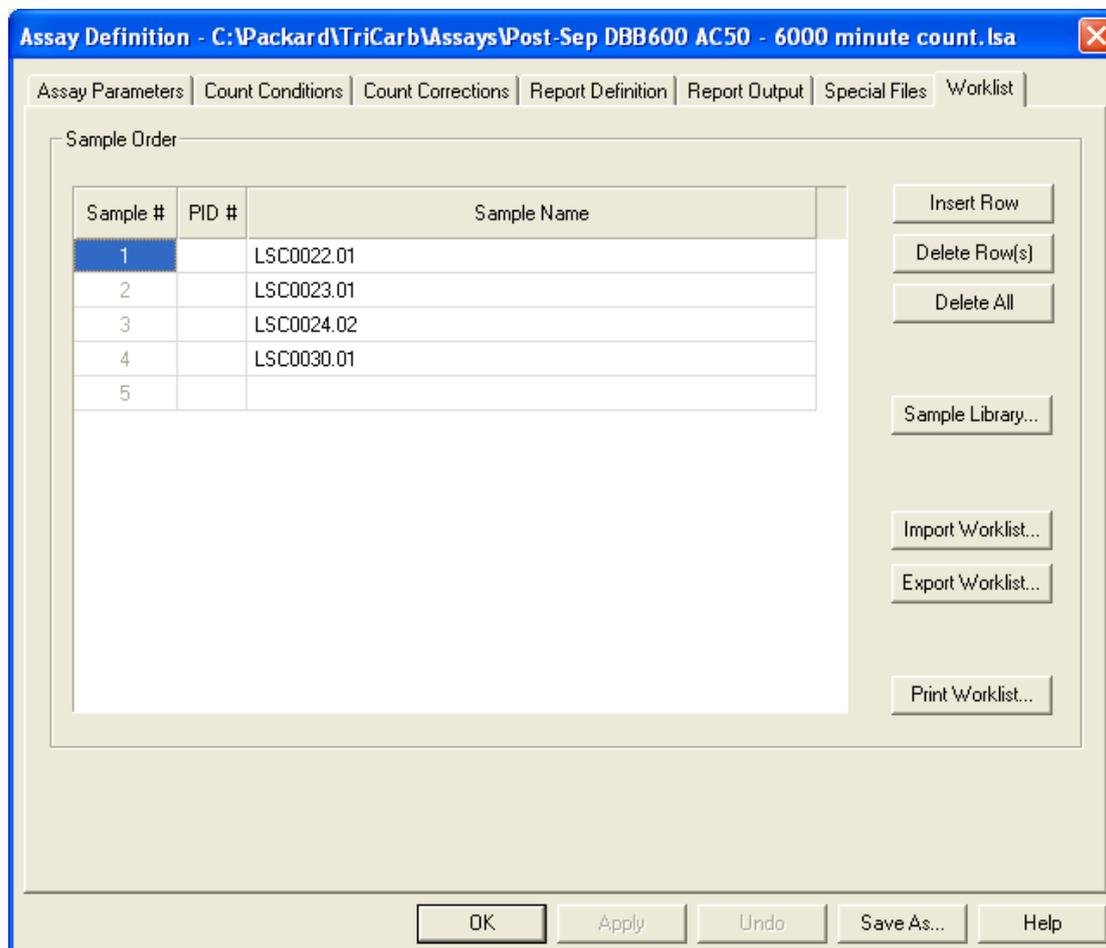


Figure 6 Worklist tab for entering sample details

- 10) Select 'Apply' then select 'OK' from the buttons at the bottom of the Assay Definition tab (highlighted in figure 7), after selecting 'OK' the program will return to the home screen. **NOTE:** If 'Apply' is not selected first then any changes made will not be saved



Figure 7 The 'Apply' and 'OK' buttons at the bottom of the Assay Definition tab

- 11) Start counting the selected flag by selecting the green flag button at the top left of the home screen (figure 1). When the green flag is selected, all protocols with the flag protocol pushed to the left will be counted in order. The SNC (Standardisation/Normalisation/Calibration) standards will automatically be counted if it has been more than 35 hours since they were last counted, these should not be removed from the LSC if it can be avoided.
- 12) When counting has finished use method **CRR05** to calculate the activity concentration of ²¹⁰Pb in the sample

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3.3 Disposal of organic waste

Holding times for samples or standards prepared for ^{210}Pb analysis via LSC are routinely 12 months after the preparation date unless otherwise specified. The disposal date is recorded in the 'LSC ^{210}Pb – Method batch log' logbook (form S6), including all blanks. When the disposal date is approaching follow this method to prepare the samples for disposal. Prior to combining any potentially radioactive organic waste, refer to the Radiation Safety Officer for advice on disposal.

- 1) Locate a pre-labelled glass bottle (if available) by checking the 'Time Sensitive Chemical and Organic Waste Register' (form L7). For a current LSC waste disposal container. If unavailable, prepare a new pre-labelled glass bottle using the label 'LSC Acid-OrganicWaste (UGAB, Ethanol, Hydrochloric and Phosphoric acids)', located on SPIRE at:

Supervising Scientist\Management and Administration\Laboratory and Sample Management\Manuals and Procedures\EnRad – Procedure Manual – Current Procedures and Signs

For newly prepared waste bottles the disposal date to be recorded in the 'Time Sensitive Chemical and Organic Waste Register' should be the earliest disposal date of any sample that is combined in the bottle. Bottles prepared for disposal of waste from this method **[LSC01]** are also suitable for waste generated from method **[LSC02]**.

- 2) In the pre-labelled glass Winchester empty the contents of the LSC vial.
- 3) Triple rinse the vial with 60% Ethanol and empty the rinses into the pre-labelled glass bottle
- 4) Combine as many samples as will reasonable be able to fit into the labelled bottle
- 5) Arrange for disposal of the combined organic waste via a licensed chemical waste disposal contractor

5. References

PerkinElmer 2004. QuantaSmart™ for the TriCarb Liquid Scintillation. PerkinElmer. Reference Manual.

6. Definitions

LSC Liquid Scintillation Counting/Counter

SOP Standard Operating Procedure