

THE DETERMINATION OF ^{234}Th IN OCEANIC TRACER STUDIES BY LIQUID SCINTILLATION SPECTROMETRY EMPLOYING α/β SEPARATION TECHNIQUES

J. M. PATES, ROBERT ANDERSON, G. T. COOK and A. B. MACKENZIE

Scottish Universities Research and Reactor Centre, East Kilbride, G75 0QU, Scotland

ABSTRACT. ^{234}Th has considerable potential for investigating a range of important marine processes, including euphotic zone production rates, nearshore scavenging processes, particle fluxes and sediment reworking rates. Our previous work demonstrated that ^{234}Th measurement by liquid scintillation spectrometry (LSS) using a ^{230}Th yield tracer is a significant improvement over more traditional methods. These require the ^{234}Th to be measured by end-window beta counting or gamma spectrometry and ^{230}Th by alpha spectrometry. Traditional techniques also require intercalibration of the ^{234}Th and ^{230}Th analytical methods, more rigorous chemistry and larger samples than necessary for the LSS method, which has higher counting efficiencies and requires only one count. One disadvantage is the spectral overlap between the β spectrum of ^{234}Th (in equilibrium with $^{234\text{m}}\text{Pa}$) and the α spectrum of ^{230}Th , thus requiring crossover calculations. We present results here of an adaptation to the method using techniques to discriminate the α from β events on the basis of pulse shaping, thus removing the crossover calculations. We discuss results in relation to limits of detection, improvements in precision and minimum sample size requirement.

INTRODUCTION

Uranium and thorium have markedly differing solubilities in seawater under oxidizing conditions. U is relatively soluble as an anionic carbonate complex of the uranyl ion, whereas Th is highly insoluble and susceptible to removal by such processes as hydrolysis, sorption and scavenging by oxyhydroxide precipitates. The disequilibrium induced between ^{234}U and ^{230}Th has been recognized as a means of estimating sedimentation rates (Ku 1976; Kadko 1980); ^{230}Th is produced by decay of ^{234}U from a constant U concentration in seawater, and is removed relatively rapidly from the water column to sediments, principally by sorption, onto settling particles. This results in an excess of ^{230}Th in sediment over that which is supported by *in-situ* ^{234}U . In the simplest situation, we assume that excess ^{230}Th decays exponentially as a function of time, and this can be related directly to sediment depth. The relation between time and depth of sediment may be computed from a best-fit linear function of $\ln(^{230}\text{Th}_{(\text{excess})})$ versus depth. This method assumes steady-state conditions for both the supply of $^{230}\text{Th}_{(\text{excess})}$ and all other sedimentary components. More recently, the technique has been applied to non-steady-state situations. In this instance, the $^{230}\text{Th}_{(\text{excess})}$ serves as an indicator of past periods of enhanced bioproductivity. The ^{230}Th must be decay-corrected to initial values by using an independent chronology, such as ^{14}C (De Master 1981; Scholten *et al.* 1990).

In addition to ^{230}Th , the short half-life isotope, ^{234}Th , has considerable potential for investigating other processes, *e.g.*, particle fluxes and reworking at the deep-sea floor, the demonstration of a stratification in the euphotic zone, euphotic zone production rates and nearshore scavenging processes (Coale & Bruland 1987; De Master *et al.* 1985; Aller & De Master 1984; Tanaka, Takeda & Tsunogai 1983). However, significant difficulties are associated with the analyses: ^{234}Th is a weak beta emitter ($E\beta_{\text{max}} = 190 \text{ keV}$), which decays with a 24.1 day half-life to its daughter, $^{234\text{m}}\text{Pa}$, which emits energetic β particles ($E\beta_{\text{max}} = 2.33 \text{ MeV}$), and has a half-life of 1.17 min. Thus, $^{234\text{m}}\text{Pa}$ is generally present in secular equilibrium during the ^{234}Th analyses. The conventional approach to its analysis in seawater has been to collect and filter samples of 30–40 liter volume. For analysis of the dissolved fraction, the seawater is then spiked with a ^{230}Th (alpha emitter) yield tracer, equilibrated and co-precipitated with $\text{Fe}(\text{OH})_3$. The precipitate is then collected, dissolved in HCl and the Th isotopes separated by anion exchange. This is followed by electrodeposition of the near weightless source onto a stainless steel or platinum planchette. The ^{230}Th activity is deter-

mined using a calibrated silicon surface barrier or passivated implanted planar detector; $^{234}\text{Th}/^{234\text{m}}\text{Pa}$ activity is determined by calibrated gas-flow proportional counting. Major limitations in this methodology are that both counting systems are $2\text{-}\pi$ geometries and require intercalibration. An alternative approach is to use low-level liquid scintillation spectrometry (LSS) (Anderson *et al.* 1991), which has several advantages: 1) much higher detection efficiencies and consequently, shorter counting times; 2) simultaneous counting of the ^{230}Th and $^{234}\text{Th}/^{234\text{m}}\text{Pa}$; and 3) simpler separation and source preparation techniques may be employed. We developed this initial method using a Packard 2000CA/LL. Two disadvantages are: 1) the spectral overlap between the $^{234\text{m}}\text{Pa}$ and the ^{230}Th yield tracer makes the calculation of individual contributions in this overlap area an absolute requirement; and 2) when using the burst counting circuitry (BCC) feature to reduce background, one loses some β efficiency and even more α efficiency. The latter means that some degree of over-spiking with yield tracer is required.

A more elegant approach is to use LSS with α/β separation capabilities. Thus, in theory, the α events should be sent to one multichannel analyzer (MCA) and the β events to a second, obviating the need for overlap calculations. The α events will be detected at near 100% counting efficiency, and the β counting efficiency will also be relatively high since BCC is not used; however, because BCC is not used, background count rates in the β MCA may be significant.

Initially, we developed this α/β method using a Packard 2250CA/AB, and later continued with a Packard 2550TR/AB. The latter has features that simplify and enhance the technique: 1) the optimum pulse-decay-discrimination (PDD) time setting can be calculated automatically; and 2) BCC can be used on β -classified events, thereby reducing background. On the 2000 and 2200 series instruments, BCC has a fixed delay of 75 nsec after initiation of the prompt pulse, whereas the 2500 series instruments have a variable delay. We have already shown (Cook & Anderson 1993) that this feature can improve the limits of detection for ^{14}C , using a cocktail not really suitable for this type of instrument. Following the separation of α from β activity, this feature could conceivably allow us to carry out further pulse-shape analyses on β -classified events to remove some of the background component without significantly reducing the β efficiency.

METHODS

Isolation of ^{230}Th and ^{234}Th for α/β Standards and Yield Tracer

We performed the isolations by ion exchange separation as described previously (Anderson *et al.* 1991). Briefly, for ^{230}Th , we isolated Th from a mineralized U nodule in which the ^{238}U decay chain was in equilibrium, at least to the ^{230}Th member, and the ^{232}Th content was below the limit of detection. The Th fraction was retained in dilute nitric acid with aluminum carrier for >2 yr. This aging ensures the decay of ^{227}Th , ^{231}Th and ^{234}Th and the succeeding daughters in the respective decay chains to a negligible level of activity (Fig. 1). We also retained the U fraction; aging for a similar period allows ^{234}Th to reach secular equilibrium with ^{238}U . The ^{230}Th activity is negligible because of the relatively long half-lives of both ^{230}Th and its parent, ^{234}U . Therefore, this provides a source of ^{234}Th free from ^{230}Th . Following the isolation of ^{234}Th from ^{238}U , we allow several days' aging before use. During this time, ^{231}Th , formed from ^{235}U (also present in the U fraction), decays to a negligible level.

Liquid Scintillation Counting of ^{230}Th and ^{234}Th Using α/β Separation

The degree of separation of α from β events depends greatly on cocktail composition. For this study, we used a cocktail developed specifically for this type of work (Cocktail 07A) (Pates *et al.* 1993). We set up two 7-ml glass vials, as follows, to determine the percentage misclassification

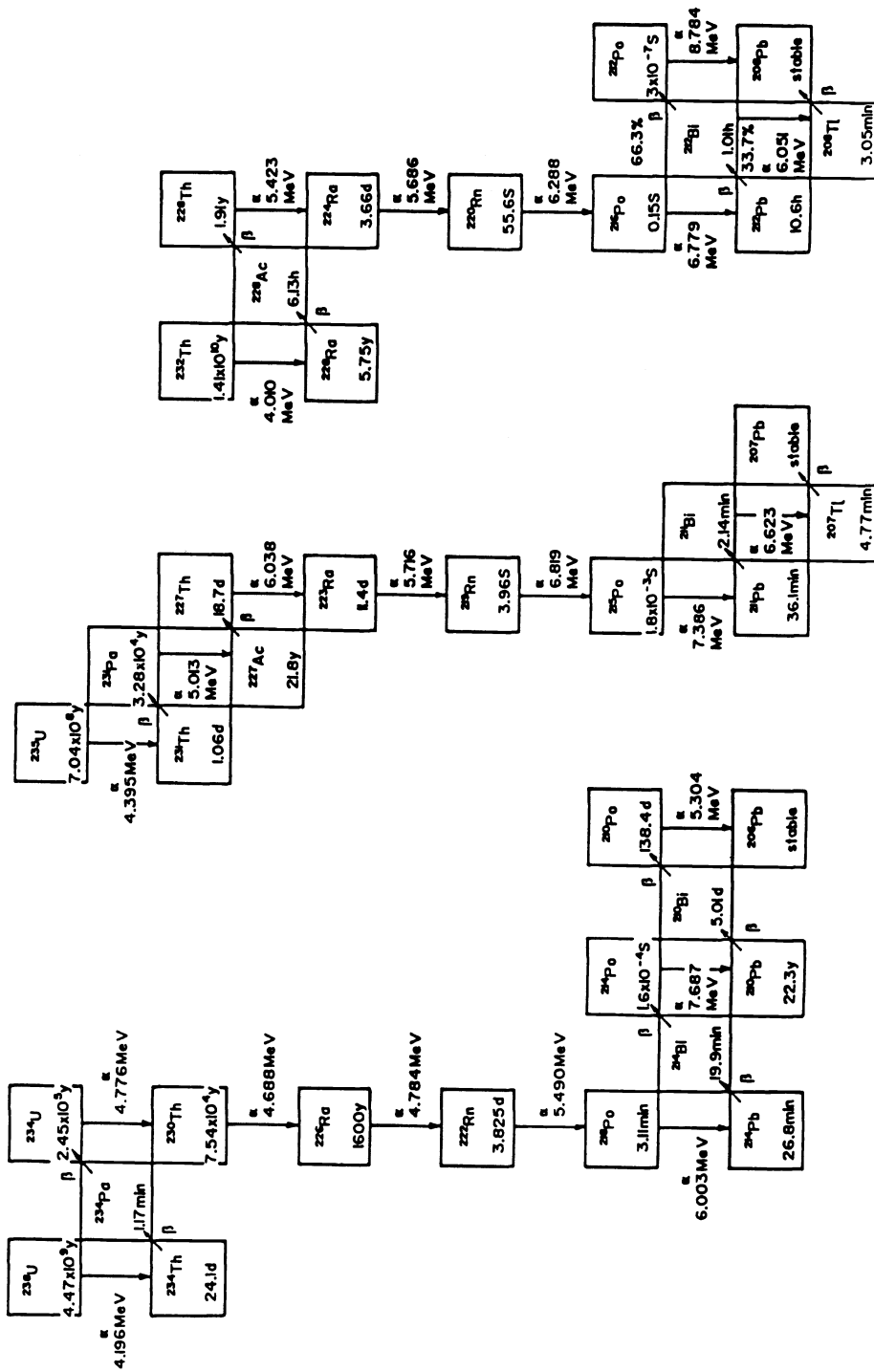


Fig. 1. Natural decay series (branching schemes)

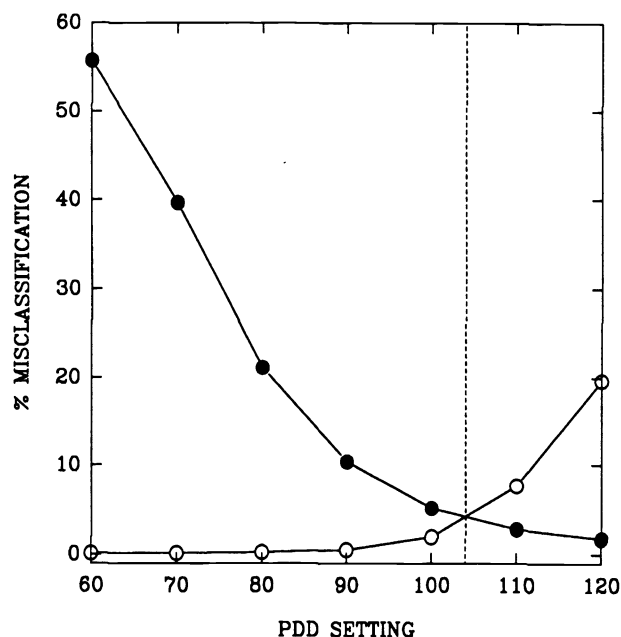


Fig. 2. Misclassification curve for ^{230}Th and ^{234}Th using a Packard 2550TR/AB. --- = the computed optimum PDD setting, at which the spillover from α to β MCA is 3.57%, and from β to α MCA is 3.92% for the 0–2000 keV window. \circ = α in β MCA; \bullet = β in α MCA.

of events: Vial 1 contained $^{234}\text{Th}/^{234\text{m}}\text{Pa}$ in 0.5 ml of 0.1 M HCl and 5 ml of Cocktail 07A; Vial 2 contained ^{230}Th in 0.5 ml of 0.1 M HCl and 5 ml of Cocktail 07A. We calculated optimum misclassification in the Tri-Carb® 2550TR/AB by programming the PDD time-setting range to be studied and the number of points within that range. Figure 2 shows these results.

Seawater Analysis

We collected replicate 20-liter samples of seawater from the River Clyde estuary on the west coast of Scotland and determined the ^{238}U content by ICP-MS to be 2.27 dpm liter $^{-1}$. In seawater, U exists principally as the dissolved $\text{UO}_2(\text{CO}_3)_3^{4-}$ species, and is relatively unreactive to particle sorption (Hodge, Koide & Goldberg 1979). As a result, U is conservative in seawater, so that its concentration varies with salinity, and can be calculated indirectly from: ^{238}U (dpm liter $^{-1}$) = 0.07081 \times salinity) (Coale & Bruland 1985). For open ocean water (salinity = 35‰), the ^{238}U content is 2.5 dpm liter $^{-1}$. Back-calculation of our ^{238}U value yields a salinity of ca. 28‰, which is typical for this area.

Upon returning to the laboratory, we filtered the samples using a 0.2 μm membrane filter and adjusted the pH to ~ 2 by adding 50 ml of concentrated HCl, and then added 50 dpm of ^{230}Th . At this stage, we analyzed one sample; the remaining four were left for varying periods of time to allow different degrees of ^{234}Th ingrowth. Because we obtained these samples from a near-shore environment with a high suspended inorganic flux and high productivity, it is reasonable to assume that virtually all the ^{234}Th had been removed from solution by adsorption on suspended material. The analysis consisted of the following: adding 500 mg of ferric chloride hexahydrate as a scavenger, followed by stirring, and then adding ammonia to raise the pH to 9, with further stirring to maximize the recovery. We allowed the ferric hydroxide precipitate to settle, then filtered it. We dissolved the precipitate in 9 M HCl and passed it through a Bio-Rad AG 1 \times 8 chloride form column to remove Fe and U. We then reduced the eluate containing Th to a few ml, made the volume to 20 ml with water, and added 50 mg of hydrated aluminium nitrate. We then raised the pH with ammonia and centrifuged the sample to bring down the aluminium hydroxide precipitate

containing the Th. We then washed the precipitate with de-ionized water and repeated the process to remove all traces of chloride. We redissolved the precipitate in 8 M HNO_3 , and passed it through a column of the nitrate form of the Bio-Rad resin. The Th was retained on this column, and after suitable washing with 8 M HNO_3 , we eluted it with 9 M HCl. We took the volume almost to dryness and transferred the Th quantitatively to a 7-ml glass scintillation vial. We then dried the Th completely and added 0.5 ml of 0.1 M HCl, followed by 5 ml of Cocktail 07A.

We prepared appropriate background vials using 0.5 ml of 0.1 M HCl and 5 ml of cocktail. We dispensed aliquots of ^{230}Th yield tracer into vials, which we then dried and prepared for counting as above. These were used to determine the counting efficiency in the α MCA. We determined ^{234}Th counting efficiencies in the β MCA using a known activity of ^{238}U in equilibrium with ^{234}Th , following the same chemical procedure as the samples, obviously without the initial large-volume scavenging step. We then counted all vials for 200 min at the optimum PDD setting. We set counting windows of 10–140 keV for ^{234}Th in the β MCA and 140–300 keV for ^{230}Th in the α MCA.

RESULTS

Figure 2 shows the optimum misclassification for the 2550TR/AB and a 3.57% spillover of α events into the β MCA and 3.92% of β events into the α MCA. These misclassification values are higher than expected, based on earlier work performed on the 2250CA/AB using ^{238}Pu and $^{90}\text{Sr}/^{90}\text{Y}$, which have similar energy distributions. This may be due, in part, to Pa following the U chemistry (we are investigating this) and to differences in the two instruments that we have used. The 2550TR/AB has no facility for background subtraction in its misclassification routine, whereas we carried out the entire calculation manually, including background subtraction, in the 2250CA/AB. However, these misclassification values are for 0–2000 keV. For ^{230}Th in the selected α window (140–300 keV), only 0.9% of the α events are misclassified; this has an almost negligible effect on counting efficiency, and the misclassified events go into a part of the β MCA that is not used in the analysis. No ^{230}Th counts appear in the 10–140 keV region (β window used in the analysis). For ^{234}Th in the 10–140 keV window, 5.4% of the total number of events are misclassified into the α MCA, and the β counting efficiency will be reduced by this amount. Again, however, the misclassified events appear in a part of the α MCA that is not used in the ^{230}Th determination. Also misclassified into the α MCA are 11.3% of the β events in the 140–300 keV window. Here, the misclassification is relevant, as these events are included with those from the ^{230}Th yield tracer and will give an inaccurate yield determination. However, this misclassification represents only 1.4% of the total β activity in the 0–2000 keV window of the β MCA.

By adding 50 dpm of ^{230}Th yield tracer to 20 liter of seawater with a maximum 2.5 dpm liter⁻¹ of ^{234}Th (*i.e.*, 50 dpm total activity), 1.4% will be the maximum error introduced; of course, with samples where ^{234}Th scavenging has occurred, the error will be smaller. Also, the shape of the spectrum of misclassified events suggests that true α activity may be present from the decay products of ^{231}Pa , and the actual error in real samples will be less where ^{231}Pa is virtually absent from the water column. The results presented in Figure 3 demonstrate the relation between the measured ^{234}Th activities and the theoretical ingrowth. Using the equation of the best-fit line through the data, we calculate a value of 2.19 dpm liter⁻¹ at the theoretical maximum of 2.27 dpm liter⁻¹. The intercept on the x-axis is -0.2 dpm liter⁻¹, indicating $\sim 90\%$ removal of ^{234}Th from seawater in the estuary.

Table 1 shows the effect on ^{234}Th counting efficiency of increasing the burst delay. By introducing the BCC with the normal delay of 75 nsec, the relative counting efficiency in the 0–140 keV win-

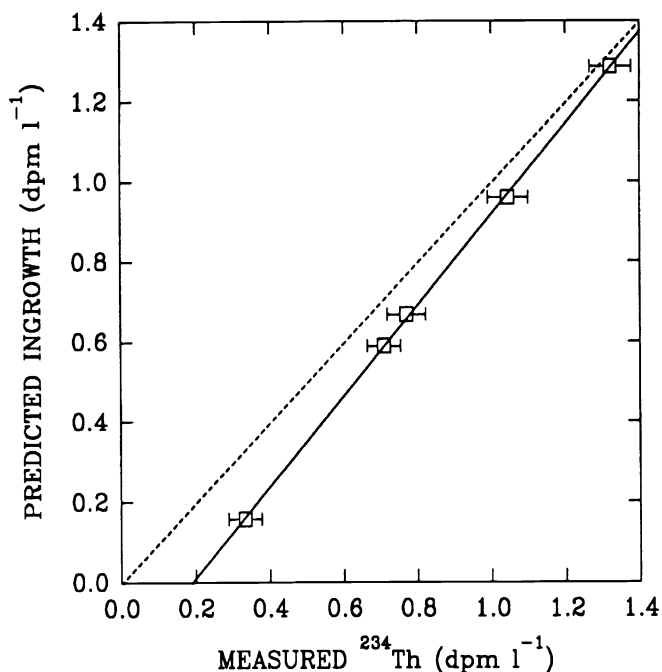


Fig. 3. Measured vs. predicted ingrowth of ^{234}Th . --- = predicted; — = measured; the dashed line indicates the theoretical ingrowth (with the assumption of zero ^{234}Th at t_0). The solid line indicates the best fit through the results. Note that this line is tending towards the dashed line and should intercept it at 2.27, which is the maximum ^{234}Th activity in dpm liter^{-1} that can be supported by the ^{238}U .

dow is massively reduced, and, despite a >3-fold reduction in background, the relative E^2/B factor is significantly reduced. However, relative efficiency is more than doubled by applying a delay of 400 nsec. This has the effect, despite some increase in background, of increasing the relative E^2/B factor to a value significantly greater than when the BCC is disabled, or when BCC and the standard 75 nsec delay are invoked. Increasing the delay beyond 400 nsec causes no further increase in E^2/B .

TABLE 1. Effect of Increasing the Burst Delay on ^{234}Th Efficiency and Background Following α/β Separation

BCC	Delay (nsec)	Fraction of cpm in 0–140 keV window, BCC off	Background (cpm)	Relative E^2/B (cpm) $\pm 2\sigma$
Off	N/A	1	21.23	471 \pm 20
On	Normal	0.418	6.07	288 \pm 16
On	400	0.875	9.61	797 \pm 36
On	600	0.923	10.73	794 \pm 34
On	800	0.938	11.11	792 \pm 34

CONCLUSIONS

Our results demonstrate the potential of α/β separation LSS for measuring ^{234}Th in oceanic water column studies. The advantages of this over the traditional methods are: 1) simpler preparative chemistry; 2) both the ^{234}Th and its yield tracer (^{230}Th) can be measured in a single count on equipment employing automatic sample changing; and 3) counting efficiencies are much higher, making possible determinations on much smaller samples. ^{234}Th measurements are entirely possible

on 5-liter samples by this method. The advantages of the α/β separation technique using the Packard Tri-Carb® 2550TR/AB over the standard LSS method are: 1) no spectral overlap calculations are required. The results can simply be calculated from a 10–140 keV window in the β MCA and a 140–300 keV window in the α MCA; 2) using the delay-before-burst feature halves background, losing only about 10% of the relative efficiency. This has the overall effect of lowering the detection limit for a 200-min count from 0.63 dpm to 0.49 dpm total ^{234}Th activity.

Several factors require more investigation. These include: 1) optimizing the cocktail/acid ratio to improve the α/β separation; 2) possible improvements in the α/β discrimination circuitry; 3) removal of possible contaminant ^{231}Pa from ^{238}U , used as a source of ^{234}Th ; and 4) fully optimizing the delay-before-burst feature.

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