

The Determination of ^{234}Th in Water Column Studies by Liquid Scintillation Counting

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INTRODUCTION

As a result of the pronounced differences in their geochemical properties, uranium and thorium exhibit markedly different solubilities in seawater under oxidizing conditions. Uranium is relatively soluble in seawater, with an average open ocean ^{238}U concentration of 0.04 Bq l^{-1} ($3.2 \mu\text{g}^{-1}$) and it exists as an anionic carbonate complex of the uranyl ion. In contrast, ^{232}Th is highly insoluble in seawater, with a concentration of about $2 \times 10^{-7} \text{ Bq l}^{-1}$ ($6 \times 10^{-5} \mu\text{g l}^{-1}$) and it is highly susceptible to removal from solution by hydrolysis or by sorption on, and incorporation in, particulate material. Similarly, thorium isotopes produced *in situ* in seawater by decay of soluble parent radionuclides also have a very short residence time in solution. The resulting situations of radioactive disequilibrium which develop in the marine environment, eg., between ^{230}Th and ^{234}U , (members of the ^{238}U decay series shown in Figure 1), have long been recognized as a means of investigating the rates and mechanisms of a variety of oceanographic processes. For example, the systematics of $^{230}\text{Th}/^{234}\text{U}$ disequilibria have been used in the development of oceanic sediment chronologies,^{1,2} investigation of uranium diagenetic chemistry and mobility in sediments,^{3,4} and study of the efficiency of particulate scavenging of thorium and protactinium in different areas of the oceans.⁵⁻⁷

In recent years, however, it has become apparent that the short-half-life ^{234}Th (Figure 1) also has considerable potential for investigating the rates of a range of important marine processes; $^{234}\text{Th}/^{238}\text{U}$ disequilibrium has been used to investigate open ocean euphotic zone productivity rates,⁸ nearshore scavenging processes,^{9,10} and particle fluxes and reworking rates in deep ocean sediments.¹¹

^{234}Th is therefore an extremely useful natural radio-tracer. There are, however, difficulties associated with its analysis; it is a weak β -emitter ($E_{\beta\text{MAX}} = 190\text{keV}$), it gives rise to a daughter nuclide, $^{234\text{m}}\text{Pa}$, which is also a β -emitter ($E_{\beta\text{MAX}} = 2.33 \text{ MeV}$), and it has a half life of 1.17 minutes. $^{234\text{m}}\text{Pa}$ is generally

present in secular equilibrium with ^{234}Th during its analysis. The conventional approach to the analysis of ^{234}Th concentrations in seawater involves spiking the filtered sample (typically of volume $\sim 40\text{L}$) with ^{230}Th as a yield tracer, scavenging the thorium from solution by coprecipitation with ferric hydroxide, redissolution and extraction of the thorium by anion exchange separation, electrodeposition of the thorium on a planchette, and measurement of the combined ^{234}Th plus $^{234\text{m}}\text{Pa}$ activity using a G.M. or proportional counter. The ^{230}Th activity is subsequently determined by alpha spectroscopy using a surface barrier detector. The limitation on detection efficiency using these 2π counting systems is one of the main factors affecting the sensitivity of this analysis, and the method also requires intercalibration of the alpha and beta counting systems.

Gamma spectroscopy analysis of ^{234}Th using its gamma photon of energy (63.2 keV) offers an alternative method of determining ^{234}Th concentrations, but the intensity of 2.5% for this decay mode, in conjunction with the low efficiency of gamma photon detectors, gives rise to a relatively low sensitivity for this method (e.g. typical detection efficiency using a 130 cc Ge (Li) detector = 0.5%).

Modern liquid scintillation counters offer a highly attractive alternative for the analysis of ^{234}Th in that much higher detection efficiencies can be obtained and simpler chemical separation and source preparation techniques can be employed. The low-level analysis capability now routinely available with modern liquid scintillation counters provides suitably low backgrounds for the determination of ^{234}Th , and the provision of spectroscopy capability simplifies simultaneous counting of alpha and beta particles so that ^{234}Th and the ^{230}Th yield tracer can be analyzed in a single count. A description is provided below of the development of a liquid scintillation method for analysis of ^{234}Th in seawater. The work is being undertaken as part of the U.K. BOFS (Biogeochemical Ocean Flux Study) program which is associated with the international JGOFS (Joint Geochemical Ocean Flux Study) program.

Development of the method was performed using a Packard 2000CA/LL liquid scintillation counter. Comparison was made between the low level count mode which employs pulse shape analysis to discriminate true β events from background events¹² and the normal counting mode. As a result of this pulse shape discrimination, a small percentage of the β -efficiency is lost, together with a proportionately higher percentage of the α events. The latter are well documented as having much broader pulse widths and therefore being more liable to discrimination. Despite this, it was envisaged that the achievable reductions in background would more than compensate for the loss of efficiency.

EXPERIMENTAL

Isolations of ^{230}Th and ^{234}Th

The ^{230}Th spike was prepared by anion exchange isolation of Th, from a mineralized uranium nodule in which the ^{238}U decay chain was in equilibrium,

at least to ^{230}Th . The concentration of ^{232}Th was below the limit of detection as well. The ^{230}Th fraction was retained in dilute nitric acid with aluminium carrier. Aging for approximately 12 months ensures decay of ^{234}Th , ^{231}Th , ^{227}Th , and the corresponding decay products to a negligible level (Figure 1).

The uranium fraction was also retained and similar aging allows ^{234}Th to come to secular equilibrium with the ^{238}U . This provides a source of ^{234}Th free from ^{230}Th for method development. Following isolation of ^{234}Th from ^{238}U , a period of a few days should be allowed for decay of ^{231}Th ($t_{1/2} = 1.06\text{d}$) formed by decay of ^{235}U which was also present in the solution. The purities of both the ^{230}Th and the $\text{U}/^{234}\text{Th}$ aged solutions were confirmed by electrodeposition and alpha spectroscopy. The work presented here was performed with spikes which were not completely aged, however, so an allowance was made for this in calculations.

Liquid Scintillation Counting of ^{230}Th and ^{234}Th

To obtain representative spectra, suitable aliquots of ^{234}Th , ^{230}Th , the combination of ^{234}Th and ^{230}Th , and background were prepared as follows:

- Aliquots were added to 7 mL Packard low potassium glass vials and gently taken to dryness.
- The Th was redissolved in 0.5 mL of 1 mol dm^{-3} HCl, and 5 g Packard Hionic Fluor was added.
- Each sample was counted on a Packard 2000 CA/LL liquid scintillation counter for 300 minutes, first in the low level mode and then in the normal mode.
- Spectra were saved for subsequent analysis using the Packard Spectragraph software package.

Following measurement of the ^{234}U activity, the ^{234}Th activity was calculated based on the ingrowth time since U/Th separation. To determine the counting efficiency of ^{234}Th ($^{234\text{m}}\text{Pa}$) the following steps were carried out: a known aliquot of $^{238}\text{U}/^{234}\text{Th}$ was spiked with the ^{230}Th yield tracer, and the Th was isolated again by anion exchange. The volume was reduced to 1 to 2 mL and quantitatively transferred to a 7 mL scintillation vial, taken to dryness, and prepared for counting as previously described. The same activity of ^{230}Th yield tracer was added directly to a further vial, taken to dryness, and similarly prepared.

Seawater analysis

Replicate 20 L seawater samples were collected from the River Clyde estuary. The ^{238}U concentration was determined by anion exchange separation and conventional alpha spectroscopy. The samples were filtered through 0.45 μm millipore membrane filters to remove particulate material, and the pH was lowered to 2 with HCl to maintain Th solubility. Three of these samples were then analyzed for ^{234}Th almost immediately, while a further four were stored to

allow ^{234}Th ingrowth (23 to 25 days). Samples were first spiked with ^{230}Th and thereafter 500 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added to scavenge out Fe/U/Th etc. by pH adjustment to 9. To maximize recovery, the 20 L samples were stirred for approximately 2 hr and left overnight for precipitate settling. Th separation and vialing/scintillation counting was as previously described.

RESULTS

The spectra obtained from counting ^{234}Th , ^{230}Th , the combination of ^{234}Th and ^{230}Th , and a background, in both counting modes, are presented in Figure 2. Although there is a reasonable degree of spectral separation, it is not complete. There is some interference in the ^{230}Th region from the high energy $^{234\text{m}}\text{Pa}$ β^- emissions. Conversely, residual ^{234}Th in the ^{230}Th yield tracer brings about a small interference in the ^{234}Th region. Provided that the degree of sample quenching remains constant, the extent of interference will remain constant, and indeed this has been the case throughout the study. Using Spectragraph, windows of 0 to 80 keV and 100 to 220 keV were selected for ^{234}Th and ^{230}Th , respectively. For the ^{234}Th spectrum obtained under low-level conditions, a fully optimized window of 10 to 70 keV was determined using software developed at SURRC. The respective crossovers were then calculated in both counting modes and for both 0 to 80 and 10 to 70 keV counting windows. The ^{230}Th contribution into the ^{234}Th region will decrease with aging, i.e., as the residual ^{234}Th decays. The contribution of $^{234}\text{Th}/^{234\text{m}}\text{Pa}$ will remain a constant percentage of the net count rates in the 0 to 80 and 10 to 70 keV windows. As an example of this, under low-level conditions and using a 0 to 80 keV window, the contribution $^{234}\text{Th}/^{234\text{m}}\text{Pa}$ under the ^{230}Th peak was estimated at $16.5 \pm 0.002\%$. The contribution, at the time of counting of ^{230}Th in the ^{234}Th region was $3.9 \pm 0.93\%$. Using the low level option there is an approximate 10% loss in ^{234}Th counting efficiency and a 45% loss in ^{230}Th efficiency.

^{234}Th efficiencies were determined as follows: (1) gross counts in appropriate regions were obtained for all vials from stored spectra using Spectragraph. (2) Appropriate backgrounds were subtracted from each region and corrections for crossover interferences were made, thus yielding net $^{234}\text{Th}/^{234\text{m}}\text{Pa}$ and ^{230}Th count rates. (3) Yields were determined from the ratio of sample ^{230}Th count rates to those of ^{230}Th added directly to scintillation vials. (4) The count rates in the $^{234}\text{Th}/^{234\text{m}}\text{Pa}$ region were corrected for decay and the yield factor was applied. (5) The activity of ^{234}Th was calculated from the ^{238}U activity as 470.5 ± 7.6 dpm ml^{-1} . Since $^{234\text{m}}\text{Pa}$ is in equilibrium with ^{234}Th , the gross activity will be 941 dpm mL^{-1} . Table 1 presents triplicate values of the overall counting efficiency for $^{234}\text{Th}/^{234\text{m}}\text{Pa}$ in the two counting windows and in both counting modes together with yields representing the efficiency of the chemistry.

Table 2 indicates background count rates and E^2/B values for relevant counting windows and in both counting modes. The results show that E^2/B is maximized using a 10 to 70 keV window in the low level mode. However, this

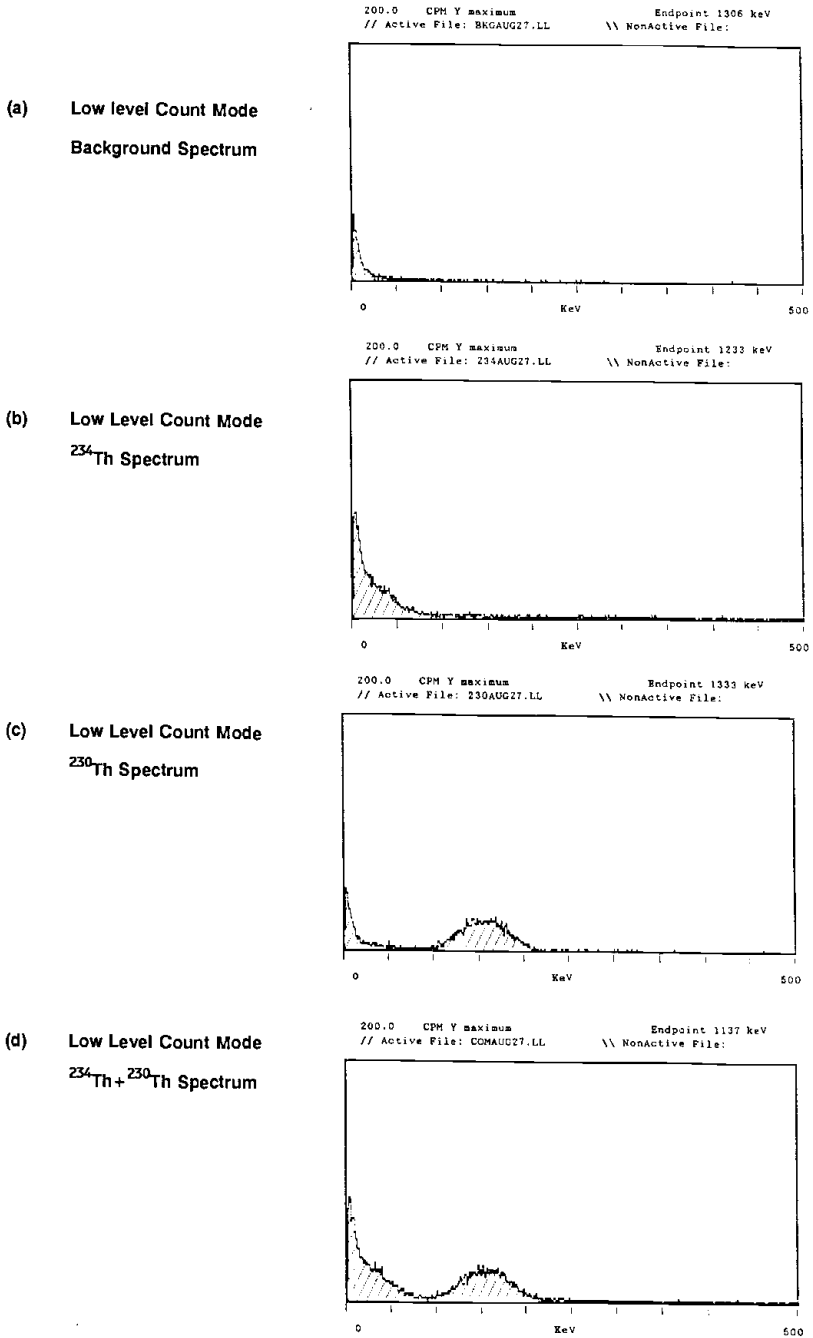
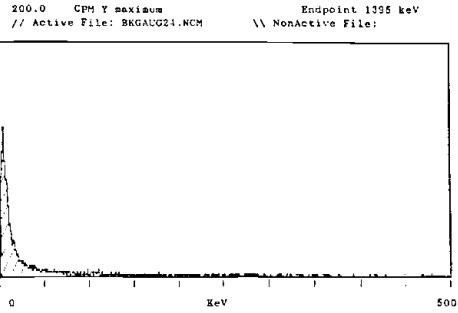
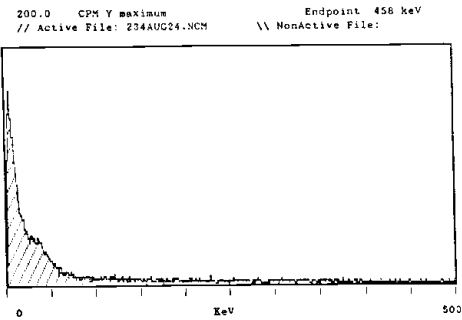


Figure 2a. Low-level count mode spectra for background, ²³⁴Th, ²³⁰Th, and ²³⁴Th + ²³⁰Th.

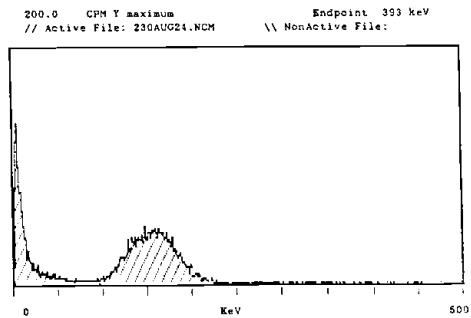
(e) Normal Count Mode
Background Spectrum



(f) Normal Count Mode
 ^{234}Th Spectrum



(g) Normal Count Mode
 ^{230}Th Spectrum



(h) Normal Count Mode
 $^{234}\text{Th} + ^{230}\text{Th}$ Spectrum

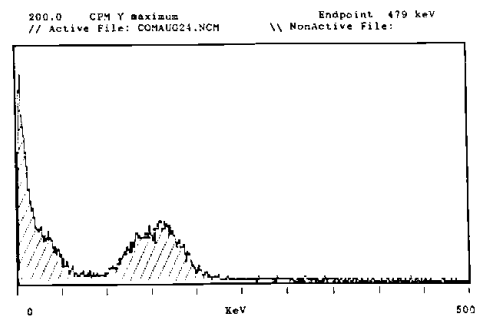


Figure 2b. Normal count mode spectra for background, ^{234}Th , ^{230}Th , and $^{234}\text{Th} + ^{230}\text{Th}$.

Table 1. ^{234}Th Chemical Yields and Counting Efficiencies Using Both the Low-Level and Normal Counting Modes and 0 to 80 and 10 to 70 keV Counting Windows

Replicate	Chemical Yield (%)	Normal Mode % Eff.		Low Level Mode % Eff.	
		0-80 keV	10-70 keV	0-80 keV	10-70 keV
1	80.0	136.9	100.3	115.5	85.0
2	79.1	138.7	102.0	118.2	85.7
3	73.0	137.8	101.3	120.0	88.2

Table 2. Background Count Rates and E^2/B Factors for ^{234}Th and Background Count Rates for ^{230}Th Using Both the Normal and Low-Level Counting Modes

	Normal Count Mode			Low Level Count Mode		
	^{234}Th	^{234}Th	^{230}Th	^{234}Th	^{234}Th	^{230}Th
	(0-80 keV)	(10-70 keV)	(100-220 keV)	(0-80 keV)	(10-70 keV)	(100-220 keV)
Background (cpm)	16.75	6.73	2.27	6.46	2.77	0.93
E^2/B	1134	1522	—	2152	2689	—

improvement is partly negated at present by larger errors in the final net count rate calculations because the ^{230}Th spike is not fully aged. With a fully aged spike, overspiking with ^{230}Th , followed by counting in the low level mode, should be the optimum method.

Table 3 represents the measured ^{234}Th concentrations and the predicted values based upon the assumption of insignificant ^{234}Th activity initially present in these high suspended particulate content, shallow waters.¹⁰ The results for the short term ingrowth of ^{234}Th are generally consistent with the predicted values, whereas systematically lower values of 80 to 90% of predicted values are observed for longer ingrowth periods. This is probably a result of partial scavenging during the longer ingrowth periods. This would not represent a problem in practical applications of the technique in which ^{234}Th separation is effected as quickly as possible after sample collection.

Table 3. Predicted and Measured ^{234}Th Concentrations in Replicate 20 L Estuarine Seawater Samples (Errors Quoted at the ± 1 Sigma Level of Confidence)

Replicate Number	Ingrowth time (days)	Predicted ^{234}Th (dpm L ⁻¹)	Measured ^{234}Th (dpm L ⁻¹)			
			Normal Mode		Low Level Mode	
			0-80 keV	10-70 keV	0-80 keV	10-70 keV
1	2.0	0.11(0.01)	0.12(0.03)	0.15(0.03)	0.16(0.02)	0.16(0.02)
2	4.7	0.25(0.01)	0.25(0.03)	0.28(0.03)	0.26(0.02)	0.26(0.02)
3	4.7	0.25(0.01)	0.35(0.03)	0.36(0.03)	0.37(0.03)	0.36(0.03)
4	23.8	0.98(0.02)	0.87(0.02)	0.89(0.04)	0.90(0.03)	0.93(0.03)
5	23.8	0.98(0.02)	0.86(0.04)	0.88(0.04)	0.85(0.03)	0.84(0.03)
6	25.7	1.03(0.02)	0.82(0.03)	0.84(0.03)	0.81(0.03)	0.82(0.03)
7	25.7	1.03(0.02)	0.82(0.03)	0.88(0.03)	0.82(0.03)	0.83(0.03)

DISCUSSION AND CONCLUSIONS

The results to date indicate that ^{234}Th measurements from seawater samples are indeed feasible by this technique. The advantages of the method are that (1) the preparation chemistry is simpler, since no electrodeposition is required, (2) both isotopes may be measured in a single count on equipment employing an automatic sample changing facility, and (3) counting efficiencies are much higher for both isotopes of the order of 100% for ^{230}Th and 137% relative to ^{234}Th activity for combined $^{234}\text{Th}/^{234\text{m}}\text{Pa}$. As a result of these, a higher throughput of samples can be achieved with greater precision. The possibility also therefore exists of carrying out the determinations on much smaller samples. This is a major advantage for seawater analysis, where sample size is often a limiting factor. Five litre samples should be well within the capabilities of this method.

In order to validate the method yield factors can and will be confirmed when all ^{234}Th has decayed. Where a fast turnaround time of results is not required, this should enable higher precision to be obtained. The possibility also exists of using scintillation counters employing simultaneous α/β separation and counting which should in theory virtually eliminate the need for crossover calculations.

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