



Rapid and Accurate Method for Determining ^{234}Th in Seawater: Fe Co-precipitation, UTEVA Extraction, and Micro-precipitation

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Abstract

Thorium-234 (^{234}Th ; $t_{1/2} = 24.1$ days) has been widely used as a tracer of particle settling and organic carbon export in the ocean. However, the use of ^{234}Th in the ocean has been hampered by labor-intensive procedures, low throughputs, and large uncertainties related to source impurities. Here, we demonstrate a more efficient technique developed to analyze ^{234}Th in seawater by modifying the traditional $\text{Fe}(\text{OH})_3$ co-precipitation method. The advantages and shortcomings of this method were compared with the ^{234}Th analytical method using MnO_2 precipitation. In the new method, following the equilibration of the ^{230}Th spike with ^{234}Th , Th was co-precipitated with Fe. Although the precipitates include a fraction of U, Fe precipitation was fast, and the supernatant can be easily siphoned off, allowing simple handling of several samples simultaneously. The Th adsorbed onto particles, collected by Fe precipitation, was desorbed in ~ 4 M HNO_3 solution by heating at 230°C for 30 min in a sealed Teflon bottle. Then, Th was separated from U using UTEVA resin. The counting source of Th was prepared by micro-precipitation of Ce. We were able to process ~ 60 samples for 5 days onboard, and the first counting was completed within a week upon returning to the laboratory. The main advantages of this method include (1) easy increase in the sample volume, (2) rapid Fe precipitation, (3) high-purity Th sources for beta and alpha counting, (4) no need for mass spectrometry, and (5) the high throughput.

Keywords Th-234 · Seawater · UTEVA resin · Fe co-precipitation · Particle flux

1 Introduction

Naturally occurring ^{234}Th (half-life = 24.1 days) is constantly produced in seawater by its parent ^{238}U (half-life = 4.5×10^9 years). Although Th is particle-reactive, U is conservative in seawater by forming $\text{UO}_2(\text{CO}_3)$. Thus, the disequilibrium of ^{234}Th and ^{238}U in seawater has been widely utilized to estimate the scavenging rates of elements and settling rates of particles in a variety of marine regimes such as the upper open ocean (Buesseler 1998; Coale and Bruland 1985; Owens et al. 2015), benthic boundary layer (Bacon and van der Loeff 1989; Inthorn et al. 2006; van der Loeff et al. 2002), continental shelf (Buesseler et al. 2010;

Charette et al. 2001; Feng et al. 2021), and coastal ocean (Gustafsson et al. 1998; Stukel et al. 2013).

Over the last few decades, several methods have been developed for determination of ^{234}Th in seawater. Bhat et al. (1968) developed a conventional method that utilizes $\text{Fe}(\text{OH})_3$ co-precipitation, followed by sequential processes of Th purification using HCl and HNO_3 anion-exchange columns, electrodeposition on a stainless-steel disc, beta counting of ^{234}Th , and alpha counting of ^{230}Th for the Th recovery. One defect of this method is co-precipitation of ^{238}U with Fe, with variable efficiency (Buesseler et al. 2001), which requires measurement of ^{238}U in Fe precipitates to correct for the ingrowth of ^{234}Th during the period between the Fe precipitation and Th separation (Kim et al. 1999). On the other hand, Buesseler et al. (1992) used the MnO_2 filter cartridge method for the selective extraction of Th from large volume seawater samples (1000–4000 L) for gamma counting. Although the interference of U can be avoided, it is difficult to process several samples simultaneously using such a large water volume.

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Buesseler et al. (2001) later developed a simple method that utilizes MnO_2 co-precipitation for smaller volume samples (2–5 L), which takes about 2 days for the precipitation and filtration of each sample. This method has been widely adopted to determine particulate organic carbon export in the ocean (Black et al. 2018; Owens et al. 2015). Cai et al. (2006) reduced the precipitation and filtration time significantly by heating the precipitation samples onboard a ship. However, the recovery of Th using the Mn co-precipitation method varied from 86 to 95% ($n=5$), necessitating more labor-intensive and skillful steps after beta counting: i.e., the second spike (^{228}Th or ^{229}Th) addition, chemical separation, and the measurement of ^{228}Th by alpha counting or ^{229}Th by mass spectrometry.

In this study, we designed experiments to improve and modify the traditional Fe co-precipitation method using UTEVA extraction chromatography (Eichrom Industries, Darien, IL), followed by Ce micro-precipitation. We aimed to achieve a rapid and accurate determination of ^{234}Th in seawater, with high sample throughput, which is crucial for obtaining high-resolution vertical profiles of ^{234}Th in the ocean for a given cruise period.

2 Materials and Methods

2.1 Sampling and Onboard Procedures

The analyses of ^{234}Th in seawater samples were conducted during three cruises in the shelf of the East China Sea from 10 to 20 August 2020 onboard the *R/V Onnuri*, in the north-western Pacific Ocean from 8 to 25 September 2020 onboard the *R/V Isabu*, and in the East Sea (Japan Sea) from 4 to 11 November 2020 onboard the *R/V Onnuri*. Seawater samples (6–15 L) were collected using Niskin samplers mounted on a rosette sampler with a CTD (Seabird, SBE-911 plus). We used our new Fe co-precipitation method as described below.

Within 1 h of collection, the unfiltered seawater was transferred into 20-L plastic buckets and acidified with HNO_3 to a pH ~ 1. After a ^{230}Th spike (6.5 dpm, disintegration per minute) and Fe^{3+} carrier (70 mg) were added, the sample was allowed to stand for at least 12 h for isotopic equilibration. Then, the pH of the sample was raised to ~ 8 by adding NH_4OH . The sample was stirred vigorously when $\text{Fe}(\text{OH})_3$ precipitates were formed, then allowed to settle for > 3 h. At this stage, Th in the sample is co-precipitated with Fe.

After the settling of Fe precipitates, the supernatant was siphoned off, and the precipitates in the residual sample (~ 500 mL) were collected on a filter (Whatman Grade 54, 22 μm pore size, and 185 mm diameter). The precipitates on the filter were dissolved with 20 mL of 8 M HNO_3 , adjusted to ~ 4 M HNO_3 solution in a Teflon acid-cycle digestion vessel (ODLAB, Korea), and heated (~ 30 min)

at 230 °C using a 12-hole graphite hot block (ODLAB, Korea) for the release of Th to the solution. The solution was passed through a column filled with 2 mL of UTEVA resin, which was preconditioned with 15 mL of 4 M HNO_3 , at a flow rate of 2 mL min^{-1} using a 6-channel peristaltic pump. Subsequently, three aliquots of 15 mL of 3 M HNO_3 were passed through the column to wash out the unretained species in the column. Then, Th in the column was eluted with three aliquots of 20 mL of 6 M HCl to a 50-mL polyethylene bottle. A simplified flowchart of the analytical procedure is shown in Fig. 1.

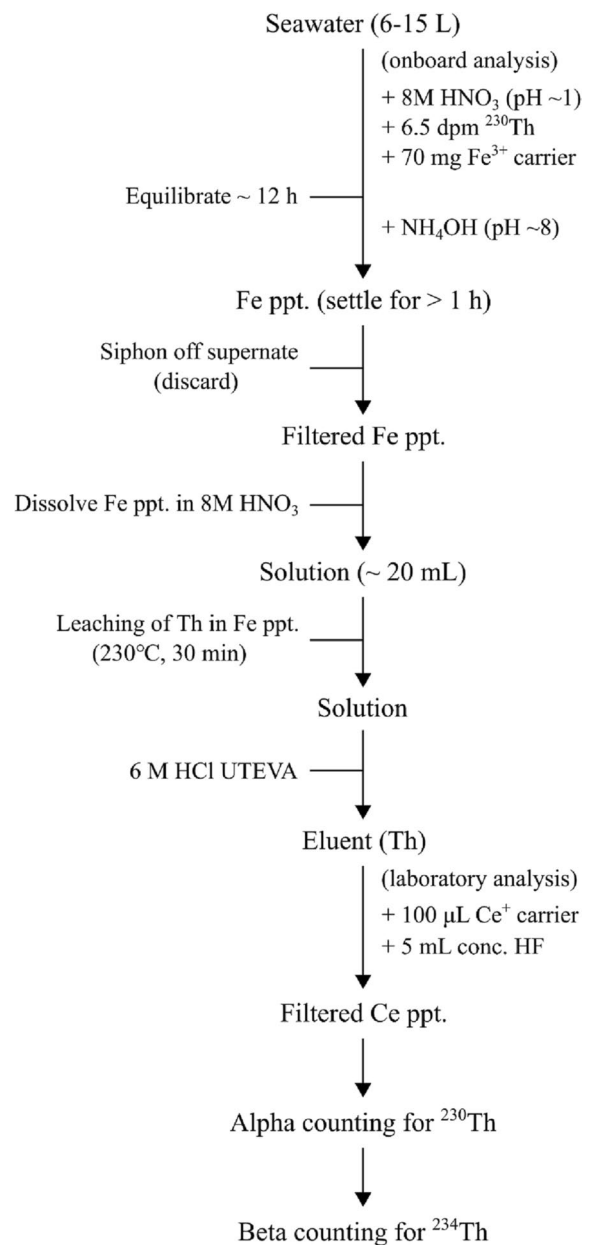


Fig. 1 A flowchart of the newly developed ^{234}Th analysis method using the Fe co-precipitation

2.2 Land-Based Laboratory Procedures

In the land-based laboratory, 100 μL of Ce^{3+} carrier was added to the purified sample and stirred well for equilibration between Ce and Th. Then, 5 mL of concentrated HF was added to form CeF_3 , which co-precipitates Th (Sill 1987). The precipitates were collected on a filter (Eichrom, 0.1 μm pore size, and 25 mm diameter), which was preconditioned with 80% ethanol solution. After removing the funnel, two drops of 80% ethanol solution were placed on the filter under vacuum to remove the residual HF solution. The filter was then allowed to air dry for at least 15 min and placed on a stainless-steel plate.

2.3 Alpha Spectrometry and Beta Counting

The alpha counting of ^{230}Th was performed first. Then the beta counting of ^{234}Th was performed after the filter was covered with two layers of aluminum foils (0.03 mm thickness) to prevent the interference of alphas on beta counting. The ^{230}Th peak appeared from 4617 to 4684 keV in alpha spectrometry (Canberra Alpha Analyst with a PIPS detector, USA), and ^{234}Th was measured via $^{234\text{m}}\text{Pa}$ by a beta counter (low-level RISØ beta counter, Denmark). A series of ^{234}Th measurements was conducted to verify the purity.

3 Results

3.1 Standardization and In Situ ^{234}Th Activity Calculations

The efficiencies of alpha and beta counters used in this study were in the range of 18–22% and 42–45%, respectively, based on the analysis of ^{230}Th standard (Eckert & Ziegler isotope Products, USA) and $^{234}\text{Th}/^{238}\text{U}$ standard (Inorganic ventures, USA). To minimize the uncertainties arising from different geometries between the standards and the samples, we prepared a Ce micro-precipitation source with ^{238}U in equilibrium with ^{234}Th , which has the same geometry as the sample. Equilibrium was confirmed by counting three times at 1-month intervals. Then, the ratio of alpha and beta counting efficiencies was obtained for each set of alpha and beta detectors used for the measurement of the samples. The activity of in situ ^{234}Th in the water sample was calculated using an equation modified from Kim et al. (1999):

$$^{234}\text{Th}(t_0) = \left(\frac{C_{\text{Th-234}} \times ^{230}\text{Th}_{\text{std}}}{C_{\text{Th-230}} \times \text{DE}_{\beta/\alpha} \times V} \right) \times e^{\lambda(t_2-t_0)} - U \left(e^{\lambda(t_1-t_0)} - 1 \right) \quad (1)$$

where $^{234}\text{Th}(t_0)$ is the ^{234}Th activity in the sample at the initial time, $C_{\text{Th-234}}$ is the ^{234}Th count rate at the time of beta counting, $^{230}\text{Th}_{\text{std}}$ is the ^{230}Th spiked activity (6.5 dpm), $C_{\text{Th-230}}$ is the ^{230}Th count rate, $\text{DE}_{\beta/\alpha}$ is the ratio of detector efficiency, V is the sample volume, λ is the decay constant of ^{234}Th , and U is the activity of uranium calculated from the salinity (Owens et al. 2011); t_0 , t_1 , and t_2 are the time of sample collection, U/Th separation, and beta counting, respectively. The error propagation was based on 2-sigma counting statistics. The blank values were 0.14 ± 0.03 cpm (counts per minute) for ^{234}Th and 0.003 ± 0.001 cpm for ^{230}Th which were applied for the net count rate of samples. The detection limit of this method was ~ 0.01 dpm L^{-1} based on procedure blanks, and the overall measurement uncertainty was $\sim 1\%$ based on replicate analyses.

A series of beta counting of ^{234}Th for all samples from the three cruises using our new method showed good linear regression curves and a similar y-intercept range (0.1–0.3 cpm). The decay curves of ^{234}Th for all samples (the data are shown in Table 1) using our new method confirmed the purity of the ^{234}Th sources. We used the slope values and standard deviations of the slopes for calculating the activities and uncertainties of ^{234}Th , respectively, for all samples. The decay curves were shown only for the East Sea samples as representative data because other results were all similar (Fig. 2). This method is further verified using old seawater samples, which have the equilibrium activities between ^{234}Th and ^{238}U . The activity ratios of the measured and the expected ^{234}Th (^{238}U) activity were 1.00 ± 0.01 , which confirms the accuracy and applicability of this technique in seawater samples (Table 2).

3.2 Field Observations

After the sample collection, ^{234}Th activity changes with time by ingrowth and decay toward equilibrium between ^{234}Th and ^{238}U . In this experiment, the equilibration time between ^{234}Th and ^{230}Th took ~ 12 h, which produced $< 1\%$ of in situ ^{234}Th . Then, a further ~ 6 h elapsed from Fe precipitation to the UTEVA column chromatography. Additional uncertainties may arise from the fact that we did not measure U content in the Fe precipitates. Kim et al. (1999) showed that the efficiency of U co-precipitation with Fe ranged from 17 to 60%. Even if the maximum efficiency is applied, it is less than 1% of the in situ ^{234}Th . Thus, we ignored this ingrowth contribution in the final calculation. Then, the decay during the period (5–20 days) from separation to beta counting was corrected in the final calculations. We increased the counting time in the case of low activities of ^{234}Th to obtain counting errors $< 2\%$ in beta counting.

The three representative ^{234}Th profiles are listed in Table 1. The chemical recovery varied from 82 to 93%, with an average of 85% ($n = 15$). The activities were in the range

Table 1 Results of ^{234}Th analyses for seawater samples from the East China Sea, East Sea (Japan Sea), and the northwestern Pacific Ocean. Errors are calculated based on 2-sigma counting statistics

Locations	Longitude ($^{\circ}\text{E}$)	Latitude ($^{\circ}\text{N}$)	Depth (m)	^{234}Th (dpm L^{-1})	$^{238}\text{U}^{\text{a}}$ (dpm L^{-1})
East China Sea	129 $^{\circ}$ 48	35 $^{\circ}$ 25	0	0.44 ± 0.03	2.11
			10	0.67 ± 0.04	2.26
			30	1.31 ± 0.06	2.37
			50	0.35 ± 0.02	2.38
			75	0.69 ± 0.04	2.39
East Sea (Japan Sea)	130 $^{\circ}$ 45	36 $^{\circ}$ 37	1000	2.50 ± 0.06	2.36
			1566	2.41 ± 0.06	2.36
			1816	2.33 ± 0.06	2.36
			2016	2.10 ± 0.02	2.36
			2036	1.68 ± 0.02	2.36
Northwestern Pacific	127 $^{\circ}$ 30	16 $^{\circ}$ 30	0	2.15 ± 0.04	2.40
			30	2.11 ± 0.04	2.41
			50	2.28 ± 0.04	2.41
			100	1.86 ± 0.04	2.42
			140	2.40 ± 0.05	2.42

^aCalculated from the salinity (Owens et al. 2011)

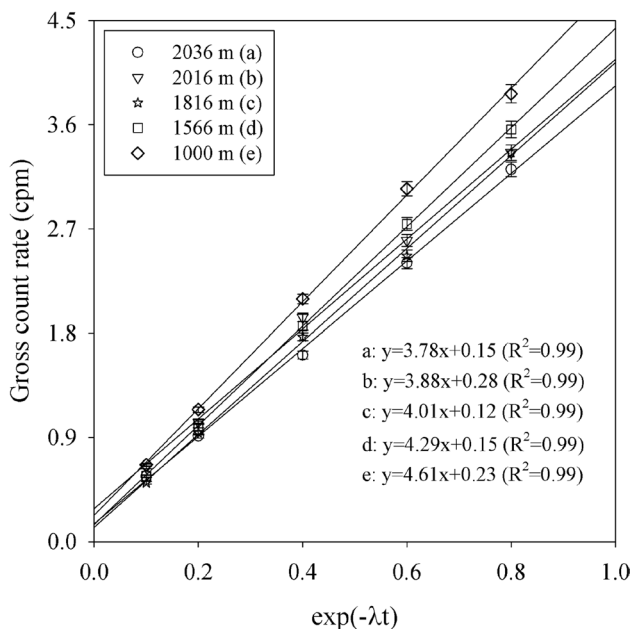


Fig. 2 A plot of gross count rate versus $\exp(-\lambda t)$ for samples from a field observation (East/Japan sea). Linear lines show the decay curves of ^{234}Th activities, and the intercepts are the blank activities. High correlation coefficient values ($R^2=0.99$) indicate the high purity of the sources

of $0.35\text{--}1.31$ dpm L^{-1} in the entire depth of the East China Sea shelf water, $1.86\text{--}2.40$ dpm L^{-1} in the upper northwestern Pacific Ocean, and $1.68\text{--}2.50$ dpm L^{-1} in the East Sea deep water. As previously documented, shelf water showed the largest deficiency of ^{234}Th due to the rapid removal of ^{234}Th in this environment (Charette et al. 2001). In the

northwestern Pacific Ocean, there was a large ^{234}Th deficiency in the upper euphotic zone, but ^{234}Th was close to the activity of ^{238}U at a depth of 140 m. This is typical of ^{234}Th profiles occurring in the upper ocean of the oligotrophic ocean (Black et al. 2018). In the bottom layer of the East Sea (2080 m total depth), ^{234}Th was in equilibrium with ^{238}U at a depth of 250 m from the seafloor and then decreased gradually toward the seafloor, implying the resuspension and settling of particles from the bottom sediments (Bacon and van der Loeff 1989). Further detailed data interpretation of these profiles, together with the full dataset, will be published elsewhere.

4 Discussion

The new method was compared with the Mn co-precipitation method (Buesseler et al. 2001; Cai et al. 2006), commonly used for ^{234}Th measurements in seawater (Table 3). The pre-concentration with Fe precipitation was relatively rapid (3 h without heating). With a small sample volume (~ 500 mL) after the supernatant was siphoned off, several samples could be processed simultaneously for filtration using a 6-channel filtration set, acid dissolution in a 12-hole hot block, and UTEVA separation using a 6-channel peristaltic pump (Fig. 3). The entire processing time is about 6 h, excluding the isotopic equilibration time between ^{234}Th and ^{230}Th . In comparison, the Mn co-precipitation method (Buesseler et al. 2001) takes ~ 1 h for precipitation and > 12 h for filtration. The filtration time of the Mn precipitates varies significantly for different samples (> 24 h for some samples). Although Cai et al. (2006) reduced the precipitation and

Table 2 Accuracy of the Fe precipitation method for ^{234}Th measurements in seawater

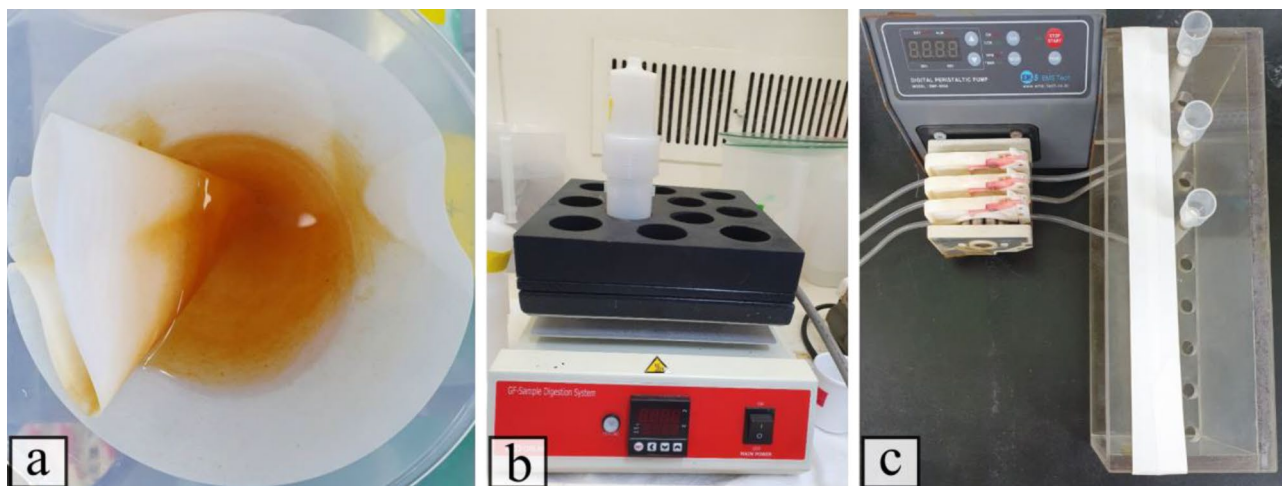
Seawater standard	Expected ^{234}Th activity (dpm L $^{-1}$)	Measured ^{234}Th activity (dpm L $^{-1}$)	Activity ratio (measured/expected)
Seawater (4 L) ^a	2.39 ± 0.02	2.40 ± 0.05	1.00
Seawater (6 L) ^a	2.39 ± 0.02	2.42 ± 0.03	1.01
Seawater (4 L) ^b	2.30 ± 0.01	2.31 ± 0.05	1.00
Seawater (6 L) ^b	2.30 ± 0.01	2.28 ± 0.04	0.99

^aSeawater samples were collected at 1000 m water depths from the Northwestern Pacific Ocean (130.49° E, 30.03° N)

^bSurface seawater samples were taken from the East China Sea (128.60° E, 34.40° N)

Table 3 Main advantages and disadvantages of this method in comparison with the Mn co-precipitation methods (Buesseler et al. 2001; Cai et al. 2006) with respect to labor, analytical skills, accuracy, and throughputs

Procedure	Fe ppt. (this method)	Mn ppt. (Cai et al. 2006)	Mn ppt. (Buesseler et al. 2001)
Sample volume	Up to 20 L	4 L	2–5 L
Carrier and spike	Fe(OH) ₃ ^{230}Th	0 ^{228}Th and ^{230}Th	0 Not added
Pre-concentration	Equilibration time: ~ 12 h	Equilibration time: ~ 12 h	Unnecessary
	Co-precipitation (> 1 h)	Co-precipitation with heating (> 1 h)	Co-precipitation (1 h)
	Siphon off and filtration (~ 1 h)	Filtration (~ 1 h)	Filtration (> 12 h)
Dissolution	Leaching of Th in Fe ppt. after filtration (230 °C, 30 min) on board	Total digestion of filters after beta counting (~ 3 h) in land-based laboratory	Not performed
Chemical purification	UTEVA column (~ 1 h)	Anion exchange column (~ 6 h)	Not performed
Source preparation	Ce micro-precipitation (~ 30 min)	Unnecessary	Unnecessary
Advantages	High throughputs Pure ^{234}Th source	No U co-precipitation	No U co-precipitation
Disadvantages	U co-precipitation with Fe ppt	Impure ^{234}Th source	Impure ^{234}Th source
	Chemical procedures onboard	Chemical procedures after beta counting	Recovery is unknown

**Fig. 3** Photograph of experimental setups used in this study: **a** Fe(OH)₃ precipitates, **b** heating of the Teflon acid-cycle digestion vessel, and **c** UTEVA resin purification using a peristaltic pump

filtration time to ~ 1 h by heating the total volume of the water sample, heating the water sample onboard is often not convenient.

The water volume for this method can be increased even up to 20 L (Kim et al. 1999) because the supernatant of Fe precipitates can be easily siphoned off. In contrast, the water volume for Mn co-precipitation method is practically limited to 3–5 L, due to a safety of onboard heating (Cai et al. 2006) or for the completion filtration of Mn precipitates without heating within 1–2 days (Buesseler et al. 2001). The increase of a sample water volume is advantageous for low activity samples, particularly in coastal waters, and for the open-ocean samples for which extended time is needed between the onboard and laboratory analyses.

Due to the purification of ^{234}Th conducted in this Fe co-precipitation method, we obtained very low blank values (i.e., similar to the detector backgrounds) and a pure ^{234}Th decay curve (Fig. 2). However, the Mn co-precipitation method can produce large uncertainties in beta counting because of the self-absorption of ^{234}Th in particles and interference of other beta emitters (^{214}Bi from ^{226}Ra) (Benitez-Nelson et al. 2001). Such problems may be more significant for coastal water samples with high particle concentrations.

For the recovery experiments in a land-based laboratory, the Fe co-precipitation method can be easily conducted using traditional alpha spectrometry without further separation. Instead, the Mn co-precipitation method (Cai et al. 2006; Pike et al. 2005) requires additional labor-intensive chemical purification steps, including the addition of ^{228}Th (for alpha spectrometry) or ^{229}Th (for mass spectrometry) as an internal standard, acid digestion of the filter, and purification using an anion-exchange column. The measurement of ^{228}Th is necessary for alpha spectrometry since ^{229}Th produces many alpha daughters (^{225}Ac , ^{221}Fr , ^{217}At , and ^{213}Po), which further complicates alpha spectrometry.

5 Conclusion

It appears that the entire process time and separation steps required from the sampling to the separation are similar for the three methods (Fe co-precipitation, Mn co-precipitation without heating, and Mn co-precipitation with heating). However, the Fe co-precipitation method seems to be more advantageous with respect to handling, accuracy, and throughput. We successfully processed 60 samples in 5 days using the Fe co-precipitation method. More importantly, using the Fe co-precipitation method, pure ^{234}Th sources can be obtained since it is purified before beta counting, and larger water volume can be used. Thus, if the samples contain a large amount of particles (i.e., coastal water) with low ^{234}Th activities, our method is much more advantageous since the self-absorption of ^{234}Th can be avoided. However,

in this case, the complete digestion of particulate matter is necessary before the column separation. For the measurements of ^{234}Th in particulate samples, the same procedure suggested in this study may be used after the acid digestion of particulate samples.

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