

# An improvement in the small-volume technique for determining thorium-234 in seawater

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## Abstract

The recently developed 2-5 L small-volume MnO<sub>2</sub> coprecipitation method for determining <sup>234</sup>Th in seawater has provided a new way to substantially increase, both temporally and spatially, the sampling resolution of <sup>234</sup>Th and <sup>234</sup>Th-based particulate organic carbon export estimates in the upper ocean. In this study, we further optimize the technique by reducing reagent quantities and the use of an additional water bath heating step. This optimization allows the filtration of the MnO<sub>2</sub> precipitate onto a 25-mm diameter, 1.0 μm pore size QMA filter to be completed within < 30 minutes for unfiltered waters from the South China Sea. In addition, we have modified the MnO<sub>2</sub> purification procedure to allow for alpha spectrometric measurements of <sup>234</sup>Th recoveries. Results from recovery experiments suggest that reagent amounts can be reduced to 0.0375 mg KMnO<sub>4</sub> and 0.1 mg MnCl<sub>2</sub>·4H<sub>2</sub>O per liter of sample, while still maintaining high <sup>234</sup>Th recovery. This study further confirms that the addition of a yield monitor is necessary for the application of this small-volume method.

Keywords: Thorium-234; MnO<sub>2</sub> coprecipitation; Beta counting

## 1. Introduction

Thorium-234 ( $^{234}\text{Th}$ ,  $t_{1/2}=24.1$  days) has been widely used as a tracer for scavenging processes of upper ocean particles over time scales of days to weeks (e.g. Bhat et al., 1969; Coale and Bruland, 1985; Buesseler et al., 1992; Santschi et al., 1999; Cochran and Masque, 2003). Over the past decade, the widest application of  $^{234}\text{Th}$  in a variety of marine regimes has been related to its use in quantifying the downward flux of particulate organic carbon (POC) from the surface ocean (e.g. Bacon et al., 1996; Buesseler, 1998; Charette and Moran, 1999; Moran and Smith, 2000; Cai et al., 2002; Coppola et al., 2005).

The determination of  $^{234}\text{Th}$  in seawater used to require either an iron hydroxide ( $\text{Fe}(\text{OH})_3$ ) coprecipitation of  $^{234}\text{Th}$  from 20 to 30 L of seawater, or scavenging of this nuclide onto  $\text{MnO}_2$ -impregnated acrylic fibers from > 200 L of seawater. More recently, Rutgers van der Loeff and Moore (1999) developed a 20-L  $\text{MnO}_2$  technique that allows for onboard beta counting for  $^{234}\text{Th}$  with a portable beta counter. This procedure was further modified into a 2-5 L small volume technique by Buesseler et al. (2001) and Benitez-Nelson et al. (2001a) and uses the lowest sample volumes of all known  $^{234}\text{Th}$  methods to date. As a result, this method can be easily applied at sea using samples obtained through CTD rosette water samplers that are available on most research vessels. Hence, it has the potential to substantially enhance both spatial and temporal sampling, which is crucial in constraining POC export rates in the upper ocean, especially in areas where non steady state and physical processes cannot be ignored, such as in the

marginal sea.

The small volume technique has been successfully applied in a number of field experiments (e.g. Benitez-Nelson et al., 2001b; Buesseler et al., 2004; Savoye et al., 2004). Two issues that must be considered in applying the small volume technique are recovery correction and the extensive sample processing time commonly required for filtering the MnO<sub>2</sub> precipitate (ppt). With respect to recovery correction, Pike et al. (2005) has proposed an acidification of the samples followed by an addition of <sup>230</sup>Th as a yield monitor, the recovery of which, is quantified by ICP-MS. The advantage of this modified approach is a precise knowledge of <sup>234</sup>Th recovery, leading to an enhancement in data quality of <sup>234</sup>Th. However, the prolonged time period associated with filtration of the MnO<sub>2</sub> ppt remains unresolved.

In order for the MnO<sub>2</sub> ppt to undergo beta counting, it is necessary to filter the ppt onto small diameter (i.e., 25-mm) membrane filters such as silver or quartz fiber filters so that they fit into the 25-mm-diameter sample windows of the RISØ beta counter commonly used by the marine science community. As a consequence, the time invested in this apparently easy filtration step becomes a major bottleneck in applying this technique. The situation becomes even more severe for samples from particle-laden environments, where filtration of the MnO<sub>2</sub> ppt from a 4-L sample may become prohibitive without prefiltration. Even with prefiltration, the ppt filtration process might still be lengthy, up to 12 hrs even under ideal conditions (Pike et al., 2005). Finally, there are other drawbacks associated with sample prefiltration, such as the so-called “wall

effect” as pointed out by Benitez-Nelson et al. (2001a), who have demonstrated that significant adsorption of  $^{234}\text{Th}$  onto bottle walls may occur when the time period between sample collection and reagent addition is longer than 6 hours. Regardless, the slow rate of ppt filtration hampers our ability to process large numbers of  $^{234}\text{Th}$  samples in a given program. In this study, experiments were designed to increase the  $\text{MnO}_2$  ppt filtration rate in order to achieve a rapid, easily accessible and reproducible protocol for  $^{234}\text{Th}$  collection in seawater.

## **2. Materials and method**

### **2.1 Material**

Seawater samples used in our testing experiments were mostly taken from the northern South China Sea (SCS) at  $21^{\circ}10'11''\text{N}$ ,  $117^{\circ}49'12''\text{E}$  on board the R/V *Yanpin-II* on July 17, 2003. Water depth at this location is 936 m. Surface seawater (1 m) was collected into twelve 20-L polyethylene carboys through an on-deck pumping system. Within 1 h of collection, the unfiltered seawater was acidified to  $\text{pH}\approx 1$  with concentrated  $\text{HNO}_3$ . The sample was then transported to a land-based laboratory for subsequent experiments. Suspended particle concentration in the surface water was measured by weighing and found to be  $0.54 \text{ mg L}^{-1}$ . During the recovery test (see below), we also used surface seawater samples from a shallow station ( $24^{\circ}26'30''\text{N}$ ,  $118^{\circ}03'30''\text{E}$ ) at Xiamen Harbor.

In the laboratory, all comparison experiments were conducted using 4-L samples collected from the same bulk seawater into 4-L fluorinated polyethylene bottles where

the MnO<sub>2</sub> precipitation took place. This 4-L bottle can be directly attached to a specially designed vacuum filter manifold for filtration with little attendance.

## **2.2 Experimental**

The sample processing procedure is the same as that of Buesseler et al. (2001), with the exception of minor modifications (see Figure 1). Briefly, KMnO<sub>4</sub> and MnCl<sub>2</sub> solutions were added to a 4-L aliquot of seawater to form a suspension of MnO<sub>2</sub>. Samples were heated in a water bath (>80 °C) without stirring. After the samples were allowed to cool to room temperature (this step generally takes 3-5 hours), the suspension was filtered onto a 25-mm-diameter, 1 µm pore size quartz fiber membrane filters (QMA, Whatman). In this study, the 1.0 µm pore size QMA filters were selected over GF/F filters or GMF filters because they have a much lower background (~0.2 cpm) than GF/F filters (~0.7 cpm) or GMF filters (~1.4 cpm). The filter was dried and then prepared for beta counting (see below). The water bath used in this study can accommodate 5, 4-L bottles. It is specially designed and makes the heating step fairly practical at sea.

### **2.2.1 The effect of water-bath heating and reagent amount**

The goal of this series of experiments was to optimize the MnO<sub>2</sub> precipitation procedure for the formation of a coarse MnO<sub>2</sub> ppt that is rapidly filterable for on site applications, while maintaining a ppt amount that is sufficient for co-precipitation of <sup>234</sup>Th in the samples, i.e. a reasonable recovery of <sup>234</sup>Th can be achieved within a

relatively short time frame applicable for at-sea operations. Hence, experiments were conducted to examine the effects of temperature on the formation of  $\text{MnO}_2$  ppts as well as how ppt reagent amount affects the filtration rate. A total of 9 sets of 4-L unfiltered subsamples, with 5 replicates in each set, were collected from the same bulk seawater from the northern SCS (Table 1). Sets 1-3 were run without water bath heating, sets 4-5 had 1 hr of heating time, and sets 6-9 were heated for 2 hrs. Set 10 consists of 15 samples and had  $\geq 3$  hrs of heating time. Samples in set 10 were collected at different sites and depths in the northern SCS during February 8 – March 8, 2004.  $^{234}\text{Th}$  data for these samples are not presented in this paper, i.e., we only report the effect of filtration time. Within each temperature set, different amounts of reagent were added. As shown in Table 1, 1.00, 0.50, 0.25 ml of  $\text{KMnO}_4$  solution ( $3.0 \text{ g L}^{-1}$ ) and 1.00, 0.50, 0.25 ml of  $\text{MnCl}_2$  solution ( $8.0 \text{ g MnCl}_2 \cdot 4\text{H}_2\text{O L}^{-1}$ ) were added into sample sets 1, 2 and 3, respectively. Note that 1.00 ml of the  $\text{KMnO}_4$  and  $\text{MnCl}_2$  solutions conform to the amount of reagent addition used in the protocol of Buessler et al. (2001). Upon mixing, a suspension of  $\text{MnO}_2$  was formed. The non-heated samples were placed at room temperature for 24 hrs to allow the  $\text{MnO}_2$  suspension to nucleate. Then, the  $\text{MnO}_2$  ppt was filtered onto the QMA filters. For those samples that were subject to water bath heating, ppt filtration was conducted as soon as the samples cooled to room temperature. To eliminate possible effects associated with vacuum filtration, the vacuum was kept at 0.3 atm during all filtrations.

### 2.2.2 Analysis

The MnO<sub>2</sub> ppt was counted on a 5-sample, gas-flow proportional low-level RISØ beta counter (Model GM-5-25, RISØ National Laboratory) in Xiamen University, China. It utilizes an anti-coincidence shield above 25-mm-diameter sample windows. The entire unit is surrounded by approximately 10-cm of low-radiated BOLIDEN lead bricks (JL Goslar, Germany), which reduce background count rates to ~ 0.11-0.16 cpm. In this study, detector efficiency of the beta counter was calibrated using open ocean water with salinity > 34, which was filtered and acidified to pH≈1 with concentrated HNO<sub>3</sub> immediately after collection. Subsequently, the seawater was transported to a land-based laboratory and stored for > 5 months to ensure that <sup>234</sup>Th was in equilibrium with <sup>238</sup>U. Five replicates of 4-L aged seawater were taken and ~ 10 dpm of <sup>230</sup>Th was added to each. Subsequent sample processing followed the procedure depicted in Figure 1. A recovery correction was performed using alpha spectrometry as described in section 2.2.3. Samples were also corrected for the ingrowth of <sup>234</sup>Th between suspension formation and filtration, which generally accounted for <3% of the total <sup>234</sup>Th activity. The efficiencies of the detectors for the MnO<sub>2</sub> precipitate covered with one layer of Mylar film and two layers of aluminum foil (density = 3.6 mg cm<sup>-2</sup>) were determined to be 0.50 ± 0.01 and vary by < 2 % among detectors. The MnO<sub>2</sub> precipitate used for the determination of detector efficiency was formed by using 0.25 ml of reagent addition. We have monitored the RISØ counter periodically and found the detectors to be very stable, without any detectable changes in efficiency or background since the instrument was purchased (in



2003).

Our procedure for data processing was identical to the “multi-count” method used by Buesseler et al. (2001). Each sample was beta-counted 5 times over a period of 60 days in order to follow the decay of  $^{234}\text{Th}$ . The data were then decay-corrected to the midpoint of  $\text{MnO}_2$  filtration and reported with the standard error associated with the  $^{234}\text{Th}$  fitting curve (see Table 1). The typical background activity as determined from the curve regression is around 0.4 – 0.5 cpm, and is the result of a combination of detector background and other non- $^{234}\text{Th}$  high-energy beta emitters not removed during sample processing (Benitez-Nelson et al. 2001a; Buesseler et al. 2001).

### **2.2.3 $^{234}\text{Th}$ recovery experiment**

Pike et al. (2005) have presented a procedure suitable for analysis by ICP-MS. In this study, the procedure was modified to allow for alpha spectrometric measurement, given the limited accessibility of high-resolution ICP-MS instruments. In contrast, alpha spectrometry is widely available at most institutions although the sample throughput is lower due to its longer counting time.

Selected samples were spiked with  $^{230}\text{Th}$  for the purpose of monitoring Th-recovery. After counting, the  $\text{MnO}_2$  ppt was disassembled and placed in a 100 ml Teflon beaker. Approximately 10 dpm of  $^{228}\text{Th}$  internal standard was added. To ensure that any particulate matter or residual ppt entrained in the filter mesh was released, the filter was digested using a mixture of concentrated acids ( $\text{HNO}_3:\text{H}_2\text{O}_2:\text{HF}=10:1:1$ ). The digested

solution was evaporated to near dryness and ~1 ml of HClO<sub>4</sub> was added to remove SiF<sub>4</sub>. After further evaporation, the final solution was re-dissolved with 3×10 ml of 3 M HCl, which was then transferred into a 50-ml centrifugal tube for subsequent processing.

Buesseler et al. (2001) pointed out that the presence of Mn<sup>2+</sup> on ion exchange columns might interfere with the standard radiochemical purification of Th, resulting in a failure of <sup>230</sup>Th recovery experiment by alpha counting. Our own experiments had similar problems. As such, there is a need to remove the Mn<sup>2+</sup> prior to the purification of Th using ion-exchange columns. Ten mg of Fe<sup>3+</sup> carrier was added to the acid digested solution, and the pH adjusted to ~ 7 with NH<sub>3</sub>·H<sub>2</sub>O. A ppt of Fe(OH)<sub>3</sub> formed and Th was coprecipitated, while Mn<sup>2+</sup> remained in the supernatant. The supernatant was discarded after the ppt was centrifuged. Concentrated HCl was then added to re-dissolved the Fe(OH)<sub>3</sub> ppt, followed by an addition of NH<sub>3</sub>·H<sub>2</sub>O to reform the Fe(OH)<sub>3</sub>. To ensure complete removal of Mn<sup>2+</sup>, this step was repeated 2-3 times.

The final Fe(OH)<sub>3</sub> ppt was dissolved with concentrated HCl and processed using the routine ion-exchange chemistry for Th (Anderson and Fleer, 1982). Finally, Th was extracted into a 0.25 M TTA/benzene solution, and evaporated onto a stainless steel disc. The disc was counted via alpha spectrometry on ultra ion-planted detectors (Octête™ PC) until the error of <sup>230</sup>Th/<sup>228</sup>Th ratio was lower than 3%.

### 3. Results and Discussion

#### 3.1 MnO<sub>2</sub> ppt filtration rate

Results in Table 1 indicate that a reduction in reagent combined with sample heating in a water bath (>80 °C) substantially reduces the time duration for filtration of the MnO<sub>2</sub> ppt. We want to point out that the time listed in Table 1 corresponds to the total time during which the samples are in a heated bath. For sample set 1, the addition of 1.00 ml of reagents and no heating caused the filtration process to be prohibitive (>72 hrs). In sample set 2, the reagent addition was halved and the ppt filtration took 30.9 to 36.0 hrs, with an average of 34.2 hrs. In sample set 3, the reagent addition was further reduced to 0.25 ml of the KMnO<sub>4</sub> and MnCl<sub>2</sub> solutions, but the filtration process remained long, up to 19.4 hrs on average.

By comparison, the ppt filtration rate was substantially faster for heated samples. It took 25.4 to 2.8 hrs for sample sets 6, 7, 8, and 9, which is a significant reduction in terms of filtration length. For sample set 8, in which 0.375 ml of the reagents were added, and samples were heated for 2 hrs, the ppt filtration took an average of ~5 hrs. For sample set 9 with 0.25 ml of the reagent addition, it took only ~2.8 hrs.

If heating time was extended to > 3 hrs, the filtration length can be further reduced. Results in set 10 show that MnO<sub>2</sub> ppt filtration time can be reduced to as low as < 30 minutes. In contrast, if the heating time was limited to 1 hr (sets 4 and 5), the “temperature effect” was not as obvious. The ppt filtration took 27.2 and 5.6 hrs, respectively. Therefore, we conclude that samples should be heated for >2 hrs to reach

optimum time reduction in ppt filtration.

It is quite clear that a reduction in reagent addition decreases the amount of the ppt, and thus shortens the filtration length. At the same time, higher temperature increases the collision rate between colloidal and larger size particles and hence increases the probability of forming coarser MnO<sub>2</sub> particles which filter more rapidly.

It must be pointed out that the filtration rate or time listed in Table 1 is not strictly quantitative since ppt filtration always depends on the matrix of original samples, such as the initial particle load. The samples presented here were not prefiltered and are from a marginal sea with a particle load of 0.54 mg L<sup>-1</sup>. In such a context, our conclusion is that a reduction in reagent addition combined with sample heating in hot water baths substantially decreases the MnO<sub>2</sub> ppt filtration time and hence enhances the application potential of this small volume technique, in this near shore area and is presumably applicable to open ocean sites as well.

A major problem in the non-destructive beta measurement technique is the self-absorption of beta radiation by natural particles and the MnO<sub>2</sub> ppt. In this study, a uranium standard (with <sup>234</sup>Th in equilibrium) was covered by “blank” samples which had Mn ppts formed using different reagent amounts. These U standards were then beta-counted. As shown in Figure 2, it appears that there is no negative correlation between the <sup>234</sup>Th count rates and the reagent amount. This implies that in the range of 0.25 - 1.0 ml of reagent addition (i.e. 1.0 - 4.0 mg of MnO<sub>2</sub> suspension), the self-absorption effect is negligible. However, if the particle load in seawater is higher

than the reagent addition, the self-absorption effect due to the combination of natural particles and MnO<sub>2</sub> suspension may not be negligible.

### 3.2 <sup>234</sup>Th recovery based on alpha spectrometric measurement

Since reagent concentrations were reduced, we need to ensure that there were no variations in <sup>234</sup>Th recovery. This was done with the aid of a yield monitor of <sup>230</sup>Th following the procedure described in section 2.2.3. Figure 3 shows the relationship of <sup>234</sup>Th recovery vs. reagent addition. Samples for this test experiment were collected from Xiamen Harbor and prefiltered. The recovery varies from 86% to 95%, with an average of  $90.8 \pm 3.2\%$  (n=5). The mean recovery is comparable to that presented by Pike et al. (2005), who reported an average recovery of 91.3% (n=104) for filtered samples collected from the Southern Ocean. Figure 3 demonstrates that reagent amount can be reduced to 0.05 ml (i.e. 0.0375 mg KMnO<sub>4</sub>+0.1mg MnCl<sub>2</sub>·4H<sub>2</sub>O per liter of samples) or even lower, while still maintaining high <sup>234</sup>Th recovery.

The potential of this modified small volume technique in elucidating upper ocean-particulate export is shown from a <sup>234</sup>Th depth profile (Figure 4) taken from a station (20°06.42'N, 115°47.81'E) in the SCS in February, 2004. <sup>234</sup>Th activities are lower than equilibrium in the upper 100 m, indicating particle export is occurring. It is evident that under normal conditions, un-corrected <sup>234</sup>Th activity may be too low by up to 10%, e.g. see uncorrected <sup>234</sup>Th activities at 300 m, which would result in an artificial deficit of <sup>234</sup>Th at that depth.

## 5. Conclusions

In this study, we have succeeded in reducing the MnO<sub>2</sub> ppt filtration time by using a combination of water bath heating and a reduction in reagent quantities. This protocol allows filtration of the MnO<sub>2</sub> ppt to be completed within 30 minutes for seawater samples without prefiltration. Consequently, the total time associated with all the steps involved in the procedure (acidification – equilibration – heating – cooling – filtration) can be reduced to < 24 hours. As such, this modified protocol not only improve our ability to process a larger number of <sup>234</sup>Th samples onboard, but also substantially reduce the uncertainty caused by the correction for <sup>234</sup>Th ingrowth.

This study confirms that the addition of a yield monitor is necessary for the application of this small-volume method. In doing so, we have also modified the typical ion-exchange chemistry to allow for the alpha spectrometric measurement of <sup>230</sup>Th recovery by converting the MnO<sub>2</sub> ppt to an Fe(OH)<sub>3</sub> ppt. This procedure can serve as an alternative to the ICP-MS based method presented by Pike et al. (2005).

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Table 1

Comparison of the MnO<sub>2</sub> precipitate filtration length under different experiment conditions in terms of reagent amount and water bath heating duration. Also shown are count rates of <sup>234</sup>Th, decay corrected to the midpoint of precipitate filtration.

Sample set I.D.*	Reagent <sup>&amp;</sup> (ml)	Heating (hrs)	Filtration length (hrs)		<sup>234</sup> Th		
			Range	Average	Count rates (cpm)	Standard deviation (±)	Standard deviation (%)
1	1	0	> 72	>72	—	—	—
2	0.5	0	30.9-36.0	34.2	1.79	0.096	5.4
3	0.25	0	11.7-37.3	19.4	1.87	0.066	3.5
4	0.5	1	20.6-40.5	27.2	2.05	0.162	7.9
5	0.25	1	2.4-8.7	5.6	1.86	0.069	3.7
6	1	2	21.3-30.6	25.4	1.51	0.068	4.5
7	0.5	2	11.6-13.8	12.5	1.69	0.1	5.9
8	0.375	2	2.9-8.8	4.9	1.66	0.101	6.1
9	0.25	2	0.5-6.4	2.8	1.76	0.066	3.8
10 <sup>∇</sup>	0.25	≥3	0.2-3.5	1	—	—	—

\*Each sample set consists of 5 replicates except for set 10.

&Reagent amount, 1.0 represents the addition of 1.0 ml of the KMnO<sub>4</sub> and MnCl<sub>2</sub> solutions.

∇ This set consists of 15 samples collected from northern South China Sea during February 8 – March 6, 2004. <sup>234</sup>Th data will be published elsewhere.

## Figure Captions

Figure 1. A flowchart showing the modified procedure for the small volume MnO<sub>2</sub> technique.

Figure 2. The self-absorption effect due to the reagent addition. The error bar represents 1 sigma standard deviation for the measurements of five replicates.

Figure 3. <sup>234</sup>Th recovery vs. reagent amount. Note that 1.00 ml of the KMnO<sub>4</sub> and MnCl<sub>2</sub> solutions is equivalent to the reagent amount used in prior protocols (Buesseler et al. 2001).

Figure 4. Profiles of recovery-corrected and uncorrected <sup>234</sup>Th activities at a station (115°47.83'E, 20°05.71'N) in the northern South China Sea.

Fig 1.

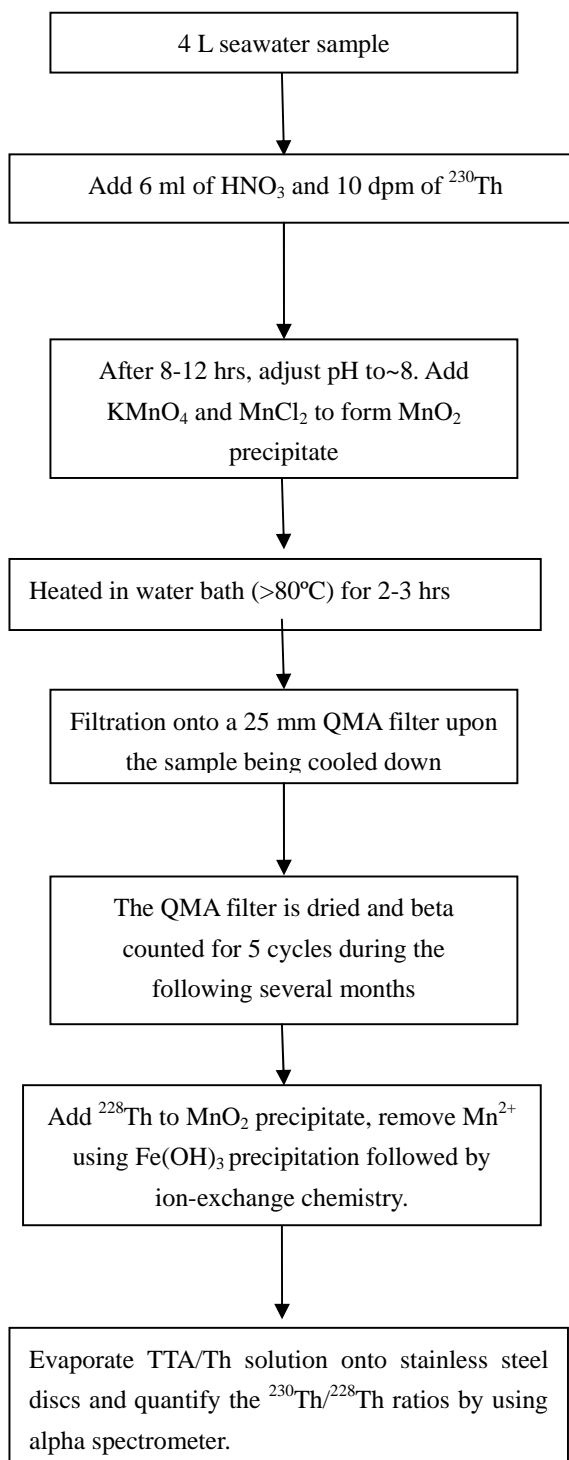


Fig 2

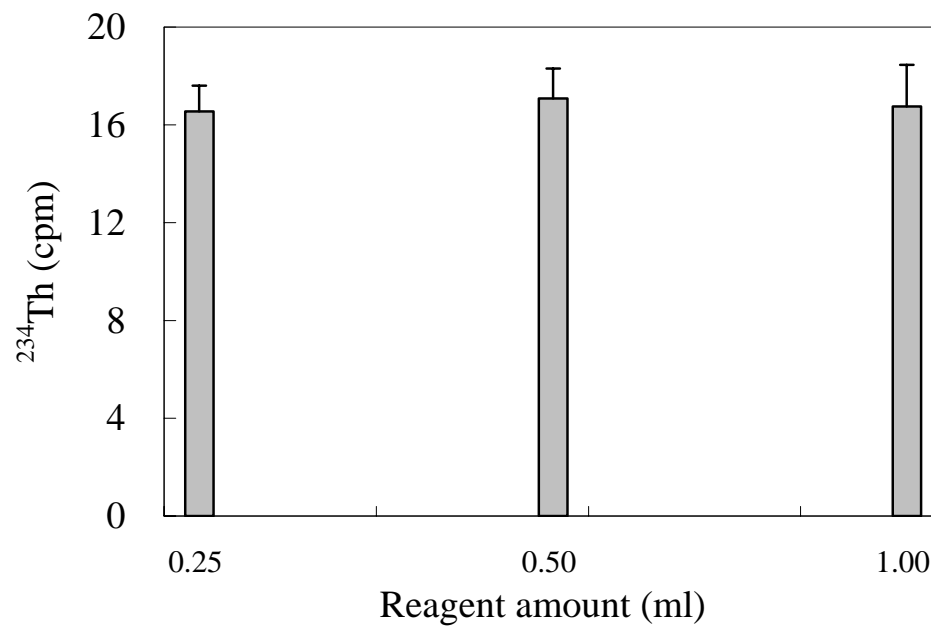


Fig 3

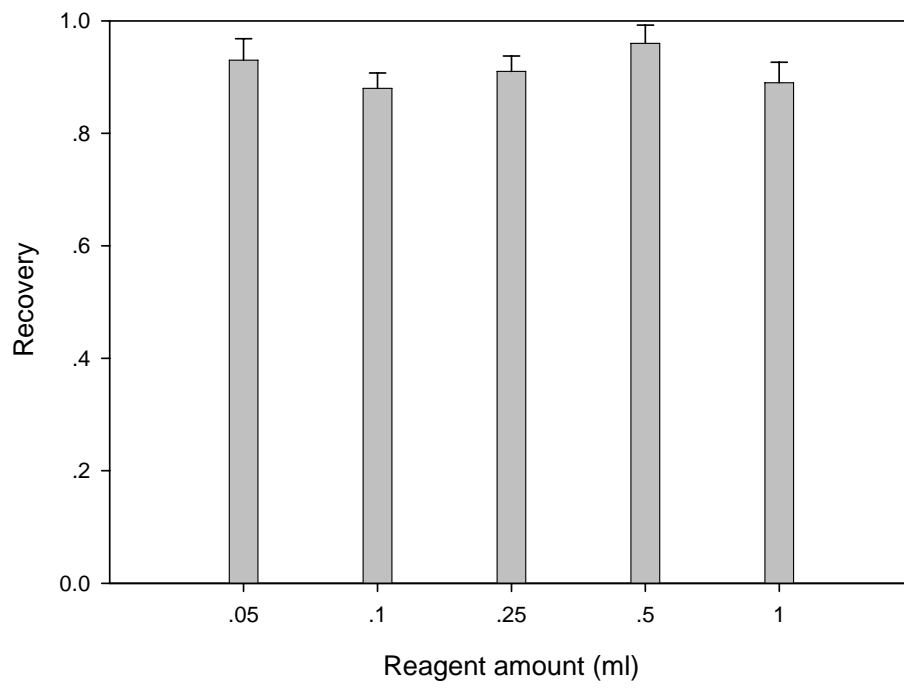


Fig 4

