

A Single vs. Double Spike Approach to Improve the Accuracy of ^{234}Th Measurements in Small-Volume Seawater Samples.

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Abstract

^{234}Th is a particle-reactive radionuclide widely used to trace biogeochemical oceanic processes occurring over short timescales. During the last few years, small-volume techniques based on the co-precipitation of ^{234}Th with MnO_2 coupled with beta-counting have been developed as an alternative to large volume gamma-spectrometric techniques. Here a procedure has been developed to enhance quantitative measurement of ^{234}Th in MnO_2 precipitates. The main objectives were to obtain a purified Th fraction for beta-counting and to determine the chemical recovery of ^{234}Th using Th spikes and alpha-spectrometry as an alternative to ICP-MS based methods. Two variations of the procedure are presented. In the first “1 spike” method a ^{230}Th tracer is added to the sample prior to precipitation of MnO_2 , and UTEVA[®] extraction chromatography is used to obtain a $\text{NdF}_3(\text{Th})$ purified source that can be used for both beta-counting of ^{234}Th and alpha-spectrometry of ^{230}Th . In the “2 spike” method a ^{230}Th spike is added and the $\text{MnO}_2(\text{Th})$ precipitate is directly beta-counted for ^{234}Th and subsequently spiked with ^{228}Th or ^{229}Th prior to UTEVA[®] purification and alpha-spectrometry. The results confirm the need to process small-volume seawater samples for ^{234}Th measurement in presence of a yield tracer, and show that both the 1 spike and 2 spike methods allow an accurate and precise determination of ^{234}Th (relative percent difference, RPD, between expected and mean measured value < 1%; CV between replicate samples < 3%). Our work also suggests that, although the combined analytical uncertainty on total ^{234}Th measurements accomplished with both versions of the NdF_3 procedure is promising (~ 6% for 2-L samples), the precision of the ^{234}Th flux estimation will ultimately depend on the degree of disequilibrium between ^{234}Th and ^{238}U .

Keywords: ^{234}Th ; Extraction Chromatography; Beta-counting; Alpha-Spectrometry;

DYFAMED

1. Introduction

^{234}Th is a naturally occurring radionuclide constantly produced in seawater by its soluble parent ^{238}U . Due to its high particle reactivity (e.g. Santschi et al., 1983) and relatively short half-life ($t_{1/2} = 24.1$ days), ^{234}Th is a suitable tracer of biogeochemical processes occurring over timescales of days to weeks (Bhat et al., 1969; Matsumoto, 1975; Cochran and Masque, 2003). ^{234}Th is commonly used as a proxy to estimate POC export from the upper oceanic water column (Coale and Bruland, 1985; Eppley, 1989; Murray et al., 1989; Buesseler et al., 1992; Benitez-Nelson et al., 2001a). This export is usually assessed by quantifying ^{234}Th deficits with respect to its conservative parent nuclide ^{238}U in large volumes of seawater (100–1000 L), filtered through a series of filters and MnO_2 impregnated cartridges that scavenge ^{234}Th (e.g. Baskaran et al., 1993). Determination of ^{234}Th has been usually performed by gamma-spectrometry of compressed or ashed cartridges. However, over the last few years, it has been recognized that beta-counting of ^{234}Th can improve sensitivity and enable reduced samples sizes. As a result, the co-precipitation of ^{234}Th with MnO_2 from small volumes (2–20 L) of seawater has been increasingly used as an alternative to large volume sampling (e.g. *in-situ* pumping) (Rugters van der Loeff and Moore, 1999; Buesseler et al., 2001; Benitez-Nelson et al., 2001b; Savoye et al., 2004). These techniques have improved precision and have made the acquisition of higher temporal and spatial resolution ^{234}Th depth profiles easier, greatly increasing the potential of using this radionuclide in particle export studies (Rugters Van der Loeff et al., 2005). Yet, only Pike et al. (2005) explicitly proposed the use of internal standards (^{229}Th and ^{230}Th) to assess the accuracy of the radiochemical analysis. By quantifying the yield-tracers by ICP-MS, these authors have shown the

procedure to yield high (mean = 85.6%; n = 123), but variable (as low as 24.8%) recoveries, which strongly recommend the use of yield-tracers in all ^{234}Th measurements performed on small volumes (4 L) of seawater.

Here we present a detailed procedure developed to enhance quantitative measurement of ^{234}Th in MnO_2 precipitates from small volume seawater samples (down to 2 L) according to the technique pioneered by Rutgers van der Loeff and Moore (1999) and further developed by Buesseler et al. (2001) and Benitez-Nelson et al. (2001b). It addresses the problems of (1) ensuring a purified Th fraction for beta-activity measurement, (2) determining the chemical recovery of Th, and (3) using alpha-spectrometry as originally proposed by Bhat et al. (1969). It further utilizes extraction chromatography as an alternative to ICP-MS based methods. Due to the short half-life of ^{234}Th , the original version of the procedure requires purification to be performed as soon as possible. However, since onboard ship purification is a challenging task, we adapted the technique to render it useful during longer scientific cruises when immediate processing is not possible. Thus, we present and compare two variations of the procedure, based on the use of one (original version) or two (onboard adaptation) yield-tracers, henceforth referred to as the “1 spike” and “2 spike” methods respectively.

2. Methods

We initially designed the procedures given below and summarized in Fig. 1 to handle at least two 47 mm MnO_2 -loaded quartz fiber filters (La Rosa et al., unpublished data). These procedures were later modified in order for them to become applicable to other type of filters (i.e. plastic and smaller diameter quartz fiber filters). High purity

nitric, hydrochloric and hydrofluoric acids (Romil Ultra-Pure®) were used throughout the procedure. Other reagents were of analytical grade quality. Procedure blanks were made with new quartz fiber filters and all of the reagents.

2.1. Sample collection and preparation

The procedures described in sections 2.2 and 2.3 (including the addition of 1 mg Zr^{4+} , see section 2.2. step 8) were applied to 2-L natural seawater samples collected between December 2003 and October 2004 in the Eastern Weddell Sea, Antarctica (n = 216) and NW Mediterranean (n = 36).

All samples were pretreated with slight adaptations using the procedure described by Buesseler et al. (2001). Briefly, within one hour of collection, 2-L samples (volume determined with a precision $\leq 1\%$ by either volumetric techniques on board ship or by weight upon return to the laboratory) were acidified with 5 mL of concentrated HCl to $pH < 2$ (this promotes radiochemical exchange between tracer and analyte Th by preventing hydrolysis of Th ions and by decreasing the strength of Th-organic complexes; any strong acid can be used for this purpose), spiked with 200 μL of a ^{230}Th standard solution (0.4302 ± 0.0047 Bq mL^{-1} in 2M HNO_3), and allowed to stand for at least 12 h in order for isotopic equilibrium to be reached (in future, one may consider constantly shaking the samples during this step of the procedure in order to accelerate the expulsion of CO_2 and allow isotopic equilibrium to be achieved in a shorter time, i.e. < 3 h). Subsequently, the sample pH was raised to 8.0 ± 0.2 by addition of ~ 4.5 mL of 25% wt. NH_3 , spiked with 250 μL $KMnO_4$ (6 g L^{-1}), and mixed vigorously. The solution, which by then displayed a magenta color, was subsequently spiked with 100 μL $MnCl_2$ (40 g L^{-1}). Following vigorous mixing, the color of the samples turned amber indicating

the presence of the newly formed MnO_2 suspension. This non-settling precipitate was collected by vacuum filtration, generally within one hour of the start of nucleation, onto 25-mm diameter Whatman Multigrade QM-A filters with a 1 μm nominal pore-size. Upon completion of the filtration (4 to 8 h per sample), the filters and sampling bottles were rinsed 3 times with either distilled (onboard ship) or Milli-Q (laboratory) water and air-dried for at least 3 h (until the precipitate turned from dark to light brown) before being mounted for beta-counting. Drying in an oven at elevated temperatures should be avoided to prevent “cracking” and possible losses of the MnO_2 precipitate. All filtration equipment was rinsed between samples with a 10% H_2O_2 /2N HCl solution followed by distilled/Milli-Q water.

2.2. Procedure for MnO_2 -loaded quartz fiber filter dissolution, Th separation and $\text{NdF}_3(\text{Th})$ source preparation: 1 spike method

1. Introduce 1 or 2 MnO_2 -loaded quartz fiber (QF) filters containing the ^{234}Th and ^{230}Th (spike) scavenged from the water sample into a PTFE beaker. Add 1–2 mL of 1M HNO_3 to wet the filter(s).
2. Carefully add 1 mL of concentrated (40–48%) HF drop wise followed by 2 drops of concentrated (32–37%) HCl. Heat to dissolve and evaporate to dryness to expel SiF_4 and excess HF.
3. Add 8 drops of concentrated HCl to the residue and heat. Then add 1 mL of concentrated HF, heat and evaporate to dryness to expedite SiF_4 removal.
4. Add 2 mL of concentrated (65–70%) HNO_3 and 1 drop of $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution (0.1 g mL^{-1}). Heat and evaporate to dryness to remove excess HF and weakly bound fluoride.

5. Repeat step 4.
6. Add 5 mL of 4M HNO₃ containing 10 mg H₃BO₃ mL⁻¹ and 1 drop of the NH₂OH·HCl solution to the residue. Cover and heat to effect solution with minimal evaporation. (The NH₂OH·HCl assists in re-dissolving any oxidized Mn. H₃BO₃ complexes any traces of fluoride remaining at this point, which might otherwise interfere in the subsequent Th chemistry.)
7. Dilute the sample solution to 10 mL with 4M HNO₃. At this point the solution should be clear. If not, filter to remove any insoluble matter and use the filtrate.
8. Add to the solution 1 mg of Zr⁴⁺ or of Ti⁴⁺ (this step is not required when dealing with two or more 47 mm MnO₂-loaded quartz fiber filters; see Discussion 4.1.).
9. Pass the sample solution through a 2 mL bed volume UTEVA[®] extraction chromatography column, previously conditioned with 20 mL of 4M HNO₃. Rinse the sample solution vessel with a total of 5 mL 4M HNO₃ in 3 portions, passing each rinse successively through the column.
10. Rinse the column successively with 2.5, 2.5 and 15 mL of 3M HNO₃ to wash out the feed solution and any non-retained species. Collect all feed and rinse solutions together, which will be subsequently discarded.
11. Elute Th from the UTEVA[®] column by passing 6M HCl, typically in successive portions of 2.5, 2.5 and 15 mL. Collect this Th strip in a new, clean plastic vial.
12. Add 100 μL of a solution of 1 mg Nd³⁺ mL⁻¹ (as NdCl₃ in 1M HCl) to the Th strip solution, mix well, and add 5 mL of concentrated HF with brief but vigorous mixing. Th is co-precipitated with the NdF₃ (Sill, 1987) that is rapidly formed. Allow the suspension (not visible to the eye under ordinary conditions) to stand

- for 0.5 to 2 h without further agitation to digest at room temperature.
13. Filter the $\text{NdF}_3(\text{Th})$ suspension through a 0.1 μm porosity, 25 mm diameter polypropylene membrane filter (e.g. Pall – Gelman Metrical product no. M5PU025 membrane filters) in a plastic vacuum filtration system at a rate of 1–2 drops s^{-1} . Wash the precipitate (not directly visible on the filter) with three 2-mL portions of dilute (ca. 4%) HF followed by two 1.5–2 mL portions of 80% ethanol solution. With vacuum still applied, remove the filter chimney/funnel and add drops of 80% ethanol around the perimeter of the filter to ensure that traces of the HF solution are removed.
 14. Release the applied vacuum as soon as possible after this last perimeter rinse (to avoid collecting radon daughters attached to aerosol particles within the atmosphere) and place the $\text{NdF}_3(\text{Th})$ -loaded filter on a clean paper towel. Allow to air dry for at least 15 min. Drying in an oven at an elevated temperature should be avoided to prevent possible “curling” of the filter.
 15. For beta-counting of ^{234}Th (via its highly-energetic daughter $^{234\text{m}}\text{Pa}$) in this $\text{NdF}_3(\text{Th})$ source, mount the source on an aluminum absorber ($\sim 7 \text{ mg cm}^{-2}$) to prevent contamination via alpha decay.
 16. For later alpha-measurement of the ^{230}Th tracer, the aluminum absorber must be removed and the source uncovered. It should be measured in an alpha-spectrometer with a calibrated efficiency for the particular NdF_3 source geometry used.

2.3. Procedure for MnO₂-loaded quartz fiber filter dissolution, Th separation and NdF₃(Th) source preparation: 2 spike method

In this method, the MnO₂-loaded filter is first analyzed in a proportional counter to determine the beta-activity from ²³⁴Th. Afterwards, it is dissolved and a NdF₃(Th) source prepared for alpha-spectrometry to determine the Th chemical yield. The procedure for dissolution, chemical separation of Th by UTEVA[®] column, and co-precipitation of Th with NdF₃ is identical to the one used for the 1 spike method (steps 1 through 14) except that a known amount of either ²²⁸Th or ²²⁹Th tracer is added in the first step. The final NdF₃(Th) source will not be beta-counted, but will be measured by alpha-spectrometry to determine the amount of ²³⁰Th that was present in the MnO₂ precipitate.

2.4. Detector calibration

2.4.1. Alpha-detector efficiencies

Three sources, hereafter called “1st NdF₃”, were prepared by spiking 20 mL of 6M HCl with a weighed amount (corresponding to ~ 6 Bq) of ²³⁰Th tracer (33.19 ± 0.32 Bq mL⁻¹ in 2M HNO₃) and precipitating NdF₃(Th) with 100 µg of Nd³⁺. The filtrate from these 1st NdF₃ (containing HF and traces of ²³⁰Th/NdF₃ that passed through the filter) were spiked with another portion of Nd carrier (the same amount as used in 1st NdF₃), shaken well and filtered to produce 2nd NdF₃ sources (after the same time interval elapsed between precipitation and filtration of 1st NdF₃ sources). 1st and 2nd NdF₃ sources were counted on the same detector in the same geometry. In all 3 cases the ²³⁰Th activity measured in the 2nd NdF₃ sources contained negligible activity relative to the 1st NdF₃ ones (< 0.1%), indicating ²³⁰Th had been quantitatively extracted from the solution during

the first NdF_3 co-precipitation step. The 1st NdF_3 sources were used to calibrate 14 different surface barrier Si alpha-detectors (EG&G Ortec).

We assumed that the average of the efficiencies obtained by counting the three external standards in each detector is the best estimate for the true efficiency of the detector itself. Although the total uncertainty on the detector efficiency, as determined by combining uncertainties on standard activities (1%), counting statistics ($\sim 1.8\%$) and geometry (0.3%) should result in $\sim 1.5\%$, the coefficient of variation (CV) of the efficiency values obtained by counting the three standards in each detector averaged 3.6%. This suggested the presence, at least in some detectors, of an unknown source of variability not accounted for in the above mentioned uncertainty computation. The CV determined for a given detector was therefore included in all further uncertainty computations. The counting efficiencies for a $\text{NdF}_3(\text{Th})$ 25-mm diameter source ranged from $19 \pm 1\%$ to $26 \pm 1\%$, for the 14 alpha-detectors used in this work.

2.4.2. Beta-detector efficiencies: 1 spike method

A gas-flow proportional beta-counter with five sample-holders manufactured by RISO National Laboratory (Roskilde, Denmark) MC-3 (hereto referred as MC-3) was calibrated using a $\text{NdF}_3(^{230}\text{Th}-^{234}\text{Th})$ external standard. The source was prepared by adding weighed amounts of ^{230}Th standard solution ($11.8 \pm 0.1 \text{ Bq}$; $33.19 \pm 0.32 \text{ Bq g}^{-1}$ in 2M HNO_3) and of uranyl nitrate solution ($12.4 \pm 0.4 \text{ Bq}$; $[^{238}\text{U}] = [^{234}\text{Th}] = 227 \pm 7 \text{ Bq g}^{-1}$ in 2M HNO_3) to a QMA 25-mm diameter filter in a PTFE 50 mL beaker together with 1 mL of 2M HNO_3 . The sample was then processed according to the 1 spike method before undergoing extraction chromatography separation with UTEVA[®] resin. The source was mounted in the same geometry as the samples and counted in each of the five detectors of

RISO beta counting system MC-3 at 7, 11 and 38 days after purification. The net beta-count rate was corrected for Th chemical recovery ($81 \pm 4\%$), and for ^{234}Th decay at the mid-time of purification and compared with the nominal added ^{238}U activity. The mean efficiency value ($\pm 1\sigma$) averaged for all 5 detectors of system MC-3 was estimated to be $51 \pm 1\%$.

2.4.3. Beta-detector efficiencies: 2 spike method

In the 2 spike method, three different RISO beta-counters, hereafter referred to as MC-1, MC-2 and MC-3, were calibrated using three different techniques: (1) a weighed amount (corresponding to 22.7 ± 0.7 Bq) of uranyl nitrate standard solution in 2M HNO_3 ($[^{238}\text{U}] = [^{234}\text{Th}] = 227 \pm 7$ Bq mL^{-1}) spiked onto filters containing MnO_2 precipitates using the same mounting procedure as the samples (in order to reproduce the self-absorption characteristics of the samples, the MnO_2 standards were prepared by spiking aged MnO_2 sources obtained by co-precipitating Th in seawater from different particle regime environments); (2) five sources obtained by gravimetric addition of different amounts (5 to 30 mg) of a U_3O_8 primary standard to filters mounted with the same geometry as the samples; and (3) five standards obtained from acidified Antarctic deep water, aged for > 6 months to allow for ^{234}Th and ^{238}U to be in secular equilibrium and processed in the same way as the samples. In this last technique ^{238}U was determined by ICP-MS (Wyse et al., 2004). The external standards were counted multiple times and the data combined. The mean efficiency value ($\pm 1\sigma$) averaged for all 5 detectors of systems MC-1, MC-2 and MC-3, was estimated to be $50 \pm 1\%$, $40 \pm 4\%$ and $51 \pm 1\%$, respectively.

2.5. Data analysis

2.5.1. Alpha-spectrometry

^{228}Th was chosen as the 2nd tracer in the 2 spike method because its mean alpha-peaks (5.423 MeV [72.7%] and 5.341 [26.7%] MeV) are well defined and easily discriminated from those of ^{230}Th (4.688 MeV [76.3%] and 4.621 [23.4%] MeV), whereas the ^{229}Th spectrum quasi-overlaps with that of ^{230}Th and is broader due to its multiple branching ratios between 4.814 and 5.050 MeV. The ^{228}Th gross count rate must be corrected for a small interference due to the ^{228}Th daughter nuclide ^{224}Ra , which has a branching ratio of 4.9% at 5.449 MeV (see Fig. 2). A Region Of Interest (ROI) of 100-150 channels and corresponding to 500-600 keV was used to integrate the peak areas of both ^{228}Th and ^{230}Th .

The chemical recovery of the MnO_2 co-precipitation, and thus the percentage of ^{234}Th initially present in the sample and actually beta-counted, was estimated according to the following formula:

$$^{234}\text{Th}_{\text{yield}} = ^{230}\text{Th}_{\text{net}} * (^{228}\text{Th}_{\text{net}})^{-1} * ^{228}\text{Th}_{\text{std}} * (^{230}\text{Th}_{\text{std}})^{-1} * 100 \quad \text{Eq. 1}$$

where:

$$^{228}\text{Th}_{\text{net}} = ^{228}\text{Th net count rate as determined by alpha-spectrometry (s}^{-1}\text{)}$$

$$^{230}\text{Th}_{\text{net}} = ^{230}\text{Th net count rate as determined by alpha-spectrometry (s}^{-1}\text{)}$$

$$^{228}\text{Th}_{\text{std}} = ^{228}\text{Th spiked activity (Bq)}$$

$$^{230}\text{Th}_{\text{std}} = ^{230}\text{Th spiked activity (Bq)}$$

$$^{234}\text{Th}_{\text{yield}} = ^{234}\text{Th chemical recovery (\%)} \text{ at initial counting time.}$$

The same formula is applicable to the 1 spike method by simply deleting the ^{228}Th terms and dividing by the effective efficiency of the detector ($\text{s}^{-1} \text{ Bq}^{-1}$).

It should to be noted that net count rates take into account a small correction for the ^{230}Th and ^{228}Th contributions derived from the QM-A filters, e.g. $\sim 8 \times 10^{-5}$ and $\sim 3 \times 10^{-5}$ s^{-1} respectively. Uncertainties in chemical recoveries were obtained by propagating uncertainties from counting statistics and the counting efficiency of each individual alpha-detector (includes uncertainties from counting, spike volume and activity of the standard) and were on the order of 5% and 4% for the 1 spike and 2 spike methods, respectively.

2.5.2. Beta-Counting

Initial ^{234}Th net count rates and background count rates from the detector and other beta-emitters present in the sample were estimated with an approach similar to the “multi-count technique” described by Buesseler et al. (2001) and the “multiple beta-count method” described by Waples et al. (2003). Briefly, raw count rates were plotted against the exponential decay of ^{234}Th over time, $e^{-\lambda t}$ (λ being the decay constant of ^{234}Th and t the time interval between the sampling and the average of the counting time) and a weighed least squares regression line was fitted to the data (Zar, 1996). ^{234}Th net count rates at the time of MnO_2 co-precipitation were estimated as the slope of the regression line and the background as the Y-intercept (Fig. 3). Successful completion of a reduced- χ^2 test on each set of repeated counts validated the quality of the estimates (Zar, 1996). Uncertainties propagated from counting statistics and based upon the fit to the raw counts resulted in an overall uncertainty on the estimated ^{234}Th net count rate of $\sim 3\%$ for both versions of the procedure (this value corresponds to a 1000 min beta-counting session).

^{234}Th activity at the time of sampling ($^{234}\text{Th}_{t_0}$; Bq) was estimated using the following equation, which combines data on the ^{234}Th net count rate, chemical recovery

of the MnO₂ co-precipitation, efficiency of the beta-detectors (calculated for each individual beta-counter to be ~3.5%), and ingrowth from ²³⁸U activity in the sample:

$${}^{234}\text{Th}_{\text{to}} = {}^{234}\text{Th}_{\text{net}} * ({}^{234}\text{Th}_{\text{yield}})^{-1} * (\beta \text{ efficiency})^{-1} * (e^{-\lambda t})^{-1} - {}^{238}\text{U}_{\text{to}} * (1 - e^{-\lambda t}) \quad \text{Eq. 2}$$

where:

- ${}^{234}\text{Th}_{\text{net}}$ = ²³⁴Th net count rate at the time of MnO₂ co-precipitation as determined by beta-counting and least-squares regression (s⁻¹)
- ${}^{234}\text{Th}_{\text{yield}}$ = ²³⁴Th_{yield} chemical recovery as determined by alpha-spectrometry of ²³⁰Th tracer present in the sample
- β-efficiency = effective efficiency of each gas-proportional counter (s⁻¹ Bq⁻¹)
- λ = decay constant of ²³⁴Th [t⁻¹]
- t = interval between sampling and the MnO₂ co-precipitation [t].
- ${}^{238}\text{U}_{\text{to}}$ = ²³⁸U activity at the time of sampling (Bq).

3. Results

3.1. Double spike

A total of 228 2-L seawater samples from 21 different stations (Eastern Weddell Sea, Antarctica) and 5 spiked 2-L seawater samples were processed using the 2 spike method described in section 2.1. The average recovery for the MnO₂ precipitation was 91% with a CV of 11% (range from 34 ± 3% to 109 ± 11%; n = 228) for the natural samples and 91% with a CV of 2% (range from 88 ± 2% to 92 ± 2%; n = 5) for the spiked ones. The average recovery for the UTEVA[®] purification was 96% with a CV of 7%

(range from $62 \pm 3\%$ to $113 \pm 7\%$; $n = 216$) and 99% (range from $95 \pm 4\%$ to $101 \pm 4\%$) with a CV of 2% for the natural and spiked seawater samples, respectively.

Five replicates of spiked seawater (activity of ^{230}Th tracer = $1.01 \pm 0.01 \text{ Bq L}^{-1}$; activity of ^{234}Th tracer = $1.09 \pm 0.04 \text{ Bq L}^{-1}$ [from a $\text{UO}_2(\text{NO}_3)_2$ standard solution with nominal ^{238}U activity of $227 \pm 7 \text{ Bq mL}^{-1}$]) were processed using the 2 spike method in order to test accuracy and precision of the procedure. The results of this experiment, shown in Fig. 4, indicate that the method has very good accuracy (RPD between the expected and mean measured ^{234}Th activities of 1.6%) and high precision (CV $< 1\%$).

3.2. Single spike

The 1 spike method was applied to both natural ($n = 24$) and spiked ($n = 5$) 2-L seawater samples. The average recovery for the MnO_2 precipitation and UTEVA[®] purification combination for the spiked samples was 86% with a CV of 3% (range from $80 \pm 4\%$ to $92 \pm 4\%$) and 89% with a CV of 7% (range from $74 \pm 4\%$ to $99 \pm 6\%$) for the natural ones.

Five replicates of spiked seawater (activity of ^{230}Th tracer = $3.25 \pm 0.03 \text{ Bq L}^{-1}$; activity of ^{234}Th tracer = $3.11 \pm 0.09 \text{ Bq L}^{-1}$) were processed according to the 1 spike method in order to test accuracy and precision of the procedure. This method has the advantage that it is not sensitive to slight variations in the beta-counter background ($\sim 0.003 \text{ s}^{-1}$). However, it is sensitive to the variability in the chemical recovery determination, which in this case depends on the reproducibility of the NdF_3 source geometry. Results indicate that both the precision (CV $< 1\%$) and accuracy (RPD = 1.9%) of the method are very good (Fig. 5).

In order to test the integrity of the NdF₃ precipitate and the sensitivity of the detector efficiency to slight variations in the position of the sample relative to the Si detector, a ²³⁰Th source was re-positioned 17 times consecutively in the same alpha-tray in different positions (uppermost, lowermost, leftmost, rightmost and center) in the 26 mm cavity. Between each operation, the sample was counted in a selected detector long enough to reach satisfactory counting statistics ($1\sigma = 1.8\%$). The results showed variability similar to that expected from counting statistics alone ($1\sigma = 2.1\%$).

Each of the 5 spiked seawater sources was counted 7 times over a period of 1 month in each of the 5 sample holders of MC-3 beta-counting system and again at least 2 times in 5 different alpha-chambers. Estimated activities displayed a mean CV of 1.1% among sources (range from 0.6 to 1.5%) and 1.3% among detectors (range from 0.8 to 1.7%) for beta-counting (²³⁴Th) and 3.2% among sources (range from 2.1 to 3.7%) and 2.1% among detectors (range from 1.4 to 3.0%) for alpha-counting (²³⁰Th). The excellent reproducibility and narrow uncertainty ranges confirm the quality of intercalibration and resilience of the processed samples during careful handling (the samples were removed from the beta-holders and alpha-trays 3 times during the above mentioned operations).

3.3. In-field reproducibility

On 26 October 2004, during one of the monthly samplings at the DYFAMED station of the *Service d'Observation DYFAMED* (SODYF), 2-L samples (n = 36; 12 depths with 3 replicates) were collected and processed following the 1 spike (n = 24) and the 2 spike (n = 12) methods (Fig. 6). The average RPD between each pair of 1 spike replicates resulted in $2.4 \pm 1.7\%$ (range from 0.2 to 6.0%) and the CV between the

triplicates was $2.7 \pm 0.8\%$ (range from 0.7 to 6.3%), indicating excellent in-field reproducibility of the two techniques.

4. Discussion

4.1. Radiochemical considerations

Extraction chromatography with 2 mL UTEVA[®] resin columns was used to purify Th because mono-, di- and trivalent ions, including those of Mn, Fe, Ca, Pb, Bi, Ra and Ac, are not retained by UTEVA[®] from 4M HNO₃, whereas hexavalent U and tetravalent Th ions are. Th⁴⁺ is rapidly and selectively stripped from UTEVA[®] by 6M HCl, while U⁶⁺ is strongly retained (Horwitz et al., 1992). Our experiments with the separation of Th from MnO₂-loaded, 47 mm diameter quartz fiber filters gave excellent results for both Th purification and chemical recovery.

However, in later experiments with pure ²²⁸Th and ²³⁰Th tracers (i.e., without dissolved QF filter), the Th tracers could not be recovered from the UTEVA[®] column with 6M HCl. It was subsequently found that the addition of 1 mg of either Ti⁴⁺ or Zr⁴⁺, chemical analogues of Th⁴⁺, to the ²²⁸Th and ²³⁰Th spikes into the 4M HNO₃ feed solution allowed the tracers to be quantitatively stripped with 6M HCl. This suggested that at least some UTEVA[®] batches contained an extractant, perhaps an impurity, which had an affinity for Th⁴⁺ much greater than that specifically attributed to UTEVA[®]. The 1 mg of Ti⁴⁺ or Zr⁴⁺ was apparently able to saturate this non-UTEVA[®] extractant, thereby permitting the Th to be stripped from UTEVA[®] in 6M HCl. Using semi-quantitative X-ray fluorescence, we found that the quartz fiber filters in our experiments contained small but definite amounts of Ti and Zr, which are likely to have facilitated the 6M HCl

stripping of Th from the UTEVA[®] columns. Thus, if a cellulose or plastic filter is used, or if the quartz fiber filter does not contain any Ti or Zr, it may be necessary to add 1 mg of Ti or Zr to the dissolved MnO₂-filter solution in 4M HNO₃ before passing it through the UTEVA[®] column. Any Ti or Zr that might accompany the Th in the 6M HCl will not hinder subsequent NdF₃(Th) precipitation because both Ti⁴⁺ and Zr⁴⁺ form stable fluoride complexes that are soluble in excess HF.

4.2. Self-absorption characteristics of NdF₃ sources

The average thickness of 140 µg of NdF₃ (corresponding to 100 µg Nd) in a 2.3-cm diameter source (i.e., slightly less than the 2.5-cm diameter filter) is 34 µg cm⁻², assuming uniform deposition. The range of a 5 MeV alpha particle in NdF₃ is calculated to be ~8 mg cm⁻² of NdF₃ (Fig. 4-4 and equations 4-8 and 4-9; Friedlander et al., 1981). Therefore, in principle, no alpha particle is absorbed by the NdF₃ deposit: even an alpha particle originating at the bottom of the NdF₃ layer and passing through twice the average thickness (68 µg cm⁻²) would be counted by the detector. It would, however, lose some energy, contributing to the poorer resolution observed for NdF₃ sources compared to "weightless" electrodeposited sources. Nonetheless, the resolution obtained with NdF₃ sources (typically 60–120 keV FWHM) is more than satisfactory for alpha spectrometry measurements, easily resolving ²³⁰Th alphas from those of ²²⁹Th, ²²⁸Th and ²³²Th. The adequacy of this resolving power is illustrated in Fig. 2.

In turn, the self-absorption of the high-energy beta emission of ^{234m}Pa (1.1 min daughter of ²³⁴Th) in the NdF₃ is negligible. The maximum beta energy of the ^{234m}Pa beta particle is 2.3 MeV, corresponding to half-thickness of 160 mg cm⁻² Al absorber.

Considering the average thickness of the NdF₃ to be 34 µg cm⁻², we can neglect any self-

absorption. There will be a slight attenuation of beta particles in the external Al absorber used to remove the ^{230}Th spike alpha particles, which is taken into account during the efficiency calibration for the proportional beta counter.

4.3. Verification of methods and uncertainties

Experimental evidence has indicated that both methods enable precise and accurate determination of ^{234}Th in small volume samples. Provided there are adequate laboratory facilities (i.e., alpha-detectors, multiple column rack and filtering device), both methods easily allow a throughput of 12 samples per person per day from UTEVA[®] purification to spectrometric measurements, which generally last about 24 h, long enough to reach satisfactory counting statistics (uncertainty $\leq 3\%$).

The combined uncertainty of each ^{234}Th activity concentration was calculated using the traditional numerical method of error propagation, which is based on the following relationship between the uncertainty $u(y)$ of the value $y(x_1, \dots, x_n)$ and the uncertainty of the independent parameters x_1, \dots, x_n on which it depends:

$$u(y(x_1, \dots, x_n)) = ((\delta y / \delta x_1)^2 * (u(x_1))^2 + \dots + (\delta y / \delta x_n)^2 * (u(x_n))^2)^{0.5} \quad \text{Eq. 3}$$

where $\delta y / \delta x_i$ is the partial differential of y with respect to x_i (EURACHEM-CITAC Guide, 1995). However Tables 1 and 2 present the results obtained when computing the uncertainties associated with ^{234}Th activity values (for both variants of the procedure) by using the “spreadsheet method” described by Kragten (1994) because, by showing the contribution of the individual uncertainty components to the overall uncertainty, it allows all significant components (last line of Tables 1 and 2) to be easily identified. This method takes advantage of an approximate numerical method of differentiation and only requires knowledge of (a) the equation to calculate the final result, and (b) the parameters

with their associated individual uncertainties. In essence, it is based on the principle that, with reference to Eq. 3, if either the term $y(x_1, x_2, \dots, x_n)$ is linear in (x_1, \dots, x_n) or $u(x_1, \dots, x_n)$ is small compared to (x_1, \dots, x_n) , then the differentials $(\delta y / \delta x_i)$ can be simplified as follows:

$$(\delta y / \delta x_i) \approx (y(x_i + u(x_i)) - y(x_i)) / u(x_i) \quad \text{Eq. 4}$$

and thus the $u(y, x_i)$ can be approximated as the difference between the values of y calculated for $[x_i + u(x_i)]$ and x_i respectively. This simplified method has been used to generate the matrices on the left side of Tables 1 and 2, where the numbers in bold in each line-vector represent the varied value $[x_i + u(x_i)]$ of the corresponding independent variable (x_i) (terms in bold on the right side of the tables).

The 1 spike method has several advantages; (1) the $\text{NdF}_3(\text{Th})$ source is used for both beta-counting and alpha-spectrometry; (2) it can be applied to measure ^{234}Th in different amounts of MnO_2 precipitate (since ^{234}Th is measured in the NdF_3 source, it is not necessary to limit the filtration of the MnO_2 to a 25 mm filter diameter; in principle, one could use one or more paper membrane filters of larger diameter to collect the precipitate) and, with slight modifications, even in gram-quantities of biological samples (Rodriguez y Baena and Boudjenoun, unpublished procedure); and (3) it contains a purified Th fraction in which self-absorption induced effects are greatly reduced (in the NdF_3 source there is essentially no attenuation compared to MnO_2 sources where there may be extra material from insoluble matter in unfiltered seawater to cause variable attenuation). The average beta-counting background of all three counters ($0.0033 \pm 0.0008 \text{ s}^{-1}$; $n = 24$) matches within uncertainty the count rate of the procedure blank ($0.0037 \pm 0.0008 \text{ s}^{-1}$; $n = 5$), and is about 40% lower than those associated with MnO_2

sources ($0.006 \pm 0.001 \text{ s}^{-1}$; $n = 216$) for sources in this geometry. This helps to reduce the “determination limit” of the technique (Currie, 1968). Since the background is low and consistent, it also suggests that estimating ^{234}Th activity ($^{234}\text{Th}_{\text{to}}$; Bq) using a “single beta-counting method” may be possible. This estimation process would be based on the following equation:

$$^{234}\text{Th}_{\text{to}} = (^{234}\text{Th}_{\text{gross}} - ^{234}\text{Th}_{\text{blk}}) * (^{234}\text{Th}_{\text{yield}})^{-1} * (\beta \text{ eff.})^{-1} * (e^{-\lambda t_1})^{-1} - ^{238}\text{U} * (1 - e^{-\lambda t_2}) \quad \text{Eq. 5}$$

where:

- $^{234}\text{Th}_{\text{gross}}$ = ^{234}Th gross count rate as determined by beta-counting (s^{-1})
- $^{234}\text{Th}_{\text{blk}}$ = procedure-blank and instrumental contribution to ^{234}Th count rate (s^{-1})
- $^{234}\text{Th}_{\text{yield}}$ = $^{234}\text{Th}_{\text{yield}}$ chemical recovery as determined by alpha-spectrometry of ^{230}Th tracer present in the sample
- β -eff. = effective efficiency of each gas-proportional counter ($\text{s}^{-1} \text{ Bq}^{-1}$)
- λ = decay constant of ^{234}Th [t^{-1}]
- t_1 = time interval between sampling and the average of counting time [t].
- ^{238}U = ^{238}U activity in sample (Bq)
- t_2 = time interval between sampling and MnO_2 co-precipitation [t].

This equation is an alternative to Eq. 2 described in section 2.5.2. The former must be applied when one has to monitor the decay behavior of a ^{234}Th source due to the presence of highly energetic beta-emitting nuclides other than ^{234}Th ($^{234\text{m}}\text{Pa}$) that coprecipitate with MnO_2 and may bias ^{234}Th measurements. In contrast, in the case of a purified NdF_3 source shielded with an appropriate absorber (used to decrease alpha- and weak beta-

emissions), interferences are limited to only Th isotopes, which may have progeny that emit energetic beta-particles (e.g., ^{228}Th , ^{229}Th , and ^{231}Th). Given that ^{229}Th is an anthropogenic radionuclide and that ^{231}Th is extremely rare (Friedlander et al., 1983), ^{228}Th remains the only radionuclide that may interfere with ^{234}Th beta-counting. In case non-negligible amounts of this isotope are present in the sample (a seldom occurrence in marine samples), it can be easily detected by alpha-spectrometry of the NdF_3 source prior to beta-counting, and one may decide to estimate ^{234}Th activity by applying the combined beta-count method. Alternatively, the same result can be achieved by quantifying and correcting for ^{228}Th progeny contributions to the total beta-count rate (Waples et al., 2003). When applied to the set of data obtained from the DYFAMED site with the 1 spike method, the single count method always yielded ^{234}Th activity values matching (within uncertainty) those estimated using the combined beta-count approach (average RPD for each pair of measurements is 2.1%, range from 0.2 to 6.2%, $n = 24$). As can be seen from the example reported in Table 1, the uncertainty associated with the single count method is slightly lower than that associated with the combined beta-count method. The contribution of alpha-spectrometry and beta-counting uncertainties in the single count method accounts for about 86% of the total uncertainty on ^{234}Th activity, whereas it represents slightly less, $\sim 80\%$ total uncertainty, in the combined beta-count method. This phenomenon can be explained by the fact that the uncertainty of the “Net cnt rate” parameter in Table 1A results from the combination of the counting uncertainties associated with 6 different beta-counting times, which can only be greater than the uncertainty associated with a single measurement. By allowing the identification of beta-interferences, including those that could have been accidentally overlooked during the

earlier phases of the procedure (i.e., false single measurement due to temporary beta-counter misbehavior or short-lived contamination in the source), repeated counts will improve method accuracy and are strongly recommended. However, the 1 spike method requires chemical separation soon after the MnO₂ sample is prepared in order to measure ²³⁴Th, and it depends on the alpha-spectrometer calibration, thus displaying a slightly higher uncertainty than the 2 spike method in ²³⁴Th determinations (see Tables 1A and 2).

The 2 spike method uses the MnO₂ source for direct beta-counting and has several practical advantages, namely (1) it can be applied onboard during long cruises if a beta-detector is available (laboratory facilities for chemical separation may not be), (2) it does not require the MnO₂ source to be purified without delay prior to beta-counting to prevent problems related to ²³⁴Th decay, and (3) it does not rely on the calibration of the alpha-detectors. Besides the fact that the procedure requires a second Th tracer and subsequent chemical separation for alpha-source preparation, the MnO₂ source displays a higher beta-background (as mentioned earlier) and is likely to be sensitive to self-absorption induced biases in beta-counting due to differences in the quality/quantity of the MnO₂ precipitate.

A practical example of how the analytical uncertainty on ²³⁴Th activity may impact the uncertainty on ²³⁴Th fluxes was generated by computing a steady state ²³⁴Th flux at 100 m for the set of data presented in Fig. 6, i.e. $5.0 \pm 5.1 \text{ Bq m}^{-2} \text{ d}^{-1}$. This error appears quite high, since the combined analytical uncertainty of the ²³⁴Th activity concentration for these samples is only ~6%. Rather, the 100% uncertainty is only partially due to the analytical uncertainty, it mainly depends on the very low (~3.9%) deficit of ²³⁴Th with respect to ²³⁸U at the sampling site. For instance, if one was to

reduce the analytical uncertainty by a factor 2, the uncertainty on the flux would only be reduced to ~65%. The same result could be obtained by doubling the number of sampled depths. However, if a ^{234}Th deficit a factor of two larger is assumed, the uncertainty would decrease to 45% and would continue doing so in an exponential manner until reaching values $\leq 15\%$ for deficits $\geq 20\%$. Further discussion on the subject would exceed the scope of this paper. However, it is important to point out that even though the analytical uncertainty on ^{234}Th measurements obtained by both versions of the NdF_3 procedure is very good, a precise estimation of ^{234}Th export can only be reached in regions characterized by particle export regimes generating relatively large ^{234}Th deficits.

5. Conclusion

This study has shown that small volume MnO_2 co-precipitation techniques yield high mean recoveries, in good agreement with the results of Pike et al. (2005). Our results further suggest that recoveries may vary occasionally. Thus, it is strongly recommended that ^{234}Th measurements in small volume samples use a yield tracer. This enables reliable data to be obtained regardless of any technical/analytical problem that may occur during sample processing. The data presented shows that (1) UTEVA[®] separation of Th yields excellent average chemical recoveries (96%); (2) both the 1 spike and 2 spike methods enable an accurate (RPD between expected and mean measured value $<1\%$) and precise (CV for spiked seawater samples $<2\%$; mean CV between natural seawater samples $<3\%$) determination of ^{234}Th in small-volume seawater samples; (3) the combined uncertainty on ^{234}Th activity concentration values is comparable for the two methods (~

6% for 2-L samples), and (4) confirm the versatility of the NdF₃(Th) procedure.

Choosing which method to use will mainly depend upon facilities available for the experiments. However, if logistics are not a limiting factor, the 1 spike and multiple count procedure is preferred as (1) problems associated with the potential presence in the source of highly energetic beta-emitting nuclides other than ²³⁴Th (^{234m}Pa) are avoided; (2) it is possible to assess ²³⁴Th activity in the sample with good approximation after having beta-counted the sources only once; and (3) the geometry of the NdF₃ sources is highly reproducible and their beta background is low and consistent.

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References

- Baskaran, M., Murphy, D.J., Santschi, P.H., Orr, J.C. and Schink, D.R., 1993. A method for rapid in situ extraction and laboratory determination of Th, Pb, and Ra isotopes from large volumes of seawater. *Deep Sea Res. Part I* 40, 849-865.
- Benitez-Nelson, C., Buesseler, K.O., Karl, D.M. and Andrews, J., 2001a. A time-series study of particulate matter export in the North Pacific Subtropical Gyre based on ^{234}Th : ^{238}U disequilibrium. *Deep Sea Res. Part I* 48, 2595-2611.
- Benitez-Nelson, C.R. et al., 2001b. Testing a new small-volume technique for determining thorium-234 in seawater. *J. Radioanal. Nucl. Chem.* 248, 795-799.
- Bhat, S.G., Krishnaswami, S., Lal, D., Rama, D. and More, W.S., 1969. $^{234}\text{Th}/^{238}\text{U}$ ratios in the ocean. *Earth Planet. Sci. Lett.* 5, 483-491.
- Buesseler, K.O., Bacon, M.P., Kirk Cochran, J. and Livingston, H.D., 1992. Carbon and nitrogen export during the JGOFS North Atlantic Bloom experiment estimated from ^{234}Th : ^{238}U disequilibria. *Deep Sea Res. Part I* 39, 1115-1137.
- Buesseler, K.O., Benitez-Nelson, C., Rutgers van der Loeff, M., Andrews, J., Ball, L., Crossin, G. and Charette, M., 2001. An intercomparison of small- and large-volume techniques for thorium-234 in seawater. *Mar. Chem.* 74, 15-28.
- Chen, J.H., Lawrence Edwards, R. and Wasserburg, G.J., 1986. ^{238}U , ^{234}U and ^{232}Th in seawater. *Earth Planet. Sci. Lett.* 80, 241-251.
- Coale, K.H. and Bruland, K.W., 1985. ^{234}Th : ^{238}U disequilibria within the California Current. *Limnol. Oceanog.* 30, 22-33.

- Cochran, J.K. and Masque, P., 2003. Short-lived U/Th series radionuclides in the ocean: Tracers for scavenging rates, export fluxes and particle dynamics, Uranium-Series Geochemistry. *Rev. Mineral. Geochem.* 52, 461-492.
- Currie, L.A., 1968. Limits of qualitative detection and quantitative determination. *Anal. Chem.* 40, 586-593.
- Eppley, R., 1989. New production: history, methods and problems. In: W.H. Berger, V. Smetacek and O. Wefer (Editors), *Productivity of the Ocean: Present and Past: Dahlem Workshop Reports*. John Wiley & Sons Inc, New York, USA, pp. 85-97.
- EURACHEM-CITAC Guide, 1995. Quantifying uncertainty in analytical measurements. EURACHEM.
- Friedlander, G., Kennedy, J.W., Macias, E.S. and Miller, J.M., 1981. *Nuclear and Radiochemistry*. John Wiley & Sons Inc, New York, USA.
- Horwitz, E.P., Dietz, M.L., Chiarizia, R., Diamond, H., Essling, A.M. and Graczyk, D., 1992. Separation and preconcentration of uranium from acidic media by extraction chromatography. *Anal. Chim. Acta.* 266, 25-37.
- Kragten, J., 1994. Calculating Standard Deviations and Confidence Intervals with a Universally Applicable Spreadsheet Technique. *Analyst* 119, 2161-2166.
- Matsumoto, E., 1975. ^{234}Th - ^{238}U radioactive disequilibrium in the surface layer of the ocean. *Geochim. Cosmochim. Acta* 39, 205-212.
- Murray, J.W., Downes, J.N., Strom, S., Wei, C. and Jannash, H.W., 1989. Nutrient assimilation, export production and ^{234}Th scavenging in the eastern equatorial Pacific. *Deep Sea Res. Part I* 36, 1471-1489.

- Pike, S.M., Buesseler, K.O., Andrews, J.A. and Savoye, N., 2005. Quantification of ^{234}Th recovery in small volume sea water samples by inductively coupled plasma mass spectrometry. *J. Radioanal. Nucl. Chem.* 263, 355-360.
- Quigley, M.S., Santschi, P.H., Guo, L. and Honeyman, B.D., 2001. Sorption irreversibility and coagulation behaviour of ^{234}Th with marine organic matter. *Mar. Chem.* 76, 27-45.
- Rutgers van der Loeff, M.M., Moore, W.S., 1999. Determination of natural radioactive tracers. In: Grasshoff, K., Kremling, K., Ehrhardt, M. (Eds.), *Methods of Seawater Analysis*. Wiley-VCH, Weinheim, pp. 365– 397. Chapter 13.
- Rutgers van der Loeff, M., Sarin, M.M., Baskaran, M., Benitez-Nelson, C., Buesseler, K.O., Charette, M., Dai, M., Gustafsson, O., Masque, P., Morris, P., Orlandini, K., Rodriguez y Baena, A.M., Savoye, N., Schmidt, S., Turnewitsch, R., Vöge, I., and Waples, J. T., 2005. A review of present techniques and methodological advances in analyzing ^{234}Th in aquatic systems, *Marine Chemistry*, FATE special issue.
- Santschi, P.H., Li, Y.-H., Adler, D.M., Amdurer, M., Bell, J. and Nyffeler, U.P., 1983. The relative mobility of natural (Th, Pb and Po) and fallout (Pu, Am, Cs) radionuclides in the coastal marine environment: results from model ecosystems (MERL) and Narragansett Bay. *Geochim. Cosmochim. Acta* 47, 201-210.
- Savoye, N., Buesseler, K.O., Cardinal, D. and Dehairs, F., 2004. ^{234}Th deficit and excess in the Southern Ocean during spring 2001: Particle export and remineralisation. *Geophys. Res. Lett.* 31, L12301.

- Sill, C.W., 1987. Precipitation of actinides as fluorides or hydroxides for high-resolution alpha spectrometry. Nucl. Chem. Waste Manag. 7, 201-215.
- Waples, J.T., Orlandini, K.A., Weckerly, K.M., Edgington, D.N. and Val Klump, J., 2003. Measuring low concentrations of ^{234}Th in water and sediment. Mar. Chem. 80, 265-281.
- Wyse, E., Lee, S.-H., Rodriguez y Baena, A.M., Azemard, S., Miquel, J.C., Povinec, P.P., De Mora, S., in press. Measurement of Radioisotopes in Marine Samples by Sector Field ICP-MS. In: Proceedings of the Aquatic Forum 2004 IAEA Conference, Monaco (Principality of Monaco).
- Zar, J.H., 1996. Biostatistical Analysis. Prentice Hall International, Upper Saddle River, New Jersey.

Captions to Figures

Fig. 1. Flow diagram summarizing the 1 spike and 2 spike methods.

Fig. 2. Example of a ^{228}Th - ^{230}Th alpha-spectrum obtained by counting for $\sim 87\,000$ s a 25-mm diameter $\text{NdF}_3(\text{Th})$ source relative to a 2-L seawater sample from the DYFAMED site treated following the 2 spike method.

Fig. 3. Plot of ^{234}Th count rate vs. $e^{-\lambda t}$ (λ : ^{234}Th decay constant, [t^{-1}]; t : time interval between sampling and mid-counting time, [t]) for a sample from the DYFAMED site analyzed using the 1 spike method. The parameters (initial ^{234}Th net count rate [$\text{CR}_0^{234}\text{Th}$] and overall background) of the weighed least square regression are reported; reduced- χ^2 value indicates the goodness of the fit.

Fig. 4. ^{234}Th analytical reproducibility using the 2 spike method with spiked seawater samples. Shaded area: expected $[^{234}\text{Th}] \pm 1\sigma$; black dots: measured $[^{234}\text{Th}] \pm 1\sigma$ (analytical uncertainty); dashed lines: $\pm 1\sigma$ of the 5 replicates distribution.

Fig. 5. ^{234}Th analytical reproducibility using the 1 spike method with spiked seawater samples. Symbols as in Fig. 3.

Fig. 6. Vertical profiles of ^{234}Th concentration ($\pm 1\sigma$) at the DYFAMED site, NW Mediterranean Sea, obtained by analyzing replicate 2-L seawater samples according to the 1 spike (gray dots) and 2 spike (black dots) methods. Full line: average $[^{234}\text{Th}]$; dashed line: $[^{238}\text{U}]$ as estimated from salinity (Chen et al., 1986).

Table 1. Example of uncertainty calculation for (A) the one-spike multiple count method (^{234}Th activity at sampling time [$^{234}\text{Th}_{t_0}$] is calculated based on Eq. 2) and (B) the one-spike single count method ($^{234}\text{Th}_{t_0}$ is calculated based on Eq. 5), according to the spreadsheet method of Kragten (1994) for a sample from the DYFAMED site.

Net count rate: net initial ^{234}Th count rate estimated from the weighed least squares regression ($n = 6$); **α -factor:** chemical recovery as estimated by alpha-spectrometry; **β -factor:** beta-detection efficiency; **Volume:** volume of the sample; **Gross count Rate:** ^{234}Th count rate at first counting time; **Blank:** procedure blank count rate; $^{238}\text{U}_{t_0}$: ^{238}U activity in sample. Uncertainties of the parameters (1σ) include all propagated errors.

A. One-spike "multiple count method"

Parameter	Value	Standard Absolute Uncertainty	Net cnt rate	α -factor	β -factor	Volume	$^{238}\text{U}_{t_0}$	
Net cnt rate (s^{-1})	0.039	0.001	0.040	0.039	0.039	0.039	0.039	
α -factor	0.89	0.04	0.89	0.93	0.89	0.89	0.89	
β -factor	0.51	0.02	0.51	0.51	0.53	0.51	0.51	
Volume (L)	1.97	0.01	1.97	1.97	1.97	1.98	1.98	
$^{238}\text{U}_{t_0}$ (Bq L^{-1})	0.043	0.001	0.043	0.043	0.043	0.043	0.044	
$^{234}\text{Th}_{t_0}$ (Bq L^{-1})	0.042		Varied	4.34E-02	4.06E-02	4.09E-02	4.21E-02	4.21E-02
			Residuals	1.08E-03	-1.77E-03	-1.42E-03	-2.17E-04	-2.35E-04
			Residual Squared	1.16E-06	3.13E-06	2.00E-06	4.72E-08	5.53E-08
			Sum of Squares	6.34E-06			Uncertainty Abs	2.52E-03
							Uncertainty %	5.9
			% Contributions	18.3	49.4	31.6	0.7	0.9

B. One-spike "single count method"

Parameter	Value	Standard Absolute Uncertainty	Gross cnt rate	α -factor	β -factor	Volume	Blank	$^{238}\text{U}_{t_0}$	
Gross cnt rate (s^{-1})	0.028	0.001	0.028	0.028	0.028	0.028	0.028	0.028	
α -factor	0.89	0.04	0.89	0.93	0.89	0.89	0.89	0.89	
β -factor	0.51	0.02	0.51	0.51	0.53	0.51	0.51	0.51	
Volume (L)	1.97	0.01	1.97	1.97	1.97	1.98	1.97	1.97	
Blank (s^{-1})	0.0032	0.0002	0.0034	0.0032	0.0032	0.0032	0.0034	0.0032	
$^{238}\text{U}_{t_0}$ (Bq L^{-1})	0.043	0.001	0.044	0.043	0.043	0.043	0.043	0.044	
$^{234}\text{Th}_{t_0}$ (Bq L^{-1})	0.042		Varied	4.24E-02	3.99E-02	4.03E-02	4.15E-02	4.13E-02	4.17E-02
			Residuals	7.70E-04	-1.74E-03	-1.39E-03	-2.14E-04	-3.81E-04	-1.79E-05
			Residual Squared	5.93E-07	3.04E-06	1.94E-06	4.58E-08	1.45E-07	3.22E-10
			Sum of Squares	5.76E-06			Uncertainty Abs	2.40E-03	
							Uncertainty %	5.8	
			% Contributions	10.3	52.7	33.7	0.8	2.5	0.0

Table 2. Example of uncertainty calculation for the two-spike multiple count method ($^{234}\text{Th}_{\text{to}}$ is calculated based on Eq. 2), according to the spreadsheet method of Kragten (1994) for a sample from the DYFAMED site.

Abbreviations as in Table 1. Uncertainties of the parameters include all propagated errors.

Parameter	Value	Standard Absolute Uncertainty	Net cnt rate	α -factor	β -factor	Volume	$^{238}\text{U}_{\text{to}}$
Net cnt rate (s^{-1})	0.039	0.001	0.040	0.039	0.039	0.039	0.039
α -factor	0.92	0.03	0.92	0.95	0.92	0.92	0.92
β -factor	0.51	0.02	0.51	0.51	0.52	0.51	0.51
Volume (L)	1.96	0.01	1.96	1.96	1.96	1.97	1.97
$^{238}\text{U}_{\text{to}}$ (Bq L^{-1})	0.043	0.001	0.043	0.043	0.043	0.043	0.044
$^{234}\text{Th}_{\text{to}}$ (Bq L^{-1})	0.042		Varied	4.29E-02	4.03E-02	4.04E-02	4.16E-02
			Residuals	1.11E-03	-1.55E-03	-1.39E-03	-2.16E-04
			Residual Squared	1.23E-06	2.41E-06	1.92E-06	4.65E-08
			Sum of Squares	5.61E-06			Uncertainty Abs
							Uncertainty %
							5.7
			% Contributions	21.9	43.0	34.3	0.8
							1.0

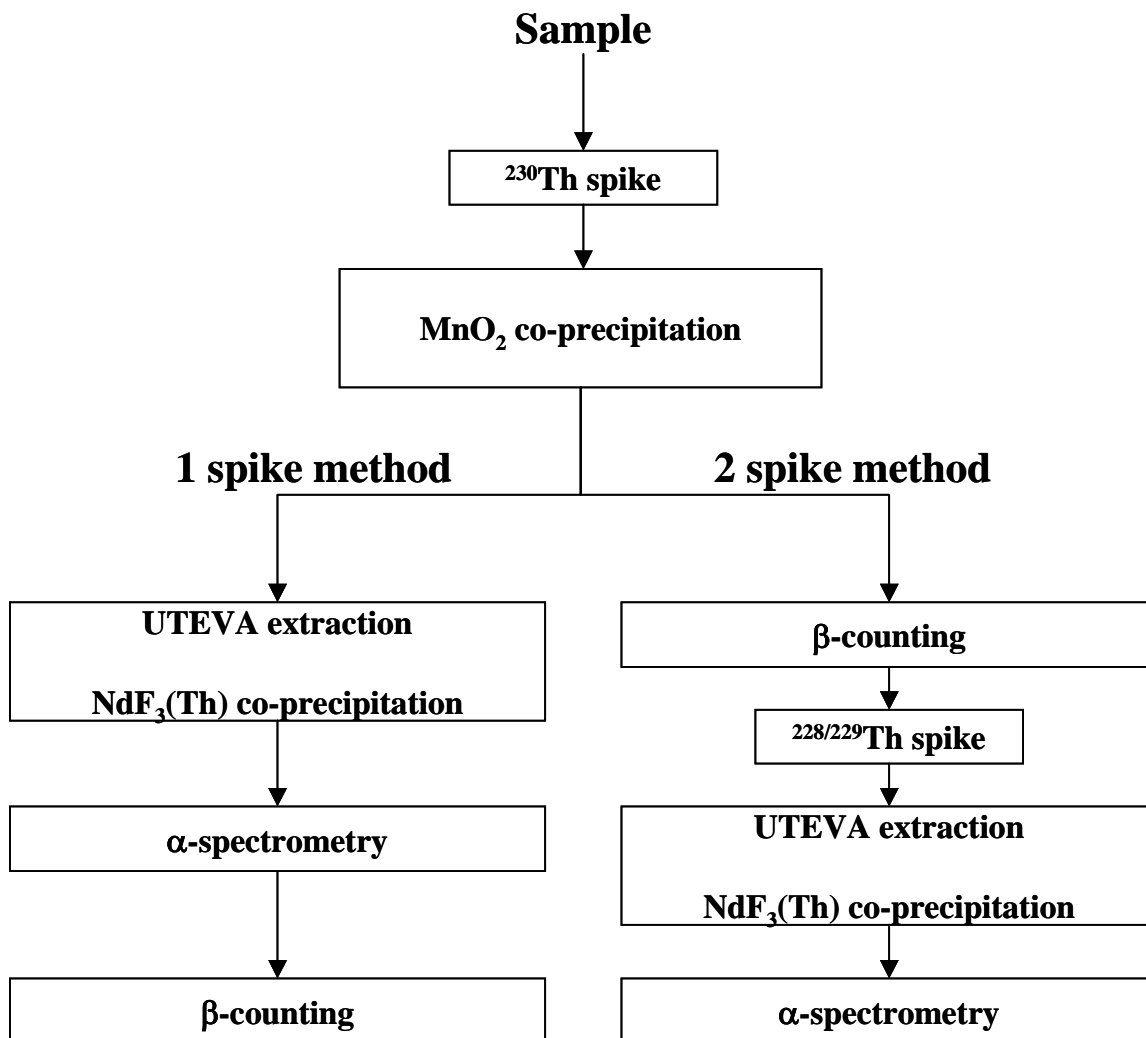


Fig. 1

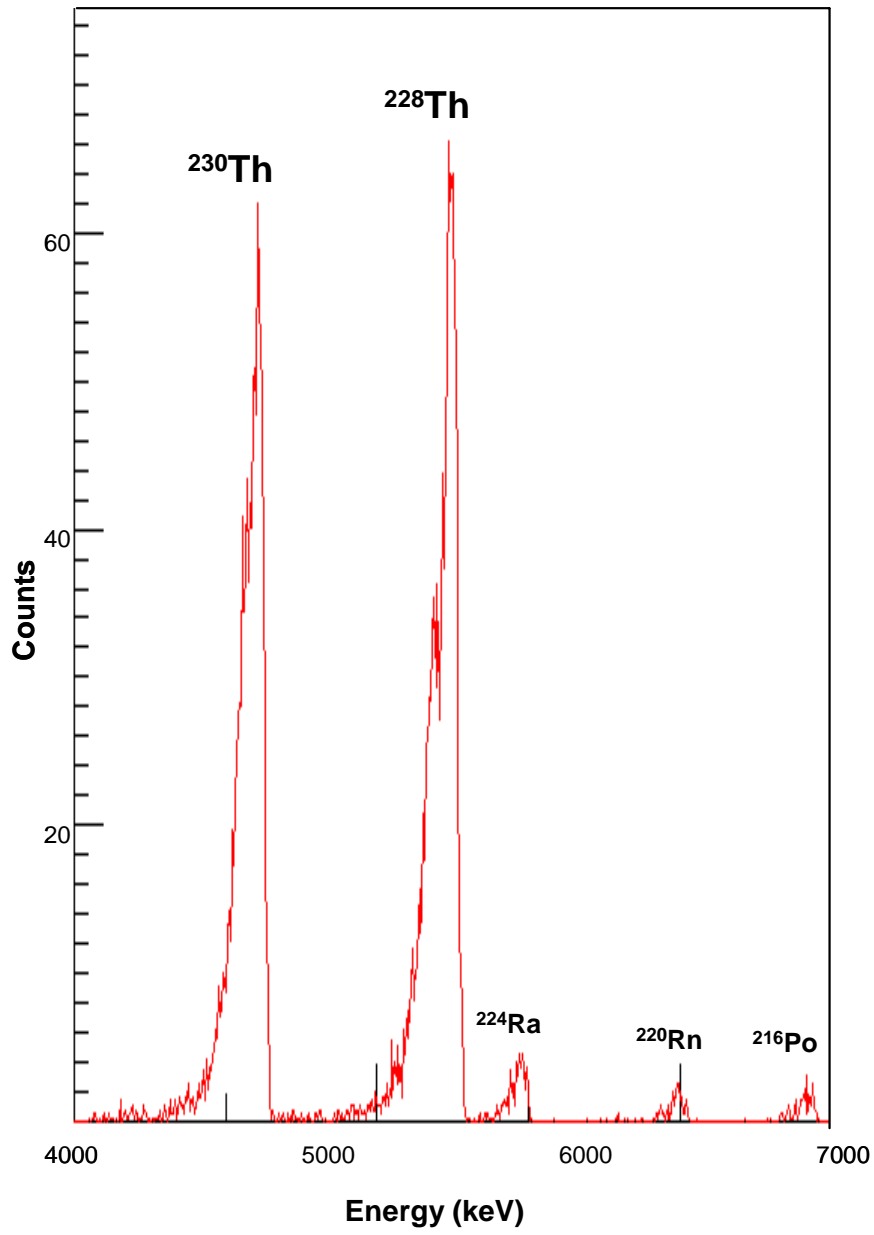


Fig. 2

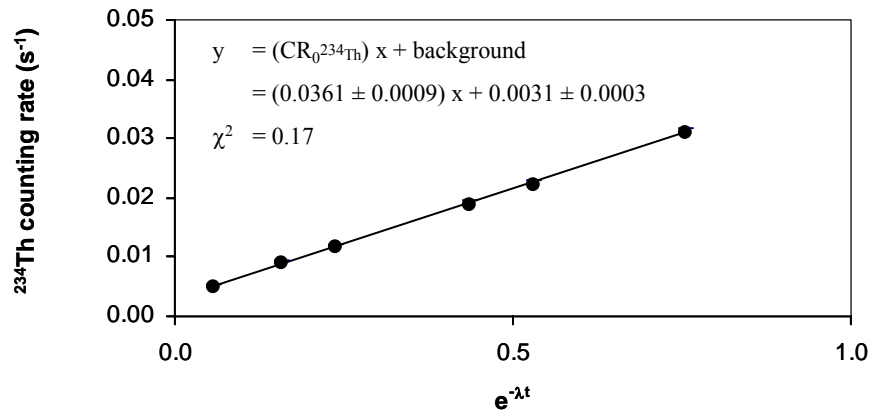


Fig. 3

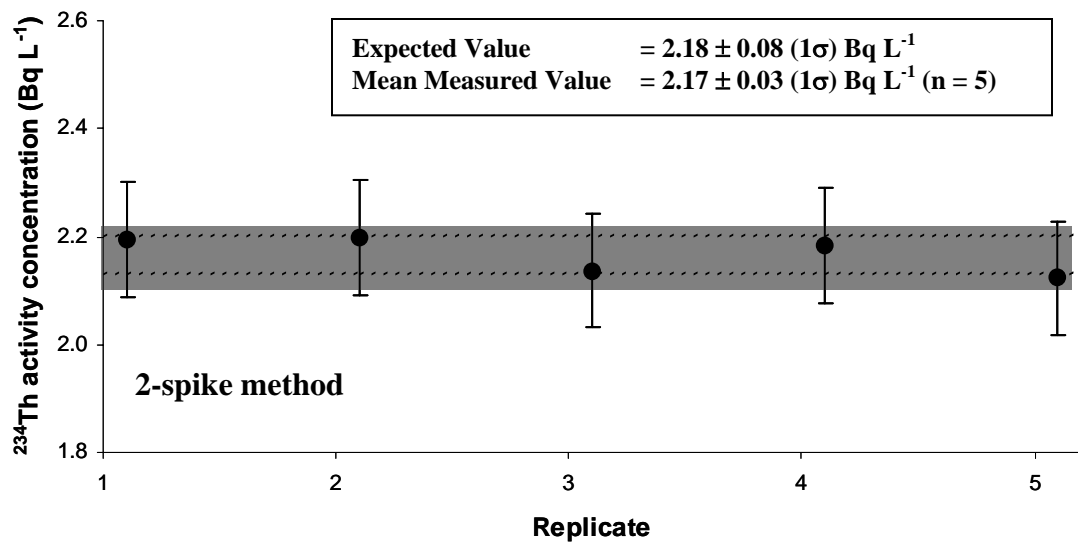


Fig. 4

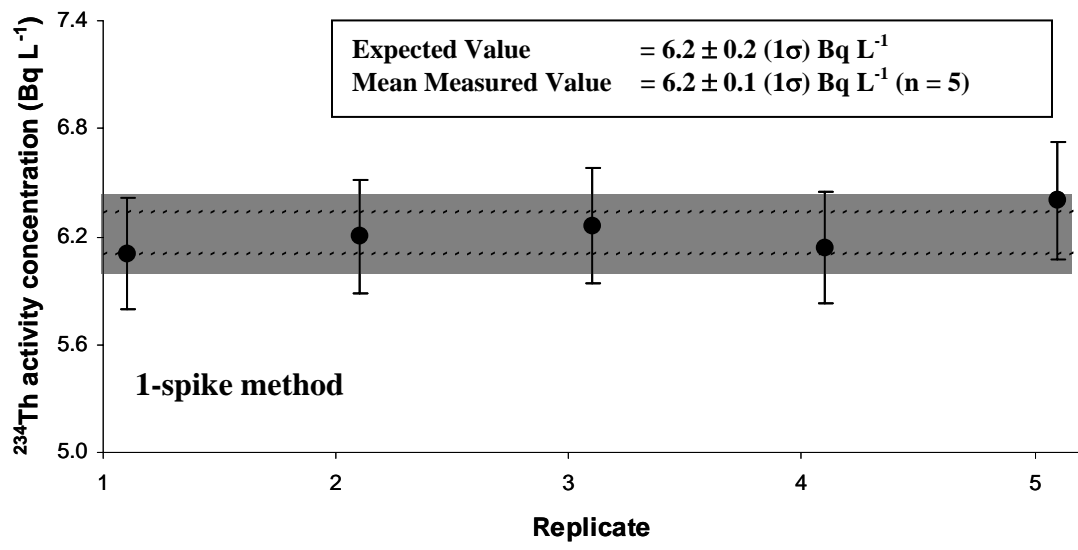


Fig. 5

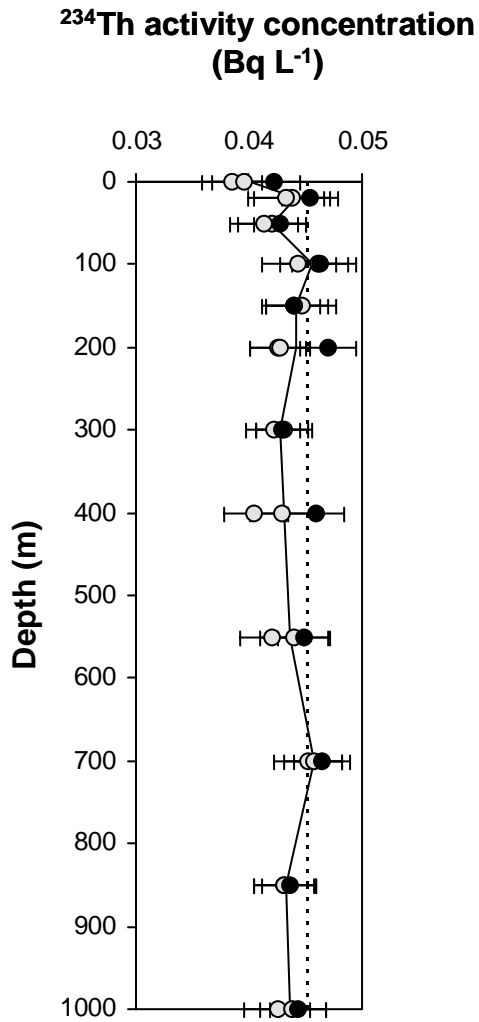


Fig. 6