

Quantification of ^{234}Th Recovery in Small Volume Sea Water Samples by Inductively Coupled Plasma Mass Spectrometry

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Development of a small volume (2-4l) technique for measuring ^{234}Th in sea water has been instrumental in bringing to light small-scale structures in upper-ocean particle removal processes previously missed by standard ^{234}Th measurement techniques. Further development of this method to evaluate removal efficiencies of ^{234}Th via MnO_2 precipitation quantified using ICP mass spectrometry are presented in this work. Advantages to this approach are precise knowledge of ^{234}Th recovery, while maintaining high sample throughput afforded by ICP-MS analyses. The improved technique includes the acidification of 4-l sea water samples and the addition of ^{230}Th as a yield monitor prior to MnO_2 precipitation. Subsequent filtration and beta counting of the high-energy daughter, $^{234\text{m}}\text{Pa}$, was followed by a final background count after 6 half-lives (144 days) of decay. Filtered precipitates were dissolved with H_2O_2 , and an internal standard of ^{229}Th was added. Samples were purified using anion exchange chromatography to remove high levels of manganese, and recoveries were determined by measured ratios of $^{230}\text{Th}/^{229}\text{Th}$ by ICP-MS. Application of this procedure for ^{234}Th derived export in the recent Southern Ocean Iron Experiment showed average recoveries of 91%. Corrections for rare low recoveries (25-80%) noticeably change ^{234}Th profiles, thus impacting subsequent elemental flux calculations.

Introduction

Thorium-234 ($T_{1/2}=24.1$ d) has been used widely as a tracer of surface-ocean particle fluxes and to calculate particulate organic carbon (POC) export in the upper ocean.¹⁻⁷ Thorium-234 activities are generally lower than its parent ^{238}U activity ($T_{1/2}=4.5\times 10^9$ y) in the upper 100-200m, due primarily to particle scavenging and particle sinking, with this deficit tending to be largest in coastal settings and during blooms. Thorium-234 fluxes on sinking particles are calculated from knowledge of the source (from ^{238}U decay) and loss terms (^{234}Th decay and sinking). By multiplying the ^{234}Th

export rate by the measured ratio of ^{234}Th to carbon and other elements, export fluxes via sinking particles can be determined.⁷

Development of the small-volume technique for ^{234}Th measurements, based on the 20-l method developed by RUTGERS VAN DER LOEFF and MOORE⁸, allowed for rapid at-sea analysis and increased sample throughput. Both aspects contribute to improved spatial and temporal resolution of particle export estimates. However, as a result of not adding a yield tracer, this approach was dependent upon the reproducibility of MnO_2 recovery. BUESSELER et al.⁹ concluded that reproducibility of 3-7% in small-volume samples was possible when close attention is paid to all processing steps. Furthermore, these high rates of reproducibility would be most affected by experimental error. Other factors influencing reproducibility such as sample pre-filtration, counting errors, background activities, times of reagent addition and sample filtration, and sorptive loss of ^{234}Th to bottle walls have been addressed and the method amended.¹⁰

While the issues mentioned above were closely monitored throughout developmental stages of the procedure, during routine application to large numbers of samples in the field it is not always possible to maintain this level of scrutiny of processing. Also, there are other means where sample loss can occur which can not be prevented by close adherence to the methods. In field applications we have encountered sample loss due to torn filters, leaking filter holders and spilled sample bottles. All of the results from these samples could never be quantified without the addition of a yield tracer. This paper describes modifications made to the existing small-volume technique for dissolved as well as total (dissolved + particulate) ^{234}Th collection that includes the

addition of a yield tracer and the methods for digestion and analysis by ICP-MS to quantify ^{234}Th recoveries.

Experimental

Th recovery and ^{234}Th counting

Within 1 hour of collection, 4 liter samples are acidified to a $\text{pH} \approx 2$ with concentrated HNO_3 at 1.5 ml/liter and shaken vigorously. Thorium-230 yield monitor is then added (1 g/sample at 0.167 Bq g^{-1} (10 dpm g^{-1})). The sample is shaken again and allowed to equilibrate for 12 hours. After equilibration, the pH is brought up to 8 ± 0.15 using concentrated NH_4OH . A precipitate is formed by the addition of $100 \mu\text{l}$ of KMnO_4 ($7.5 \text{ grams KMnO}_4 \text{ l}^{-1} \text{ Q-H}_2\text{O}$) and $100 \mu\text{l}$ of MnCl_2 ($33.3 \text{ grams MnCl}_2\cdot 5\text{H}_2\text{O l}^{-1} \text{ Q-H}_2\text{O}$) for Th adsorption. Samples are vigorously shaken between each addition and allowed to stand for 12 hours followed by filtration.

Filtered precipitates were dried and mounted for counting. Subsequent beta counting of the high-energy daughter, $^{234\text{m}}\text{Pa}$, was performed at sea. All measurements for ^{234}Th at sea and in the lab were made using gas-flow proportional beta counters manufactured by Risø National Laboratories (Roskilde, Denmark) following methods described in Buesseler et al. (2001).⁹ Initial counting was followed by a final background count after 6 half-lives (144 days) of decay.

Sample preparation before ICP-MS measurement

The first step of this new yield process is to take samples of MnO_2 precipitate after the final background beta counting has been performed, dismount them, and place them in 50 ml beakers. It should be noted that all acids and reagents used for equilibration, columns and ICP preparations were Fisher Optima grade. Dissolution of

the Mn precipitate was accomplished by adding 10 ml of 8M HNO₃/ 10% H₂O₂ solution followed by gravimetric addition of ²²⁹Th at 1 g/sample. The ²²⁹Th tracer activity was 1.13 Bq g⁻¹ (67.7 dpm g⁻¹). To make certain any particulate matter and residual precipitate entrained within the filter mesh were released and both Th isotopes able to equilibrate, samples were sonicated for 20 minutes and allowed to stand covered overnight. As long as filters remained relatively intact through this process, there was no need to filter the samples prior to loading onto the columns.

A 2 ml bed-volume anion exchange column was prepared using Poly-Prep Chromatography columns (Bio-Rad Laboratories, Hercules, CA) and AG 1-X8, 100-200 mesh, chloride form resin (Bio-Rad Laboratories, Hercules, CA). The following steps were used to wash and precondition columns: first, wash column with 2x3 ml of concentrated HCl. Wait 10 minutes after addition of 3 ml of conc. HCl to dissolve trace impurities that may be present. Add another 3 ml and allow HCl to drain completely. Further wash column with 3x4 ml of 1.2 M HCl allowing column to drain completely between additions. Rinse column 3 times with 4 ml Milli-Q water. Final column preconditioning was accomplished by passing 3x4 ml of 8 M HNO₃ just prior to introduction of sample.

Transfer the sample into column, taking care to keep the filter in the beaker. Make sure the transfer is quantitative by rinsing the filter and beaker 3 times with 4 ml of 8 M HNO₃, transferring the solution to the column after each rinse. Further wash impurities from the column, particularly Mn, with 4x10 ml of 8 M HNO₃. Discard the wash effluent and replace waste beaker with an acid-cleaned beaker. Elute the Th into a 50 ml beaker with 4x5 ml of 9 M HCl.

Prior to analyses by ICP-MS, HCl is removed and the sample diluted in a nitric acid matrix.¹¹ Evaporate sample to a volume of about 1 ml. Rinse the sample from the walls of the beaker by rinsing with 1 ml of conc. HNO₃. Evaporate sample to a volume of about 1 ml. Further rinse the beaker with 4 ml of 8M HNO₃, evaporate to <0.5 ml, and let cool. Bring up sample with 2 ml of 10% HNO₃/1%HF solution for analysis by ICP-MS. The final analyte solution is filtered using Acrodisc 0.2 µm HT Tuffryn membrane syringe filters (Gelman Laboratory) to minimize potential clogging of capillary tubing during sample uptake.

ICP-MS measurements

Measurements were made using a magnetic sector inductively coupled mass spectrometer (Element1, Thermo Finnigan MAT GmbH, Bremen, Germany) at low resolution (LR: $R=300$ where $R=M/\Delta M$ at 10% peak height). Detailed operation methods are listed in Table 1. A free-aspirating micro-concentric desolvation system (MCN-6000, Cetac Technologies, Omaha, NE, USA) coupled with a T1 free-aspirating micro-concentric nebulizer (Cetac Technologies) was used for sample introduction. Sample flow rates through this nebulizer were approximately $120\mu\text{l min}^{-1}$. To ensure that there was no blank carry over, the method included a 5-minute washing with 10% HNO₃ complete washout.

Of primary concern for application of ²³⁰Th recoveries calculated from ICP-MS data was to minimize the statistical impact of errors introduced in ²³⁴Th activity calculations. To that end, measured ratio errors of 2% or less were determined to be necessary from ICP-MS measurements.

Study Site

The experimental results discussed in this paper are from samples collected during the Southern Ocean Iron Enrichment Experiment (SOFeX). Sampling on board the *RV Melville* and *USCG Polar Star* took place over a 4 week period from January to February, 2002 in the vicinity of 66°1'S, 172°7'W. Four liter samples were taken from Go-Flow and Niskin bottles deployed by rosette or single bottles strung on Kevlar line to below the mixed-layer water column depth. The use of SF₆ as a tracer added along with iron to the experimental patch (15x15 km initially) allowed for sampling in a lagrangian fashion over time.¹² As such, subsequent estimates of export were not constrained by unresolved physical effects on the ²³⁴Th balance, and high-resolution time series sampling allowed for non-steady state modeling.

Results and Discussion

Advantages / disadvantages of the 4-l method

The 4-l method described in this paper was adopted for several reasons and introduces some procedural changes to the 2-l method described by BUESSELER et al..⁹ We have determined through laboratory tests that ²³⁴Th is efficiently removed from samples with an even more dilute solution of reagents. This reduces the amount of precipitate that has to be filtered through the small diameter filters and can be a significant time-saving step in samples with high concentrations of particulate matter. Filtration of the MnO₂ precipitate onto a 25-mm-diameter Whatman QMA filter with a 1 µm nominal pore size was a further improvement over the 20-l method⁸ as it limits sampling volume. Consequently, water can be easily sampled using Niskin or Go Flow bottles and ²³⁴Th measurement can be performed from the same collection bottle as other parameters. This reduces sampling uncertainty since one is comparing different data from

the exact same sample bottle. While prefiltration of samples is recommended in particle rich regimes, the precipitate filtration process can be quite lengthy: up to 12 hours even under ideal conditions. Development of filter holders that attach directly to sample bottles and vacuum manifolds has eliminated the need for close observation during filtering.

The primary advantage in doubling the sample volume from 2 to 4-l was to reduce by near half the time required to obtain a count rate that is an order of magnitude higher than the beta detector background. Given current detector efficiencies, a ^{234}Th activity in open-ocean seawater near that of ^{238}U will be 33-42 mBq l^{-1} (2.0-2.5 dpm l^{-1}), which translates to 3-5 cpm per 4 liter sample. With these count rates, beta counting time is 6-12 hours to obtain counting errors near 2%. In ocean settings with low particle concentrations, the increase in sample volume to 4 liters combined with smaller amounts of precipitate resulting from the reduction in reagent additions, does not add significant time to the filtration step. However, as previously stated, in high particle regimes this increased volume may prohibit filtering samples through a 25-mm filter without prefiltration. A deep-water comparison of 1, 2 and 4-l samples showed similar recoveries, and activities that were statistically identical.

Earlier methods for coprecipitation of ^{234}Th using $\text{Fe}(\text{OH})_3$ used ^{230}Th as a yield tracer.¹³ While this method proved to be effective, at sea sample processing was extensive and required rigorous radiochemical purification of ^{234}Th from ^{238}U and other natural radionuclides. This becomes a limiting factor when handling large numbers of samples. By adding ^{230}Th as a yield monitor of MnO_2 precipitate in the small-volume technique, the impact of experimental error on final ^{234}Th activities is greatly reduced.

Specifically, concerns of temperature, pH, and time of precipitate formation and filtration noted in prior publications are effectively eliminated by the yield monitor addition.⁹⁻¹⁰ Final determination of ^{230}Th via ICP-MS involves anion exchange column chemistry to remove high levels of manganese in redissolved samples. However, the clean-up chemistry is performed in the laboratory under stable conditions and not until final counts for ^{234}Th background assessment have been conducted. The high sample throughput afforded by ICP-MS analysis allows for large numbers of samples to be processed.

Lab experiments: Equilibration of ^{230}Th and ^{229}Th

Concerns regarding spike equilibration of the ^{230}Th yield monitor and ^{229}Th internal standard were addressed in several lab experiments. Tests included vigorous heating of the combined spikes with HClO_4 alone, HClO_4 and HF , and simple combination of the two spikes without the addition of these acids. Where perchloric acid was used in the equilibration step, NaNO_2 was added or withheld prior to introduction to the column to evaluate the impact of residual HClO_4 on the performance of the anion resin. Each of the described combinations was treated with and without column chromatography to determine if isotope-specific fractionation occurred during column processing. Comparative results indicated that there was no fractionation of either isotope during anion exchange chemistry (Table 2). Also, both isotopes equilibrated without the need for vigorous heating or the addition of perchloric or hydrofluoric acids. These tests resulted in a considerable amount of processing time eliminated from the procedure.

Comparison of corrected and uncorrected data: some examples from SOFeX cruise

Between January and February, 2002 in the Southern Ocean some 272 samples were collected and processed for ^{234}Th using this new method. The addition of a yield tracer effectively eliminated concerns regarding reagent addition times, sorptive loss to bottle walls and other uncontrolled variables due to the large number of samples.

Recoveries via ^{230}Th were assessed on all deep-water samples used for calibration of our method and on selected shallow water profiles where there were apparent low yields evident from beta counting results. Ratios of $^{230}\text{Th}/^{229}\text{Th}$ obtained by ICP-MS were normalized to ^{229}Th atom concentrations to determine efficiency of ^{230}Th recovery in samples. Results presented in this paper are from analysis of N=123 samples. The $^{230}\text{Th}:^{229}\text{Th}$ ratio errors from these data range from 0.2-1.7% with a calculated mean error of 0.7%. Aliquots of ^{230}Th tracers used in the field were calibrated against weight calculated atom concentrations of ^{229}Th internal standards. Results showed that recoveries were generally greater than 85% with a mean recovery of 91.3% for these samples (n=104). Recoveries below 85% ranged from 24.8-84.2% with a mean of 60.7% (n=19). Low recoveries were likely a combined result of sample loss during processing at sea and poor chemistry yields. In some samples precipitate was noticeably lighter in color, and lower recoveries were expected. These findings were noted in the field, leading to selection for recovery processing. We found, however, that lower yields were not always associated with samples that were observed to have lighter precipitate. Other suspected low recovery samples were identified after construction of ^{234}Th activity profiles from counting results. As is evident in Figure 1, poor recoveries can only have a negative impact on the calculated activity. A mean recovery of 91% was applied to samples not processed and analyzed by ICP-MS.

Development of the small-volume technique for measuring ^{234}Th made possible the ability to obtain multiple high-resolution vertical profiles of ^{234}Th . Improved spatial and temporal resolution in the vertical distribution of ^{234}Th afforded by this method increased the accuracy of upper-ocean particle export calculated from ^{234}Th . In profiles obtained during SOFeX, these improvements become quite evident. A comparison of ^{234}Th activity profiles from the Southern Ocean before and after recovery corrections is illustrated in Figure 1. In the three profiles, significant corrections were made in ^{234}Th activities of single samples from the upper 100 m. These corrections ranged from 40-60% of the measured ^{234}Th . The resulting impact on ^{234}Th flux calculations would have been an overestimation of ^{234}Th flux by 39-63% at 100 m. Without the applied corrections, any derived elemental particle fluxes would reflect these overestimates.

Conclusions

As has been demonstrated in development of this small-volume technique for measuring ^{234}Th , high-level precision is obtainable but is dependent upon control of experimental error. During large-scale application of this technique at sea with hundreds of samples being processed, uncontrollable physical factors were shown to have the greatest impact on the accuracy of counting results. Specifically, precipitate loss from filters seated improperly or that fractured during the filtration process was observed. It was not uncommon to find some precipitate adhering to the base of the filtration apparatus, especially those with high particulate loading that added to the height of precipitate on the filter. Also, loss of sample from leaking bottles or filter holders had the potential for affecting precipitate recoveries. It is clear that without the addition of the yield monitor, these samples would have produced erroneous data. This new protocol

demonstrates that recovery corrections increase the confidence placed in ^{234}Th activities obtained from standard beta counting methods. We feel the advancements introduced in this paper have significantly improved the sampling and processing protocols for this method.

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Table 1. Element 1 instrument method for determination of $^{230}\text{Th}/^{229}\text{Th}$ ratios.

isotope	accurate mass	mass window	mass range	magnet mass	settling time	sample time
Th229	229.0312	5	229.012-229.050	229.031	0.300	0.0600
Th230	230.0326	5	230.013-230.052	229.031	0.001	0.0600

isotope	samples per peak	segment duration	search window	integration window	scan type	detection mode
Th229	200	0.600	150	5	Escan	both
Th230	200	0.600	150	5	Escan	both

Table 2. Comparison of measured and calculated $^{230}\text{Th}/^{229}\text{Th}$ spike ratios.

Sample ID	treatment	measured/ calculated ^a	% error ^b
lab 1	HClO ₄ /NaNO ₂ /column	100.7%	1.4%
lab 2	HClO ₄ /column	100.6%	1.2%
lab 3	HClO ₄ /no column	100.7%	3.6%
lab 4	HClO ₄ /HF/NaNO ₂ /column	100.5%	3.1%
lab 5	HClO ₄ /HF/column	103.9%	4.5%
lab 6	HClO ₄ /HF/no column	100.3%	1.0%
PS Spike 1-1	no HClO ₄ /no HF/column	100.0%	0.7%
PS Spike 1-2	no HClO ₄ /no HF/column	99.84%	0.3%
PS Spike 1-3	no HClO ₄ /no HF/column	100.1%	0.3%
PS Spike 2-4	no HClO ₄ /no HF/column	100.0%	0.3%
PS Spike 2-5	no HClO ₄ /no HF/column	99.96%	0.3%
PS Spike 2-6	no HClO ₄ /no HF/column	100.1%	0.3%
MEL Spike 1-1	no HClO ₄ /no HF/column	100.0%	1.0%
MEL Spike 1-2	no HClO ₄ /no HF/column	100.2%	0.6%
MEL Spike 1-3	no HClO ₄ /no HF/column	100.2%	0.8%
MEL Spike 2-1	no HClO ₄ /no HF/column	99.8%	1.0%
MEL Spike 2-2	no HClO ₄ /no HF/column	100.0%	0.9%
MEL Spike 2-3	no HClO ₄ /no HF/column	99.6%	1.0%

a) values not corrected for final spike calibration

b) error propagated from spike weights and RSD from ICP analysis

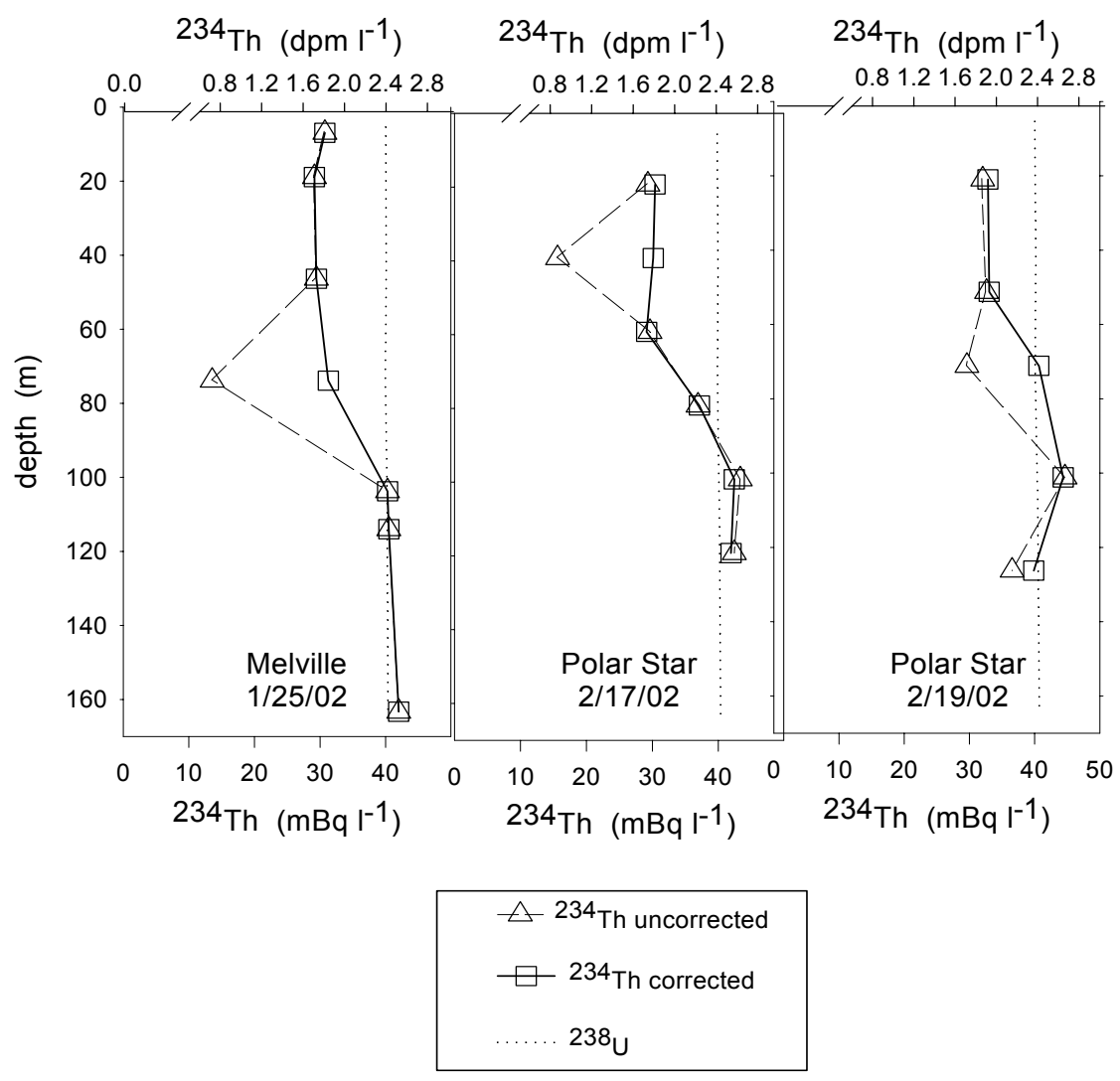


Figure 1.

Table 1. Element 1 instrument method for determination of $^{230}\text{Th}/^{229}\text{Th}$ ratios.

Table 2. Comparison of measured and calculated $^{230}\text{Th}/^{229}\text{Th}$ spike ratios. Spike equilibration experiments are indicated by specific treatments applied during preparation. Included are individual batch results of spike behavior monitoring. Variations seen in %error reflect daily instrument sensitivity differences between runs.

Figure 1. Profiles of ^{234}Th and ^{238}U activities from the Southern Ocean. Recoveries were quantified by ICP-MS on all Polar Star samples. The mean recovery of 91% was applied to all Melville samples with the exception of the 72.5 meter sample. Open triangles indicate sample activity prior to recovery corrections. Activities are given in mBq and dpm per liter. Note: error bars are \leq symbol size.