

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 .

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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;

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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) (Rutgers 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 (Rutgers 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 com-

pare 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 types 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 $\text{pH} < 2$ (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 ($0.4302 \pm 0.0047 \text{ Bq mL}^{-1}$ 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. $< 3 \text{ h}$). Subsequently, the sample pH was raised to 8.0 ± 0.2 by addition of $\sim 4.5 \text{ mL}$ 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

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