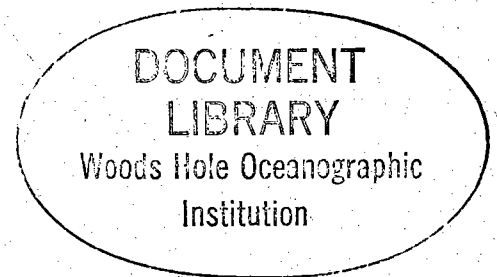
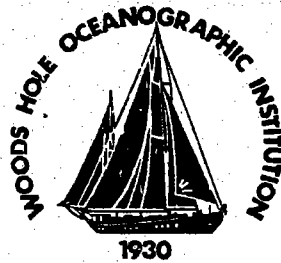


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**Woods Hole
Oceanographic
Institution**



**Adsorbers for In-Situ Collection and At-Sea Gamma
Analysis of Dissolved Thorium-234 in Seawater**

by

M. C. Hartman and K. O. Buesseler

July 1994

Technical Report

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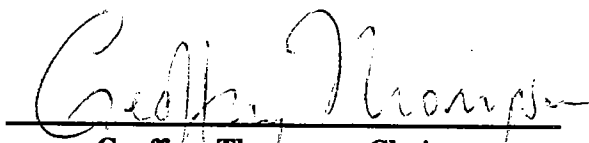
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Geoffrey Thompson, Chair
Department of Marine Chemistry and Geochemistry



**ADSORBERS FOR IN-SITU COLLECTION AND AT-SEA
GAMMA ANALYSIS OF DISSOLVED THORIUM-234 IN SEAWATER**

Abstract:

Two polypropylene cartridge types (Beta Pure and Hytrex II) were tested in the laboratory as adsorbers for in-situ collection of dissolved Thorium-234 (^{234}Th) in seawater. Using a uranyl nitrate tracer, we determined that a MnO_2 impregnated 3.25-inch Hytrex II cartridge with a flow rate of 8 liters/minute would collect ^{234}Th with a greater than 60% efficiency. The smaller size and composition of the 3.25 inch Hytrex II cartridge enabled it to be pressed into a permanent 1-inch "puck" for direct gamma counting. This protocol significantly reduced the handling between collection and counting. When field tested in the Gulf of Maine as a large volume (> 500 liters) collector, the new adsorbers produced a greater than 80% collection efficiency and a dissolved ^{234}Th concentration which was consistent with independent samples collected at the same station and depth. These adsorbers were used successfully for the in-situ collection of ^{234}Th in large volumes of seawater during the 1992 NOAA and NSF sponsored JGOFS EqPac program, with a mean collection efficiency of 0.79 +/- 9% (n = 104 cartridge pairs).

INTRODUCTION

Large volumes of seawater are necessary for the detection of Thorium-234 (^{234}Th) via gamma spectroscopy. This laboratory has sampled 1000 to 4000 liters of seawater through polypropylene cartridges, using in-situ pumps (Winget et al., 1982, Sachs et al., 1989). A 10-inch 0.5 μm wound polypropylene prefilter (CUNO Micro-wynd II DPPPZ) is used to collect the particulate phase and two in-line MnO_2 impregnated CUNO Micro-wynd II 1 μm cartridge adsorbers (Livingston and Cochran, 1987; Buessler et al., 1992a) efficiently collect dissolved ^{234}Th (Buesseler et al., 1992b). To obtain the best possible gamma detector efficiency, the sample cartridges are either melted into a solid form or ashed. The latter method, while providing the best detector efficiency, involves the time consuming method of melting each cartridge in an oven, ashing it in a muffle furnace and quantitatively transferring the ash to an 8oz. polystyrene counting jar (Buesseler et al., 1992a). The melting method may not ensure a uniform counting matrix. A MnO_2 impregnated cartridge was developed which significantly lowers the sample handling time between in-situ collection and at-sea gamma counting for dissolved ^{234}Th , while retaining high collection and detector efficiencies.

BACKGROUND

The priorities in determining a suitable adsorber for dissolved ^{234}Th included:

- ability to be used for in-situ sample collection
- efficient ^{234}Th collection in large volumes (500 liters) within a two hour sampling interval (4.2 liters/min)
- minimum handling between sampling and counting
- efficient gamma counting geometry

In order to limit the sample handling between collection and counting, we examined smaller sized cartridges that might be pressed into a puck-like form for acceptable gamma counting efficiencies. Knowing that a pair of MnO_2 impregnated 10-inch 1 μm CUNO MicroWynd II cartridges were efficient in-situ collectors of ^{234}Th in 3000-liters of seawater, we estimated that a 1.5-inch cartridge would efficiently collect ^{234}Th in 500 liters of seawater. The CUNO Micro-wynd II cartridge is not manufactured at this length and cannot be manually cut to a uniform length, since it is composed of wound polypropylene fibers.

Based on prior research on cartridges within our laboratory, two other polypropylene cartridge types were examined:

1. Hytrex II

The Hytrex II cartridge is manufactured by Osmonics, Inc. (Minnetonka, MN). The cartridge filter is composed of thermally bonded polypropylene microfibers (Eric Stone, Osmonics, Inc., (800) 848-1750; distributed through Pure Flow, Inc., NH (603) 924-4008). The 1.5-inch 1 um cartridge can only handle 0.5 gal/min (1.9 l/min), with a 6 psi pressure drop, while the 10-inch 1 um cartridge can easily handle 3-4 gal/min (11.4 - 15.1 l/min) (Technical Report, Osmonics, Inc.). The 5 um Hytrex II cartridge should be of equal performance to a 1 um wound polypropylene cartridge, such as the Micro-wynd II cartridge (Skip Itezh, Pure Flow, Inc., personal communication) and a 10-inch 5 um cartridge can handle 5 gal/min (19 l/min) with a 3 psi pressure drop (Technical Report, Osmonics, Inc.).

2. Beta Pure

The Beta Pure cartridge is manufactured by CUNO, Inc. (Meriden, CT). The cartridge filter is composed of thermally bonded polypropylene with a polypropylene coating (distributed through MWM Company, Inc., Quincy, MA (617) 328-1920). The cartridge is available in 3 um, 5 um and 10 um sizes. Since there is no central core, a Beta Pure cartridge with less than 3 um size would require additional gasketing in order for the cartridge to work properly (Greg McCarthy, MWM Company, Inc., personal communication). The 10-inch 3 um cartridge can handle 3-4 gal/min (11.4 - 15.1 l/min) with a 6 psi pressure drop (Technical Report, CUNO, Inc.).

METHODS

MnO₂ Impregnation

The standard method of manganese dioxide (MnO₂) impregnation of CUNO Micro-wynd II cartridges involves soaking the cartridges in three separate 16-hour baths containing strong soap (25 mls Micro/5 liters distilled water), 1M NaOH and 0.5 M HCl solutions, with thorough rinsing with distilled water between the soaking steps. The cartridges are placed in a continuously stirred 35°C supersaturated potassium permanganate (KMnO₄) bath for 24 hours and allowed to cool, then rinsed of excess MnO₂ with distilled water and sealed in plastic bags to maintain moisture (Buessler et al., 1992a). Based on other studies which demonstrated effective MnO₂ impregnation with only the soap and KMnO₄ steps (van der Loeff and Berger, personal communication), we tried both impregnation methods for Hytrex II and Beta Pure cartridges.

We found that the Hytrex II cartridges effectively and uniformly absorbed KMnO_4 with the standard impregnation method as well as the shortened impregnation method presented in Appendix 1. The shortened method reduced the impregnation time from 5 days to 2.5 days, reducing the man-hour costs by 40% and the chemical costs by 10%. The Beta Pure cartridges did not impregnate well with either impregnation method and lost much of the KMnO_4 upon rinsing with distilled water.

Laboratory Studies

Six preliminary studies of 5 um Hytrex II and Beta Pure cartridges were conducted in the laboratory at the Woods Hole Oceanographic Institution (WHOI). A known volume of 0.5 um filtered seawater (approximately 800 liters) was passed through each Mn cartridge pair at flow rates of 8 to 15 liters/minute (Table 1). The various cartridge sizes were achieved by sawing a 10-inch cartridge into the desired size prior to Mn impregnation. Since we were unable to locate plastic cartridge housings which could accommodate the smaller cartridge sizes, PVC inserts were manufactured at WHOI, allowing us to use our 10-inch plastic cartridge housings. However, a new 5-inch plastic cartridge housing is now available (Cole Parmer Instrument Company), which reduces the dead volume in the housing (a small PVC insert is still required). After collection, the cartridges were ashed for 4 hours in a 500°C muffle furnace. The ash was quantitatively transferred to an 8-ounce styrene counting jar and then directly counted on a calibrated germanium detector.

The cartridge collection efficiency of ^{234}Th is determined using the equation:

$$\text{Collection Efficiency} = 1 - (B / A)$$

where "A" and "B" designate the activities on the first and second Mn cartridge in the cartridge pair, respectively (Livingston and Cochran, 1987).

Since the comparison experiments of Hytrex II and Beta Pure cartridges showed that the Hytrex II cartridges were more efficient in collecting ^{234}Th , experiments on the Beta Pure cartridges were stopped. The Hytrex II cartridge appeared to be the most efficient at collecting ^{234}Th at slower flow rates (8 l/min) and longer cartridge lengths (2.5 inches).

The Hytrex II cartridges were further tested using a uranyl nitrate solution containing a known activity of ^{234}Th in secular equilibrium with its parent, ^{238}U . Each tracer experiment consisted of approximately 230 liters of 0.5 um filtered seawater which was spiked with uranyl nitrate solution and passed through a Mn cartridge pair (Table 2). Various flow rates were used in order to test the affect on cartridge efficiency. Two cartridge sizes (2.5 and 3.25 inches) were tested to see if the increased cartridge size affected the collection efficiency.

The cartridges were ashed for 4 hours in 500°C muffle furnace and the ash was counted on a calibrated germanium detector. The cartridge ash was gamma counted again after one week

to ensure that the ^{234}Th activity was unsupported. There appears to be no difference in collection efficiency between the 2.5-inch and 3.25-inch cartridges, while the slower flow rate (4 liter/min) produces a decrease in collection efficiency. This decrease in collection efficiency could be the result of a poor fit between the cartridge in the PVC insert since, during these initial tests, the cartridges were roughly cut to the appropriate length using a hand held hacksaw. At the higher flow rate, the cartridge may have been held more firmly onto the housing, resulting in an increased cartridge efficiency. In any case, it is important that the cartridge be properly seated in the housing, and that a consistent flow rate be maintained for the duration of the sampling, to ensure that there is no cartridge bypass. The MnO_2 impregnated 3.25-inch Hytrex II cartridge with a flow rate of 5 - 8 liters/minute was determined to be the most efficient absorber of dissolved ^{234}Th (we have subsequently seen efficient dissolved ^{234}Th collection on 3.25-inch Hytrex II cartridges at flow rates as low as 1 liter/min).

Field Studies

The Hytrex II cartridges were field tested during a July 1991 cruise in the Gulf of Maine aboard the R/V *Cape Hatteras*. Approximately 3200 liters was pumped on deck through a 1 μm 10-inch DPPPY Micro-wynd II prefilter cartridge, followed by two 5 μm 3.25-inch Hytrex II MnO_2 impregnated cartridges at approximately 9 liters/minute. The cartridges were returned to WHOI, where they were ashed in a 500°C muffle furnace. The ash was quantitatively transferred to a polystyrene counting jar and gamma counted on a calibrated germanium detector. The cartridge collection efficiency of ^{234}Th was 0.81 +/- 2.2 % and the dissolved ^{234}Th concentration was consistent with independent samples from the same station and depth.

The new adsorbers were used to collect dissolved ^{234}Th samples during the spring and fall legs of the 1992 Equatorial Pacific (EqPac) program aboard the NOAA ships R/V *Malcolm Baldrige* and R/V *Discoverer*. An in-situ pumping system was used to collect samples at a fixed depth (100m) and an integrated depth (0-100m). Particulate and dissolved samples were collected at 75 stations between 10°S and 15°N latitude and 95-170°W longitude. The standard sampling protocol involved pumping 300 - 600 liters of seawater, at approximately 5 liters/min, in-situ through a 53 μm Nitex screen followed by a precombusted Whatman 0.7 μm GFF filter (both 142 mm diameter) and a 3.25-inch in-line MnO_2 impregnated Hytrex II cartridge pair. By raising and lowering the pump between the surface and 100m depth, at a constant winch and pumping speed, samples were obtained which represented the average concentration at a given station. This "vertical integrating" approach coupled with the new Hytrex II cartridges, and an at-sea germanium detector, enabled us to obtain near real-time ^{234}Th data from a large number of stations.

At sea, the cartridges were dried overnight in a 65°C oven, then pressed into a stainless steel mold (2.75" I.D.) at 10 tons of pressure for 1 minute using a hydraulic press (it is important to maintain the 65°C oven temperature, since the cartridge becomes brittle at higher temperatures and may be impossible to press into a uniform matrix). The resulting "puck" was wrapped in plastic film and directly gamma counted for ^{234}Th on a precalibrated at-sea germanium detector. The puck remained in a permanent shape (height = approximately 1-inch), showing no measurable evidence of sample expansion. The precalibration and initial efficiency of the at-sea gamma

detector was established using a pressed MnO₂ cartridge containing a known activity of uranyl nitrate solution (^{238}U dpm = ^{234}Th dpm). Typical counting times for the "A" and "B" cartridges were 4 hours (5% uncertainty) and 10 hours (15% uncertainty), respectively. Field blanks (cartridges which were not exposed to seawater, but otherwise processed as samples) were insignificant relative to the detector background of 0.030 counts/minute +/- 50% at 63.3 keV.

A number of the sample cartridges (n=18) were gamma counted at sea, then returned to WHOI for radiochemical purification and low level beta counting, to confirm the at-sea counting efficiency (0.063 +/- 9%). The low level beta counters have a higher counting efficiency (> 50%) than gamma detectors and are not affected by branching ratio (3.9% at 63.3 keV gamma), thereby producing a ^{234}Th value with relatively low uncertainty. In the laboratory, ion-exchange chemistry and electroplating were used to isolate thorium (see Appendix 2 for chemical procedures). The samples were then beta counted over a 5-week counting period, tracking the distinctive ^{234}Th decay rate ($t_{1/2} = 24.1$ days). The counts were fit to a ^{234}Th decay regression using a curve fitting routine (Sigma Plot Scientific Graph System, Jandel Scientific) in order to calculate ^{234}Th at the time of collection, and associated error. The chemical efficiency was determined by alpha counting ^{230}Th which was added at the start of the chemistry. The calibration of the at-sea detector was further confirmed by a deep water (167m) "standard" cartridge pair, which was gamma counted at sea, then returned to WHOI for radiochemical processing. At >150m depths, ^{234}Th and ^{238}U should approach equilibrium. The conservative ^{238}U relationship with salinity ($S_{\text{‰}} \times 0.07097 = ^{238}\text{U}$ dpm/l; Chen et al., 1986) enabled us to calculate the ^{238}U activity at 167m. We found a $^{234}\text{Th} / ^{238}\text{U}$ ratio of 1.03 +/- 0.06.

RESULTS

The 3.25 inch MnO₂ impregnated Hytrex II cartridges were used to obtain 62 (spring) and 53 (fall) dissolved ^{234}Th values during six legs of the 1992 NOAA and NFS sponsored JGOFS (Joint Global Ocean Flux Study) EqPac program. The ranges and mean cartridge collection efficiencies for the spring and fall legs are listed in Table 3. The pump speed behaved erratically during one part of a fall leg (11 samples), disrupting the flow of seawater through the cartridge housings, and the efficiencies are therefore not included in Table 3. The lowest spring collection efficiency (0.500) appears to be an anomaly, since there is a difference of 30% between it and the next highest efficiency (0.648). All other collection efficiencies are within 5% of the next highest efficiency. A plot of the spring and fall ^{234}Th collection efficiencies (Figure 1) illustrates the distribution of efficiencies around the mean. The percent cartridge efficiencies are rounded to the nearest 5% (for example, a cartridge pair with a 73% collection efficiency is represented in the 75% group). The collection efficiencies for the spring and fall legs plot into a typical Gaussian distribution, with the highest number of cartridge pairs falling at or near the mean collection efficiency of 0.789 +/- 9.3% (n=104). If the low collection efficiency of 0.500 from the spring leg is omitted from the data set, the mean for the spring and fall legs is 0.792 +/- 8.6% (n=103). This mean collection efficiency is consistent with the collection efficiencies of 10-inch Micro-wynd cartridges, which were used by this laboratory to measure ^{234}Th in the 1990 North Atlantic Bloom Experiment (mean = 0.87 +/- 8%, n=40; Buesseler et al., 1992b).

We found a small fraction of ^{238}U on the cartridges, which only became significant on the few cartridges which were analyzed for ^{234}Th after more than 3 half-lives. A correction of less than 5% of the signal (at 80 days) was made to account for the supported ^{234}Th in these samples. This ^{238}U "contamination" may be a result of seawater which remains on the cartridge as it is removed from the housing, and therefore might be minimized by rinsing the cartridges with distilled water prior to further processing. Since there is some evidence that MnO_2 impregnated Micro-wynd II cartridges might collect a small fraction of ^{238}U (collection efficiency approximately 0.5%; Buessler et al., 1992a), this possibility must also be considered for the Hytrex II cartridges. In any case, the correction was significant for less than 10% of the cartridges (n=22) and was accounted for during calculations for the at-sea detector efficiency.

CONCLUSIONS

We tested two MnO_2 impregnated polypropylene cartridge types (Beta Pure and Hytrex II, both with 5 μm pore size) in order to determine the best adsorber for the in-situ collection of dissolved ^{234}Th in large volumes (> 500 liters) of seawater. We were able to reduce the steps in the MnO_2 impregnation procedure so that the Hytrex II cartridges could be successfully impregnated in 2.5 days as compared with the previous impregnation procedure which required 5 days. The cost per- MnO_2 impregnated cartridge was significantly reduced by using the 3.25-inch Hytrex II cartridge and shortened impregnation procedure: 90% in cartridge cost (one 10-inch cartridge produces three 3.25-inch cartridges) over the 10-inch Micro-wynd II cartridges, 40% in man-hours and 10% in chemicals. This reduction in labor and savings in cartridge and chemical costs becomes most significant during preparation for large sampling programs. The Beta Pure cartridges did not impregnate uniformly with MnO_2 .

The MnO_2 impregnated Hytrex II cartridges were tested in the laboratory for efficiency of ^{234}Th collection using 0.5 μm filtered seawater and radiochemically spiked filtered seawater. Different flow rates and cartridge sizes were used in order to determine the most effective parameters for dissolved ^{234}Th collection. We determined that a 3.25-inch cartridge with a flow rate of approximately 8 liters/minute would collect ^{234}Th with a greater than 60% efficiency. The same size cartridges and flow rate used on a 1991 Gulf of Maine cruise resulted in a greater than 80% collection efficiency, and produced a dissolved ^{234}Th concentration consistent with independent samples collected at the same station and depth.

The MnO_2 impregnated 3.25-inch Hytrex II cartridges efficiently collected ^{234}Th in-situ during the 1992 NOAA and NSF sponsored JGOFS EqPac program, with a mean collection efficiency of $0.79 \pm 9\%$ (n= 104 cartridge pairs). These collection efficiencies are consistent with those for 10-inch Micro-wynd II cartridges which were previously used by this laboratory (Buessler et al., 1992b). Using a flow rate of 5 liters/minute enabled samples to be collected in a two hour sampling period. These 300-600 liter samples produced acceptable counting statistics on the "A" and "B" cartridges within a 14 hour gamma counting period (5% and 15%, respectively). The smaller size and composition of the 3.25 inch Hytrex II cartridge enabled it to

be pressed into a permanent 1-inch "puck" for direct gamma counting at sea. This protocol significantly decreases the handling between collection and counting, reducing handling errors and producing more consistent counting data than previous non-destructive techniques. Radiochemical procedures and low level beta counting at WHOI were used to establish the at-sea gamma detector efficiency for this new counting matrix. A deep water "standard" was also collected to confirm that the collection and counting efficiencies were correct.

Acknowledgments:

We are pleased to acknowledge the assistance of J. Andrews, S. B. Moran, S. Casso and J. Todd for their participation in the EqPac sampling cruises. The officers and crew of the R/V *Cape Hatteras*, R/V *Malcolm Baldrige* and R/V *Discoverer* contributed greatly to the success of the field work for this project. This work was supported by a grant from NOAA's Office of Global Programs (OCE-920395200).

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Table 1

Collection Efficiency of Dissolved ^{234}Th on MnO_2 Impregnated Cartridges

<u>size (inches)</u>	<u>liters/min</u>	<u>Collection Efficiency</u>	
		<u>Hytrex II</u>	<u>Beta Pure</u>
1.8	15	0.42	0
2.5	8	0.86	0.70
2.5	10	0.39	n/a
2.5	15	0.40	n/a

Collection efficiency of MnO_2 impregnated Hytrex II and Beta Pure cartridges relative to the length of the cartridge and flow rate through the cartridge pair. The Hytrex II cartridge pair consistently produced a higher ^{234}Th collection efficiency than the Beta Pure cartridge pair (n/a = not analyzed).

Table 2

Collection Efficiency of Dissolved ^{234}Th on MnO_2 Impregnated Hytrex II Cartridges.

<u>size (inches)</u>	<u>liters/min</u>	<u>collection efficiency</u>
2.5	7.4	0.638 +/- 2.1%
2.5	4.3	0.467 +/- 4.8%
3.25	7.9	0.621 +/- 2.4%
3.25	3.9	0.427 +/- 3.2%

The cartridge collection efficiency of dissolved ^{234}Th increases with increased flow rate through the Hytrex II cartridge pair. This increased efficiency could be anomalous, since we have subsequently seen efficient ^{234}Th collection in the field at flow rates as low as 1 liter/min. There appears to be no difference in the collection efficiency of the 2.5 inch and the 3.25 inch cartridge pair.

Table 3

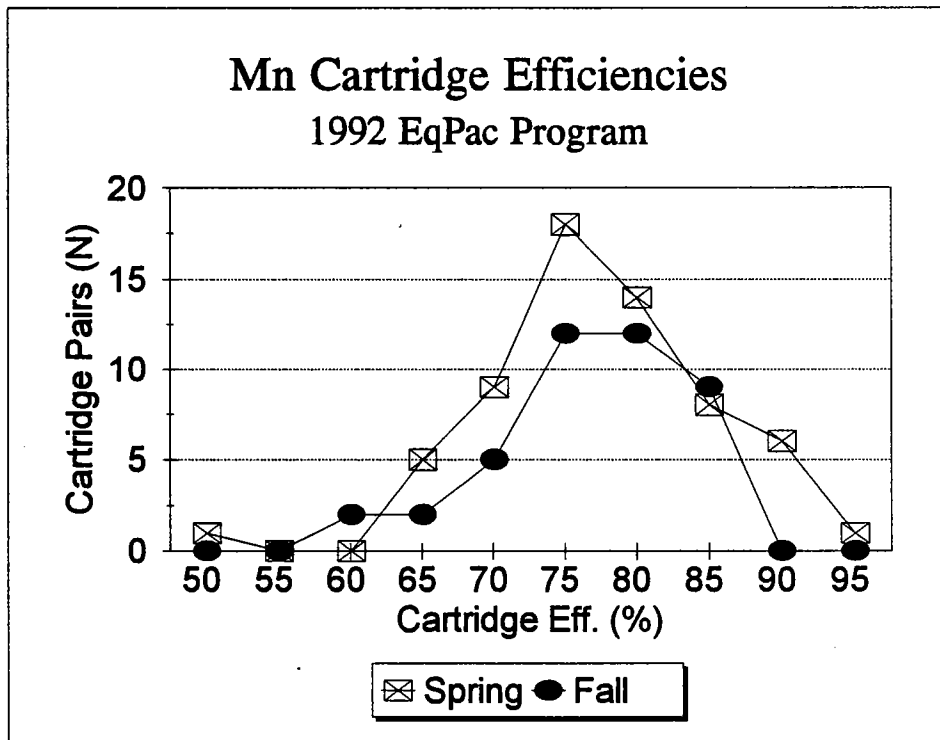
**Collection Efficiencies of Dissolved ^{234}Th on MnO_2 Impregnated
3.25-inch Hytrex II Cartridges for the 1992 EqPac Program.**

	<u>Spring (n=62)</u>	<u>Fall (n=42)</u>
Mean	0.791	0.787
Standard Deviation	0.081	0.062
% variation	10.2	7.9
Median	0.793	0.794
Range	0.500 - 0.922	0.639 - 0.867

The mean collection efficiency and standard deviation is consistent for the spring and fall samplings. The lowest collection efficiency (0.500) for the spring legs appears to be an anomaly, and if omitted from the data set, the mean dissolved ^{234}Th collection efficiency for the combined spring and fall legs becomes 0.792 +/- 8.6% (range 0.639 - 0.922).

Figure 1

Percent Collection Efficiencies of Dissolved Th-234
plotted against number of 3.25-inch Hytrex II pairs



The collection efficiencies for the spring and fall legs plot into a typical Gaussian distribution, with the highest number of cartridge pairs falling at or near the mean collection efficiency of $0.79 \pm 9\%$ (percent cartridge efficiencies are rounded to the nearest 5%). This mean collection efficiency is consistent with that of the 10-inch Micro-wynd II, previously used by this laboratory ($0.87 \pm 8\%$, $n = 40$; Buessler et al., 1992b).

Appendix 1

MN CARTRIDGE IMPREGNATION

The procedure for impregnating Osmonics Hytrex II (polypropylene) cartridges with MnO_2 is modified from a method previously used by this laboratory for another polypropylene cartridge, CUNO Micro-wynd II (Buessler et al., 1992a). The cartridges are submerged overnight in a large bath containing 25 mls Micro soap/ 5 liters distilled water. After a thorough rinse with distilled water, the cartridges are submerged in a supersaturated $KMnO_4$ bath, which has been heated to $35^{\circ}C$. The bath is continually stirred for 24 hours with heat and an additional 16 hours without heat. A system of 3 filter holders in series is used for the final rinse with approximately 30 liters of distilled water. It is important that the cartridges remain wet throughout the Mn impregnation. After the final rinse, the cartridges are drained of excess water and placed in individual plastic zip lock bags. The date and batch number is recorded on the bag.

Appendix 2
PROCEDURE FOR THE SEPARATION/PURIFICATION
OF TH-234 ON MN CARTRIDGE SAMPLES

****ASH THE CARTRIDGES INDIVIDUALLY IN A 600 ML BEAKER AT 500°C FOR 4 HOURS.****

1. Add approximately 50 ml 8N HNO₃ to the ashed sample in the 600ml beaker and warm on a hot plate to solubilize the ash. Add UP TO 0.5 ML 30% H₂O₂ dropwise to reduce the MnO₂ and clear the solution.
2. Add 12 dpm (by weight) Th-230 and heat at a low temperature (~ 50°C) for 5 hours to equilibrate the solution.
3. Add 8N HNO₃ and continue warming to solubilize all salts (if necessary), then filter through a Whatman 934-AH glass fiber filter, rinsing the beaker and filter with an additional 10 ml of 8N HNO₃.
4. Condition a 1cm ID x 20cm long gooseneck column (see note 1) containing 17 ml AG1-X8 50 - 100 mesh (BioRad) resin with 100 ml 8N HNO₃ (flow rate = 1 - 2 ml/min)
5. Pass the solution through the column (1 - 2 ml/min), collecting the eluant in a waste beaker. This fraction contains Ra and should be discarded.
6. Rinse the filter flask 3x with 5 ml 8N HNO₃, then rinse the column with 150 ml 8N HNO₃, collecting in a waste beaker.
7. Change from the waste beaker to a 250 ml beaker and elute Th with 100 ml 8N HCl.
8. Evaporate the Th fraction to dryness and resolubilize in 40 ml 8N HCl.
9. Condition a 1cm ID x 10cm long column containing 10 ml of AG1-X8 100 - 200 mesh resin with 50 ml 8N HCl (flow rate = 1 - 2 ml/min).
10. Pass the 40 ml Th fraction through the column (1 - 2 ml/min), collecting in a 100 ml beaker.
11. Rinse the 250 ml beaker 3x with 2 ml 8N HCl, then rinse the column with 20 ml 8N HCl, collecting in the same 100 ml beaker as step 10.
12. Evaporate the Th fraction to dryness and resolubilize in 5 ml 8N HNO₃. Repeat twice.
13. Condition a 1cm ID x 5cm long column containing 2 ml of AG1-X8 100 - 200 mesh resin with 10 ml 8N HNO₃ (flow rate = 1 - 2 ml/min).
14. Pass the 5 ml Th fraction through the column (1 - 2 ml/min), collecting the eluate in a waste beaker (trace amounts of Ra).
15. Rinse the beaker 3x with 2ml 8N HNO₃, then pass an additional 10 ml 8N HNO₃ through the column, collecting as waste.

16. Change from the waste beaker to a 50 ml beaker and elute the Th with 15 ml 8N HCl.
17. Add 5 drops of concentrated H₂SO₄ to the Th fraction and evaporate to dryness. Cool and hold for electroplating.

ELECTROPLATING PROCEDURE

1. Clean and label the plating disks with ID#. Assemble the plating cells, allowing time for each to sit with 5 ml of distilled-deionized water (DDW), to check for leaking (See note 2). Remove the DDW.
2. Add exactly 5 ml of DDW to the dried Th fraction from step 17, washing down the walls of the beaker with a disposable pipette.
3. Add 4 drops of 0.02% thymol blue indicator and 10 drops of 14M NH₄OH. The solution should turn blue, indicating a basic pH. Mix the solution using a disposable pipette.
*** It is important that the same amount of NH₄OH be added to each cell per plating run, since the (NH₄)₂SO₄ concentration establishes the electrical resistance of the solution and thus affects the current for each cell.
4. Neutralize the solution with 18M H₂SO₄ and add one drop in excess of the neutral point. The solution should be slightly pink.
5. Transfer the solution to the plating cell, rinsing the beaker twice with 2 ml of 0.02M H₂SO₄.
6. Adjust the pH to 2 - 3, using 2M NH₄OH (mix with a disposable pipette). The end point indicator is a light orange color. Check the pH. If the pH is greater than 3, the solution may be adjusted with dilute H₂SO₄ (1 drop concentrated H₂SO₄ in 50 ml DDW).
7. Plate for 2 hours at 1 amp per cell. Check periodically, adjusting the voltage, if necessary.
8. At the end of the plating period, add 1 ml of 14M NH₄OH to each sample, wait 1 minute, then switch off.
9. Disassemble the cells as quickly as possible. Wash the plating disk with DDW and acetone. Dry and store for counting in a labeled glassine envelope.
** Save the plating solution until the chemical efficiency has been established**

Place the plating apparatus in a beaker with warm soapy water and warm on a hot plate. Cool overnight, rinse with tap water and put everything but the brass bottoms into a beaker with 2N HCl, warming on a hot plate. Put the brass bottoms into a cool 2N HCl bath overnight. Rinse the plating equipment with distilled water, dry and store in plastic bags.

Notes:

1. The gooseneck modification maintains moisture throughout the resin bed, thereby limiting the possibility of the column channeling due to the resin going dry (Suprenant et. al., 1983). The gooseneck columns used for separation chemistry are made by Anderson Glass, Fitzwilliams, N.H. (603) 585-7771.
2. The plating cell is adapted from those described in DOE procedures manual HASL-300 (United States Department of Energy, 1992). The stainless steel disks are made by A.F. Murphy Die & Machine Co., Inc., North Quincy, MA (617) 328-3820.

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REPORT DOCUMENTATION PAGE	1. REPORT NO. WHOI-94-15	2	3. Recipient's Accession No.
4. Title and Subtitle Adsorbers for In-Situ Collection and At-Sea Gamma Analysis of Dissolved Thorium-234 in Seawater			5. Report Date July 1994
7. Author(s) M. C. Hartman and K. O. Buesseler			6.
9. Performing Organization Name and Address Woods Hole Oceanographic Institution Woods Hole, Massachusetts 02543			8. Performing Organization Rept. No. WHOI-94-15
12. Sponsoring Organization Name and Address National Oceanic and Atmospheric Administration			10. Project/Task/Work Unit No.
			11. Contract(C) or Grant(G) No. (C) OCE-920395200 (G)
			13. Type of Report & Period Covered Technical Report
15. Supplementary Notes This report should be cited as: Woods Hole Oceanog. Inst. Tech. Rept., WHOI-94-15.			14.
16. Abstract (Limit: 200 words) Two polypropylene cartridge types (Beta Pure and Hytrex II) were tested in the laboratory as adsorbers for in-situ collection of dissolved Thorium-234 (²³⁴ Th) in seawater. Using a uranyl nitrate tracer, we determined that a MnO ₂ impregnated 3.25-inch Hytrex II cartridge with a flow rate of 8 liters/minute would collect ²³⁴ Th with a greater than 60% efficiency. The smaller size and composition of the 3.25 inch Hytrex II cartridge enabled it to be pressed into a permanent 1-inch "puck" for direct gamma counting. This protocol significantly reduced the handling between collection and counting. When field tested in the Gulf of Maine as a large volume (>500 liters) collector, the new adsorbers produced a greater than 80% collection efficiency and a dissolved ²³⁴ Th concentration which was consistent with independent samples collected at the same station and depth. These adsorbers were used successfully for the in-situ collection of ²³⁴ Th in large volumes of seawater during the 1992 NOAA and NSF sponsored JGOFS EqPac program, with a mean collection efficiency of 0.79 +/- 9% (n=104 cartridge pairs).			
17. Document Analysis			
a. Descriptors Thorium-234 MnO ₂ adsorber seawater			
b. Identifiers/Open-Ended Terms			
c. COSATI Field/Group			
18. Availability Statement Approved for public release; distribution unlimited.		19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 19
		20. Security Class (This Page)	22. Price