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Measurement of Attogram Quantities of ^{231}Pa in Dissolved and Particulate Fractions of Seawater by Isotope Dilution Thermal Ionization Mass Spectroscopy

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A technique has been developed to quantify ultratrace ^{231}Pa (50−2000 ag; 1 ag = 10^{-18} g) concentrations in seawater using isotope-dilution thermal ionization mass spectrometry (TIMS). The method is a modification of a process developed by Pickett et al. (Pickett, D. A.; Murrell, M. T.; Williams, R. W. *Anal. Chem.* 1994, *66*, 1044−1049) and extends the technique to very low levels of protactinium. The procedural blank is 16 ± 15 ag (2σ), and the ionization efficiency (ions generated/atom loaded) approaches 0.5%. Measurement time is <1 h. The amount of ^{231}Pa needed to produce ^{231}Pa data with an uncertainty of ±4−12% is 100−1000 ag (~3 × 10^5 to 3 × 10^6 atoms). Replicate measurements made on known standards and seawater samples demonstrate that the analytical precision approximates that expected from counting statistics and that, based on detection limits of 38 and 49 ag, protactinium can be detected in a minimum sample size of surface seawater of ~2 L for suspended particulate matter and <0.1 L for filtered (<0.4 μm) seawater, respectively. The concentration of ^{231}Pa (tens of attograms per liter) can be determined with an uncertainty of ±5−10% (2σ) for suspended particulate matter filtered from 5 to 10 L of seawater. For the dissolved fraction, 0.5−1 L of seawater yields ^{231}Pa measurements with a precision of 1−10%. Sample size requirements are orders of magnitude less than traditional decay-counting techniques and significantly less than previously reported ICP-MS techniques. Our technique can also be applied to other environmental samples, including cave waters, rivers, and igneous rocks.

^{231}Pa, the only long-lived intermediate daughter ($t_{1/2}$ = 32 760 years[2]) of ^{235}U, has been applied as a geochemical tracer in diverse fields of Earth sciences, including geochronology, volcanology, oceanography, and paleoclimatology.[3−10] In particular, concentrations and isotopic ratios of ^{231}Pa and ^{230}Th in seawater and ocean sediments have been used to elucidate the processes responsible for the removal of particle-reactive elements from the ocean.[10−18] Seawater ^{231}Pa and ^{230}Th data have also improved our understanding of processes ranging from boundary scavenging[19] to ventilation of the modern[10,20−23] and last-glacial[20] Atlantic Oceans.

The utility of ^{231}Pa as a tracer in marine science has been constrained by its extremely low natural abundance. For example,

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seawater contains only 10 ag/L (~10^{-20} molar or 10^4 atoms/L) in the surface particulate fraction and about 500 ag/L (~10^{-18} molar or 10^6 atoms/L) in the surface dissolved fraction.[10,22-24] Traditional α and β counting techniques[25] typically yield a precision of ±9-28% (2σ) for samples containing 100-4000 fg ^{231}Pa (10^8-10^9 atoms). These methods require very large sample sizes, typically several thousand liters for measurement of the suspended particulate fraction, and long (weeks to months) counting times.[13-16,19,25] Recently, Choi et al.[26] developed an ICP-MS method that improves detections limits and sample size requirements by large amounts compared to traditional decay-counting techniques and is applicable to ^{231}Pa measurement of total seawater. Here, we present a thermal ionization mass spectrometric (TIMS) technique with lower detection limits and, hence, sample size requirements. This method is applicable to the measurement of ^{231}Pa in both dissolved and particulate forms throughout the ocean water column. Pickett et al.[1] were the first to develop a TIMS method to perform Pa measurements with a precision of better than ±1% for sample sizes of hundreds of femtograms of ^{231}Pa. Since then, the TIMS technique has been used to analyze ^{231}Pa in different natural materials, such as carbonates, silicates, and seawater.[6,7,9,10]

On the basis of the lowest values of previous reported blanks, 100 ± 100 ag,[10] the detection limit is 250 ag, which corresponds to the concentration of ^{231}Pa in the suspended particulate matter of 15 L of surface seawater or in the dissolved fraction of 0.5 L of surface seawater.[22] Here, we present a modified version of the Pickett et al. method.[1] Our main contribution is the characterization and testing of this method for very small protactinium loads. The application of a TIMS method to the analysis of particulate and dissolved fractions of seawater containing as little as tens of attograms of Pa remains a challenge because of the following reasons. First, the procedural blank needs to be reduced as much as possible and characterized at these low levels. Second, the ionization efficiency must be maintained at high levels (e.g., tenths of a percent[1]). Third, small ion beams must be measured precisely and accurately, requiring, among other characteristics, low detector dark noise. The dark noise inevitably increases after introducing ^{233}Pa ($t_{1/2} = 27.0$ days[27]), which is used as a spike, into the TIMS instrument. Fourth, high sample throughput is desirable in order to obtain large-scale ocean ^{231}Pa data. A method that requires small sample sizes with short measurement times and has a low procedural blank, high instrumental sensitivity, and high signal/noise ratio is necessary for analyzing ultratrace ^{231}Pa in seawater.

EXPERIMENTAL SECTION

Reagents and Materials. All chemical procedures were performed in a clean room at the Minnesota Isotope Laboratory (MIL). Deionized/distilled water was purified using a Super-Q purification system. Bottles and beakers were cleaned in acid baths.[28] Ultrapure reagents, including HNO_3, HF, $HClO_4$, and NH_4OH, were obtained from Seastar Chemicals. Ultrapure HCl was double-distilled from analytical reagent (AR) grade acid. Redistilled HNO_3 and HCl were obtained from GFS Chemicals Inc.

A 200-g portion of anion-exchange resin (Spectrum Spectra/Gel, AG 1-X8, 75-150 μm) was packed in a quartz column and successively cleaned with GFS HCl (6 N, 1 L), H_2O (1 L), GFS HNO_3 (6 N, 0.5 L), Seastar HNO_3 (0.1 N, 1 L), and H_2O (1 L). The column used for ion separation, made from a heat-shrink Teflon tubing (4:1, 1/2-in.) from Texloc Ltd., was successively cleaned by boiling in aqua regia, AR HNO_3 (6 N), and GFS HCl (0.2 N). Colloidal graphite (Ted Pella, Inc.), used for covering the Pa sample on the Re filament, was placed in a 180-mL Teflon beaker and successively cleaned with aqua regia (overnight, 10 times), HNO_3 (0.5 N, overnight, 2 times) and H_2O (10 times) at 90 °C.

Preparation of ^{233}Pa Spike Solution. To obtain the internal standard, ^{233}Pa, we modified the ^{237}Np milking method described by Pickett et al.,[1] as described in the following paragraph. Six ion-exchange columns with different capacities of cleaned AG 1-X8 resin (850 μL for column 1 and 350 μL for the others), were used to perform the separation steps.

(1) 4 drops of $HClO_4$ and 1 drop of H_3BO_3 were added to the ^{237}Np solution (2.5 mg in 1 mL of 1 N HCl + 0.5 N HF) to oxidize $^{237}Np^{3+}$ to $^{237}Np^{5+}$ and to remove F^-, which is reactive with both Np and Pa. (2) In a closed hood, the solution was dried and redissolved with 1 column volume (cv) of 9 N HCl, followed by 1 drop of H_3BO_3 and 1 drop of 35% ultrapure H_2O_2 to keep the Np oxidized. This solution was passed through column 1, and the eluant was collected in a vial (Np vial). (3) The Pa fraction was eluted with 2 cv of 9 N HCl + 0.05 N HF two times in another vial (Pa vial). The collected Pa solution with 1 drop of $HClO_4$ and 1 drop of H_3BO_3 was dried. (4) The Np fraction was eluted in the Np vial by adding 8 cv of 1 N HCl + 0.5 N HF. (5) The collected Pa fraction was dissolved with 2 cv of 9 N HCl, and loaded on column 2. (6) Continue with steps (3), (4), and (5) four times with columns 3-6 to purify Pa from Np. Pa was collected in the Pa vial.

After collecting the last Pa fraction, the solution was dried and redissolved with 4-5 drops of HNO_3. In a clean room, the Pa solution was diluted with 3 N HNO_3 + 0.05 N HF to 100-200 mL and heated at 70 °C overnight to equilibrate the spike solution. Typically, 10^3-10^4 fg (10^9-10^{10} atoms) of ^{233}Pa was used to prepare a 10-100 fg/g spike solution. The decay of the ^{233}Pa spike was monitored with multiple calibrations, and no ^{237}Np was found to bias ^{233}Pa concentration for as long as 2 months. The collected Np solution remained in the sealed glovebox and was dried to 0.1-0.2 mL with 4-5 drops of $HClO_4$. The Np beaker was then stored, still in the glovebox, for the next milking.

After we had milked the ^{237}Np solution five times, we modified our milking procedure as follows. H_3BO_3 and H_2O_2 were no longer used, and steps 1-4 were simplified. (1) The solution in the stored Np vial was dried, and 2 drops of $HClO_4$ were added to the vial. (2) The solution was dried, redissolved with 1 cv of 9 N HCl, and passed through an 850-μL ion-exchange column, and the eluant was collected in the Np vial. (3) The Pa fraction was eluted twice with 2 cv of 9 N HCl + 0.05 N HF into the Pa vial. The collected Pa solution was dried with 1 drop of $HClO_4$. (4) The Np fraction was eluted into the Np vial by adding 8 cv of 1 N HCl + 0.5 N HF.

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Safety Considerations. Strong acids and bases, including HNO_3, HCl, aqua regia, HF, and NH_4OH, are toxic and corrosive and can burn skin and respiratory organs. A fume hood, goggles, and protective gloves are required to avoid inhalation and contact with skin and eyes. Eye-wash stations and safety showers should be available in case of accidental external exposure to any of these reagents. In case of exposure, immediate rinsing with water is necessary. Calcium gluconate gel, which neutralizes HF, should be immediately available in case of accidental HF exposure. This gel should be applied to the affected area immediately after rinsing with water. Fume hoods should be periodically scrubbed and washed down to remove $HClO_4$, a strongly oxidizating acid, and to avoid possible explosions or fires. ^{233}Pa and ^{237}Np are radioactive nuclides. The ^{237}Np milking procedure should be performed in a glovebox that is sealed except for HEPA filtered incoming air and hepa and charcoal filtered outgoing air. Furthermore, all vapors from dry-down procedures should be immediately scrubbed inside the glovebox by bubbling through aqueous solutions in gas washing bottles. After scrubbing, HEPA filtration, and charcoal filtration, outgoing air should be released into a fume hood. All acidic or basic solutions should be neutralized prior to disposal. Any neutralized solutions that may contain radioactive nuclides should be disposed as radioactive waste.

Standards and Samples. Two ^{231}Pa solutions (Pa-I, 3.00×10^9 atoms/g; Pa-II, 4.09×10^9 atoms/g) were separated from solutions of uranium ore. The ^{231}Pa concentrations were calibrated with a ^{233}Pa tracer solution,[6] which was calibrated with a solution of a zircon from the Piper Gulch Granodiorite that records concordant U−Pa ages[29] and is likely in secular equilibrium for ^{234}U and ^{230}Th.[30] Interlaboratory calibration (between the Minnesota Isotope Lab (based on the zircon solution) and Los Alamos National Laboratory (based on Table Mountain Latite)) demonstrated that independent calibrations were reproducible to better than 0.5%.[6] A more dilute standard (Pa-III, 4.71×10^6 (±0.5%) atoms/g (or 1808 ag/g)) was prepared by dilution of an aliquot of Pa-I.

The particulate fraction of seawater samples (12−18 L) collected from three depths (100, 750, and 2500 m) in the Labrador Sea[23] were used in replicate analyses. Another 35 seawater samples, including both dissolved and particulate fractions, were collected in the Equatorial and South Atlantic Ocean during the 1996 International Oceanographic Commission Trace Metals Baseline Expedition.[22,23] The particulate fraction was collected by filtering 10−20 L seawater on an acid-cleaned 0.4-μm-pore-sized Teflon filter.[23] Filtered seawater samples were stored and acidified (1 mL Seastar HNO_3/L) in acid-cleaned polyethylene bottles.

Chemistry and Analysis. Chemical procedures were modified from previous studies.[1,6,10,28] In some cases, Th was also collected, and one aliquot was split for U analysis. For the dissolved fraction, seawater was acidified to pH ∼2 with concentrated HNO_3, spiked with 10−20 fg of ^{233}Pa tracer, and 10 mg of Fe was added. This solution was heated at 75 °C for several days to ensure sample−spike equilibration. The quantity of ^{233}Pa tracer added to the sample was minimized to limit the increase of the SEM dark noise during the course of the analyses. Pa was then coprecipitated with $Fe(OH)_3$ by addition of NH_4OH to the seawater solution (pH of 8−9). The precipitate was isolated by centrifugation and taken up in 1 mL of 8 N HNO_3. Two anion-exchange columns were used, each containing an 800-μL bed of AG 1-X8 resin. The columns were preconditioned with 3 cv of 8 N HCl, 3 cv of H_2O, and 3 cv of 8 N HNO_3. The dissolved precipitate was loaded onto the column. Fe was eluted by adding 3 cv of 8 N HNO_3, and Th was then collected with 3 cv of 9 N HCl for instrumental analysis.[24] The Pa fraction was collected with 3 cv of 9 N HCl + 0.05 N HF. The eluant was dried and dissolved in 8 N HNO_3, then loaded on the second column, which was conditioned with the same process as the first column. The column was then washed with 3 cv of 8 N HNO_3 to remove residual Fe, 3 cv of 9 N HCl to remove Th, and 3 cv of 9 N HCl + 0.05 N HF to collect Pa.

For the filtered particulate fraction, the sample was digested twice, in HNO_3 + HF (2:1) and in 1% HNO_3 + 3% HCl overnight at 85−90 °C. Typically, 10 fg of ^{233}Pa and 3 mg of Fe were added, and the solution was dried and redissolved in 2 N HCl. Approximately 70% of the sample solution was used for Pa analysis, and the remaining fraction was used for other trace element analyses. Pa was separated from other elements with a single column using the Fe coprecipitation and anion-exchange chromatography methods described above. Chemical recoveries were typically 90−95% for both dissolved and particulate fractions.

After chemical separation, the Pa fraction was spiked with 200 fg of ^{229}Th. This added Th was used as an aid in focusing the ion beam during data acquisition and was found to contribute no Pa contamination. The spiked Pa fraction was dried, loaded in 1 N HNO_3 + 0.4 N HF on a single Re-filament, and then covered with graphite for TIMS analysis. To check the reproducibility of very low [^{231}Pa] analyses, we quantified 11 aliquots of the ^{231}Pa-III standard (150−2000 ag), which had been processed using the same chemical procedure as the dissolved seawater fraction. Replicate measurements were also performed on three particulate fractions collected from the Labrador Sea.

Instrumentation. A Finnigan MAT-262 equipped with an electron multiplier and a Retarding Potential Quadrupole (RPQ) energy filter was used for all analyses. Analysis was conducted by magnet-controlled peak jumping with the electron multiplier (Cu−Be dynode multiplier from MassCom; see Cheng et al.[30]) operated in ion-counting mode. Scan cycles were 20−50 s, and 50−200 sets of data were measured for each sample. Because the centering of peaks could not be verified easily with small ion beams of ^{231}Pa and ^{233}Pa, one additional filament, loaded with ^{231}Pa and ^{233}U, was used for this purpose. Instrumental analyses were conducted within 24 h of chemical processing at 1850−1950 °C (filament temperature). The small amount of ^{233}U, produced by decay of ^{233}Pa during this interval, was evaporated off the filament at low temperatures prior to commencing data acquisition to diminish this isobaric interference.[6]

Multiplier dark noise gradually increased from an initial value of <0.1 count per second (cps) to 0.12−0.14 cps throughout the course of all of the analyses as a result of the introduction of the short-lived ^{233}Pa radionuclide. This background dark noise was tracked between samples, and a correction was applied during data processing.

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An ionization efficiency of several per mil has been reported for protactinium extracted from silicate and carbonate samples,[1,6] as compared to values of 1−2‰ for our earlier seawater studies.[10] To increase sensitivity, we improved the loading technique. Pa was loaded in 1 N HNO_3 + 0.4 N HF. One drop of cleaned colloidal graphite was then loaded on a single spot, followed by 5−7 layers of graphite (total ~0.2 mg). Measurements of 70 samples, including 35 particulate samples and 35 filtered samples, indicated an improved and more consistent ionization efficiency of 3−5‰. Additional advantages include a reduced measurement time, from 2−3 h[6,10] to <1 h, and increased ion beam intensity. Typical beam intensities for ^{231}Pa and ^{233}Pa were 0.5−30 and 30−90 cps, respectively, such that signal/dark noise ratio was increased by a factor of 2−3, as compared to our earlier work.[10]

Data Processing. Data reduction was done off-line. Uncertainties in this paper were all calculated at the 2σ level and represent the maximum of run statistics or counting statistics fully propagated through corrections for dark noise and blanks. The abundance sensitivity was 2.0×10^{-8} at one atomic mass unit (amu) difference and 6.7×10^{-9} at 2 amu difference after the RPQ filter. $^{232}Th^+$, one of the major ion beams in these measurements, was typically between 500 and 2000 cps and never over 10 000 cps and, thus, would contribute $<2 \times 10^{-4}$ cps at masses 231 and 233. $^{229}Th^+$ was <1000 cps. Therefore, the influence of the abundance sensitivity is insignificant. Because the ^{233}Pa ion beam was <100 cps and ^{231}Pa/^{233}Pa ratios ranged from 0.005 to 0.2, intensity and mass biases[30] were negligible. A correction for mass fractionation was not applied, because its magnitude is <0.2% on the basis of tests using Pb and U. Ion beams were counted until Pa was completely burned off, which also minimized any bias from mass fractionation. [^{233}Pa] in the spike solution was corrected for radioactive decay between the time of calibration and the time of analysis.

RESULTS AND DISCUSSION

Blank and Detection Limit. Initially, a significant quantity of ^{231}Pa was found in the ^{233}Pa spike solutions milked from our ^{237}Np solution. Initial ^{231}Pa/^{233}Pa ratios ranged from 0.001 to 0.004 in the ^{233}Pa spike, corresponding to 10−80 ag/sample of ^{231}Pa. However, after milking five batches of ^{233}Pa spike from the ^{237}Np solution, ^{231}Pa was no longer detectable (^{231}Pa/^{233}Pa < 5 ppm), contributing negligible ^{231}Pa to each sample. The total amount of ^{231}Pa blank derived from chemicals, including the spike, resin, Fe, and acids, was <10 ag. We tested three different filters for use in isolating the suspended particulate material from the dissolved fraction in seawater. The total procedural blank including filtering was 16 ± 15 ag, 90 ± 20 ag, and 150 ± 20 ag for an acid-cleaned Teflon filter (0.4-μm, 90-mm diameter), a Nuclepore filter (0.4-μm, 47-mm diameter), and another Nuclepore filter (0.4-μm, 142-mm diameter), respectively, all of which are routinely used for sampling particulate matter in seawater. Acid-cleaned Teflon filters have the lowest blank and are therefore recommended. For the dissolved fraction, the larger amount of added Fe (10 mg instead of 3 mg) and the use of a second anion exchange column increased the total ^{231}Pa procedural blank to 29 ± 13 ag.

The dark noise in our system was ~0.1 cps and generally contributed <10% of the total uncertainty (Figure 1). On the basis of the general definition of the detection limit, blank + 3 × δ_B, where δ_B is the standard deviation of the blank,[31] the minimum detectable amount of ^{231}Pa is 38 ag for the particulate fraction, using a Teflon filter, and 49 ag for the dissolved fraction, both of which are limited by our blank and our ability to characterize the blank (see below for details).

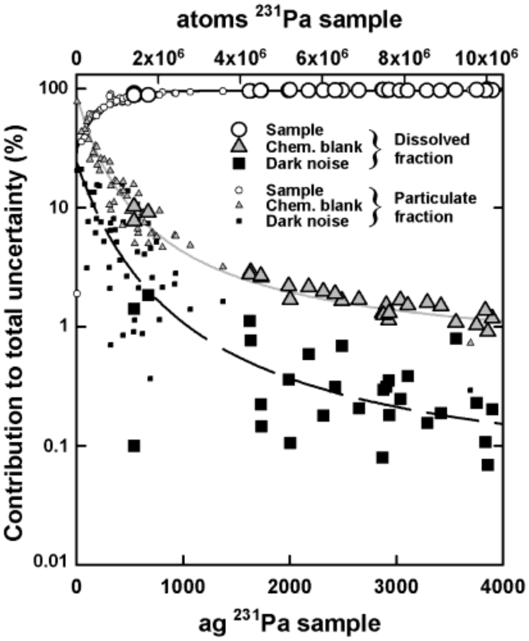

Figure 1. Relationship among analytical uncertainty for sample (circles), chemical blank (triangles), and secondary electron multiplier (SEM) dark noise (squares) and the amount of ^{231}Pa measured in the dissolved fraction (bigger symbols) and suspended particulate fraction (smaller symbols) of 35 seawater samples. Samples were collected from the South Atlantic Ocean.[22,23]

Precision and Accuracy. Precision is ultimately limited by counting statistics: $2\sigma = 2(N^{-1/2})$, where N is the total number of ions counted. Because of the high ionization efficiency (5‰), high ^{231}Pa ion beam to dark noise ratio (10−20), and low procedural blank (<30 ag), measurement precisions of 3−5% are obtained with 1000 ag (4×10^{-18} mol or 3 million atoms) of ^{231}Pa, including the counting error for ^{233}Pa.

The relationship between the sources of error, including sample size, chemical blank and dark noise, and total analytical uncertainty for both the particulate and dissolved fractions for the South Atlantic seawater samples is illustrated in Figure 1. For samples with ^{231}Pa >300 ag, the Pa counting error dominates the total uncertainties, with <15% contribution from the procedural blank and <5% from dark noise. The intensity of the ^{231}Pa ion beam is always <1 cps for samples with <300 ag ^{231}Pa, and the uncertainty contributions from the blank and dark noise become more significant. When ^{231}Pa is <100 ag, the contribution to the total uncertainty is <45% from counting errors, >45% from the blank, and >10% from dark noise.

Results from replicate analyses of the Pa-III standard are illustrated in Figure 2. The internal precision (within-run) were 2.5, 4, 6, 10, and 15% for sample sizes of 2000, 1000, 500, 250, and 150 ag, respectively. For sample sizes with multiple measurements (1000, 500, and 150 ag quantities), external uncertainties (between-

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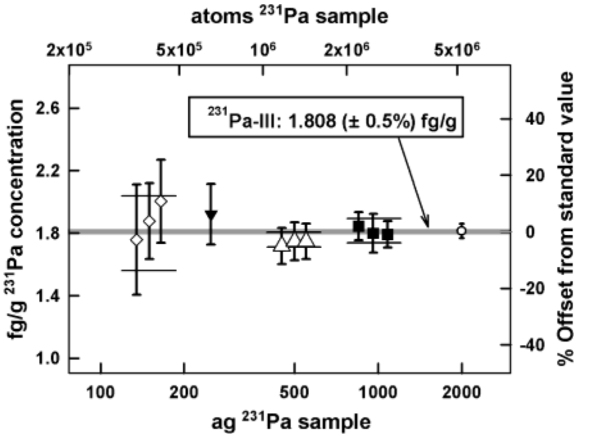

Figure 2. Replicate measurements of Pa-III standard. Aliquots containing different amounts of ^{231}Pa (150 (diamonds), 250 (black triangle), 500 (white triangles), 1000 (squares), and 2000 ag (circle)) were used. External uncertainties of the means of aliquots containing 150, 500, and 1000 ag are indicated (horizontal black lines). The between-run errors are similar to the within-run statistical errors, indicating that the precision follows counting statistics. There is no significant difference between the measured concentrations and gravimetric value (gray bar), demonstrating the overall accuracy of the technique.

run) are comparable to internal uncertainties. These results indicate that the internal uncertainty represents an accurate measure of the true uncertainty. The main sources of this uncertainty are counting statistics (dominant for samples larger than 300 ag) and uncertainty in the blank correction (dominant for samples <100 ag). The measured concentration for all replicates is consistent with the gravimetric value, which demonstrates the overall accuracy of the TIMS technique.

Analysis of Seawater Samples. For ^{231}Pa analysis by TIMS with an ionization efficiency of 5‰, a precision of ±1−10% can be obtained for a sample size containing 100−2000 ag ^{231}Pa. Thus, for a suspended particulate matter sample obtained by filtration, this would require 5 L of surface seawater ([^{231}Pa] ~ 20 ag/L[22,23]) or 2 L of deep seawater ([^{231}Pa] ~ 50 ag/L[22,23]) to achieve such a precision. For the dissolved fraction, 0.2 L of seawater ([^{231}Pa] ~ 500−4000 ag/L[22,23]) would be required. With respect to the detection limit, the minimum surface water sample size would be 2 L for the particulate fraction and 0.1 L for the dissolved fraction. To perform routine seawater ^{231}Pa analyses, 0.5−1 L is recommended for the dissolved fraction and 5−10 L for the suspended particulate fraction.

Results from replicate analysis of seawater particulate samples from the Labrador Sea are plotted in Figure 3. Data from each sampling depth are consistent within error. The external uncertainty for each sample is similar in magnitude to the individual internal uncertainty, which further indicates that the internal error is representative of the true precision. A measurement precision of ±10−15% is indicated for three replicates containing 130 ag of ^{231}Pa in suspended particulate matter obtained from filtration of 4 L seawater from a depth of 100 m. At a depth of 750 m, a precision of ±10−50% was obtained on three replicates of one particulate sample, which had 40, 80, and 150 ag of ^{231}Pa from filtration of 1.9, 3.9, and 7.7 L seawater, respectively. An analytical precision of ±4−10% was achieved for three replicates which had 200−800 ag ^{231}Pa in 2.5−10 L seawater from 2500 m. These results indicate that analytical capabilities for ^{231}Pa that is chemically separated from seawater are essentially identical to those performed on ^{231}Pa in standard solutions.

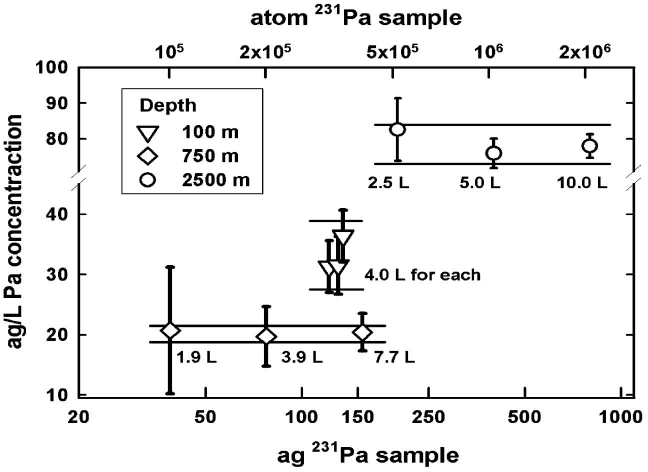

Figure 3. Replicate measurements of the particulate fraction filtered from seawater collected at depths of 100 m (triangles), 750 m (diamonds) and 2,500 m (circles) in the Labrador Sea. The external uncertainty of the mean for each depth is shown as horizontal black lines. The percentage of ^{231}Pa associated with the particulate fraction is on the order of 1−5% and the total ^{231}Pa concentrations in the 100 and 750 m samples are a factor of 2−10 less than typical deep waters.[22,23] Thus, ^{231}Pa concentrations in the two particulate fractions are among the lowest in the ocean. Dissolved deep water fractions typically have concentrations that are higher by 2 orders of magnitude or more than the values depicted in this figure. Seawater volumes corresponding to the amount of ^{231}Pa analyzed are shown adjacent to the symbols. The amount of ^{231}Pa analyzed ranges from 38 to 800 ag.

CONCLUSIONS

We have modified and characterized a TIMS technique for measuring attogram-sized ^{231}Pa samples in filtered and particulate seawater samples. Compared to previous TIMS methods,[1,10] we have characterized our chemical blanks at low levels, and we have relatively high ion beam signal to dark noise ratios considering sample size and comparable ionization efficiencies of 3−5‰, which, taken together, results in reduced sample size capabilities (<100 ag ^{231}Pa). To perform routine seawater ^{231}Pa analyses, 0.5−1 L is recommended for the dissolved phase and 5−10 L for the suspended particulate matter. The method is applicable to both deep waters and surface waters. The method also has broad applications to other fields of Earth sciences, including ^{235}U−^{231}Pa geochronology, igneous geochemistry, and paleoclimatology.

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