Rapid Determination of Actinides in Seawater Samples

Sherrod L. Maxwell[1], Brian K. Culligan [1], Jay B. Hutchison[1], Robin C. Utsey[1] and
Daniel R. McAlister[2]
Savannah River National Laboratory, Building 735-B, Aiken, SC 29808, USA
[2]PG Research Foundation, Inc. Lisle, IL 60532

Savannah River National Laboratory, Building 735-B, Aiken, SC 29808, USA

[1] Author for correspondence (email: sherrod.maxwell@srs.gov)
phone 803-952-7473
fax 803-952-7881

Keywords: Actinides, plutonium, isotopes, seawater, rapid, ICP-MS

Abstract

A new rapid method for the determination of actinides in seawater samples has been developed at the Savannah River National Laboratory (SRNL). The actinides can be measured by alpha spectrometry or inductively-coupled plasma mass spectrometry (ICP-MS). The new method employs novel pre-concentration steps to collect the actinide isotopes quickly from 80L or more of seawater. Actinides are co-precipitated using an iron hydroxide co-precipitation step enhanced with Ti^{+3}reductant, followed by lanthanum fluoride co-precipitation. Stacked TEVA Resin and TRU Resin cartridges are used to rapidly separate Pu, U, and Np isotopes from seawater samples. TEVA Resin and DGA Resin were used to separate and measure Pu, Am and Cm isotopes in seawater volumes up to 80 liters. This robust method is ideal for emergency seawater samples following a radiological incident. It can also be used, however, for the routine analysis of seawater samples for oceanographic studies to enhance efficiency and productivity. In contrast, many current methods to determine actinides in seawater can take one to two weeks and provide chemical yields of ~30-60%. This new sample preparation method can be performed in 4-8 hours with tracer yields of ~85-95%. By employing a rapid, robust sample preparation method with high chemical yields, less seawater is needed to achieve lower or comparable detection limits for actinide isotopes with less time and effort.

Introduction

In light of the nuclear accident at Fukushima Nuclear Power Plant in March, 2011, there is a need for a rapid method to determine actinide levels in seawater samples that can be applied quickly with high chemical yields and effective removal of interferences. Laboratory methods that take one to two weeks to determine actinide levels in seawater are simply not rapid enough to determine actinides following a radiological release. Radiological information is needed immediately to allow adequate protection of the public and assess environmental contamination and damage to ecosystems. The recent theft of nuclear material in Mexico highlights the need for nuclear safeguards and raises concerns about a radiological dispersive device (RDD) or "dirty bomb", again illustrating the need for rapid environmental methods. [1]

News reports suggest that large amounts of radioactive water have leaked from the Fukushima Daiichi Nuclear Power Plant. The Japanese government has announced plans for an "underground ice wall" to prevent contaminated water from flowing out to sea. Concerns have been expressed about the potential presence of "nastier and heavier elements like uranium and plutonium" moving toward the sea. [2] Actinides are chemically and radiologically toxic. The reports that radioactive water may be leaking into the sea near Fukushima Daiichi illustrates the need for rapid methods to determine actinides in seawater to support dose mitigation and to quickly assess the impact on marine ecosystems. [3, 4]

Marine environments have been extensively contaminated by transuranics as a result of global fallout due to atmospheric nuclear-weapons testing. Knowledge of the levels and behavior of actinides in these environments is important to assess the radiological and ecological effects. In addition to radiological risk assessment and monitoring, the determination of actinide isotopes is seawater is important for radioecology and tracer studies, as they are important tools for better understanding oceanographic processes [5]

The measurement of actinide levels in seawater can be quite challenging, due to the difficulty of the seawater matrix and low detection limits required. Surface concentrations of plutonium in seawater, for example, are usually very low ($<5\ \mu BqL^{-1}$), except for contaminated areas such as in the Irish Sea. [6] While fresh water sample aliquots taken for analysis are often 1 liter or less, seawater aliquots up to 200 liters or more have been analyzed to lower detection limits as much as possible. Unfortunately, many of the methods used provide chemical yields of only 30-60%, and that is possibly one reason why such large seawater aliquots are used. If we can improve chemical yields, less seawater may be needed for easier handling and more rapid processing of aliquots. For example, a 40% chemical yield with a 150L seawater aliquot results in a higher detection limit than an 80L sample aliquot with an 85% chemical yield, under the same measurement conditions.

Actinide isotopes are often determined by alpha spectrometry and inductively coupled plasma mass spectrometry (ICP-MS). Inductively-coupled plasma mass spectrometry is an attractive tool for the measurement of actinide isotopes in seawater samples for several reasons. The measurement time for sequential assay by ICP-MS is typically shorter than alpha spectrometry, although alpha spectrometry measurements may be performed simultaneously with large numbers of detectors. ICP-MS is very effective for longer-lived actinide isotopes, where alpha spectrometry works very well for short-lived or long-lived actinide isotopes. ICP-MS, however, can be hampered by isobaric, polyatomic interferences and signal suppression. Accelerator mass spectrometry (AMS) is also an option to achieve very low detection limits for actinide isotopes. [7]

Alpha spectrometry cannot differentiate well between alpha isotopes with overlapping alpha energies. Although alpha spectrometry can measure total ^{239}Pu + ^{240}Pu, for example, it cannot differentiate between ^{239}Pu and ^{240}Pu isotopes. The measurement of ^{240}Pu /^{239}Pu isotope ratios in seawater is very important. In contrast, ^{239}Pu and ^{240}Pu are easily differentiated by ICP-MS, and often Pu isotopic ratios are needed. For seawater, which contains large amounts of ^{238}U, the measurement of ^{239}Pu can be hampered significantly due to ^{238}UH^{+} hydride formation and ^{238}U peak tailing. Effective removal of ^{238}U is therefore very important to ensure the reliable measurement of ^{239}Pu by ICP-MS.

In some cases, a hybrid approach using both alpha spectrometry and ICP-MS may be helpful. This may involve separation of longer-lived actinide isotopes for measurement by ICP-MS and short-lived actinide isotopes (^{238}Pu, ^{241}Am, ^{244}Cm) by alpha spectrometry. [8, 9] It is possible to determine ^{238}Pu by alpha spectrometry, for example, redissolve the sample test source and purify the Pu isotopes further on TEVA Resin. This allows additional removal of ^{238}U, prior to final assay of ^{239}Pu and ^{240}Pu isotopes by ICP-MS. The measurement of ^{236}U/^{238}U has been observed to be a valuable tool to identify an anthropogenic origin of radionuclide contamination. [10] ^{236}U can be separated and determined using ICP-MS or accelerator mass spectrometry (AMS).

There are a number of analytical methods reported that use ion exchange/extraction chromatography to determine the actinide content in seawater that seem to use older, more tedious sample preparation steps or need significant improvements in chemical yield. [11, 12] La Rosa et al reported a new method for ^{237}Np in seawater using multiple MnO_2 precipitations, multiple anion exchange separations and extraction chromatography. While the overall results versus reference values were good, the chemical yields varied greatly and were at times as low as ~20%. [13]

Tracer equilibration of actinide isotopes with multiple valence states is important to ensure accurate assay of the actinide content. In addition, uranium precipitation using iron hydroxide co-precipitation is enhanced by reduction of uranium to U^{+4}. Some laboratory methods use potassium metasulfite [$K_2S_2O_5$] to reduce Pu and U, while other methods do not use any reductant at all. Increasing the iron added to co-precipitate actinides may improve chemical yields, however, this can result in very large amounts of precipitate to redissolve, large column load solutions, large ion exchange columns and long separation times. Some also employ older solvent extraction methods, which often have solvent waste disposal issues. These older approaches have typically resulted in 1 to 2 week processing times, unacceptable during an emergency and inefficient for routine analytical processing of seawater samples.

Some newer methods with smaller sample aliquots have been reported. Kim [14] reported a Pu isotope method for high resolution ICP-MS, however, the method was applied to only 5 liters of spiked seawater. Typically, a larger seawater aliquot is needed to achieve lower detection limits and more reliable measurement of ^{239}Pu/^{240}Pu ratios. The chemical recoveries were ~ 60-70%, with very good assay of Pu isotopic ratios on standards tested. Zheng and Masada reported a method for Pu isotopes in seawater reference materials IAEA-443 and IAEA-381, using a highly sensitive isotope dilution sector field inductively coupled plasma mass spectrometry method. The method provided chemical yields of~ 65% using ^{242}Pu as a tracer. [15] Qiao et al reported a new rapid sequential injection method for Pu, Np and U isotopes in10L seawater aliquots, with Pu yields of ~67-78%, using multiple iron hydroxide preconcentration steps and TEVA Resin plus UTEVA Resin. The need to process much larger aliquots to meet detection limits was discussed. [16]

The time frame needed to determine actinide levels in environmental samples, including seawater samples, after an accident such as the one at the Fukushima Daiichi Power Plant in 2011, is in hours, not weeks, to allow appropriate assessment of environmental contamination as well as protection of the public and marine ecosystems.

Savannah River National Laboratory (SRNL) recently published a paper on the rapid determination of ^{89}Sr and ^{90}Sr in seawater. This new method achieves a 1 mBq L^{-1} detection limit with smaller seawater aliquots and longer gas flow proportional count times. [17]. While there has been progress in the analysis strategies for seawater, a simple, rapid method for actinide isotopes in seawater still seems to be needed that can be applied to larger aliquots, not only for emergency response, but for more efficient processing and throughput for routine analyses.

A new method has been developed by SRNL that can be used aliquots up to 80 liters of seawater, with sample preparation in 4-8 hours and high chemical yields (~85-95%). While the method was not tested with volumes greater than 80L, it can likely be applied to aliquots over 100L. Using the new SRNL method, actinide isotopes can be determined quickly in large seawater aliquots by alpha spectrometry or ICP-MS, with very low detection limits. AMS techniques could also be applied, after appropriate preparation steps.

Actinides are preconcentrated from seawater samples using an iron hydroxide co-precipitation, enhanced with Ti^{+3} reductant. This step is followed by lanthanum fluoride co-precipitation to remove the iron, titanium and seawater matrix interferences. This approach allows the use of relatively large amounts of iron and Ti^{+3} to enhance chemical yields, since the iron and titanium are removed in the subsequent LaF_3 removal step.

While alpha spectrometry was used to demonstrate the new SRNL method, the method can be used easily with ICP-MS assay, particularly if an enhanced removal step for ^{238}U is employed to ensure reliable measurement of ^{239} Pu. [18] The high chemical yields allow smaller seawater aliquots (<<200 L) to be used for easier handling and processing, while still a meeting detection limit of ~1 μBq L^{-1} or lower using alpha spectrometry , depending on the count time. When a highly sensitive APEX SF (Sector Field)-ICP-MS analytical system used by researchers such as Zheng et al and Epov [19, 20, 21] is employed, a detection limit of detection limit of <1 μBq L^{-1} can be easily met for ^{239}Pu and ^{240}Pu.

A rapid separation method was developed using stacked cartridge extraction chromatography. Stacked TEVA Resin and TRU Resin cartridges were used to separate Pu, U, and Np from the seawater samples. This sample preparation method was performed on 2-8L aliquots in <5 hours. TEVA Resin and DGA Resin were used to separate Pu, Am and Cm isotopes from seawater volumes up to 80 liters. The rapid sample preparation method for Pu, Am and Cm isotopes in 80L aliquots takes <8 hours. Pu and Np isotopes can also be separated using TEVA Resin alone, and this was tested for aliquots up to 20L.

It should also be noted that a similar approach can be applied to the collection and purification of ^{90}Y for the determination of ^{90}Sr in large seawater aliquots that is much simpler and easier than the calcium phosphate approach previously reported by this laboratory [17].

<u>Experimental</u>

<u>Reagents</u>

The extraction chromatography resins employed in this work are TEVA Resin® (Aliquat ™ 336), TRU-Resin® (tri-n-butylphosphate (TBP) and octyl (phenyl) N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)), and DGA Resin ® (N,N,N',N' tetraoctyldiglycolamide), available from Eichrom Technologies, Inc., (Lisle, Illinois, USA) and Triskem International (Bruz, France). Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc., Pittsburgh, PA, USA). All water was obtained from a Milli-Q2™ water purification system. All other materials were ACS reagent grade and were used as received. Radiochemical isotopes ^{232}U, ^{242}Pu, ^{243}Am, ^{237}Np, and ^{244}Cm were obtained from Analytics, Inc. (Atlanta, GA, USA) and diluted to the appropriate levels. ^{236}Pu was obtained from the National Physical Laboratory (Teddington, UK).

Procedures

Column preparation. TEVA Resin, TRU Resin and DGA Resin were obtained as cartridges containing 2 ml of each resin from Eichrom Technologies, Inc.. In addition, 1ml cartridges of TEVA Resin and DGA Resin were also used when a total of 3 ml of resin was required. For larger seawater aliquots where larger amounts of La were used, DGA Resin cartridges were stacked to achieve a larger resin volume (3 ml DGA Resin or 4 ml DGA Resin). Small particle size (50-100 micron) resin was employed, along with a vacuum extraction system (Eichrom Technologies).

Apparatus. Polycarbonate vacuum boxes with 24 positions and a rack to hold 50 ml plastic tubes were used. Two boxes were connected to a single vacuum source by using a T-connector and individual valves on the tubing to each box. A large volume vacuum box liner was used to collect rinses to eliminate having to change out 50 ml tubes during the load and rinse steps.

Sample Preparation. Seawater samples were obtained from Isle of Palms, South Carolina, USA. The seawater was rapidly filtered to remove sediments using Whatman 41 filter paper (20 µm pore size). Small volumes of MAPEP 23 and MAPEP 24 (Mixed Analyte Performance Evaluation Program) water standards were added to the seawater samples to test for measurement reliability. The MAPEP samples were provided by Department of Energy (DOE) – Radiological and Environmental Sciences Laboratory (RESL), Idaho, USA.

Figure 1 provides a flow chart of the initial sample preparation method for Pu, Np and U isotopes in seawater for sample volumes of 2L to 8L. If ^{237}Np assay was determined, ^{236}Pu was used instead of ^{242}Pu tracer. ^{239}Np would, of course, also be a yield measurement option for ^{237}Np. ^{232}U was added as a yield monitor for the measurement of uranium isotopes by alpha spectrometry.

Figure 2 show the sample preparation for Pu, Am and Cm isotopes for larger sample aliquots. Up to 40L sample aliquots were processed. To obtain a larger 80L aliquot, two 40L samples were each processed with an iron /titanium hydroxide step, a LaF_3 co-precipitation step and then combined together in one final LaF_3 matrix removal step. The Pu, Am and Cm isotopes were preconcentrated from 80L of seawater into a single column load solution for separation using stacked TEVA Resin + DGA Resin cartridges. As larger and larger seawater aliquots were analyzed, increasing amounts of CaF_2 (presumably) were observed at the LaF_3 matrix removal step and the initial supernatant pH was lowered to be closer to pH 8.8-9.0. Too much residual Ca from the larger seawater aliquots can cause redissolution problems with the final LaF_3 precipitate. In addition, it was found that a water rinse (pH 8.8-8.9) of the Fe/Ti solids was very effective in removing residual Ca for the larger seawater aliquots.

Column separation for Pu, Np and U. Figure 3 provides a flow chart of the rapid column separation method using TEVA Resin plus TRU Resin cartridges for the 2 L -8L sample aliquots. After valence adjustment of the column load solution, the sample was loaded to stacked TEVA Resin + TRU Resin cartridges at ~1 drop/second. It should be noted that the decontamination of uranium from Th is very good (>>1000), as Th is removed on TEVA Resin and even further with the 4M HCl-0.2M HF rinse on TRU Resin. Po^{+4} is removed from U on TEVA Resin in 3M HNO_3, and also with the 10M HNO_3 rinse on TRU Resin. [22]

A more dilute ammonium bioxalate (0.01M) can be used if ICP-MS assay is needed instead of alpha spectrometry. It is also possible to prepare samples for AMS measurement of ^{236}U in a manner similar to the method described by Qiao following the uranium purification on TRU Resin. [17]

Cerium fluoride microprecipitation was used to prepare the purified samples for alpha spectrometry counting. After adding 50 µg Ce, 0.5ml 30wt% H_2O_2 and 1 ml 28 M HF to the Pu eluent solution and waiting 15 minutes, the solution was filtered using a 25 mm polypropylene filter (0.1 µm pore size disposable Resolve™ filter funnel). Each tube was rinsed with ~5 ml deionized water, followed by ethanol to facilitate drying. The filters were heated briefly under a heat lamp to ensure dryness. A similar approach was used for the Am/ Cm and U eluents. For Am/Cm, 50 µg Ce, 0.2ml 30wt% H_2O_2 and 1 ml 28 M HF were added. To prepare the U eluents, 100 µg Ce, 0.5ml 10% $TiCl_3$ and 1 ml 28 M HF were added. The filtering protocol as described above was followed after a 15 minute wait time. Adding hydrogen peroxide to the Pu and Am/Cm precipitation steps provides additional decontamination from uranium by ensuring the U is U^{+6}, which does not carry on the CeF_3 precipitate. $TiCl_3$ is added during the uranium microprecipitation steps to reduce U^{+6} to U^{+4}, which will carry with the CeF_3.

If electrodeposition is desired, sodium formaldehyde sulfoxylate or ammonium iodide reductant in the HCl-HF Pu eluent solution can be used instead of titanium. In an emergency, the CeF_3 approach provides much more rapid results, with good peak resolution.

ICP-MS Measurement Option: Additional Uranium Removal

While alpha spectrometry is used in this work to demonstrate the effectiveness of the new method, this method can be adapted for ICP-MS. A hybrid approach is possible. The sample can be counted for ^{238}Pu by alpha spectrometry and then redissolved using warm 3M HNO_3-0.25M boric acid. The dissolved Pu isotopes processed quickly through TEVA Resin, eluted and measured by ICP-MS to determine ^{239}Pu and ^{240}Pu . The CeF_3 microprecipitation step can remove an additional 1000 x ^{238}U so this approach, in combination with another TEVA Resin separation, can result in extremely high ^{238}U decontamination factors. If the sample is reprocessed through TEVA Resin, a Pu eluent solution of 0.05M HCl-0.025M HF-0.02M hydroxlyamine hydrochloride may be used to allow ICP-MS assay.

An alternate approach without CeF_3 is available. Pu can be eluted directly from TEVA Resin as Pu^{+3} (with 3M HNO3-0.1M ascorbic acid-0.02M Fe^{+2}) through a coupled UTEVA Resin cartridge (1ml) onto a stacked DGA Resin cartridge to achieve very high uranium decontamination factors (~$1x10^7$). This eliminates eluting and reloading Pu to TEVA Resin multiple times. After a single elution and rapid clean-up on DGA Resin, Pu isotopes can be eluted from DGA Resin with a 5ml volume of 0.02M HCl-0.005M HF-0.01M hydroxylamine hydrochloride and assayed by ICP-MS. [18]

Column separation for Pu, Np, Am and Cm

Figure 4 provides a flow chart of the rapid column separation method using TEVA Resin plus DGA Resin cartridges (3ml and 4 ml) that was applied to 16L to 80L sample aliquots. After valence adjustment of the column load solution, the sample was loaded to stacked TEVA Resin + DGA Resin cartridges at ~1 drop/second. Column rinses were ~1-2 drops/second and final elution steps were performed at~1 drop/second. It should be noted that additional Th removal can be achieved by increasing the 9M HCl rinse on TEVA Resin as needed. Po^{+4} is retained on TEVA Resin in 3M HNO_3 and in all concentrations of HCl, as shown on Figure 5. The k' values for Po^{+4} on TEVA Resin were measured using the batch extraction procedure and calculations similar to what is described in reference 23. Po is not an isobaric interference for Pu or Np by ICP-MS, and does not typically form an insoluble fluoride and coprecipitate with CeF_3, which is used for the final alpha spectrometry test source. The plutonium alpha spectra did not indicate the presence of Po^{210}. For electrodeposited sources, Po removal, if needed, could likely be ensured even further by evaporation to dryness in HCl on a high temperature hot plate. For maximum removal of interferences, the final connector tips and column reservoirs on the vacuum box were replaced with new ones just prior to final elution. U is removed from DGA Resin with the 0.05M HNO_3 rinse. If any residual Th^{+4} and Po^{+4} pass through TEVA Resin onto DGA Resin, Po^{+4} is removed along with La and U in the 0.05M HNO_3 rinse, while Th is removed using 3M HNO_3-0.25M HF rinse. In addition, the 30wt% H_2O_2 added to the final Am eluent solution prevents U coprecipitation on CeF_3 by ensuring oxidized U^{+6}.

For larger seawater aliquots, if residual organic matter could not be completely dissolved, the residual solids were wet-ashed in a Teflon beaker on a hot plate using 5ml 3M HNO_3-0.25M boric acid, 5ml 15.8M HNO_3 and 5 ml 30 wt% H_2O_2. Due to the slight filtering out of a small amount of organics on TEVA Resin, increased vacuum was needed as the loading process proceeded to maintain a column flow of ~1 drop per second. As an option, the entire LaF_3/ CaF_2 precipitate can be transferred and wet-ashed in a Teflon beaker to destroy the organics more completely first. This can be done prior to dissolving the precipitate into the column load solution, instead of redissolving and centrifuging the solution first.

The amount of DGA Resin used depends on the amount of La needed to effectively precipitate the Pu, Am and Cm isotopes. When only Pu isotopes are determined using TEVA Resin, the amount of La is not a concern, since La has no retention on TEVA Resin. For 8 mg of less La, a single 2ml DGA Resin cartridge was used. For 12 mg La, used with some of the larger aliquots, 3ml DGA resin (2ml +1ml cartridges) was employed. When 40L aliquots were combined to make a total of 80L, a total of 20 mg La (10 mg La from each aliquot) was used and therefore 4ml DGA Resin was used to ensure good recovery of Am/Cm.

For the determination of Pu/Np on TEVA Resin, the amount of La added is not a problem, since La is not retained on TEVA Resin. This was tested for aliquots up to 20L. In this case, 20 mg La was added, enhanced with 75-100 mg Ca at the final LaF_3 co-precipitation step. The TEVA Resin separation method used was as described earlier, with ^{236}Pu used as a yield monitor for ^{237}Np as well.

Results and Discussion

Table 1 shows the measured values for the determination of ^{239}Pu in a set of seven seawater samples. The seawater aliquot volumes vary between 2L and 8L, spiked with MAPEP 23 standard, using the rapid

TEVA+TRU Resin method and alpha spectrometry. The average ^{236}Pu tracer yield was 89.3% ± 8.7% at 1 SD (standard deviation), and ^{239}Pu results were corrected for the ^{236}Pu tracer yield. The average bias for the seven ^{239}Pu measurements was -3.5%, with 1 SD of 3.7%. The uncertainties for the individual ^{239}Pu results were typically ± 6-8% (1 SD), with a 16 hour count time. The high ^{236}Pu tracer recoveries and excellent results for the analyte versus known values indicate the sample preparation and measurement steps were very effective. The 2L -8L sample preparation can be performed in <5 hours.

Table 2 shows the measured values for the determination of ^{237}Np in the same set of seven seawater samples using alpha spectrometry. A known amount of ^{237}Np was added to each sample aliquot and the Pu isotopes and ^{237}Np were counted together in the same purified fraction. The ^{236}Pu tracer yields were applied to the ^{237}Np results. The average bias for the seven ^{237}Np measurements was 1.8%, with 1 SD of 11.2%. The uncertainties for the individual ^{237}Np results were typically ± 8-10% (1 SD), with a 16 hour count time. Although there was more variation in the ^{237}Np results than desired, the overall average bias was only 1.8%. The use of ^{236}Pu as a tracer for Np seems feasible. ^{239}Np can be used to perhaps better compensate for any Pu-Np variation, however, this requires an additional count of the sample using gamma spectrometry. ^{237}Np can be measured by ICP-MS, if the Ti is not included in the eluent solution, using ^{242}Pu as a tracer.

Table 3 shows the measured values for the determination of ^{238}U in a set of seven seawater samples. The seawater aliquot volumes vary between 2L and 8L, spiked with MAPEP 23 standard, using the TEVA+TRU Resin method and alpha spectrometry. The average ^{232}U tracer yield was 94.7% ± 7.9% (1 SD), and the ^{238}U results were corrected for ^{232}U tracer yield. The individual ^{238}U measurements were corrected for the amount of ^{238}U determined in the unspiked sample aliquot. The average bias for the seven ^{238}U measurements was -4.4%, with 1 SD of 2.6%. The uncertainties for the individual ^{238}U results were typically ± 6-8% (1 SD), with a 16 hour count time. The tracer yields and ^{238}U measured values indicate this rapid approach can effectively collect and purify uranium for measurement. This purification technique could easily be adapted to allow measurement by ICP-MS or AMS for the determination of uranium isotopics in seawater.

Large seawater aliquots were tested for Pu, Am and Cm isotopes. Table 4 shows the measured values for the determination of ^{239}Pu in a set of eight seawater samples using the TEVA + DGA method for rapid assay of Pu, Am and Cm isotopes. The seawater aliquots vary between 16L and 80L, spiked with MAPEP 23 or MAPEP 27 standards, using this rapid method and alpha spectrometry. The average ^{242}Pu tracer yield was 86.4% ± 3.9% (1 SD) and the ^{239}Pu results were corrected for ^{242}Pu tracer yield. The average bias for the eight ^{239}Pu measurements was -0.3%, with 1SD of 8.0%. The uncertainties for the individual ^{239}Pu results were typically ± 8-10% (1 SD), with a 16 hour count time. The ^{242}Pu tracer recoveries and excellent results for ^{239}Pu versus known values indicate the sample preparation and measurement steps were very effective, despite a wide range of seawater aliquots. The 80L aliquots represent two 40L seawater aliquots that were combined in a final LaF_3 step.

The first 80L seawater aliquot shown in Table 4 was processed with 15mg La (7.5 mg per 40L) and no additional Ca added with a chemical yield of 80%. The second 80L aliquot was processed with 20 mg La (10mg per 40L) and 100mg Ca (50mg per 40L) added with a chemical yield of 90%. Other test results (not shown) with 40L aliquots also confirm the positive impact of increased La and additional Ca added. By splitting the La in half so as not to overload the DGA Resin, the Pu and Am recoveries were slightly lower, unless additional Ca was added.

Though it was not tested partly due to container limitations, combining two 50L aliquots at the final LaF_3 step to analyze 100L would seem very feasible. The amounts of Fe and Ti added can be scaled up accordingly, as they will removed during the LaF_3 step. As long as the water rinse is used to remove residual Ca, the analysis of larger aliquots still results in a very small LaF_3/CaF_2 precipitate that can be dissolved in a ~40 ml column load solution. The key step is adding enough Ca along with the LaF_3 to ensure effective precipitation since the La is reduced in each 50L aliquot, since it will be combined later.

For Pu processing only, the La does not have to be limited as with the Am/Cm separation on DGA Resin. For example, 20mg La and 50mg Ca could be used in each 50L aliquot and recombined in a final HCL/HF step representing 100L of seawater with no adverse impact on Pu retention on TEVA Resin. Being able to remove the large amounts of Fe and the Ti used to effectively control valence is a huge advantage is processing large seawater aliquots. By ensuring the initial pH is ~8.8-8.9 during the hydroxide precipitation, the amount of residual Ca can be minimized. Though not tested in this work, it is likely that an equivalent amount of fluoride added as sodium fluoride instead of hydrofluoric acid could be used for laboratories with restrictions on the use of hydrofluoric acid.

Table 5 shows the measured values for the determination of ^{241}Am in a set of eight seawater samples using the TEVA + DGA Resin method for rapid assay of Pu, Am and Cm isotopes. The seawater aliquot volumes vary between 16L and 80L, spiked with MAPEP 23 or MAPEP 27 standards, using this rapid method and alpha spectrometry. The average ^{243}Am tracer yield was 94.0% ± 3.4% (1 SD) and the ^{241}Am results were corrected for ^{243}Am tracer yield. The average bias for the eight ^{241}Am measurements was -6.0%, with 1 SD of ±2.0%. The uncertainties for the individual ^{243}Am results were typically ± 9-10% (1

SD), with a 16 hour count time. The ^{243}Am tracer recoveries and very good results for ^{241}Am versus known values indicate the rapid method was very effective, despite a wide range of seawater aliquots.

The amount of La was varied. For the 16L and 25L aliquots, 3ml DGA Resin (2ml+1ml cartridges) was employed with 12mg La added, without a water rinse of the Fe/Ti solids. For the 40L and 80L aliquots, a total of 20mg La was added and 4 ml DGA Resin (2ml+2ml cartridges) were employed. As noted above, the 80L aliquots represent two 40L seawater aliquots that were combined in a final LaF_3 step. It should be noted that the chemical yield in the final 80L aliquot was increased from 89% to 97% by adding additional La (10 mg La per 40L aliquot instead of 7.5 mg La) and also adding Ca (50mg per 40L aliquot instead of no Ca) to enhance the LaF_3 precipitation.

Table 6 shows the measured values for the determination of ^{244}Cm in a set of eight seawater samples using the TEVA + DGA Resin method for rapid assay of Pu, Am and Cm isotopes. The ^{244}Cm measurements were made on the same purified fractions containing the ^{241}Am. The ^{244}Cm results were corrected for ^{243}Am tracer yield. A known amount of ^{244}Cm was added to each aliquot, which varied from 16L to 80L. The average bias for the eight ^{244}Cm measurements was -5.1%, with 1 SD of 6.4%. The uncertainties for the individual ^{244}Cm results were typically ± 7-8% (1 SD), with a 16 hour count time. The results indicate that ^{244}Cm can be determined effectively using ^{243}Am tracer.

Figure 6 shows the results of an elution study using gamma spectrometry to look at the impact of La on ^{241}Am using the TEVA+DGA method, starting with a spiked column load solution. ^{241}Am was counted on a Packard Cobra II Auto-Gamma System. Am-241 samples (1-4 mL) in 12 x 75 mm polypropylene tubes were counted for 20 minutes or until a 1 SD counting error was achieved for the 50-100 keV energy window. The simulated column load solution contained 10 mg La and the separation was performed using 2ml TEVA Resin + 3ml DGA Resin. The results indicate 99% of the ^{241}Am activity was found in the final eluent solution. A similar elution study, however, using only 2 ml DGA Resin showed 94% of the ^{241}Am recovered in the final eluent fraction, indicating a slight adverse impact from adding 10 mg La. Another elution study was performed with 15 mg La and 50 mg Ca in the column load solution using 2ml TEVA Resin + 4ml DGA Resin, with rinse and eluent volumes increased proportionally for DGA Resin. The final eluent fraction again contained 99% of the ^{241}Am activity, indicating the effect of La under these conditions is insignificant. It may have been possible to achieve high yields for Am and Cm using only 3 ml DGA Resin when 20 mg La was added, but a conservative approach was taken. When 12 mg La was added, only 3 ml DGA Resin was used, but when 20 mg La was added with the larger seawater aliquots, 4 ml DGA Resin was used to ensure good chemical yields.

Tables 7 and 8 show ^{239}Pu and ^{237}Np results for 10L and 20L seawater aliquots spiked with 20 ml MAPEP 27 standard. ^{236}Pu tracer was used so that ^{237}Np can be determined simultaneously in the same purified fraction using TEVA Resin. The average ^{236}Pu tracer recovery was 91.1% ± 5.4% (SD) and both ^{239}Pu and ^{237}Np results were corrected for tracer recovery. The average bias for the ^{239}Pu measurements was -3.6%, with 1 SD of 8.6%. The average bias for the ^{237}Np measurements was -1.4%, with 1 SD of 6.2%, indicating that ^{236}Pu tracer can be used as a yield monitor for ^{237}Np using this method.

For the Pu/Np work, similar conditions were used as was employed in the Pu, Am and Cm method. The amount of La used was 20 mg and a water rinse of the Fe/Ti hydroxide precipitate was performed to remove residual Ca. During the final LaF_3 precipitation step, 75 -100 mg Ca was added to enhance Pu and Np recoveries. The separation was performed using TEVA Resin.

For the 20L aliquots, 3ml TEVA Resin (2ml+1ml cartridges) was used to ensure good Np recoveries, with rinses and elution volumes scaled up accordingly. It might be possible to use a single 2ml TEVA Resin cartridge for Np, but 3ml TEVA Resin (2ml+1ml) was used to provide additional assurance that Np loss would be minimized. The uncertainties for the individual ^{239}Pu and ^{237}Np results were typically ± 9-10% (1 SD), with a 16 hour count time.

Levy et al discuss strategies for seawater sampling and note that significant progress has been made regarding the assay of Pu isotopes with ICP-MS using only 20L of seawater. A discussion of the MnO_2 plus iron hydroxide sample preparation steps in combination with anion exchange separation schemes employed at the IAEA Marine Environmental Laboratory in Monaco is presented, as well as approaches used in other laboratories. [24] In an emergency, 20L seawater aliquots may be adequate, however, more rapid sample preparation are needed.

The rapid collection and purification of Pu isotopes and ^{237}Np, which takes only a few hours using this new SRNL method, can be adapted to ICP-MS assay for emergency analysis and routine oceanographic studies. This new rapid method can also be applied to 40-80L aliquots to achieve additional method sensitivity for Pu isotopes, which may be needed for ^{240}Pu. As noted earlier, additional ^{238}U removal can be performed after ^{238}Pu assay by alpha spectrometry using CeF_3, followed by a second TEVA Resin separation to prepare for ICP-MS or with a direct transfer of Pu isotopes from TEVA Resin to coupled DGA Resin, eluted as Pu^{+3}. Both methods result in rapid decontamination factors of 1×10^6 -1×10^7 for ^{238}U and provide flexibility to the laboratory for rapid assay by ICP-MS..

The MDA (Minimum Detectable Activity) for an actinide isotope using this method with alpha spectrometry was calculated according to equations prescribed by Currie: [25]

$$MDA = [3+4.65\sqrt{B}\,]/\,(CT*R*V*Eff*0.060)$$

Where B = Total Background counts, = BKG (rate) * sample count time

CT = sample count time (min)

R = Chemical Recovery

V = Sample aliquot (g)

EFF = Detector Efficiency

0.060 = conversion from dpm to mBq

In low-level counting, where a zero background count is quite common, the constant 3 is used to prevent an excessively high false positive rate.

Figure 7 shows MDA plotted vs. sample aliquot size for a 16 hour count time using ~25% efficiency alpha detectors and 90% chemical yield, with an assumption of 1 background count per 16 hours. An MDA of ~13 μBq L^{-1} can be achieved for 40L sample with a 16 hour count. During an emergency, the sample aliquot and count times can be adjusted depending on the radiological concern limit for the particular actinide isotope.

Figure 8 shows MDA plotted vs. sample aliquot size for a 7 day count time using ~25% efficiency alpha detectors and 90% chemical yield, with an assumption of 1 background count per 48 hours. An MDA of ~1 μBq L^{-1} or less can be achieved for 80L sample with a 7 day count. The MDA for the results can be adjusted as needed, by changing the sample aliquot volume and count time. Longer count times can be used for routine samples processing if desired. Selecting low background counters can be very important to facilitate achieving the lowest possible MDA.

This approach also provides a rapid sample preparation pathway for collecting ^{90}Y from large seawater aliquots for the determination of ^{90}Sr in seawater that is rapid and much easier than using calcium phosphate precipitation. An iron hydroxide /lanthanum fluoride approach to preconcentrate ^{90}Y (without titanium reductant) using only a single 2 ml DGA Resin cartridge seems feasible for aliquots up to 40L. This has been tested successfully for ^{90}Sr (^{90}Y) in 10L to 30L aliquots of seawater in this laboratory and future work will focus on the analysis of aliquots of 40L. The behavior of ^{90}Y on DGA Resin is very similar to Am and Cm so application to 40L aliquots (or larger) would seem to have a good chance for success. A verification that the sample test source displays a ^{90}Y decay profile (indicating no significant ^{91}Y present) may be required. A La removal step in combination with rinses reported previously on DGA will be investigated.

The rapid preconcentration approach for actinides in seawater described above is enhanced with stacked cartridge separations using vacuum box technology. The vacuum box approach is simultaneous instead of sequential and a large number of samples can be prepared at the same time, especially if handling facilities (space, centrifuges, etc.) for the initial preconcentration steps are available. It can process seawater samples very quickly in an emergency, and improve efficiencies for routine oceanographic studies. As an alternative, it can be adapted for use with automated sequential systems used in some laboratories.

Conclusions

A new method to determine actinide isotopes in seawater samples has been developed that allows the rapid separation of Pu, U, Np, Am and Cm isotopes in seawater samples up to 80L with effective removal of interferences. The sample method can be performed in <8 hours with high chemical yields. This method can be used for emergency seawater analyses following a radiological event or to improve sample throughput and reduce costs associated with routine analyses for oceanographic studies. The method can be used with alpha spectrometry, adapted to ICP-MS techniques, using high uranium decontamination techniques or adapted for use with AMS.

Acknowledgment

This work was performed under the auspices of the Department of Energy, DOE Contract No. DE-AC09-96SR18500. The authors wish to acknowledge Staci Britt, Phil Demaere, Jack Herrington and Becky Chavous for their assistance with this work.

References

[1] "Mexico Finds Stolen Radioactive Material Amid Dirty Bomb Fears" http://www.voanews.com/content/nuclear-material-stolen-in-mexico/1803195.html, 12/4/13

[2] "Japan to Spend Over $300M On 'Ice Wall' To Isolate Fukushima Water Leaks," http://abcnews.go.com/Technology/japan-spend-300m-ice-wall-isolate-fukushima-water/story?id=20144627, 9/3/2013

[3] Stricklin D, Tjarnhage A, and Nygren U (2002) Application of low energy gamma-spectrometry in rapid actinide analysis for emergency preparedness. J. Radioanal. Nucl.Chem. 251 (1): 69-74

[4] Maxwell S, Culligan B, and Hutchison J (2013) Rapid fusion method for determination of plutonium isotopes in large rice samples**.** J. Radioanal. Nucl.Chem, Vol 298: 1367-1374

[5] Hirose K (2009) Plutonium in the Ocean Environment: Its Distributions and Behavior. Journal of Nuclear and Radiochemical Sciences, Vol. 10, No.1: R7-R16

[6] Povinec, P, Livingston H, Shima, S, Aoyama M, Gastaud J, Goroncy I, Hirose K, Hynh-Ngoc L, Ikeuchi Y, Ito T, LaRosa J, Kwong L.L.W., Lee S.-H., Moriya H, Mulsow S, Oregioni B, Pettersson H, Togawa T (2003) IAEA '97 expedition to the NW Pacific Ocean-results of oceanographic and radionuclide investigations of the water column. Deep-Sea Res. II 50: 2607–2637

[7] Lee, S, Gastaud, J, La Rosa J, Ling Wee Kwong L, Povinec P, Wyse E , Fifield L, Hausladen P, Di Tada L, Santos G (2001) Analysis of plutonium isotopes in marine samples by radiometric, ICP-MS and AMS techniques. J. Radioanal. Nucl. Chem. 248: 757–764.

[8] Maxwell S, Jones V (2009) Rapid determination of actinides in urine by inductively coupled plasma mass spectrometry and alpha spectrometry: a hybrid approach. Talanta 80 (1): 143-150

[9] Ayranov M, Krahenbuhl U, Sahli H, Rollin S, Burger, M. (2005) Radiochemical

separation of actinides from environmental samples for determination with DF-ICP-MS and alpha spectrometry. Radiochim Acta 93 5: 249-258

[10] Quinto F, Steier P, Wallner G, Wallner A, Srncik M, Bichler M, Kutschera W, Terrasi F, Petraglia A, Sabbarese (2009) The first use of ^{236}U in the general environment and near a shutdown nuclear power plant. Applied Radiation and Isotopes 67: 1775–1780

[11] Hirose K and Sugimura Y (1985) A new method of plutonium speciation in seawater. J. Radioanal. Nucl. Chem. Articles 92: 363

[12] Sidhu R (2002) A Robust Procedure for the Determination of Plutonium and Americium in Seawater. J. Radioanal. Nucl. Chem. 256: 501-504

[13] La Rosa J, Gastaud J, Lagan L, Lee H, Levy-Palomo I, Povinec P, and Wyse E (2005) Recent developments in the analysis of transuranics (Np, Pu, Am) in seawater. Journal of Radioanalytical and Nuclear Chemistry, Vol. 263, No. 2: 427-436

[14] Kim C S and Kim CK (2002) Determination of Pu Isotopes in Seawater by an On-Line Sequential Injection Technique with Sector Field Inductively Coupled Plasma Mass Spectrometry. Anal. Chem., 2002, 74: 3824–3832.

[15] Zheng J and Yamada M (2012) Determination of plutonium isotopes in seawater reference materials using isotope. Applied Radiation and Isotopes 2012, 70, 9: 1944-1948

[16] Qiao J, Hou X, Steier P, and Golser R (2013) Sequential Injection Method for Rapid and Simultaneous Determination of ^{236}U, ^{237}Np, and Pu Isotopes in Seawater. Anal. Chem. 2013, 85: 11026−11033

[17] Maxwell S, Culligan B, and Utsey R (2013) Rapid determination of radiostrontium in seawater samples.J Radioanal Nucl Chem DOI 10.1007/s10967-013-2430-1

[18] Maxwell S, Culligan B, Noyes G, Jones V, Nichols S.T. and Bernard M. (2010), Rapid determination of ^{237}Np and Pu isotopes in urine by inductively-coupled plasma mass spectrometry and alpha spectrometry, Health Physics Journal, August 2011 Volume 101 2 : 180-186

[19] Zheng J, Yamada M (2006) Inductively coupled plasma-sector field mass spectrometry with a high-efficiency sample introduction system for the determination of Pu isotopes in settling particles at femtogram levels. Talanta 69: 1246-1253

[20] Epov V, Benkhedda K, Cornett R.J, and Evans R.D (2005) Rapid determination of plutonium in urine using flow injection on-line preconcentration and inductively-coupled plasma mass spectrometry. J. Anal. At. Spectrom., 20: 424-430

[21] Kim, C S and Vajda, N, (2007) Determination of Pu isotope concentrations and isotope ratio by inductively coupled plasma mass spectrometry: a review of analytical methodology. J. Anal. At. Spectrom. 22: 827-841

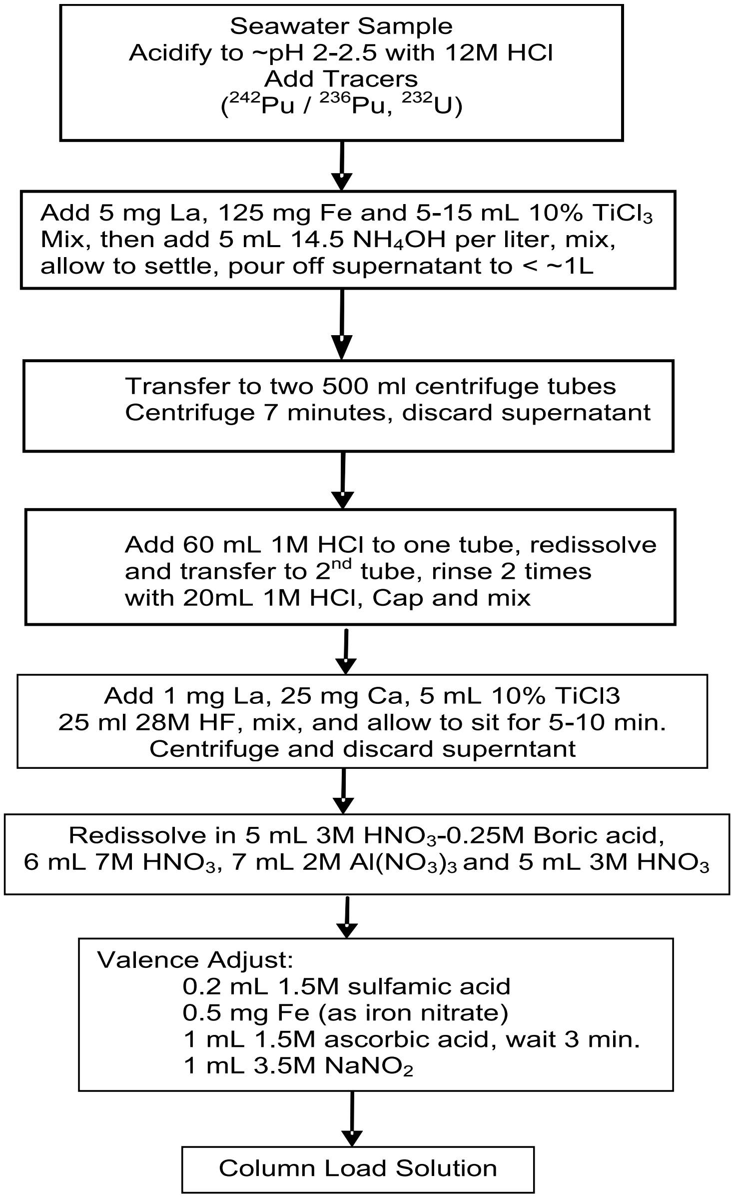
[22] Maxwell S, Culligan B, Hutchison J, Utsey R and McAlister, D (2013) Rapid determination of ^{210}Po in water samples. Journal of Radioanalytical and Nuclear Chemistry, Vol. 298, No. 3: 1977-1989

[23] Horwitz, P., McAlister, D., Bond, A., and Barrans Jr, A.B., (2005), Novel extraction chromatographic resins based on tetraalkyldiglycolamides: characterization and potential applications, *Solvent Extr. Ion Exch*., 23, (3), 319

[24] Levy I, Povinec P, Aoyama M, Hirose K, Sanchez-Cabeza J, Comanducci J, Gastaud J, Eriksson M, Hamajima Y, Kim C.S., Komura K, Osvath I, Roos P, Yim S (2011) Marine anthropogenic radiotracers in the Southern Hemisphere: New sampling and analytical strategies. Progress in Oceanography 89:120–133

[25] Currie L (1968) Limits for qualitative and quantitative determination. Anal. Chem. 40: 586-593

Figure 1 Rapid Sample Preparation Method for Pu, Np and U isotopes in Seawater (8L)



Seawater Sample
Acidify to ~pH 2-2.5 with 12M HCl
Add Tracers
(^{242}Pu / ^{236}Pu, ^{232}U)

Add 5 mg La, 125 mg Fe and 5-15 mL 10% $TiCl_3$
Mix, then add 5 mL 14.5 NH_4OH per liter, mix,
allow to settle, pour off supernatant to < ~1L

Transfer to two 500 ml centrifuge tubes
Centrifuge 7 minutes, discard supernatant

Add 60 mL 1M HCl to one tube, redissolve
and transfer to 2nd tube, rinse 2 times
with 20mL 1M HCl, Cap and mix

Add 1 mg La, 25 mg Ca, 5 mL 10% TiCl3
25 ml 28M HF, mix, and allow to sit for 5-10 min.
Centrifuge and discard superntant

Redissolve in 5 mL 3M HNO_3-0.25M Boric acid,
6 mL 7M HNO_3, 7 mL 2M $Al(NO_3)_3$ and 5 mL 3M HNO_3

Valence Adjust:
0.2 mL 1.5M sulfamic acid
0.5 mg Fe (as iron nitrate)
1 mL 1.5M ascorbic acid, wait 3 min.
1 mL 3.5M $NaNO_2$

Column Load Solution

Figure 2 Rapid Sample Preparation Method for Pu, Am and Cm in Seawater (80L)

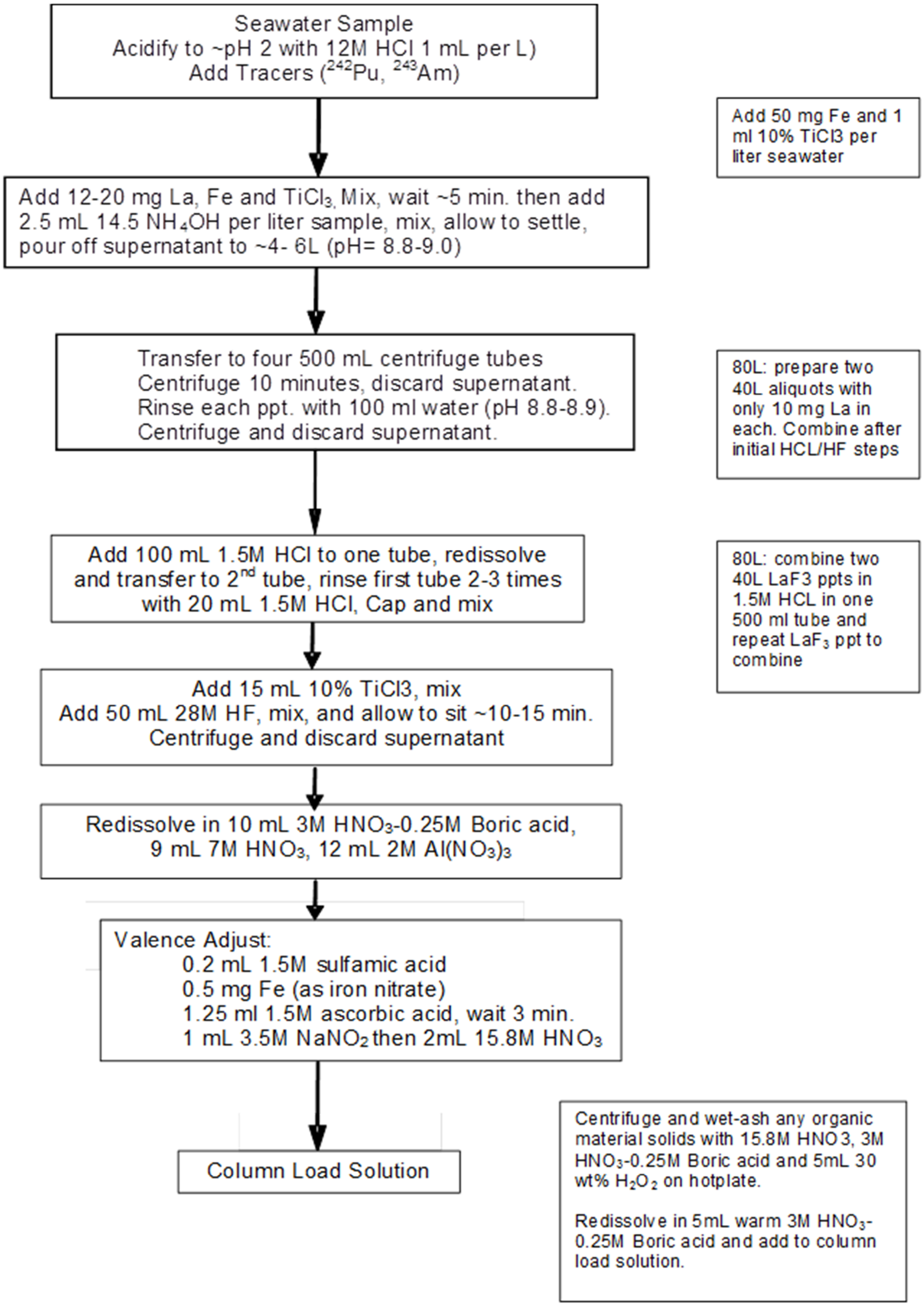
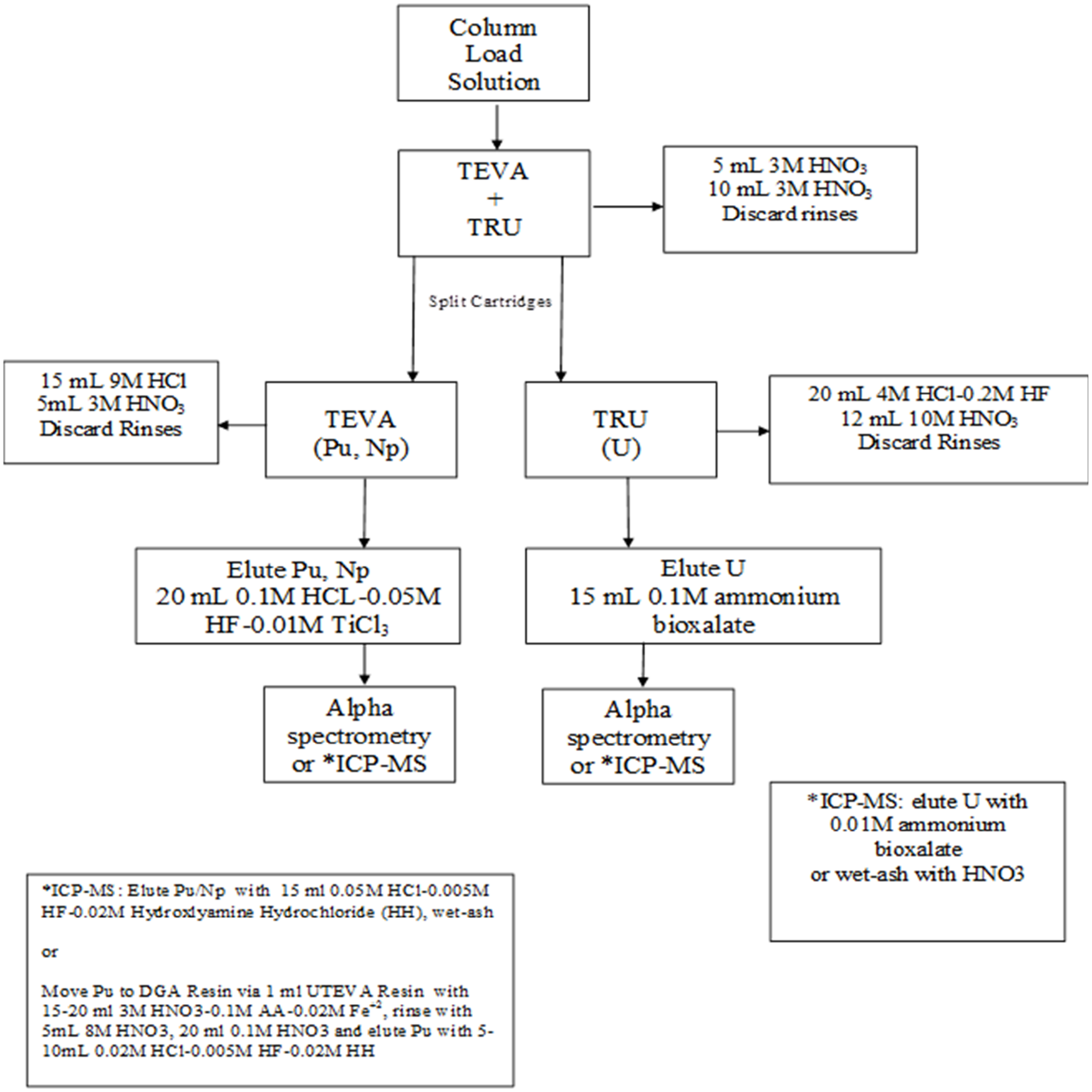


Figure 3 Rapid Column Separation Method for Pu, Np and U isotopes in Seawater (8L)



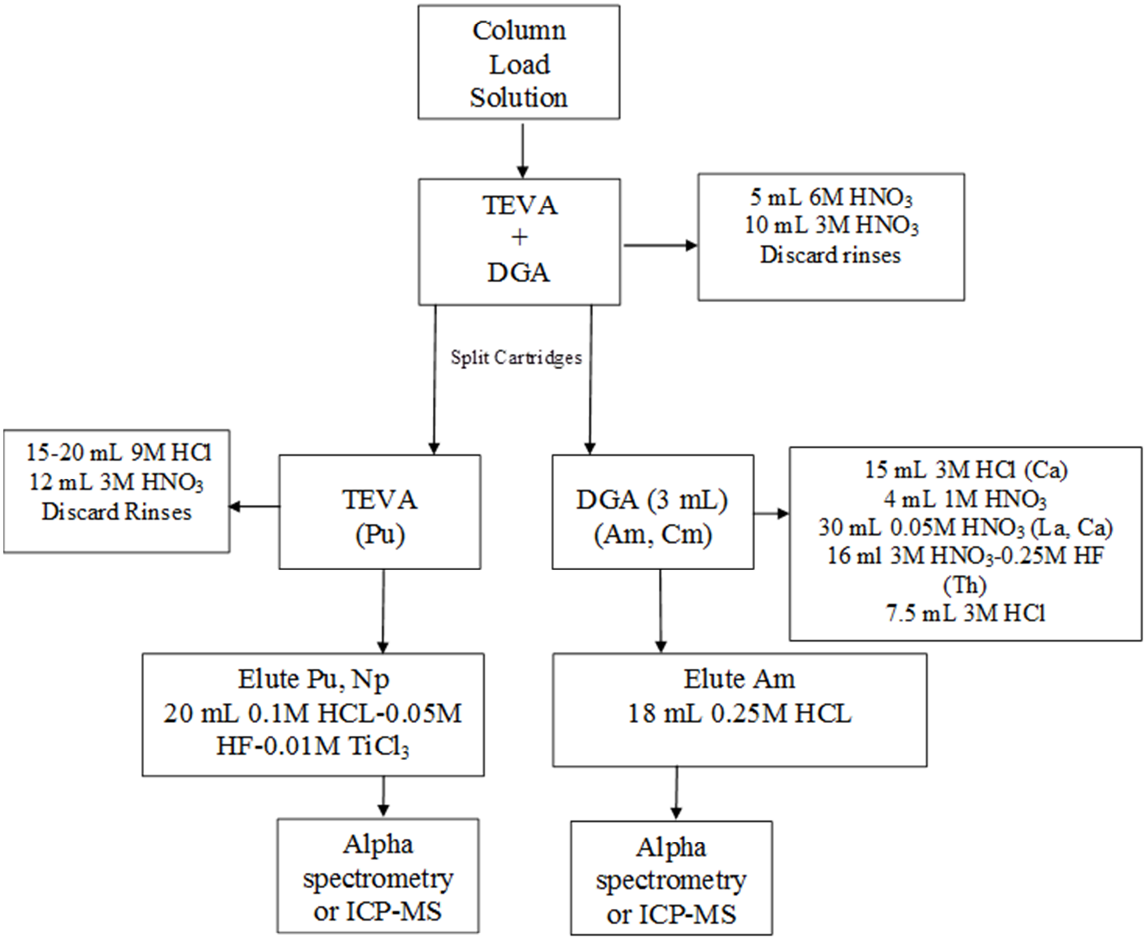
*ICP-MS: elute U with 0.01M ammonium bioxalate or wet-ash with HNO3

*ICP-MS : Elute Pu/Np with 15 ml 0.05M HCl-0.005M HF-0.02M Hydroxlyamine Hydrochloride (HH), wet-ash

or

Move Pu to DGA Resin via 1 ml UTEVA Resin with 15-20 ml 3M HNO3-0.1M AA-0.02M Fe^{+2}, rinse with 5mL 8M HNO3, 20 ml 0.1M HNO3 and elute Pu with 5-10mL 0.02M HCl-0.005M HF-0.02M HH

Figure 4 Rapid Column Separation Method for Pu, Am and Cm isotopes in Seawater (80L)



When 40L seawater aliquots are combined to get 80L, 4mL DGA Resin is needed to handle the amount of La added. DGA rinse volumes and final eluent are increased proportionally.

Figure 5 Retention of Po^{+4} on TEVA Resin in HCl and HNO_3

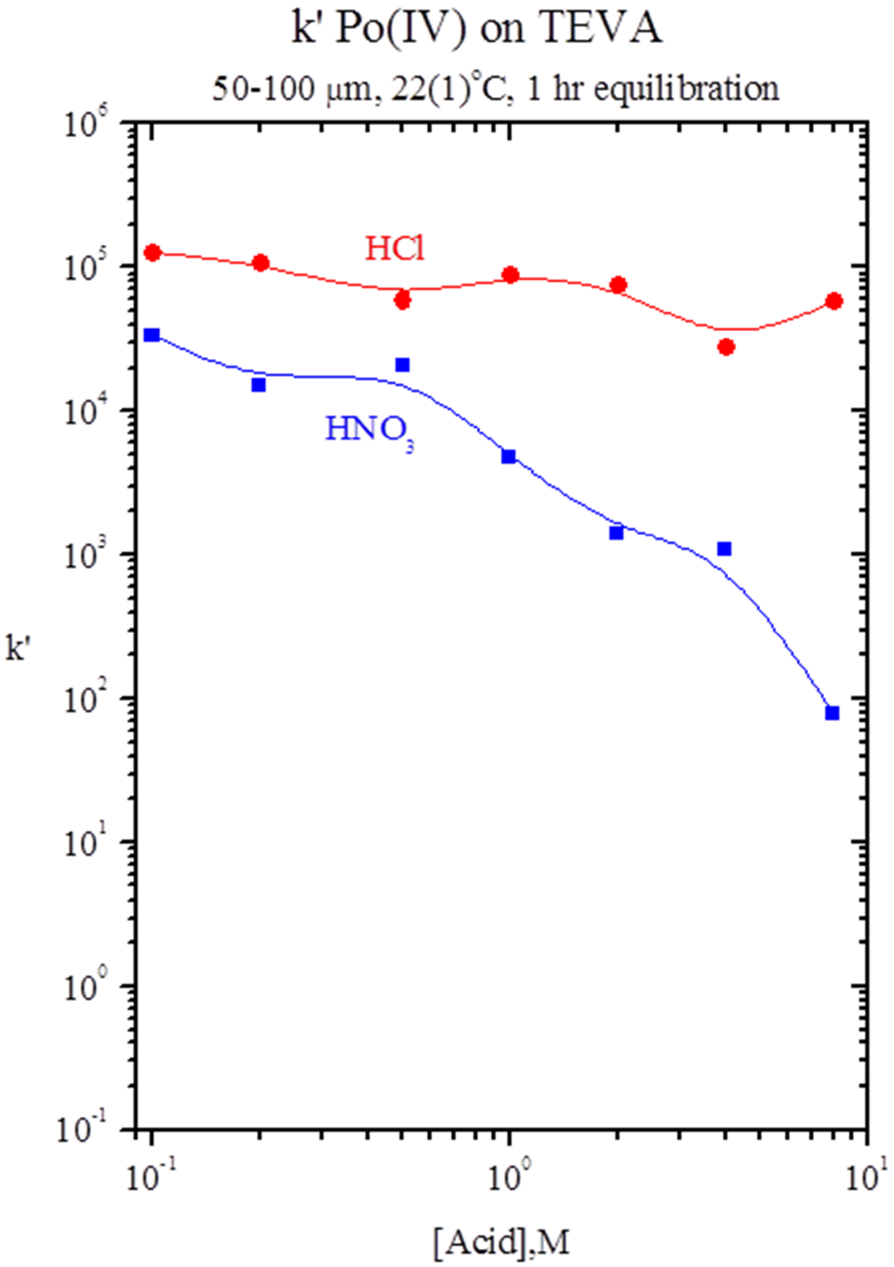


Figure 6 Elution of ^{241}Am using TEVA Resin + DGA Resin Method

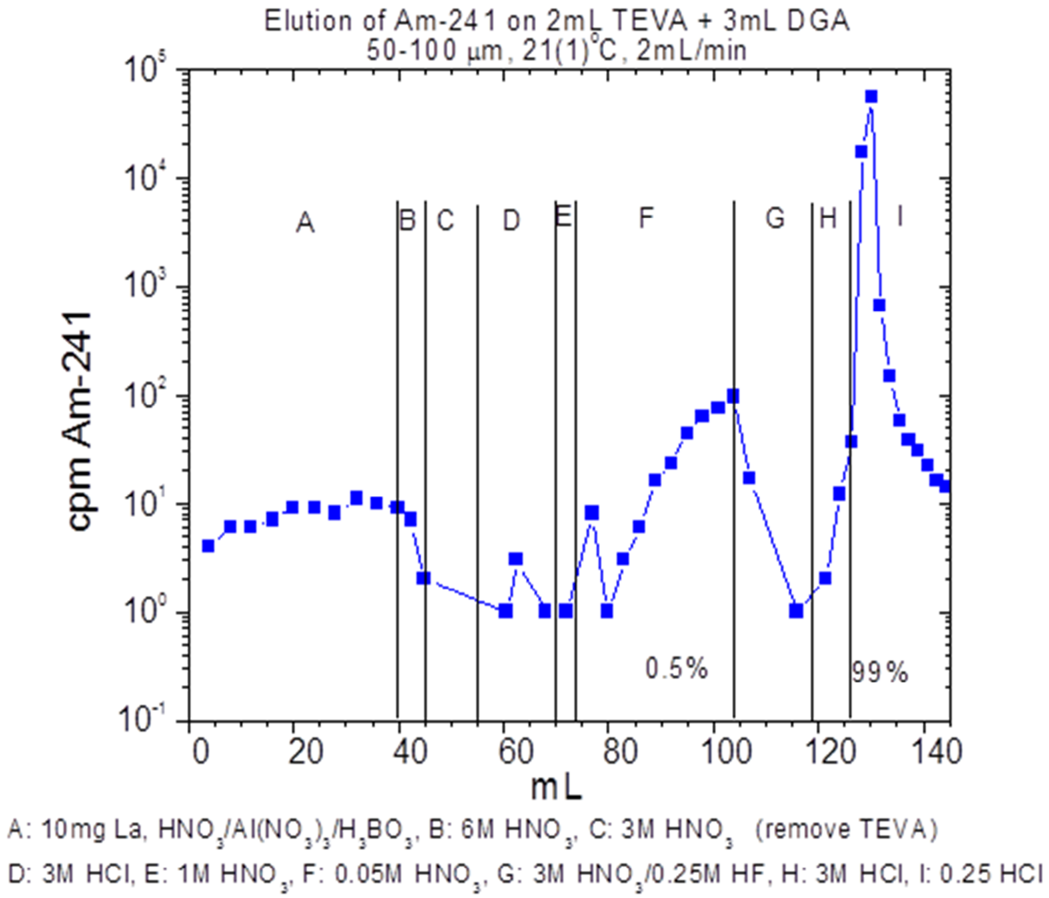


Figure 7 MDA by Alpha Spectrometry vs. Sample Size for 16 hour count

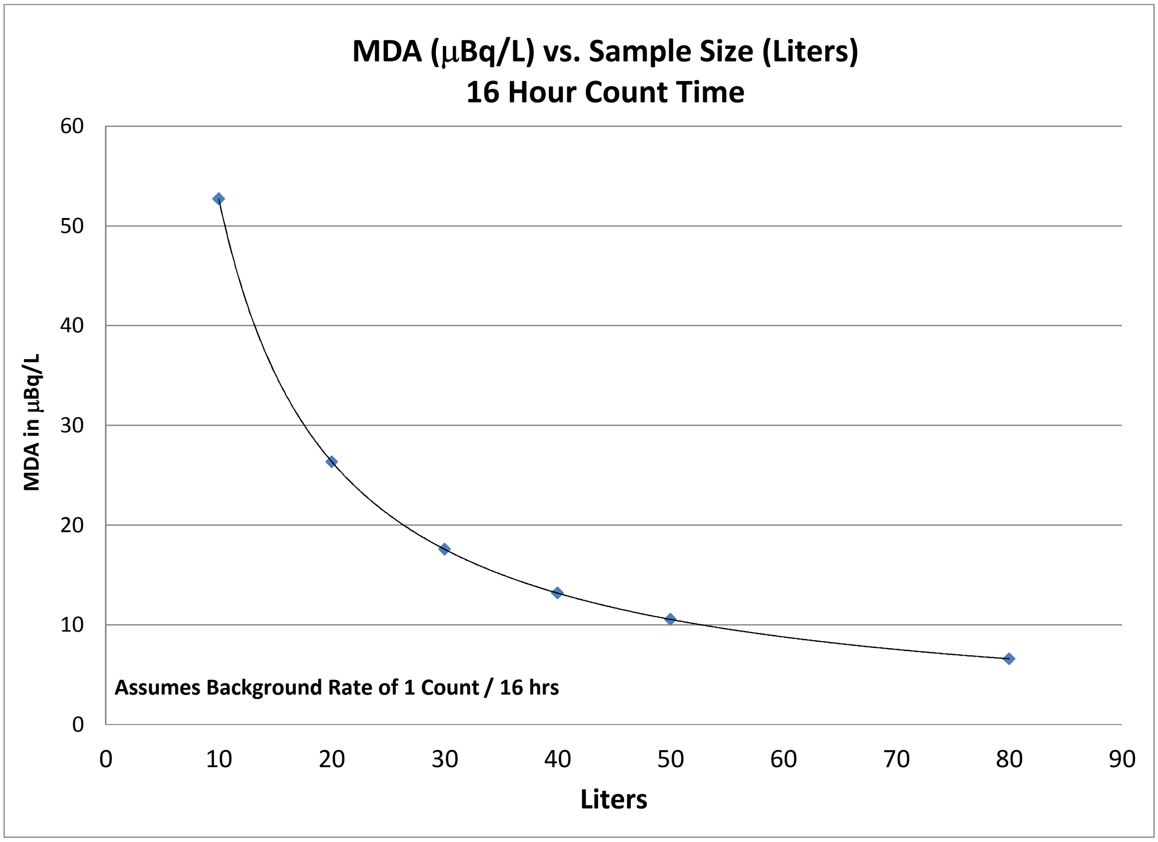


Figure 8 MDA by Alpha Spectrometry vs. Sample Size for 7 day count

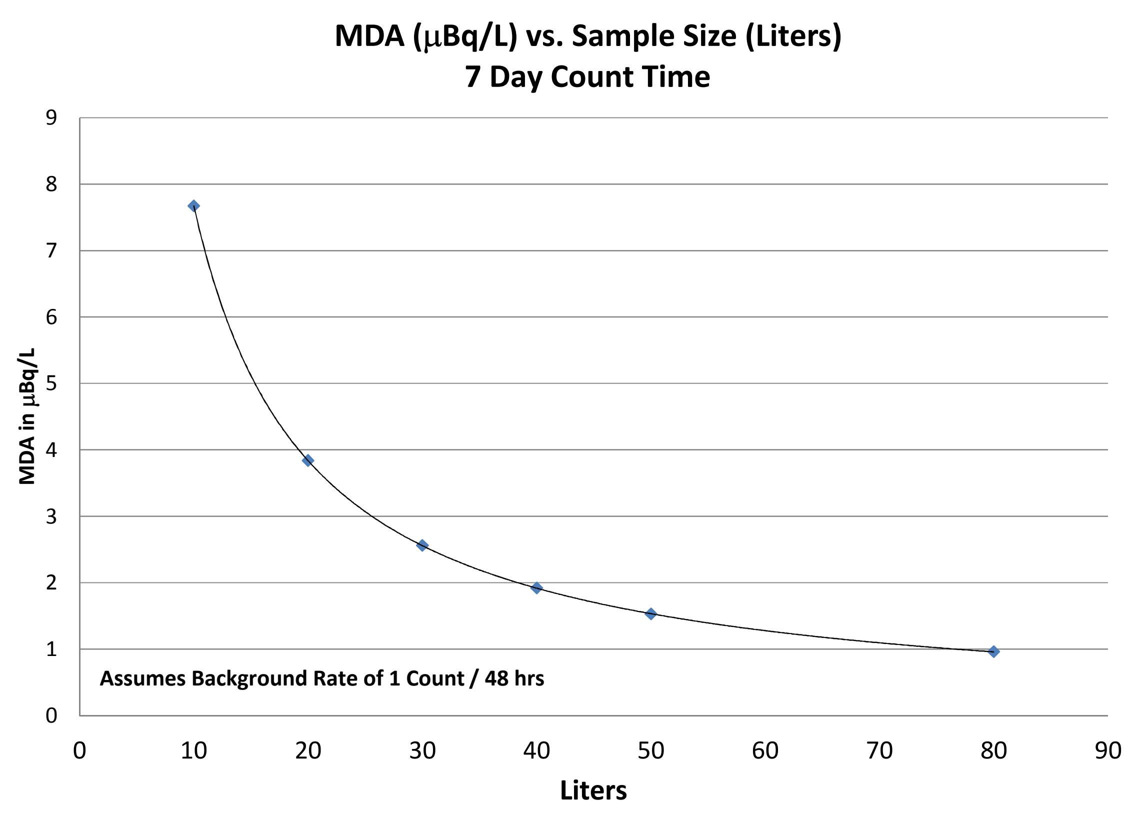


Table 1 ^{239}Pu Results using TEVA+TRU Resin Method

Sample ID	Aliquot Vol. (L)	^{236}Pu Yield (%)	^{239}Pu Reference Value (mBq L^{-1})	^{239}Pu Measured Value (pCi L^{-1})	^{239}Pu Measured Value (mBq L^{-1})	Difference (%)
1	2	102.0	Blank	0.0011	0.041	N/A
2	2	74.1	33.8	0.93	34.2	1.4
3	2	87.0	33.8	0.91	33.7	-0.1
4	2	97.7	33.8	0.84	31.1	-7.7
5	2	93.7	33.8	0.84	31.2	-7.6
6	4	86.0	16.9	0.44	16.2	-4.1
7	8	90.5	16.9	0.44	16.1	-4.7
8	8	83.7	27.8	0.75	27.6	-0.5
Avg		89.3				-3.5
SD		8.7				3.7
% RSD		9.7				

16 hr. count

Table 2 ^{237}Np Isotope Results using TEVA+TRU Resin Method

Sample ID	Aliquot Vol. (L)	^{236}Pu Yield (%)	^{237}Np Reference Value (mBq L^{-1})	^{237}Np Measured Value (pCi L^{-1})	^{237}Np Measured Value (mBq L^{-1})	Difference (%)
1	2	102.0	Blank	0.000	0.000	N/A
2	2	74.1	17.4	0.542	20.1	15.3
3	2	87.0	17.4	0.483	17.9	2.8
4	2	97.7	17.4	0.435	16.1	-7.4
5	2	93.7	17.4	0.453	16.8	-3.6
6	4	86.0	8.70	0.195	7.22	-17.1
7	8	90.5	4.35	0.104	3.83	-11.9
8	8	87.0	4.35	0.125	4.63	6.3
Avg		89.8				1.8
SD		8.5				11.2
% RSD		9.4				

16 hr. count

Table 3 ^{238}U Isotope Results using TEVA+TRU Resin Method

Sample ID	Aliquot Vol. (L)	^{232}U Yield (%)	^{238}U Reference Value (mBq L^{-1})	^{238}U Measured Value (pCi L^{-1})	Corrected Value (pCi L^{-1})	^{238}U Measured Value (mBq L^{-1})
1	1	100.9	Blank	0.98	N/A	36.3
2	2	97.7	51.8	2.31	1.33	49.3
3	2	97.7	51.8	2.33	1.35	49.8
4	2	96.7	51.8	2.36	1.38	51.1
5	2	102.3	51.8	2.25	1.27	47.0
6	4	86.3	25.9	1.64	0.67	25.0
7	8	87.0	25.9	1.63	0.66	24.3
8	8	97.7	96.3	3.51	2.54	94.0
Avg.		94.7				
SD		5.9				
% RSD		6.3				

16 hour count spiked results corrected for 0.98 pCi L-1 238U

Table 4 ^{239}Pu Results using TEVA+DGA Resin Method

Sample ID	Aliquot Vol. (L)	^{242}Pu Yield (%)	^{239}Pu Reference Value (mBq L^{-1})	^{239}Pu Measured Value (pCi L^{-1})	^{239}Pu Measured Value (mBq L^{-1})	Difference (%)
1	16	91.7	4.22	0.128	4.72	11.8
2	16	89.0	4.22	0.125	4.63	9.6
3	25	84.3	3.22	0.0888	3.29	2.0
4	25	84.8	1.29	0.0342	1.27	-1.9
5	40	88.0	0.81	0.0221	0.82	1.5
6	40	83.2	0.81	0.0202	0.75	-7.4
7	80	80.1	0.40	0.0098	0.36	-9.7
8	80	90.3	0.40	0.0100	0.37	-8.0
Avg		86.4				-0.3
SD		3.9				8.0
% RSD		4.6				

16 hour count

1,2 - spiked with 50 ml MAPEP 23 std
3 - spiked with 50 ml MAPEP 27 std
4-8 - spiked with 20 ml MAPEP 27 std

Table 5 ^{241}Am Isotope Results using TEVA+DGA Resin Method

Table 1 ^{239}Pu Results using TEVA+TRU Resin Method

Sample ID	Aliquot Vol. (L)	^{236}Pu Yield (%)	^{239}Pu Reference Value (mBq L^{-1})	^{239}Pu Measured Value (pCi L^{-1})	^{239}Pu Measured Value (mBq L^{-1})	Difference (%)
1	2	102.0	Blank	0.0011	0.041	N/A
2	2	74.1	33.8	0.93	34.2	1.4
3	2	87.0	33.8	0.91	33.7	-0.1
4	2	97.7	33.8	0.84	31.1	-7.7
5	2	93.7	33.8	0.84	31.2	-7.6
6	4	86.0	16.9	0.44	16.2	-4.1
7	8	90.5	16.9	0.44	16.1	-4.7
8	8	83.7	27.8	0.75	27.6	-0.5
Avg		89.3				-3.5
SD		8.7				3.7
% RSD		9.7				
		16 hr. count				

Table 2 ^{237}Np Isotope Results using TEVA+TRU Resin Method

Sample ID	Aliquot Vol. (L)	^{236}Pu Yield (%)	^{237}Np Reference Value (mBq L^{-1})	^{237}Np Measured Value (pCi L^{-1})	^{237}Np Measured Value (mBq L^{-1})	Difference (%)
1	2	102.0	Blank	0.000	0.000	N/A
2	2	74.1	17.4	0.542	20.1	15.3
3	2	87.0	17.4	0.483	17.9	2.8
4	2	97.7	17.4	0.435	16.1	-7.4
5	2	93.7	17.4	0.453	16.8	-3.6
6	4	86.0	8.70	0.195	7.22	-17.1
7	8	90.5	4.35	0.104	3.83	-11.9
8	8	87.0	4.35	0.125	4.63	6.3
Avg		89.8				1.8
SD		8.5				11.2
% RSD		9.4				
		16 hr. count				

Table 3 ^{238}U Isotope Results using TEVA+TRU Resin Method

Sample ID	Aliquot Vol. (L)	^{232}U Yield (%)	^{238}U Reference Value (mBq L^{-1})	^{238}U Measured Value (pCi L^{-1})	Corrected Value (pCi L^{-1})	^{238}U Measured Value (mBq L^{-1})	Difference (%)
1	1	100.9	Blank	0.98	N/A	36.3	
2	2	97.7	51.8	2.31	1.33	49.3	
3	2	97.7	51.8	2.33	1.35	49.8	
4	2	96.7	51.8	2.36	1.38	51.1	
5	2	102.3	51.8	2.25	1.27	47.0	
6	4	86.3	25.9	1.64	0.67	25.0	
7	8	87.0	25.9	1.63	0.66	24.3	
8	8	97.7	96.3	3.51	2.54	94.0	
Avg.		94.7					
SD		5.9					
% RSD		6.3					
	16 hour count	spiked results corrected for 0.98 pCi L-1 238U					

Table 4 ^{239}Pu Results using TEVA+DGA Resin Method

Sample ID	Aliquot Vol. (L)	^{242}Pu Yield (%)	^{239}Pu Reference Value (mBq L^{-1})	^{239}Pu Measured Value (pCi L^{-1})	^{239}Pu Measured Value (mBq L^{-1})	Difference (%)
1	16	91.7	4.22	0.128	4.72	11.8
2	16	89.0	4.22	0.125	4.63	9.6
3	25	84.3	3.22	0.0888	3.29	2.0
4	25	84.8	1.29	0.0342	1.27	-1.9
5	40	88.0	0.81	0.0221	0.82	1.5
6	40	83.2	0.81	0.0202	0.75	-7.4
7	80	80.1	0.40	0.0098	0.36	-9.7
8	80	90.3	0.40	0.0100	0.37	-8.0
Avg		86.4				-0.3
SD		3.9				8.0
% RSD		4.6				
		16 hour count				

1,2 - spiked with 50 ml MAPEP 23 std
3 - spiked with 50 ml MAPEP 27 std
4-8 - spiked with 20 ml MAPEP 27 std

Table 5 ^{241}Am Isotope Results using TEVA+DGA Resin Method

Sample ID	Aliquot Vol. (L)	^{243}Am Yield (%)	^{241}Am Reference Value (mBq L^{-1})	^{241}Am Measured Value (pCi L^{-1})	^{241}Am Measured Value (mBq L^{-1})	Difference (%)
1	16	89.9	3.31	0.086	3.17	-4.3
2	16	98.0	3.31	0.083	3.08	-7.1
3	25	93.1	2.12	0.052	1.94	-8.5
4	25	93.1	0.85	0.022	0.80	-5.9
5	40	94.3	0.53	0.014	0.52	-2.3
6	40	97.8	0.53	0.013	0.49	-7.8
7	80	89.2	0.27	0.0066	0.24	-7.7
8	80	96.7	0.27	0.0067	0.25	-7.2
Avg		94.0				-6.3
SD		3.4				2.1
% RSD		3.6				
		16 hr. count				

1,2 - spiked with 50 ml MAPEP 23 std
3 - spiked with 50 ml MAPEP 27 std
4-8 - spiked with 20 ml MAPEP 27 std

Table 6 ^{244}Cm Isotope Results using TEVA+DGA Resin Method

Sample ID	Aliquot Vol. (L)	^{243}Am Yield (%)	^{244}Cm Reference Value (mBq L^{-1})	^{244}Cm Measured Value (pCi L^{-1})	^{244}Cm Measured Value (mBq L^{-1})	Difference (%)
1	16	89.9	2.16	0.062	2.28	5.3
2	16	98.0	2.16	0.051	1.89	-12.6
3	25	93.1	1.35	0.033	1.21	-10.4
4	25	93.1	1.35	0.035	1.31	-2.9
5	40	94.3	0.85	0.020	0.74	-12.1
6	40	97.8	0.85	0.022	0.82	-3.0
7	80	89.2	0.42	0.0108	0.40	-5.4
8	80	96.7	0.42	0.0115	0.42	0.4
Avg		94.0				-5.1
SD		3.4				6.4
% RSD		3.6				
		16 hr. count				

Table 7 ^{239}Pu Results using TEVA Resin Method

Sample ID	Aliquot Vol. (L)	^{236}Pu Yield (%)	^{239}Pu Reference Value (mBq L^{-1})	^{239}Pu Measured Value (pCi L^{-1})	^{239}Pu Measured Value (mBq L^{-1})	Difference (%)
1	10	85.8	3.22	0.090	3.33	3.4
2	20	90.8	1.61	0.041	1.52	-5.9
3	20	96.6	1.61	0.040	1.47	-8.4
Avg		91.1				-3.6
SD		5.4				6.2
% RSD		5.9				
		16 hour count				

Table 8 ^{237}Np Results using TEVA Resin Method

Sample ID	Aliquot Vol. (L)	^{236}Pu Yield (%)	^{237}Np Reference Value (mBq L^{-1})	^{237}Np Measured Value (pCi L^{-1})	^{237}Np Measured Value (mBq L^{-1})	Difference (%)
1	10	85.8	3.48	0.102	3.77	8.4
2	20	90.8	1.74	0.045	1.66	-4.7
3	20	96.6	1.74	0.043	1.60	-7.8
Avg		91.1				-1.4
SD		5.4				8.6
% RSD		5.9				
		16 hour count				