Summary

1 Scope

This procedure describes a method for the separation and measurement plutonium isotopes in seawater samples up to 80L. 40 L aliquots may be combined to analyze 80L or larger aliquots to lower detection limits.

2 Summary of Method

Plutonium isotopes (and Np-237) are separated using TEVA resin after concentration from the sample and matrix removal via two consecutive co-precipitation steps. Pu and/or Np-237 are measured after separation on TEVA Resin by alpha spectrometry. The method may also be used with inductively-coupled mass spectrometry, with an option to remove uranium > 1E6. The sample preparation method takes <8 hours, with high chemical yields. This draft method is entirely based on a method developed by Sherrod L. Maxwell (SRNL, Savannah River, USA).

3 Significance of Use

This method is a rapid and reliable method for the determination of plutonium isotopes and Np-237 in large water samples.

4 Interferences

Uranium, americium, curium, and thorium isotopes are removed using TEVA Resin. Np-237 can also be recovered with Pu isotopes on TEVA Resin. With very large seawater aliquots (>20L), Np-237 may have a slightly lower chemical yield and may need to be traced with Np-239. The method has been used successfully to determine Pu isotopes and Np-237 together in seawater aliquots of 20 liters using alpha spectrometry, using Pu-236 tracer. Pu-242 tracer as a yield monitor for both Pu and Np can be employed if ICP-MS measurement is used for Pu and Np isotopes, but additional removal of uranium may be needed to prevent U-238 hydride interference on Pu-239 assay by ICP-MS. The amount of Np-237 in seawater does not interfere with the Pu-242 tracer measurement by alpha spectrometry since tracer activity levels are typically much higher than Np-237 activity levels. For ICP-MS assay, an enhanced purification option of Pu isotopes can be applied if needed. In this rapid high purification option, Pu can be eluted from TEVA Resin as Pu^{+3} and passed through stacked UTEVA Resin (1mL) and DGA, N Resin (2mL) cartridges to remove U with a decontamination factor of ~10E6-10E7.

5 Apparatus

5.1 *Analytical balance- 0.0001 g sensitivity*

5.2 *Centrifuge*

5.3 *Centrifuge tubes (preferably 500 mL conical tubes)*

5.4 *Fume hood*

5.5 *Heat lamp*

5.6 *Vacuum Box System- part number AC-24-BOX or AC-12-BOX*

5.7 *Luer-lock two-way valves – part number AC-12-VALVE (optional)*

5.8 *Cartridge reservoirs-10 mL Cartridge Reservoir, part number AC-25-RV10 or 20 mL Cartridge Reservoir, part number AC-25-RV20*

5.9 *Stainless steels discs - part number AC-D100-IN25*

5.10 *Tips, white inner- part number AC-1000-TUBE-PE*

5.11 *Tips, yellow outer- part number AC-1000-OT*

5.12 *Filter- 0.45 micron*

5.13 *Fume hood*

5.14 *Resolve® filter filtration unit - part number RF-DF25-25PP01*

5.15 *Hotplate*

5.16 *Stirring glass rods*

5.17 *Plastic Petri dishes, 5-1/2 x 1 cm*

5.18 *Vortex mixer*

6 Reagents

Unless otherwise indicated, all references to water should be understood to mean deionized distilled water. All reagents should be at least of analytical grade.

6.1 Ethanol

6.2 Calcium nitrate (50 mg Ca^{2+} / mL): Dissolve 51.1 g of anhydr. $Ca(NO_3)_2$ in 100 mL of water and dilute to 250 mL with water.

6.3 Iron nitrate (50 mg Fe^{3+} / mL): Dissolve 36.2 g of $Fe(NO_3)_3*9H_2O$ in 60 mL of water and dilute to 100 mL with water.

6.4 Lanthanum nitrate (10 mg La^{3+} / mL): Dissolve 3.117 g of $La(NO_3)_3 \cdot 6H_2O$ in 60 mL of water and dilute to 100 mL with water.

6.5 Cerium nitrate (1 mg Ce^{3+} / mL): Dissolve 309.9 mg of $Ce(NO_3)_3 \cdot 6H_2O$ in 60 mL of water and dilute to 100 mL with water.

6.6 Hydrogen peroxide (30%) - H_2O_2.

6.7 Ammonium hydroxide - concentrated .

6.8 Nitric acid (15.7 M) - concentrated HNO_3.

6.9 Hydrochloric acid (12M) - concentrated hydrochloric acid.

6.10 Hydrochloric acid (9M) – Add 750 mL concentrated hydrochloric acid to 100 mL of water and dilute to 1 liter with water.

6.11 Hydrofluoric acid (28.9M) - concentrated hydrofluoric acid.

6.12 Nitric acid solution (8M): Add 510 mL of concentrated nitric acid to 400 mL of water and dilute to 1 liter with water.

6.13 Nitric acid solution (2.7M-0.1M ascorbic acid-0.02M Fe^{+2}): Add 33 mL of 1.5M ascorbic acid and 22 mL 0.45M Fe^{+2} solution to 500 mL of 3M HNO_3 and dilute to 1 liter with water. 0.45M Fe^{+2} solution: Add 15 ml 50 mg/mL iron nitrate (0.9M Fe) to 15 ml 1.5M ascorbic acid and mix.

6.14 Nitric acid solution (0.05M): Add 3.2 mL of concentrated nitric acid to 900 mL of water and dilute to 1 liter with water.

6.15 Hydrochloric acid solution (3M): Add 250 mL of concentrated hydrochloric acid to 500 mL of water and dilute to 1 liter with water.

6.16 Hydrochloric acid solution (3M) - 0.25M boric acid: Add 250 mL of concentrated hydrochloric acid and15,46g boric acid to 500 mL of water and dilute to 1 liter with water.

6.17 Hydrochloric acid solution (3M) – 0.25M HF: Add 250 mL of concentrated hydrochloric acid and 8.65 mL of concentrated hydrofluoric acid to 500 mL of water and dilute to 1 liter with water. Transfer into plastic container.

6.18 Hydrochloric acid solution (1.5M): Add 125 mL of concentrated hydrochloric acid to 500 mL of water and dilute to 1 liter with water.

6.19 Hydrochloric acid solution (0.25M): Add 21 mL of concentrated hydrochloric acid to 500 mL of water and dilute to 1 liter with water.

6.20 Aluminum nitrate (2M): 428 g anhydrous aluminum nitrate to 400 mL of water and dilute to 1 liter with water.

6.21 Titanium (III) chloride (10%) in 20-30% HCl

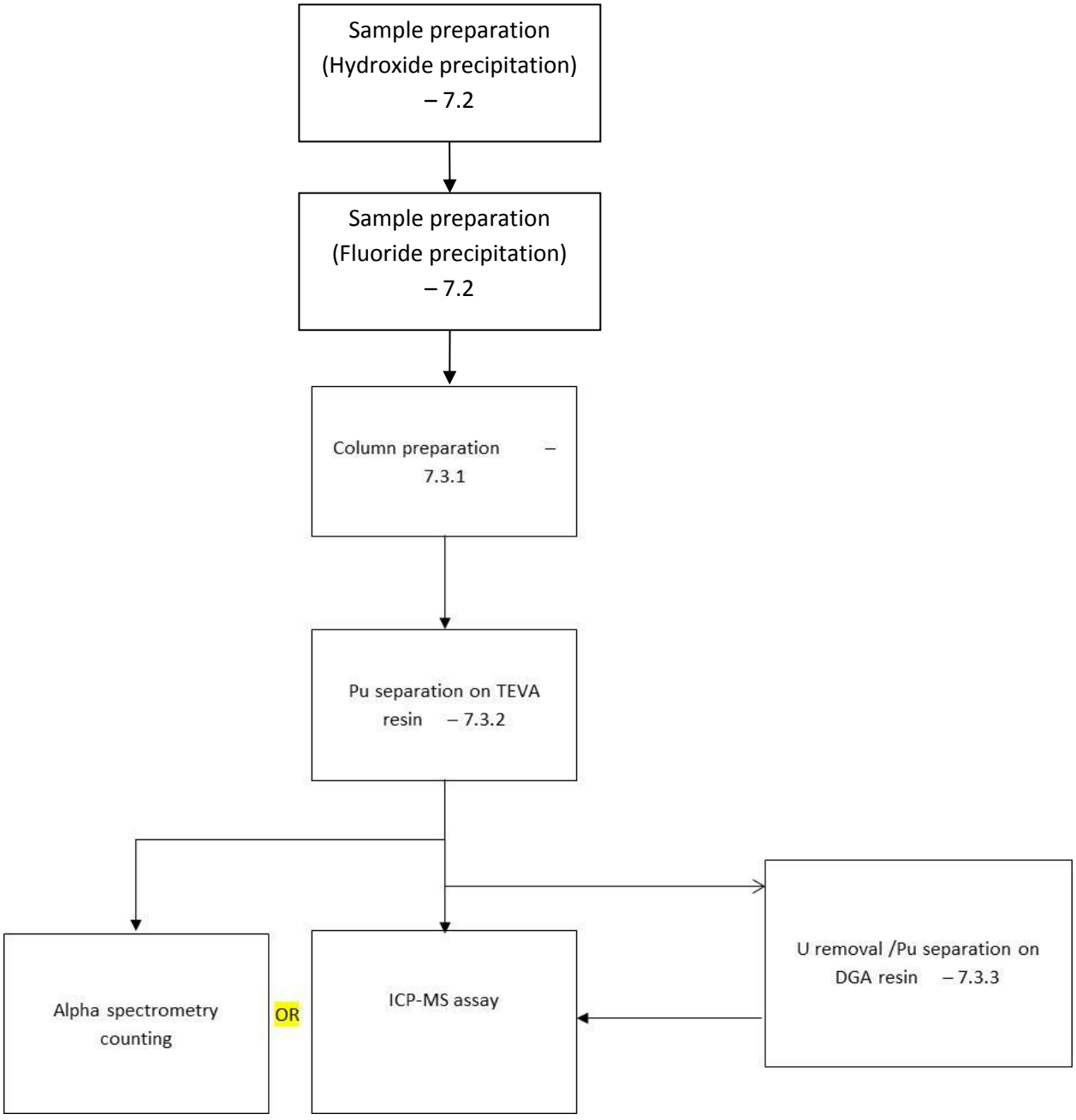
6.22 TEVA Resin- 2 mL prepacked cartridge, 50-100 μm particle size resin (s grade), part number TE-R10-S

6.23 DGA Resin -2 mL prepacked cartridge, 50-100 μm particle size resin (s grade), part number DN-R10-S

6.24 UTEVA Resin- 1 mL prepacked cartridge, 50-100 μm particle size resin (s grade), part number UT1ML-50R-S

7 Procedure

7.1 Synopsis



7.2 Sample preparation

7.2.1 If required, filter the sample through a 0.45 micron (or other appropriate size) filter.

7.2.2 Aliquot 10L to 40L of the sample (or enough to meet required detection limit) into an appropriately sized container.

Note: Large aliquots (80L or larger) may be analyzed by combining 40L aliquots later in the sample preparation process.

7.2.3 Add 1mL conc. HCl per L of sample to acidify the sample to pH 2.

7.2.4 Add Pu-242 or Pu-236 tracer into each sample aliquot.

Note: 40L aliquots may be combined at the LaF_3 step to allow 80L or larger aliquot to be analyzed. If two 40L aliquots will be combined, for example, ½ of the Pu tracer should be added to each initial aliquot.

7.2.5 Add 2 mL of 10 mg/ml lanthanum carrier into each sample aliquot.

7.2.6 Add 1mL iron nitrate (50 mg Fe^{3+} / mL) solution and 1 mL 10 wt% titanium (III) chloride ($TiCl_3$) per L of sample.

7.2.7 Add 2.5 mL conc. ammonium hydroxide (14.5M) per L of sample while stirring. Supernatant should be ~pH 8.8 – 9. Adjust pH as needed with HCl or NH_4OH.

Note: The pH should be in the range (<pH 8.8-9) to minimize Ca precipitation. If a slightly different concentrated NH_4OH is used, the volume added should be adjusted accordingly.

7.2.8 Mix well. Allow to settle for at least 1h or as needed.

7.2.9 Pour or pump off supernatant to approx. 2-4L.

7.2.10 Transfer the $Fe(OH)_2$ /$Ti(OH)_3$ precipitate into centrifugation tubes (preferably four 500 mL tubes). Centrifuge for 10 min at 2000 rpm (or higher). Discard supernatant and replace with fresh aliquot of solution/precipitate. Repeat until all precipitate has been centrifuged, rinsing container with deionized water.

7.2.11 Add 100 mL pH 8.8 – 9 water into each tube and shake to dissolve Ca from precipitate. Centrifuge 10 min at 2000 rpm (or higher). Discard supernatant.

7.2.12 Add 100 mL 1.5M HCl into the first tube to dissolve precipitate. Transfer obtained solution into 2nd centrifuge tube to dissolve precipitate. Transfer obtained solution into 3rd tube to dissolve precipitate. Transfer obtained solution into 4th tube to dissolve

precipitate. Tube 4 contains the entire $Fe(OH)_2$ precipitate dissolved in 100 mL 1.5M HCl.

7.2.13 Add 20 mL 1.5M HCl into 1st tube. Rinse tube and transfer rinsing solution into 2nd tube. Rinse tube and transfer rinsing solution into 3rd tube. Rinse tube and transfer rinsing solution into 4th tube. Repeat two more times fresh 20 mL 1.5M HCl.

7.2.14 Add 1.5ml Ca carrier solution (75 mg Ca) into 4th tube containing the dissolved precipitate and mix.

Important: The amount of Ca added can be adjusted down to decrease the precipitate size or increased to enhance chemical yield as needed. This will depend on residual Ca which is based on the pH adjustment for the hydroxide precipitation and water rinse. Typically 75-100 mg Ca is an optimal amount if good Ca removal occurs.

7.2.15 Add 50 mL conc. HF and mix well. Allow to sit for 15 min.

Remark: alternatively NH_4F or NaF might be used

7.2.16 Centrifuge for 10 minutes at 2000 rpm (or higher). Discard supernatant.

Important: If a LaF_3/CaF_2 precipitate above a volume of ~5-10 ml occurs, too much Ca may be present. This can occur if the initial hydroxide precipitation pH is higher than pH 9. If this occurs, an option to reduce Ca is to redissolve the precipitate in 100 ml 1.5M HCl, add 10 ml conc. HF, mix well, wait 10 minutes, centrifuge again and discard supernatant.

Note: It is also possible to use this option to combine 40L aliquots at the LaF_3 step to allow analysis of 80L or larger aliquots. The initial LaF_3 precipitates can be redissolved in 100 mL 1.5M HCl, combined and re-precipitated together and redissolved into a single column load solution.

7.2.17 Dissolve LaF_3 precipitate in 10 mL 3M HNO_3 – 0.25M boric acid and transfer into a 50 ml centrifuge tube. Rinse 500 ml tube with 9 mL 7M HNO_3 , then 12 mL 2M $Al(NO_3)_3$ and transfer rinses to 50 ml tube. Cap and mix well. Centrifuge 5 minutes at 2000 rpm.

Note: The sample may be loaded from the 50 ml tube or transferred to a 100 ml Teflon beaker first.

7.2.18 In case there should still be significant solid residue, rinse into glass beaker with 3mL conc. HNO_3. Add 3 mL 30% H_2O_2 to the sample and evaporate to dryness to destroy organic matter. Dissolve residue in 5 mL 3M HNO_3 – 0.25M boric acid and warm solution to dissolve residue. Transfer solution into tube/beaker used in 7.2.17.

7.3 Plutonium Separation using TEVA resin:

7.3.1 TEVA resin cartridge preparation

7.3.1.1 Prepare vacuum box following Eichrom method VBS01

7.3.1.2 For each sample to be analyzed place one 2 mL TEVA cartridge on the vacuum box.

7.3.1.3 Connect 20 mL (or larger) reservoir to each of the cartridges.

7.3.1.4 Place 50 mL centrifuge tube below each cartridge (or place vacuum box liner in box).

7.3.1.5 Pipette 5 mL of 3M HNO_3 into each cartridge, start vacuum and allow solution to drain. Adjust the vacuum to achieve a flow-rate of 1 ml per minute (~1 drop/second).

IMPORTANT: The flow rates for load and strip solutions should be 1 mL/min; for the rinse solutions ~2-3 mL/min can be used, unless specified otherwise in the step.

7.3.2 Plutonium Separation

7.3.2.1 Add 0.2 mL of 1.5M sulfamic acid to each each redissolved sample (7.2.17) solution. Swirl to mix.

7.3.2.2 Add 0.2 mL of 5 mg/mL ferric nitrate solution.

NOTE: Ferric ions are added and are reduced to ferrous ions by ascorbic acid to enhance valence reduction of Pu isotopes.

7.3.2.3 Add 1.25 mL of 1.5M ascorbic acid to each solution, swirling to mix. Wait 3 minutes.

7.3.2.4 Add 1mL 3.5M $NaNO_2$ to each sample, swirling to mix well.

NOTE: Cap and mix tubes using vortex stirrer to reduce bubbling.

7.3.2.5 Transfer each redissolved sample (7.2.17) onto the appropriate TEVA resin cartridge by pouring or by using a plastic transfer pipette and allow to drain (1 mL/min).

7.3.2.6 Add 5 mL of 3M HNO_3 to rinse each tube/beaker and transfer each solution into the appropriate TEVA resin cartridge and allow to drain (1 mL/min).

NOTE: To enhance uranium removal for ICP-MS assay, the cartridge reservoir may be replaced with a new/clean reservoir.

7.3.2.7 Add 15 mL of 3M HNO_3 to each cartridge and allow to drain (~1.5-2 mL/min, U removal).

NOTE: The 3M nitric acid rinse volume may be increased to reduce U if ICP-MS assay will be used.

7.3.2.8 Add 20 mL of 9M HCl to each cartridge and allow to drain (~1.5-2 mL/min, Th removal).

7.3.2.9 Add 12 mL of 3M HNO_3 to each cartridge and allow to drain (~1.5-2 mL, U removal).

7.3.2.10 Ensure that clean, labeled containers are placed below each cartridge. Use new connector tips for enhanced purification.

7.3.2.11 If additional uranium removal is needed for Pu isotope assay by ICP-MS, the sample may be purified further using section 7.3.3 before. Np remains on TEVA Resin as Pu is moved to DGA Resin in 7.3.3 for further purification.

7.3.2.12 Elute Pu and Np as follows:

7.3.2.12.1 For alpha spectrometry: Pipette 20 mL of 0.1M HCl -0.05M HF-0.01M $TiCl_3$ into each reservoir and allow to drain to elute the Pu (and/or Np-237) (1 mL/min or slightly slower).

7.3.2.12.2 For ICP-MS assay the Pu/Np may be eluted from TEVA Resin with 20 mL 0.05M HCl-0.005M HF-0.02M hydroxylamine hydrochloride. This may be evaporated and redissolved in small volume of dilute nitric acid for assay.

NOTE: U removal with a single TEVA Resin column separation typically a factor of 1000-2000. Enhanced U removal for ICP-MS is provided in 7.3.3 (>1E6).

7.3.2.13 Proceed to section 7.4 for sample counting

7.3.3 Enhanced Uranium Removal Option for Pu by ICP-MS

7.3.3.1 Place a 1ml UTEVA cartridge and 2mL DGA cartridge below each TEVA Resin cartridge. (TEVA+UTEVA+DGA).

NOTE: This rapid purification option typically gives ~10E6-10E7 removal of uranium. It may be used with DGA only, no UTEVA, with ~10E5-10E6 removal.

7.3.3.2 Add 20 mL 2.7M HNO_3 -0.1M ascorbic acid-0.02M Fe^{+2} to each column (Pu^{+3} to DGA) (1mL/min or less). Prepare this eluent freshly.

7.3.3.3 Remove TEVA cartridge (Np-237 may be eluted form TEVA if desired as in step 7.3.2.12).

7.3.3.4 Add 5mL 8M HNO_3 to DGA cartridge (1 mL/min) (Pu^{+3} to Pu^{+4}).

7.3.3.5 Add 15 ml 0.05M HNO_3 to each DGA cartridge (1-2 mL/min, U removal)

7.3.3.6 Place new containers/tubes below each column.

7.3.3.7 Add 5mL 0.02M HCl-0.005M HF-0.002M hydroxylamine hydrochloride to each DGA cartridge to elute highly purified Pu fraction. (very slowly ~0.5mL/min or less)

NOTE: It may be possible to elute Pu with 0.02M HCl-0.005M HF with or without hydroxylamine added. The eluents may be evaporated and redissolved in dilute nitric acid or introduced directly into the ICP-MS.

7.4 Sample preparation for counting

7.4.1 Alpha Spectrometry Option for Pu and/or Np:

7.4.1.1 Add 50µL of the Ce carrier solution (50µg Ce^{3+}) to each tube.

7.4.1.2 Add 0.5 mL 30 wt% H_2O_2 to each tube (oxidize any residual U to U(VI))

7.4.1.3 Add 1 mL conc. HF and shake. Allow to sit for 15 min.

7.4.1.4 Place Resolve® filter filtration unit on yellow outer tip, place on vacuum box. Assure that an empty centrifuge tube (or liner) is placed below the unit. Start vacuum.

7.4.1.5 Rinse unit with 2 – 3 mL 95% ethanol. Check for leaks.

7.4.1.6 Rinse unit with 2 – 3 mL water.

7.4.1.7 Pass solution through filter.

7.4.1.8 Rinse centrifuge tube with 5 mL water, transfer onto filtration unit.

7.4.1.9 Rinse filter with 2 – 3 mL water, followed by 2 – 3 mL 95% ethanol.

7.4.1.10 Stop vacuum. Remove filter from filtration unit, allow to dry and glue on planchet or steel disc.

7.4.2 ICP-MS Option for Pu and/or Np:

Introduce the purified eluents directly into the ICP-MS (if compatible) or evaporate the purified eluent solutions in clean Teflon beakers on a hot plate and redissolve in the appropriate acid solution (dilute nitric acid, etc.) for the specific ICP-MS used.

8 REFERENCES

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