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Rapid Radiochemical Method for Isotopic Uranium in Water for Environmental Remediation Following Homeland Security Events

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Revision History

Revision 0	Original release.	02/23/2010
Revision 0.1	• Corrected typographical and punctuation errors. • Improved wording consistency with other methods. • Corrected specification of analytical balance (6.1) to 10^{-4}-g readability. • Add pH paper to list of equipment and supplies (6.7). • Edited Section 8 to conform syntax and layout to other methods. • Added equations in 12.1.2 that allow theoretical calculation of the MDA and critical level for different decision error rates. • Updated footnote 9 to further clarify origin of critical value and minimum detectable concentration formulations. • Updated rounding example in 12.2.2.2 for clarity. • Deleted Appendix A (composition of Atlanta tap water) as irrelevant	10/28/2011

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ISOTOPIC URANIUM IN WATER:
RAPID METHOD FOR HIGH-ACTIVITY SAMPLES

1. Scope and Application
   1.1. The method will be applicable to samples where the source of the contamination is either known or unknown sample sources. If any filtration of the sample is performed prior to starting the analysis, those solids should be analyzed separately. The results from the analysis of these solids should be reported separately (as a suspended activity concentration for the water volume filtered), but identified with the filtrate results.
   1.2. The method is specific for ^{238}U, ^{235}U, and ^{234}U in drinking water and other aqueous samples.
   1.3. This method uses rapid radiochemical separations techniques for determining alpha-emitting uranium isotopes in water samples following a nuclear or radiological incident. Although the method can detect concentrations of ^{238}U, ^{235}U, and ^{234}U on the same order of magnitude as methods used for the Safe Drinking Water Act (SDWA), this method is not a substitute for SDWA-approved methods for isotopic uranium.
   1.4. The method is capable of satisfying a required method uncertainty for ^{238}U, ^{235}U, or ^{234}U of 2.6 pCi/L at an analytical action level of 20 pCi/L. To attain the stated measurement quality objectives (MQOs) (see Sections 9.3 and 9.4), a sample volume of approximately 200 mL and count time of at least 1 hour are recommended. The sample turnaround time and throughput may vary based on additional project MQOs, the time for analysis of the final counting form, and initial sample volume. The method must be validated prior to use following the protocols provided in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009, reference 16.5).
   1.5. The method is intended to be used for water samples that are similar in composition to drinking water. The rapid uranium method was evaluated following the guidance presented for "Level E Method Validation: Adapted or Newly Developed Methods, Including Rapid Methods" in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009, reference 16.5) and Chapter 6 of *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (MARLAP 2004, reference 16.6).
   1.6. Multi-radionuclide analysis using sequential separation may be possible using this method in conjunction with other rapid methods.
   1.7. This method is applicable to the determination of soluble uranium. This method is not applicable to the determination of uranium isotopes contained in highly insoluble particulate matter possibly present in water samples contaminated as a result of a radiological dispersion device (RDD) event.

2. Summary of Method
   2.1. This method is based on the sequential elution of interfering radionuclides as well as other components of the matrix by extraction chromatography to isolate and purify uranium in order to prepare the uranium for counting by alpha spectrometry. The method utilizes vacuum assisted flow to improve the speed of the separations. Prior to the use of the extraction resins, a water sample is filtered as necessary to remove any insoluble fractions, equilibrated with ^{232}U tracer, and concentrated by either

evaporation or calcium phosphate precipitation. The sample test source (STS) is prepared by microprecipitation with NdF_3. Standard laboratory protocol for the use of an alpha spectrometer should be used when the sample is ready for counting.

3. Definitions, Abbreviations and Acronyms
   - 3.1. Analytical Protocol Specification (APS). The output of a directed planning process that contains the project's analytical data needs and requirements in an organized, concise form.
   - 3.2. Analytical Action Level (AAL). The term "analytical action level" is used to denote the value of a quantity that will cause the decisionmaker to choose one of the alternative actions.
   - 3.3. Analytical Decision Level (ADL). The analytical decision level refers to the value that is less than the AAL based on the acceptable error rate and the required method uncertainty.
   - 3.4. Discrete Radioactive Particles (DRPs or "hot particles"). Particulate matter in a sample of any matrix where a high concentration of radioactive material is contained in a tiny particle (μm range).
   - 3.5. *Multi-Agency Radiological Analytical Laboratory Protocol Manual* (MARLAP) (see Reference 16.6.)
   - 3.6. Measurement Quality Objective (MQO). MQOs are the analytical data requirements of the data quality objectives and are project- or program-specific and can be quantitative or qualitative. These analytical data requirements serve as measurement performance criteria or objectives of the analytical process.
   - 3.7. Radiological Dispersal Device (RDD), i.e., a "dirty bomb." This is an unconventional weapon constructed to distribute radioactive material(s) into the environment either by incorporating them into a conventional bomb or by using sprays, canisters, or manual dispersal.
   - 3.8. Required Method Uncertainty (u_{MR}). The required method uncertainty is a target value for the individual measurement uncertainties, and is an estimate of uncertainty (of measurement) before the sample is actually measured. The required method uncertainty is applicable below an Analytical Action level.
   - 3.9. Relative Required Method Uncertainty (φ_{MR}). The relative required method uncertainty is the u_{MR} divided by the AAL and typically expressed as a percentage. It is applicable above the AAL.
   - 3.10. Sample Test Source (STS). This is the final form of the sample that is used for nuclear counting. This form is usually specific for the nuclear counting technique used in the method such as a solid deposited on a filter for alpha spectrometry analysis.

4. Interferences
   - 4.1. Radiological
     - 4.1.1. Spectral Overlap: Alpha-emitting radionuclides (or their short-lived decay progeny) with peaks at energies that cannot be adequately resolved from the tracer or analyte (e.g., for ^{232}U (5320, 5263 keV), ^{210}Po (5304 keV), ^{228}Th (5423, 5340 keV), and ^{243}Am (5275, 5233 keV)) must be chemically separated to enable radionuclide-specific measurements. This method separates these radionuclides effectively. The significance of peak overlap will be determined

by the individual detector's alpha energy resolution characteristics and the quality of the final precipitate that is counted.

4.2. Non-Radiological: Very high levels of competing higher valence anions (greater than divalent such as phosphates) will lead to lower yields when using the evaporation option due to competition with active sites on the resin. If higher valence anions are present, the phosphate precipitation option may need to be used initially in place of evaporation. If calcium phosphate coprecipitation is performed to collect uranium (and other potentially present actinides) from large-volume samples, the amount of phosphate added to coprecipitate the actinides (in Step 11.1.4.3) should be reduced to accommodate the sample's high phosphate concentration.

5. Safety
   5.1. General
      5.1.1. Refer to your safety manual for concerns of contamination control, personal exposure monitoring and radiation dose monitoring.
      5.1.2. Refer to the laboratory chemical hygiene plan (or equivalent) for general safety rules regarding chemicals in the workplace.
   5.2. Radiological
      5.2.1. Hot particles (DRPs)
         5.2.1.1. Hot particles, also termed "discrete radioactive particles" (DRPs), will be small, on the order of 1 mm or less. Typically, DRPs are not evenly distributed in the media and their radiation emissions are not uniform in all directions (anisotropic). Filtration using a 0.45-µm or finer filter will minimize the presence of these particles.
         5.2.1.2. Care should be taken to provide suitable containment for filter media used in the pretreatment of samples that may have DRPs, because the particles become highly statically charged as they dry out and will "jump" to other surfaces causing contamination.
         5.2.1.3. Filter media should be individually surveyed for the presence of these particles, and this information reported with the final sample results.
      5.2.2. For samples with detectable activity concentrations of these radionuclides, labware should be used only once due to potential for cross contamination.
   5.3. Procedure-Specific Non-Radiological Hazards:
      5.3.1. Particular attention should be paid to the discussion of hydrofluoric acid (HF). HF is an extremely dangerous chemical used in the preparation of some of the reagents and in the microprecipitation procedure. Appropriate personal protective equipment (PPE) must be obtained and used in strict accordance with the laboratory safety program specification.

6. Equipment and Supplies
   6.1. Analytical balance with 10^{-4}-g readability or better.
   6.2. Cartridge reservoirs, 10- or 20-mL syringe style with locking device, or equivalent.
   6.3. Centrifuge able to accommodate 250-mL flasks.
   6.4. Centrifuge flasks with 250-mL capacity.
   6.5. Filter with 0.45-µm membrane.

6.6. Filter apparatus with a 25-mm diameter, polysulfone, filtration chimney, stem support, and stainless steel support. A single-use (disposable) filter funnel/filter combination may be used, to avoid cross contamination.
6.7. pH paper.
6.8. 25-mm polypropylene filter with 0.1-µm pore size.
6.9. Stainless steel planchets or other sample mounts that are able to hold the 25-mm filter.
6.10. Tweezers.
6.11. 100-µL pipette, or equivalent, and appropriate plastic tips.
6.12. 10-mL plastic culture tubes with caps.
6.13. Vacuum pump or laboratory vacuum system.
6.14. Tips, white inner, Eichrom part number AC-1000-IT, or equivalent.
6.15. Tips, yellow outer, Eichrom part number AC-1000-OT, or equivalent.
6.16. Vacuum Box, such as Eichrom part number AC-24-BOX, or equivalent.
6.17. Vortex mixer.
6.18. Miscellaneous labware, plastic or glass, both 250 and 350 mL.

7. Reagents and Standards

Note: All reagents are American Chemical Society (ACS) reagent grade or equivalent unless otherwise specified.

Note: Unless otherwise indicated, all references to water should be understood to mean Type I Reagent water. All solutions used in microprecipitation should be prepared with water filtered through a 0.45-µm (or better) filter.

7.1. Ammonium hydrogen oxalate (0.1M): Dissolve 6.3 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) and 7.1 g of ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$) in 900 mL of water, and dilute to 1 L with water.
7.2. Ammonium hydrogen phosphate (3.2 M): Dissolve 106 g of $(NH_4)_2HPO_4$ in 200 mL of water. Heat gently to dissolve and dilute to 250 mL with water.
7.3. Ammonium hydroxide (15 M): Concentrated NH_4OH, available commercially.
7.4. Ammonium thiocyanate indicator (1 M): Dissolve 7.6 g of ammonium thiocyanate (NH_4SCN) in 90 mL of water and dilute to 100 mL with water. An appropriate quantity of sodium thiocyanate (8.1 g) or potassium thiocyanate (9.7 g) may be substituted for ammonium thiocyanate.
7.5. Ascorbic acid (1 M): Dissolve 17.6 g of ascorbic acid ($C_6H_8O_6$) in 90 mL of water and dilute to 100 mL with water. Prepare weekly.
7.6. Calcium nitrate (0.9 M): Dissolve 53 g of calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) in 100 mL of water and dilute to 250 mL with water.
7.7. Ethanol, 100 %: Anhydrous C_2H_5OH, available commercially.
7.7.1. Ethanol, (~80% v/v): Mix 80 mL 100% ethanol and 20 mL water.
7.8. Ferrous sulfamate (0.6 M): Add 57 g of sulfamic acid (NH_2SO_3H) to 150 mL of water and heat to 70 °C. Slowly add 7 g of iron powder (< 100 mesh size) while heating and stirring (magnetic stirrer should be used) until dissolved (may take as long as two hours). Filter the hot solution (using a qualitative filter), transfer to flask, and dilute to 200 mL with water. Prepare fresh weekly.
7.9. Hydrochloric acid (12 M): Concentrated HCl, available commercially.

7.9.1. Hydrochloric acid (9 M): Add 750 mL of concentrated HCl to 100 mL of water and dilute to 1 L with water.
7.9.2. Hydrochloric acid (4 M): Add 333 mL of concentrated HCl to 500 mL of water and dilute to 1 L with water.
7.9.3. Hydrochloric acid (1 M): Add 83 mL of concentrated HCl to 500 mL of water and dilute to 1 L with water.
7.10. Hydrofluoric acid (28 M): Concentrated HF, available commercially.
7.10.1. Hydrofluoric acid (0.58 M): Add 20 mL of concentrated HF to 980 mL of filtered demineralized water and mix. Store in a plastic bottle.
7.11. Neodymium standard solution (1000 µg/mL): May be purchased from a supplier of standards for atomic spectroscopy.
7.12. Neodymium carrier solution (0.50 mg/mL): Dilute 10 mL of the neodymium standard solution (7.11) to 20.0 mL with filtered demineralized water. This solution is stable for up to six months.
7.13. Neodymium fluoride substrate solution (10 µg/mL): Pipette 5.0 mL of neodymium standard solution (7.11) into a 500-mL plastic bottle. Add 460 mL of 1-M HCl to the plastic bottle. Cap the bottle and shake to mix. Measure 40 mL of concentrated HF in a plastic graduated cylinder and add to the bottle. Recap the bottle and shake to mix thoroughly. This solution is stable for up to six months.
7.14. Nitric acid (16M): Concentrated HNO_3, available commercially.
7.14.1. Nitric acid (3 M): Add 191 mL of concentrated HNO_3 to 700 mL of water and dilute to 1 L with water.
7.14.2. Nitric acid (2 M): Add 127 mL of concentrated HNO_3 to 800 mL of water and dilute to 1 L with water.
7.14.3. Nitric acid (0.5 M): Add 32 mL of concentrated HNO_3 to 900 mL of water and dilute to 1 L with water.
7.15. Nitric acid (3 M) – aluminum nitrate (1.0 M) solution: Dissolve 210 g of anhydrous aluminum nitrate ($Al(NO_3)_3$) in 700 mL of water. Add 190 mL of concentrated HNO_3 (7.14) and dilute to 1 L with water. An appropriate quantity of aluminum nitrate nonahydrate (375 g) may be substituted for anhydrous aluminum nitrate.
7.16. Phenolphthalein solution: Dissolve 1 g phenolphthalein in 100 mL 95% isopropyl alcohol and dilute with 100 mL of water.
7.17. Titanium chloride: 20 % solution, stored in an air-tight container and away from light.
7.18. Uranium-232 tracer solution: 6–10 dpm of ^{232}U per aliquant, activity added known to at least 5 % (combined standard uncertainty of no more than 5 %).
7.19. UTEVA Resin: 2-mL cartridge, 50–100 µg, Eichrom part number UT-R50-S and UT-R200-S, or equivalent.

8. Sample Collection, Preservation, and Storage
8.1. Samples should be collected in 1-L plastic containers.
8.2. No sample preservation is required if sample analysis is initiated within 3 days of sampling date/time.
8.3. If the sample is to be held for more than three days, HNO_3 shall be added until the solution pH is less than 2.0.
8.4. If the dissolved concentration of uranium is sought, the insoluble fraction must be removed by filtration before preserving with acid.

9. Quality Control
   9.1. Batch quality control results shall be evaluated and meet applicable Analytical Project Specifications (APS) prior to release of unqualified data. In the absence of project-defined APS or a project-specific quality assurance project plan (QAPP), the quality control sample acceptance criteria defined in the laboratory quality manual and procedures shall be used to determine acceptable performance for this method.
      9.1.1. A laboratory control sample (LCS) shall be run with each batch of samples. The concentration of the LCS should be at or near the action level or level of interest for the project.
      9.1.2. One method blank shall be run with each batch of samples. The laboratory blank should consist of laboratory water.
      9.1.3. One laboratory duplicate shall be run with each batch of samples. The laboratory duplicate is prepared by removing an aliquant from the original sample container.
      9.1.4. A matrix spike sample may be included as a batch quality control sample if there is concern that matrix interferences, may compromise chemical yield measurements, or overall data quality.
   9.2. The source preparation method should produce a sample test source that produces a spectrum with the full width at half maximum (FWHM) of 50–100 keV for each peak in the spectrum (with the exception of ^{235}U). Precipitate reprocessing should be considered if this range of FWHM cannot be achieved.
   9.3. This method is capable of achieving a u_{MR} of 2.6 pCi/L at or below an action level of 20 pCi/L. This may be adjusted if the event-specific MQOs are different.
   9.4. This method is capable of achieving a φ_{MR} of 13 % above 20 pCi/L. This may be adjusted if the event-specific MQOs are different.
   9.5. This method is capable of achieving a required minimum detectable concentration (MDC) of 1.5 pCi/L.

10. Calibration and Standardization
   10.1. Set up the alpha spectrometry system according to the manufacturer's recommendations. The energy range of the spectrometry system should at least include the region between 3–8 MeV.
   10.2. Calibrate each detector used to count samples according to ASTM Standard Practice D7282, Section 18, "Alpha Spectrometry Instrument Calibrations" (see reference 16.3).
   10.3. Continuing Instrument Quality Control Testing shall be performed according to ASTM Standard Practice D7282, Sections 20, 21, and 24.

11. Procedure
   11.1. Water Sample Preparation
      11.1.1. As required, filter the 100-200 mL sample aliquant through a 0.45-µm filter and collect the sample in an appropriate size beaker.
      11.1.2. Acidify the sample with concentrated HNO_3. This usually requires adding about 2 mL of concentrated HNO_3 per 1000 mL of sample. However, samples that are initially alkaline, or that may have high carbonate content, may require

substantially more acid. It is important that the pH be verified to be below 2.0, ensuring that all carbonate (a uranium complexing agent) has been removed.

11.1.3. Following the laboratory protocol, add 6–10 dpm of ^{232}U as a tracer.

Note: For a sample approximately 100 mL or less, the evaporation option is recommended. Proceed to Step 11.1.5. Otherwise continue to Step 11.1.4.

11.1.4. Calcium phosphate coprecipitation option

11.1.4.1. Add 0.5 mL of 0.9 M $Ca(NO_3)_2$ to each beaker. Place each beaker on a hot plate, cover with a watch glass, and heat until boiling.

11.1.4.2. Once the sample boils, take the watch glass off the beaker and lower the heat.

11.1.4.3. Add 2-3 drops of phenolphthalein indicator and 200 µL of 3.2 M $(NH_4)_2HPO_4$ solution.

11.1.4.4. Add enough concentrated NH_4OH with a squeeze bottle to reach the phenolphthalein end point (a persistent pink color) and form $Ca_3(PO_4)_2$ precipitate. NH_4OH should be added very slowly. Stir the solution with a glass rod. Allow the sample to heat gently to digest the precipitate for another 20–30 minutes.

Note: The calcium phosphate precipitation should be completed promptly following pH adjustment to the phenolphthalein endpoint to minimize absorption of CO_2 and formation of a soluble carbonate complex with U that will lead to incomplete precipitation of U.

11.1.4.5. If the sample volume is too large to centrifuge the entire sample, allow precipitate to settle until solution can be decanted (30 minutes to 2 hours) and go to Step 11.1.4.7.

11.1.4.6. If the volume is small enough to centrifuge go to Step 11.1.4.8.

11.1.4.7. Decant supernatant solution and discard to waste.

11.1.4.8. Transfer the precipitate to a 250-mL centrifuge tube, completing the transfer with a few milliliters of water, and centrifuge the precipitate for approximately 10 minutes at 2000 rpm.

11.1.4.9. Decant supernatant solution and discard to waste.

11.1.4.10. Wash the precipitate with an amount of water approximately twice the volume of the precipitate. Mix well using a stirring rod, breaking up the precipitate if necessary. Centrifuge for 5–10 minutes at 2000 rpm. Discard the supernatant solution.

11.1.4.11. Dissolve precipitate in approximately 5 mL concentrated HNO_3. Transfer solution to a 100 mL beaker. Rinse centrifuge tube with 2–3 mL of concentrated HNO_3 and transfer to the same beaker. Evaporate solution to dryness and go to Step 11.2.

11.1.5. Evaporation option to reduce volume and to digest organic components

11.1.5.1. Evaporate sample to less than 50 mL and transfer to a 100 mL beaker.

Note: For some water samples, $CaSO_4$ formation may occur during

evaporation. If this occurs, use the calcium phosphate precipitation option in Step 11.1.4.

11.1.5.2. Gently evaporate the sample to dryness and redissolve in approximately 5 mL of concentrated HNO_3.

11.1.5.3. Repeat Step 11.1.5.2 two more times, evaporate to dryness, and go to Step 11.2.

11.2. Actinide Separations using Eichrom Resins

11.2.1. Redissolve $Ca_3(PO_4)_2$ residue or evaporated water sample

11.2.1.1. Dissolve either residue with 10 mL of 3 M HNO_3 – 1.0 M $Al(NO_3)_3$.

Note: An additional 5 mL may be necessary if the residue volume is large.

11.2.1.2. Add 2 mL of 0.6 M ferrous sulfamate to each solution. Swirl to mix.

Note: If the additional 5 mL was used to dissolve the sample in Step 11.2.1.1, add a total of 3 mL of ferrous sulfamate solution.

11.2.1.3. Add 1 drop of 1 M ammonium thiocyanate indicator to each sample and mix.

Note: The color of the solution turns deep red, due to the formation of soluble ferric thiocyanate complex.

11.2.1.4. Add 1 mL of 1 M ascorbic acid to each solution, swirling to mix. Wait for 2-3 minutes.

Note: The red color should disappear which indicates reduction of Fe+3 to Fe^{+2}. If the red color persists, then additional ascorbic acid solution is added drop-wise with mixing until the red color disappears.

Note: If particles are observed suspended in the solution, centrifuge the sample at 2000 rpm. The supernatant solution will be transferred to the column in Step 11.2.3.1. The precipitates will be discarded.

11.2.2. Set up the vacuum box with UTEVA cartridges as follows:

Note: Steps 11.2.2.1 to 11.2.2.5 deal with a commercially available filtration system. Other vacuum systems developed by individual laboratories may be substituted here as long as the laboratory has provided guidance to analysts in their use.

11.2.2.1. Place the inner tube rack (supplied with vacuum box) into the vacuum box with the centrifuge tubes in the rack. Fit the lid to the vacuum system box.

11.2.2.2. Place the yellow outer tips into all 24 openings of the lid of the vacuum box. Fit in the inner white tip into each yellow tip.

11.2.2.3. For each sample solution, fit in the UTEVA cartridge on to the inner white tip.

11.2.2.4. Lock syringe barrels (funnels/reservoirs) to the top end of the UTEVA cartridge.

11.2.2.5. Connect the vacuum pump to the box. Turn the vacuum pump on and ensure proper fitting of the lid.

IMPORTANT: The unused openings on the vacuum box should be sealed. Yellow caps (included with the vacuum box) can be used to plug unused white tips to achieve good seal during the separation.

11.2.2.6. Add 5 mL of 3-M HNO_3 to the funnel to precondition the UTEVA cartridge.

11.2.2.7. Adjust the vacuum pressure to achieve a flow-rate of ~1 mL/min.

IMPORTANT: Unless otherwise specified in the procedure, use a flow rate of ~ 1 mL/min for load and strip solutions and ~ 3 mL/min for rinse solutions.

11.2.3. U separation from Pu, Am using UTEVA resin

11.2.3.1. Transfer each solution from Step 11.2.1.4 into the appropriate funnel by pouring or by using a plastic transfer pipette. Allow solution to pass through both the cartridges at a flow rate of ~1 mL/min.

11.2.3.2. Add 5 mL of 3-M HNO_3 to each beaker as a rinse and transfer each solution into the appropriate funnel (the flow rate can be adjusted to ~3 mL/min).

11.2.3.3. Add 5 mL of 3-M HNO_3 into each funnel as second column rinse (flow rate ~3 mL/min).

Note: Maintain the flow rate at ≤3 mL/min in the next several steps.

Note: If a high concentration of ^{210}Po is present in the sample an additional 3 M HNO_3 rinse is necessary to eliminate ^{210}Po. Add 30 mL of 3 M HNO_3 rinse to each UTEVA cartridge in increments of 10 mL. Continue with Step 11.2.3.4.

11.2.3.4. Pipette 5 mL of 9-M HCl into each UTEVA cartridge and allow it to drain. Discard this rinse.

Note: This rinse converts the resin to the chloride system. Some Np may be removed here.

11.2.3.5. Pipette 20 mL of 5-M HCl – 0.05 M oxalic acid into each UTEVA cartridge and allow it to drain. Discard this rinse.

Note: This rinse removes neptunium and thorium from the cartridge. The 9-M HCl and 5-M HCl – 0.05 M oxalic acid rinses also remove any residual

ferrous ion that might interfere with micoprecipitation.

11.2.3.6. Ensure that clean, labeled tubes are placed in the tube rack.
11.2.3.7. Pipette 15 mL of 1-M HCl into each cartridge to strip the uranium. Allow to drain.
11.2.3.8. Transfer the eluate containing uranium to a 50-mL beaker. Rinse the tube with a few milliliters of water and add to the same beaker.
11.2.3.9. Evaporate samples to near soft dryness. If a slight white residue appears, wet-ash by adding a few mL of HNO_3, heating till near dryness and repeating the process 2–3 times. Once wet-ashing is complete, convert the sample to the chloride form by treating it 2–3 times with 1–2-mL portions of HCl and evaporating to near dryness.

Note: Do not bake the residue.

11.2.3.10. Allow the beaker to cool slightly and then add a few drops of concentrated HCl followed by 1 mL of water.
11.2.3.11. Transfer the solution to a 10-mL plastic culture tube. Rinse the original sample vessel twice with 1-mL washes of 1-M HCl, transferring the rinses to a culture tube. Mix by gently swirling the solution in the tube.
11.2.3.12. Proceed to neodymium fluoride microprecipitation, Step 11.3.
11.2.3.13. Discard the UTEVA cartridge.

11.3. Preparation of the Sample Test Source

Note: Instructions below describe preparation of a single Sample Test Source. Several STSs can be prepared simultaneously if a multi-channel vacuum box (whale apparatus) is available.

11.3.1. Add 100 µL of the neodymium carrier solution (Step 7.12) to the culture tube with a micropipette. Gently swirl the tube to mix the solution.
11.3.2. Add four drops of 20% $TiCl_3$ solution to the tube and mix gently. A strong permanent violet color should appear. If the color fails to appear, add a few more drops of the $TiCl_3$ solution to provide the permanent violet color.
11.3.3. Add 1 mL of concentrated HF to the tube and mix well by gently swirling.
11.3.4. Cap the tube and place it a cold-water ice bath for at least 30 minutes.
11.3.5. Insert the polysulfone filter stem in the 250-mL vacuum flask. Place the stainless steel screen on top of the fitted plastic filter stem.
11.3.6. Place a 25-mm polymeric filter face up on the stainless steel screen. Center the filter on the stainless steel screen support and apply vacuum. Wet the filter with 100 % ethanol, followed by filtered Type I water.

Caution: There is no visible difference between the two sides of the filter. If the filter is turned over accidentally, it is recommended that the filter be discarded and a fresh one removed from the container.

11.3.7. Lock the filter chimney firmly in place on the filter screen and wash the filter with additional filtered Type I water wash.

11.3.8. Pour 5.0 mL of neodymium substrate solution (Step 7.13) down the side of the filter chimney, avoiding directing the stream at the filter. When the solution passes through the filter, wait at least 15 seconds before the next step.
11.3.9. Repeat Step 11.3.8 with an additional 5.0 mL of the substrate solution.
11.3.10. Pour the sample from Step 11.3.4 down the side of the filter chimney and allow the vacuum to draw the solution through.
11.3.11. Rinse the tube twice with 2 mL of 0.58-M HF, stirring each wash briefly using a vortex mixer and pouring each wash down the side of the filter chimney.
11.3.12. Repeat rinse using 2-mL filtered Type I water once.
11.3.13. Repeat rinse using 2-mL 80% ethyl alcohol once.
11.3.14. Wash any drops remaining on the sides of the chimney down toward the filter with a few mL 80% ethyl alcohol.

Caution: Directing a stream of liquid onto the filter will disturb the distribution of the precipitate on the filter and render the sample unsuitable for α-spectrometry resolution.

11.3.15. Without turning off the vacuum, remove the filter chimney.
11.3.16. Turn off the vacuum to remove the filter. Discard the filtrate to waste for future disposal. If the filtrate is to be retained, it should be placed in a plastic container to avoid dissolution of the glass vessel by dilute HF.
11.3.17. Place the filter on a properly labeled mounting disc, secure with a mounting ring or other device that will render the filter flat for counting.
11.3.18. Let the sample air dry for a few minutes and when dry, place in a container suitable for transfer and submit for counting.
11.3.19. Count the sample on an alpha spectrometer.

Note: Other methods for STS preparation, such as electroplating or microprecipitation with cerium fluoride, may be used in lieu of the neodymium fluoride microprecipitation, but any such substitution must be validated as described in Section 1.4.

12. Data Analysis and Calculations

12.1. Equations for determination of final result, combined standard uncertainty and radiochemical yield (if required).

The activity concentration of an analyte and its combined standard uncertainty are calculated using the following equations:

$$AC_a = \frac{A_t \times R_a \times D_t \times I_t}{V_a \times R_t \times D_a \times I_a}$$

and

$$u_c(AC_a) = \sqrt{u^2(R_a) \times \frac{A_t^2 \times D_t^2 \times I_t^2}{V_a^2 \times R_t^2 \times D_a^2 \times I_a^2} + AC_a^2 \times \left(\frac{u^2(A_t)}{A_t^2} + \frac{u^2(V_a)}{V_a^2} + \frac{u^2(R_t)}{R_t^2} \right)}$$

where:

AC_a = activity concentration of the analyte at time of count, (pCi/L)

A_t = activity of the tracer added to the sample aliquant at its reference date and time, (pCi)
R_a = net count rate of the analyte in the defined region of interest (ROI), in counts per second
R_t = net count rate of the tracer in the defined ROI, in counts per second
V_a = volume of the sample aliquant, (L)
D_t = correction factor for decay of the tracer from its reference date and time to the midpoint of the counting period
D_a = correction factor for decay of the analyte from the time of sample collection (or other reference time) to the midpoint of the counting period (if required)
I_t = probability of α emission in the defined ROI, per decay of the tracer (Table 17.1)
I_a = probability of α emission in the defined ROI, per decay of the analyte (Table 17.1)
$u_c(AC_a)$ = combined standard uncertainty of the activity concentration of the analyte (pCi/L)
$u(A_t)$ = standard uncertainty of the activity of the tracer added to the sample (pCi)
$u(V_a)$ = standard uncertainty of the volume of sample aliquant (L)
$u(R_a)$ = standard uncertainty of the net count rate of the analyte, in counts per second
$u(R_t)$ = standard uncertainty of the net count rate of the tracer, in counts per second

Note: The uncertainties of the decay-correction factors and of the probability of decay factors are assumed to be negligible.

Note: The equation for the combined standard uncertainty ($u_c(AC_a)$) calculation is arranged to eliminate the possibility of dividing by zero if $R_a = 0$.

Note: **The standard uncertainty of the activity of the tracer added to the sample must reflect that associated with the activity of the standard reference material and any other significant sources of uncertainty such as those introduced during the preparation of the tracer solution (e.g., weighing or dilution factors) and during the process of adding the tracer to the sample.**

12.1.1. The net count rate of an analyte or tracer and the associated standard uncertainties are calculated using the following equations:

$$R_x = \frac{C_x}{t_s} - \frac{C_{bx}}{t_b}$$

and

$$u(R_x) = \sqrt{\frac{C_x + 1}{t_s^2} + \frac{C_{bx} + 1}{t_b^2}}$$

where:

$u(R_x)$ = standard uncertainty of the net count rate of tracer or analyte, in counts per second[1]
R_x = net count rate of analyte or tracer, in counts per second
C_x = sample counts in the analyte or the tracer peak
t_s = sample count time (s)
C_{bx} = background counts in the same region of interest (ROI) as for x
t_b = background count time (s)

The radiochemical yield and the combined standard uncertainty can be estimated for each sample, when required, using the following equations:

$$RY = \frac{R_t}{0.037 \times A_t \times D_t \times I_t \times \varepsilon}$$

and

$$u(RY) = RY \times \sqrt{\frac{u^2(R_t)}{R_t^2} + \frac{u^2(A_t)}{A_t^2} + \frac{u^2(\varepsilon)}{\varepsilon^2}}$$

where:

RY = radiochemical yield of the tracer, expressed as a fraction
R_t = net count rate of the tracer, in counts per second
A_t = activity of the tracer added to the sample (pCi)
D_t = correction factor for decay of the tracer from its reference date and time to the midpoint of the counting period
I_t = probability of α emission in the defined ROI per decay of the tracer (Table 17.1)
ε = detector efficiency, expressed as a fraction
$u_c(RY)$ = combined standard uncertainty of the radiochemical yield
$u(R_t)$ = standard uncertainty of the net count rate of the tracer, in counts per second
$u(A_t)$ = standard uncertainty of the activity of the tracer added to the sample (pCi)
$u(\varepsilon)$ = standard uncertainty of the detector efficiency

12.1.2. If the critical level concentration (S_c) or the minimum detectable concentration (MDC) are requested (at an error rate of 5%), they can be calculated using the following equations:[2]

[1] For methods with very low counts, MARLAP Section 19.5.2.2 recommends adding one count each to the gross counts and the background counts when estimating the uncertainty of the respective net counts. This minimizes negative bias in the estimate of uncertainty and protects against calculating zero uncertainty when zero total counts are observed for the sample and background.

[2] The formulations for the critical level and minimum detectable concentrations are as recommended in MARLAP Section 20A.2.2, Equation 20.54, and Section 20A.2.3, Equation 20.74, respectively. For methods with very low numbers of counts, these expressions provide better estimates than do the traditional formulas for the critical level and MDC assuming that the observed variance of the background conforms to Poisson statistics. Consult MARLAP

$$S_c = \frac{\left[d \times \left(\frac{t_s}{t_b} - 1 \right) + \frac{z_{1-\alpha}^2}{4} \times \left(1 + \frac{t_s}{t_b} \right) + z_{1-\alpha} \sqrt{\left(R_{ba} t_b + d \right) \times \frac{t_s}{t_b} \times \left(1 + \frac{t_s}{t_b} \right)} \right] \times A_t \times D_t \ I_t}{t_s \times V_a \times R_t \times D_a \times I_a}$$

When the Type I decision error rate, α, equals 0.05, $z_{1-\alpha}$ = 1.645, and the constant, d, from the Stapleton approximation is set to 0.4, the expression above becomes:

$$S_c = \frac{\left[0.4 \times \left(\frac{t_s}{t_b} - 1 \right) + 0.677 \times \left(1 + \frac{t_s}{t_b} \right) + 1.645 \times \sqrt{\left(R_{ba} t_b + 0.4 \right) \times \frac{t_s}{t_b} \times \left(1 + \frac{t_s}{t_b} \right)} \right] \times A_t \times D_t \times I_t}{t_s \times V_a \times R_t \times D_a \times I_a}$$

$$\mathrm{MDC} = \frac{\left[\frac{\left(z_{1-\alpha} + z_{1-\beta} \right)^2}{4} \times \left(1 + \frac{t_s}{t_b} \right) + \left(z_{1-\alpha} + z_{1-\beta} \right) \times \sqrt{R_{ba} \, t_s \times \left(1 + \frac{t_s}{t_b} \right)} \right] \times A_t \times D_t \times I_t}{t_s \times V_a \times R_t \times D_a \times I_a \times 2.22}$$

When the Type I decision error rate, α, equals 0.05, $z_{1-\alpha}$ = 1.645, and the Type II decision error rate, β, equals 0.05, $z_{1-\beta}$ = 1.645, the expression above becomes:

$$\mathrm{MDC} = \frac{\left[2.71 \times \left(1 + \frac{t_s}{t_b} \right) + 3.29 \times \sqrt{R_{ba} \, t_s \times \left(1 + \frac{t_s}{t_b} \right)} \right] \times A_t \times D_t \times I_t}{t_s \times V_a \times R_t \times D_a \times I_a}$$

where:

R_{ba} = background count rate for the analyte in the defined ROI, in counts per second

12.2. Results Reporting

12.2.1. The following data should be reported for each result: volume of sample used, yield of tracer and its uncertainty, and FWHM of each peak used in the analysis.

12.2.2. The following conventions should be noted for each result:

12.2.2.1. Result in scientific notation ± combined standard uncertainty.

12.2.2.2. If solid material was filtered from the solution and analyzed separately, the results of that analysis should be reported separately

when background variance may exceed that predicted by the Poisson model or when other decision error rates may apply.

as pCi/L of the original volume from which the solids were filtered if no other guidance is provided on reporting of results for the solids. For example:

^{238}U for Sample 12-1-99:

Filtrate Result: $(1.28 \pm 0.15) \times 10^{1}$ pCi/L

Filtered Residue Result: $(2.50 \pm 0.32) \times 10^{0}$ pCi/L

13. Method Performance
    - 13.1. Method validation results are to be reported.
    - 13.2. Expected turnaround time per batch of 14 samples plus QC, assuming microprecipitations for the whole batch are performed simultaneously using a vacuum box system:
        - 13.2.1. For an analysis of a 200 mL sample aliquant, sample preparation and digestion should take ~3.5 h.
        - 13.2.2. Purification and separation of the uranium fraction using cartridges and vacuum box system should take ~1.5 h.
        - 13.2.3. The sample test source preparation takes ~1 h (longer if wet-ashing is necessary).
        - 13.2.4. A 1-h counting time should be sufficient to meet the MQOs listed in 9.3 and 9.4, assuming detector efficiency of 0.2-0.3, and radiochemical yield of at least 0.5. A different counting time may be necessary to meet these MQOs if any of the relevant parameters are significantly different.
        - 13.2.5. Data should be ready for reduction ~6 h after beginning of analysis.

14. Pollution Prevention: This method utilizes small volume (2 mL) extraction chromatographic resin columns. This approach leads to a significant reduction in the volumes of load, rinse and strip solutions, as compared to classical methods using ion exchange resins to separate and purify uranium.

15. Waste Management
    - 15.1. Types of waste generated per sample analyzed
        - 15.1.1. If calcium phosphate coprecipitation is performed, 100-1000 mL of decanted solution that is pH neutral is generated.
        - 15.1.2. Approximately 65 mL of acidic waste from loading and rinsing the extraction column will be generated. The solution may contain unknown quantities of radionuclides as may be present in the original sample. If presence of other radionuclides in the sample is suspected, combined effluents should be collected separately from other rinses to minimize quantity of mixed waste generated.
        - 15.1.3. Approximately 45 mL of slightly acidic waste, containing 1 mL of HF and ~ 8 mL ethanol are produced in the microprecipitation step.
        - 15.1.4. UTEVA cartridge – ready for appropriate disposal.
    - 15.2. Evaluate all waste streams to ensure that all local, state, and federal disposal requirements are met.

16. References

16.1. ACW02, Rev. 1.3, "Uranium in Water," Eichrom Technologies, Inc., Lisle, Illinois (April 2001).
16.2. G-03, V.1 "Microprecipitation Source Preparation for Alpha Spectrometry," HASL-300, 28th Edition, (February 1997).
16.3. ASTM D7282 "Standard Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements," ASTM Book of Standards 11.02, current version, ASTM International, West Conshohocken, PA.
16.4. VBS01, "Setup and Operation Instructions for Eichrom's Vacuum Box System (VBS)," Eichrom Technologies, Inc., Lisle, Illinois (Rev. 1.3, January 30, 2004).
16.5. U.S. Environmental Protection Agency (EPA). 2009. *Method Validation Guide for Radiological Laboratories Participating in Incident Response Activities*. Revision 0. Office of Air and Radiation, Washington, DC. EPA 402-R-09-006, June. Available at: www.epa.gov/narel/incident_guides.html and www.epa.gov/erln/radiation.html.
16.6. *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (MARLAP). 2004. EPA 402-B-1304 04-001A, July. Volume I, Chapters 6, 7, 20, Glossary; Volume II and Volume III, Appendix G. Available at: www.epa.gov/radiation/marlap/index.html.
16.7. ASTM D1193, "Standard Specification for Reagent Water" ASTM Book of Standards 11.01, current version, ASTM International, West Conshohocken, PA.

17. Tables, Diagrams, Flow Charts, and Validation Data

17.1. Nuclide Decay and Radiation Data

Table 17.1 – Decay and Radiation Data

Nuclide	Half-Life (Years)	λ (s^{-1})	Abundance	α Energy (MeV)
^{238}U	4.468×10^{9}	4.916×10^{-18}	0.79	4.198
			0.21	4.151
^{235}U	7.038×10^{8}	3.121×10^{-17}	0.050	4.596
			0.042	4.556
			0.0170	4.502
			0.0070	4.435
			0.0210	4.414
			0.55	4.398
			0.170	4.366
^{234}U	2.457×10^{5}	8.940×10^{-14}	0.7138	4.775
			0.2842	4.722
			0.002	4.604
^{232}U	68.9	3.19×10^{-10}	0.6815	5.320
			0.3155	5.263

17.2. Ingrowth Curves and Ingrowth Factors

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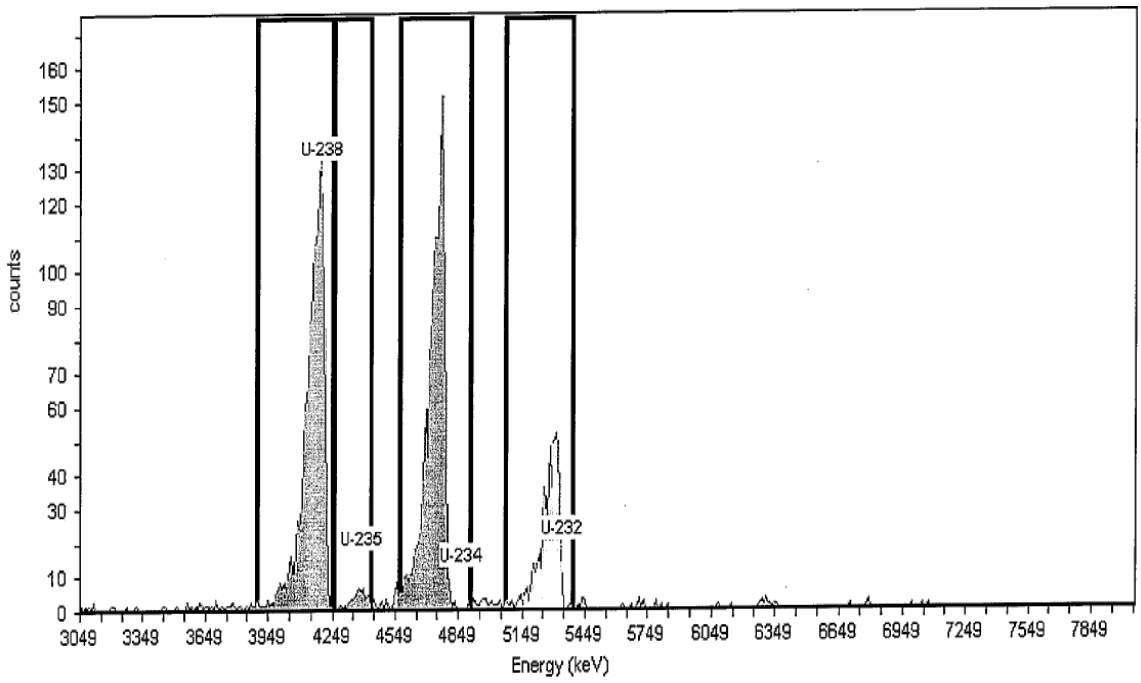
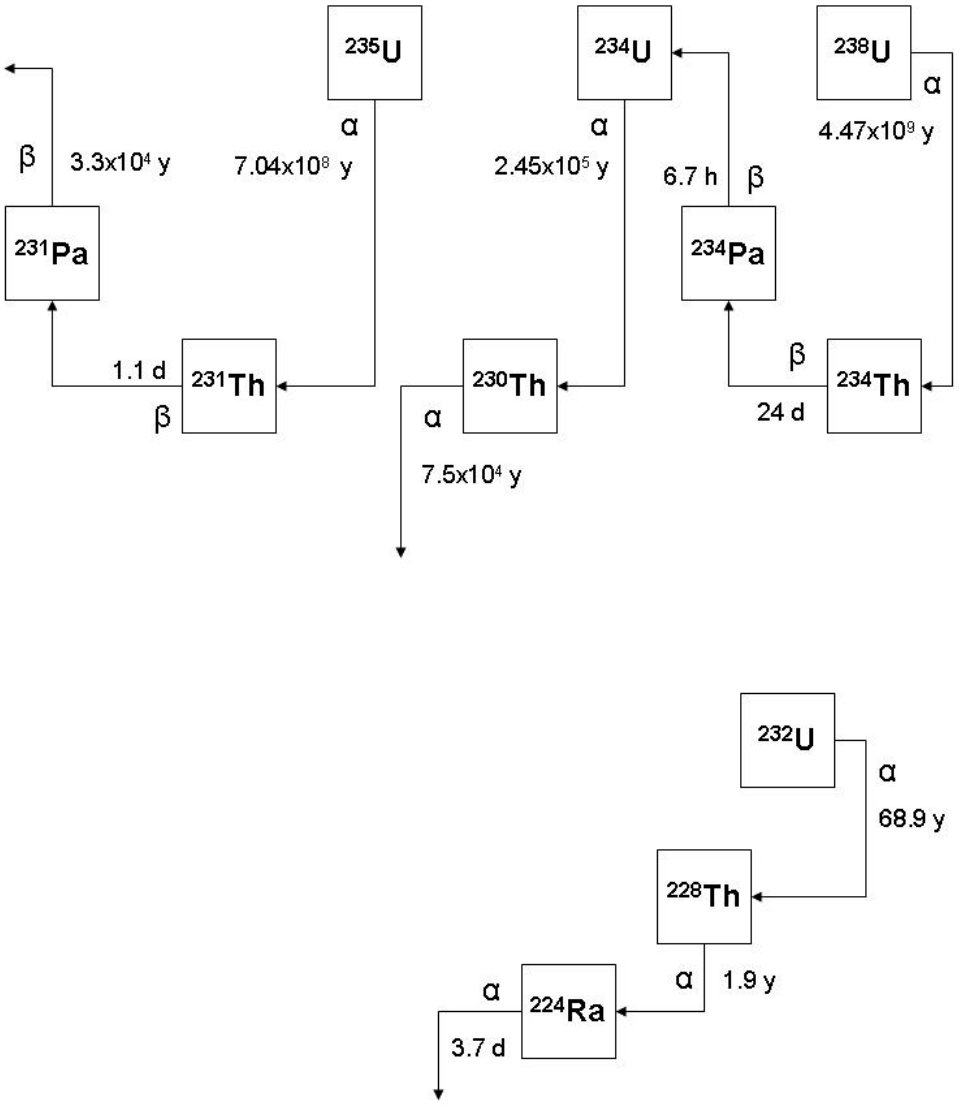
17.3. Spectrum from a Processed Sample



17.4. Decay Scheme: Ingrowth is not generally a large concern with this analysis unless one is running sequential analysis for uranium and plutonium with ^{236}Pu tracer (due to ingrowth of ^{232}U tracer) or sequential analyses for uranium and thorium (due to ^{228}Th tracer ingrowth in the ^{232}U tracer).



17.5. Flow Chart

Separation Scheme and Timeline for Determination of U Isotopes in Water Samples